Green synthesis of cellulose acetate from corncob: Physicochemical properties and assessment of environmental impacts

David Araújo [a, b, *], M. Cidália R. Castro [a], Aline Figueiredo [c], Maria Vilarinho [b, d], Ana Machado [a]

[a] Institute for Polymers and Composites/i3N, University of Minho, Guimarães, Portugal

[b] Centre for Waste Valorization, University of Minho, Guimarães, Portugal

[c] Department of Sanitary and Environmental Engineering, Federal University of Maranhão, Maranhão, Brazil

[d] Mechanical Engineering and Resources Sustainability Centre, University of Minho, Guimarães, Portugal

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Abstract

The widespread availability and chemical constitution of agroindustrial residues have stood them out as a promising source of natural chemicals and polymers, such as cellulose. However, to date, green alternative routes developed to convert the agroindustrial residues into value-added products lack environmental performance regarding the impact's quantification. In this work, promising green pretreatment (hydrothermal treatment followed by dilute sodium hydroxide reaction) and acetylation (solvent-free method catalyzed with iodine) techniques were applied to obtaining cellulose acetate (CA) from corncob. Physicochemical characterization revealed successful cellulose extraction and acetylation. CA synthesized by green and standard (acetic acid method) acetylation methods presented degree of substitutions of 2.68 and 2.89 , and yield of 60 and 40%, respectively. The storage modulus of CA film produced via this green approach (green pretreatment and acetylation) was found to be 1.89 GPa , and its operating temperature was limited to 140°C. The environmental performance of the green approach was modeled via life cycle assessment (LCA) and compared with a conventional approach (alkali-bleach pretreatment followed by standard acetylation). The LCA shows that the green approach is more advantageous than the conventional approach. The avoidance of chemicals (e.g. acetic acid, sulfuric acid, acetate buffer and aqueous chlorite) and the less use of energy throughout the pretreatment and acetylation steps of the green approach were critical to achieving environmental benefits. For instance, a reduction of 19 and 16% was attained for ionizing radiation and particulate matter emissions, respectively. Results also indicate that, for both approaches, the acetylation step was the main contributor to environmental impacts, as it accounts roughly 82 and 86% of the Global Warming Potential and Human toxicity impacts, respectively, of the green approach. The primary consumption of dichloromethane (DCM) in the purification step significantly influences this negative outlook. Moreover, sensitivity analysis demonstrates that the performance of the conventional approach only exhibits overall positive environmental effects, in comparison to the green approach, for scenarios with very high acetylation weight gains, higher than 70%.

Introduction

The use of lignocellulosic residues as feedstock for bio-based applications has been increasing as a promising alternative and essential for the functioning of modern industrial societies (Anwar

et al., 2014). Their attractiveness as a capable sustainable source of biomaterials comes mainly from their low-cost, availability and chemical composition. An unending stream of lignocellulosic residue is derived from agricultural activities. For instance, in countries where prevails an agriculture-based economy, such as Brazil, United States, China and Africa, the annual availability of lignocellulosic residues achieves remarkable values (Ullah et al., 2015). It is estimated that in Brazil an average of 108 million tonnes/year of agricultural residues are generated (Araújo et al., 2018). Although

List of abbreviations		NaOH Sodium hydroxide NaOH – LHW – CC Alkali treated LHW-CC
AGU	Anhydroglucose unit	ODP
CA	Cellulose acetate	PM
CC	corncob	POF
DCM	dichloromethane	Rf
DS	Degree of substitution	TA
ET	Freshwater Ecotoxicity	TE
E′	Storage modulus	T_g
E″	Loss modulus	Conventional pretreatment Biomass pretreatment by using

E*	Dynamic Young's modulus	alkali-bleaching technique
FE	Freshwater Eutrophication	Green pretreatment Biomass pretreatment by using combined
FU	Functional unity	LHW-Dilute NaOH solution
GWO	Global Warming Potential	Standard acetylation Cellulose acetylation through the acetic
HTc	Human toxicity, Cancer Effect	acid route
IR	Human Toxicity, non-Cancer Effect	Green acetylation Cellulose acetylation through a solvent-free
LCA	Life cycle assessment	Conventional Approach Synthesis route composed of
LCI	Life Cycle Inventory	conventional pretreatment and
LHW	Liquid Hot water	standard acetylation
LWH-CC	Liquid hot water treated corncob	Green Approach Synthesis route composed of green
ME	Marine Eutrophication	pretreatment and green acetylation

some industrial valorization techniques have already been implemented in this country, such as the production of secondgeneration ethanol and composites, the use of these residues is still very low, and they are usually inserted in the market as waste without added value, which eventually integrate the currents paths of the linear waste management systems. In a recent publication, Araújo et al. (2018) provided the availability of various crop and industry processing residues in Brazil, and highlighted, among others, the high generation of corncob, soybean straw, sugarcane top/leaves and rice straw. For instance, generation of corncob is estimated to be approximately 18.700kt/year (Araújo et al., 2018).

The agroindustrial residues are mainly composed by cellulose (30-60%), hemicellulose (14-40%) and lignin (7-20%) (Anwar et al., 2014; Kucharska et al., 2018). Cellulose is a basic structural component of plants and the most abundant renewable resource in nature. It is a high molecular weight homopolymer generated from repeating D-glucopyranose ring units linked by β-1,4-glycosidic bonds (cellobiose unit). Each glucose monomers within the cellulose chain present three hydroxyl groups positioned in the plane of the ring, which have a great influence on properties (Klemm et al., 2005). Due to the intra and intermolecular interactions of the hydroxyl groups presented in the cellobiose unit, the cellulose molecules crystallize in a horizontal plane and in parallel chains, forming microfiber packages. The elementary fibers that make up the microfiber packaging are basically organized into high order crystalline parts interspersed by amorphous regions. As a consequence of its structural organization, cellulose presents some properties that limit its application (e.g. lack of antimicrobial properties, high hydrophilicity and low dimensional stability high melting temperature). To overcome these drawbacks, cellulose is generally modified into derivatives (e.g. cellulose acetate, cellulose nitrate, methylcellulose and carboxymethyl cellulose). Due to its broad range of applications and easy processability, the modification of cellulosic biomass into cellulose acetate has been the most commonly explored approach. In 2015 the global cellulose acetate production reached the astonishing value of 4.82 billion tones and the trend is upward (Zion Market Research, 2016). While at large scale cellulose acetate is synthesized primary from wood and cotton pulp via the acetic acid route (standard acetylation), at experimental level (bench tests) the use of agroindustrial residues and environmentally friendly synthesis routes have been increasingly reported. These alternative synthesis routes are mainly focused on replacing the sulfuric and acetic acids, used respectively as catalyst and reaction media in the standard acetylation, by ecofriendly reagents, such as iodine as catalyst in the presence of acetic anhydride (Biswas et al., 2005; Das et al., 2014), phosphotungstic acid as catalyst (Fan et al., 2013), room temperature ionic liquid (Cao et al., 2007; Wu et al., 2004) and solid superacid SO2-4/ZrO2 (Yan et al., 2006). However, despite the potential environmental benefits resulting from the application of these substituent reagents, the aforementioned studies lack on environmental impact assessment through standardized and reliable tools. Moreover, almost unanimously, the authors made use of harsh chemicals and processing prior to acetylation, such as the conventional alkali and bleaching pretreatment applied to isolate the cellulose from the biomass. The extraction of cellulose through fractionation techniques is an essential step since cellulosic fibers do not occur as an isolated component in agroindustrial residues, and the other noncellulosic components (such as hemicellulose and lignin) can negatively affect the modification (Candido et al., 2017) and dissolution (Reddy et al., 2017) processes of cellulose.

The fractionation techniques, also named as pretreatment methods, can be classified into four categories, namely physical, chemical, physicochemical and biological (Hassan et al., 2018). Currently, the pretreatment step is considered one of the main bottlenecks to the cost-effective valorization of agroindustrial residues. Its application may demand, besides high energy and material consumption, the use of harsh chemicals, which implies the production of excessive wastes. These led to the development of new approaches based on the "Green Chemistry" concept, among which it is worth to mention liquid hot water (LHW), stem explosion, organosolv (Bhutto et al., 2017) and fine-tuned green solvents, such as deep eutectic solvent (Mamilla et al., 2019), ionic liquid (Yoo et al., 2017) and supercritical fluids (Farrán et al., 2015). Recently, great attention has also been focused on combining pretreatments, as reported by Araújo et al. (2019) and Sun et al. (2016). Combined treatments, carried out as multi-stage or in simultaneous, have shown to be more effective to fractionate lignocellulosic biomass than single treatments. Furthermore, they can contribute to reducing costs, time of processing, as well as the use of chemicals and energy (Kumari and Singh, 2018).

Although some recent studies have reported the application of potential less impacting process (pretreatments and acetylation techniques) to synthesized cellulose acetate from lignocellulosic biomass, for the best of our knowledge, there are no reports addressing the environmental performance of these techniques to the concerned application. Fan et al. (2009) tried to design a less impacting process by pretreating rice straw with dilute alkaline and acid solutions, followed by an acetylation reaction with acetic anhydride and phosphotungstic acid. Despite the method being effective to produce cellulose acetate with low substitution degree, conventional chemical reagents have still been used and the environmental feasibility of the approach used has not been evaluated. Cao et al. (2018) treated green landscape wastes with dilute-phosphoric-acid in an autoclave at moderate temperatures, and the solid fraction obtained was acetylated through the conventional acetic acid method. Although the developed process proved to be economically viable, mainly due to the possible separation and valorization of a xylose rich liquor after pretreatment, studies have not been carried out within the scope of environmental impacts assessment. Therefore, there is still a need to explore integrated pretreatments and acetylation solutions to prepare biomassderived cellulose acetate, and to perform environmental assessments to confirm the real environmental viability of the methods used. In this regard, life cycle assessment (LCA) has been progressively used to analyze the environmental viability of bio-based products. Moreover, LCA has proven to be reliable for the evaluation of environmental sustainability of products and methodologies within the framework of lignocellulosic biomass valorization. For instance, Arvidsson et al. (2015) used LCA to investigate the environmental impacts of three production routes to obtain cellulose nanofibrils from wood pulp. Boonterm et al. (2016) used LCA to evaluate and compare the potential environmental impacts of natural fiber thermal insulation pads produced by different ricestraw cellulose extraction processes. Recently, Benavente et al. (2017) evaluated the environmental impacts associated with the use of hydrothermal carbonization to treat olive mill wastes and compared to conventional end-of-life solid waste treatments using LCA.

In this frame, the purpose of this work is to use potential environmentally-friendly pretreatment and acetylation techniques to synthesize cellulose acetate from corncob, and further to calculate the environmental impacts related to the applied process. The pretreatment method applied is described on a recent publication of Araújo et al. (2019), who used a combined LHW-dilute NaOH solution treatment to pretreat biomass and obtained celluloseenrich final samples with great yield. The acetylation step was based on the solvent-free method as suggested by Das et al. (2014), since remarkable yields were obtained from the acetylation of rice husk. The environmental impacts resulting from this synthesis route, here named as green approach (composed of LHW-Dilute NaOH pretreatment and the solvent-free acetylation) was determined through LCA and compared with those related to a conventional route (or conventional approach), composed of alkalibleaching pretreatment and acetic acid process acetylation. The specific objectives of this work are: (1) synthesize cellulose acetate by means of green and conventional approaches; (2) investigate the physical-chemical properties of both synthesized samples in order to assess their similarities and consequent suitability to be comparable through LCA; (3) develop thin films from the cellulose acetate synthesized by the green approach to proves its potential application as a value-added product; (4) and modeling LCA scenarios in order to assess and compare the environmental impacts resulting from the green and conventional approaches.

Materials and methods

Materials

Corncob (CC) residue was supplied by local agricultural cooperatives (situated at the north of Portugal) and cellulose sheets (cellulose pulp) were provided by a local factory. Cellulose acetate (Mñ50.000 by GPC) and Sodium hydroxide (NaOH) pellets were acquired from Sigma-Aldrich. Acetic anhydride (>99%) and sodium thiosulfate ($Na_2 S_2O_3$)(98.50%) were purchased from Acros Organics. Iodine (99.80%), acetic acid glacial (99.88%), sulfuric acid (H_2SO_4)($>$ 95%), ethanol (99.80%), methanol (99.99%), dichloromethane (DCM) (99.88%) and dimethyl sulfoxide (99.99%) were purchase from Fisher Chemical. All the reactants were used without further purification.

Isolation of cellulose from corncob

The corncob was firstly milled to particles sizes from 0.25 to 0.5 mm . Cellulose extraction from dried milled corncob was carried out by applying a combined green pretreatment previously reported (Araújo et al., 2019). Briefly, a two-step process was performed by combining a first stage-liquid hot water (LHW), followed by dilute NaOH solution treatment. The LHW was performed at 190°C, 0.79MPa, for 30 min under constant mechanical stirring, in a stainless steel cylindrical reactor with an approximate volume of 2 L and feedstock loading rate of 10%(w/v). At the end of this treatment, the insoluble solid was collected, thoroughly washed with deionized water and dried at 60°C. Then, the dried liquid hot water-treated corncob (LHW - CC) was soaked in 2wt%NaOH at 90°C for 1.5 h at a 1/30 solid/liquid ratio (w/w) under magnetic stirring. The alkali treated LHW-CC (NaOH-LHW-CC) was then filtered and washed several times with deionized water until colorless. The resulting material was dried at 60°C and stored.

Synthesis of cellulose acetate

Two different acetylation methodologies were carried out, one proposed herein, referred to as a green acetylation, which is based on the method described by Das et al. (2014) with some modifications, and another one mentioned as standard acetylation, which is a commonly used technique and presents similarities with the acetic acid method (at the level of chemical components used) applied at industrial level to produce cellulose acetate. Regarding the green acetylation, basically, 0.4 g of cellulose extracted from corncob was taken into a 100 mL round bottom flask, and 20 mL of acetic anhydride and 0.6 g of iodine were added. The mixture was heated to 80°C and left reacting for 5 h with stirring. After that, the solution was allowed to cool at room temperature and treated with 10 mL saturated solution of sodium thiosulfate with stirring, in order to reduce the iodine to iodide. Then, the round bottom flask containing the mixture was place inside a beaker with cold water and 60 mL of ethanol was added to the mixture and stirred for 60 min . The product was filtered and thoroughly washed with 75% (v/v) ethanol and distilled water to remove the unreacted acetic acid and byproducts. The solid material obtained was dried at 60°C in an oven under vacuum and further dissolved in dichloromethane and filtered. Cellulose acetate was formed as a film inside the flask after evaporating the filtrate, which was easily removed without any additional treatment and dried at 60°C in a vacuum oven overnight.

The standard acetylation applied is based on methods described by Jo et al. (2016), Coletti et al. (2013), Bello et al. (2016) and Cao et al. (2018), and was carried out, initially, by reacting the extracted cellulose at different cellulose:reagents ratio (w/w) with acetic acid (1:31.5), acetic anhydride (1:14) and sulfuric acid (1:0.08) in a 100 mL round bottom flask. The mixture was heated to 40°C and magnetically stirred for 3 h . After that, the reaction was allowed to cool to room temperature, filtered and the filtrate was collected in a large beaker. Then, methanol was added, and the mixture was stirred overnight at room temperature. Further, the solution was filtrated, and the cellulose acetate was collected in a paper filter and placed in Petri dishes to evaporate and dry at 60°C in a vacuum oven overnight. The obtained dried cellulose acetate was dissolved in dichloromethane, filtered and collected as a film after evaporating the filtrate. Then, it was dried at 60°C in a vacuum oven overnight.

Chemical characterization

FTIR spectra of pretreated corncob, cellulose pulp and cellulose acetate samples were recorded on a Jasco FT/IR-4100 spectrometer, in the wavelength range of $400-4000\ \mathrm{cm}-1$ and at a resolution of 4 $\mathrm{cm}-1$, using the attenuated total reflection technique. Thermogravimetry analyses of untreated corncob extracted cellulose, cellulose pulp and CA samples were performed on TA Instruments SDT 2960 model. The sample weight was in the range of $5-10\mathrm{mg}$ and heated from 30 to $700^{\circ}\mathrm{C}$ at a rate of $10^{\circ}\mathrm{C/min}$, under purified argon. The $^{1}\mathrm{H}$ NMR spectroscopy using a Bruker Avance III, 400 MHz , and deutered dimethyl sulfoxide as solvent. The spectra were internally referenced to the residual proton tetramethylsilane (TMS, $\delta=0.00\mathrm{ppm}$) and the chemical shifts (δ) are reported as part per million (ppm). Based on Biswas et al. (2006), the average number of hydroxyl groups replaced by acetyl groups was determined from HNMR results and used for calculating the degree of substitution (DS) of synthesized CA samples. The DS was calculated by dividing $1/3$ of the three methyl proton absorbance peak area of acetyl group, in the range of $1.5-2.2$, by $1/7$ of the seven anhydrocellulose absorbance peak area, in the range of $3.5-5.2\mathrm{ppm}$ (Eq. (1)).

$$DS=\frac{7\times\int_{1.5}^{2.2}f(x)dx}{3\times\int_{3.5}^{5.2}f(x)dx} \qquad (Eq.1)$$

Chemical composition of untreated and treated biomass

The chemical composition of milled corncob and pretreated corncob were measured as follows (Araújo et al., 2019; Carrier et al., 2011; Chen et al., 2016; Saldarriaga et al., 2015; Teng et al., 1997): by means a Gaussian distribution model, the first derivative of TGA curves of samples were deconvoluted and the thermal decomposition of cellulose, hemicellulose and lignin were assessed individually; the percentage of each component on samples was calculated as the integrated area above the respective pyrolysis curve (the modeled equation, as well as graphs and parameters are available in the supplementary information A).

Cellulose acetate film preparation

Cellulose acetate films were prepared by the casting method. Initially, 50 mg of CA synthesized by the green approach was mixed with 6 g of DCM and stirred for 5 h at 35°C. After that, the mixture was sonicated for 10 min in order to remove air bubbles. Then, the solution was poured on a Teflon dish with 4 cm of diameter and placed in the vacuum oven at $40\ ^{\circ}\mathrm{C}$ to allow the solvent to evaporate.

Morphological analysis

The untreated and pretreated samples were used as stored for analysis and their surface morphologies were observed by scanning electron microscopy (SEM) using a FEI Nova 200. The samples were coated with a thin layer of Au/Pd prior to analysis. Regarding the surface morphologies and cross-section analysis of the cellulose acetate film, the same equipment and coating were used. However, the CA film was firstly frozen in liquid nitrogen and then cut in small fragments to analyze the cross-section.

Dynamic mechanical analysis of cellulose acetate film

A PerkinElmer DMA 800 Instrument was used at a dualcantilever bending mode and at a constant frequency in order to obtain the storage modulus (E'), the loss modulus (E'') and the damping capacity ($\tan\delta$) [36]. CA Films with the size of 20/5.7/ 0.04 mm , approximately, were analyzed under temperature ranging from 40 to 160°C, heating rate of 5°C/min, preload 1 N , 10μ m of displacement amplitude and 1 Hz of frequency. Dynamic Young's modulus (E*) was also determined by using Equation (2) (Menard, 1999).

$$E^{*} = \sqrt{(E')^{2} + (E'')^{2}} \qquad (Eq. 2)$$

Life cycle assessment

Goal and scope

LCA performed in this study aims to compare the environmental impact associated with two approaches used to synthesize CA from corncob. The concerned methods are distinguished by their processing design; while one takes into account strategies under the green chemistry, the other employs the use of conventional techniques. Both product systems contemplate the production of materials and energy, as well as pollutants emission, accounted at the level of laboratory scale when recorded as primary data. Corncob production and process such as transport and wastewater treatment are not considered in this study. Transportation of residues and chemicals are also not considered since processing plants, in this scope of this manufacturing purpose, are still at the laboratory stage, and consequently their locations have not yet been defined. Notwithstanding, in a scenario projected to facilitate and make feasible logistic issues, these industrial plants would be installed in proximity to companies that generate such wastes, and thus the transportation of residues at least could be disregarded. The functional unit adopted was the synthesis of 10 g of cellulose acetate. The comparison between the results of the two product systems modeled, in terms of the same FU, was validated through the physical-chemical characterization performed previously.

Modelling approach

LCA modeling was performed using the Open Life Cycle Assessment software (openLCA), developed by the GreenDelta and suitable to conducting sustainability assessment of products, process and services (Noi et al., 2017). This study followed the guidelines specified in ISO14044 (ISO, 2006), and based on elucidations about LCI framework modelling presented in the International Reference Life Cycle Data System (ILCD) Handbook (European Commission, 2011). Furthermore, it is considered an attributional

LCA, with similarities, in scope, with studies presented by Arvidsson et al. (2015) and Walser et al. (2011). As mentioned before, the cultivation, harvesting and processing of maize are not included within the system boundary as corncob is a by-product of maize with no market value, often disposed of or burned in the harvest field. Moreover, despite the potential application of the synthesized CA as a polymeric film (further presented in the subtopic 2.5), their processing and applicability have not been technically and economically defined yet, and therefore, the end-of-life of the material, as a commercial product, is also not included in the boundary system. Consequently, a gate-to-gate perspective is assigned to this study. As emphasized by Arvidsson et al. (2015), this kind of perspective is particularly important for materials that might have many subsequent applications, of which some have not yet been developed.

Scenarios description and life cycle inventory data

Two scenarios were modeled and assessed as shown in Fig. 1. The one Indicated as "Green Approach" (left branch in Fig. 1) includes corncob milling, the combined LHW-Dilute NaOH pretreatment, green acetylation based on (Das et al., 2014), washing, drying and the respective inputs (water, electricity and chemicals) and outputs. The other mentioned as "Conventional Approach" (right branch in Fig. 1), was modeled as a referential scenario since it encompasses the corncob milling, a conventional pretreatment and a standard acetylation technique commonly reported in the literature. The detailed description of the combined LHW-Dilute NaOH pretreatment, the green acetylation and the standard acetylation have already been presented in previous topics of materials and methods. When it comes to the conventional pretreatment (alkali and bleaching), it was not experimentally performed, but rather modeled according to Silvério et al. (2013), Boonsombuti et al. (2013) and Rosa et al. (2010). Succinctly, the milled dried corncob was treated with a sodium hydroxide aqueous solution of $2\%(w/w)$ for 2 h at $100^{\circ}C$ under magnetic stirring, and then filtered and washed with distilled water. After washing, the alkaline treatment was repeated, and the resulting material was dried overnight at $60^{\circ}C$ in an oven. After this treatment, the fibers were bleached with a solution made up of equal parts ($v:v$) of acetate buffer (27 g NaOH and 75 mL glacial acetic acid, dilute to 1 L of distilled water) and aqueous chlorite ($1.7 wt\% NaClO_2$ in water). This treatment was performed at $80\ ^{\circ}C$ for 6 h . The bleached fibers were filtered, washed with distilled water and dried at $60^{\circ}C$ overnight. After the alkali-bleaching treatment, it was estimated a yield of 40%.

The inventory data related to all process here modeled was sourced from previously publications, life cycle assessment studies and Ecoinvent (version 3.3), as well as calculated experimentally. Inputs or process highlighted with an asterisk in the product system flow chart do not exist in Ecoinvent database, therefore they had to be modeled as individual process in Open LCA, based on background data from previously published studies. All assumptions made, as well as input and output associated with processes in both product systems, are described in detail in supplementary information B.

Impact categories

LCA impact categories, recommended under the International Reference Life Cycle Data System (European Commission, 2011), relevant to the work, as already reported in similar studies and in accordance with the ISO 14044 (ISO, 2006), were used. The chosen categories, shown in Table 1, are segmented into non-toxicity, toxicity and resource related impact categories. In the absence of normalization references for Brazil, it was used global normalization references provided by Sala et al. (2017), for the reference year

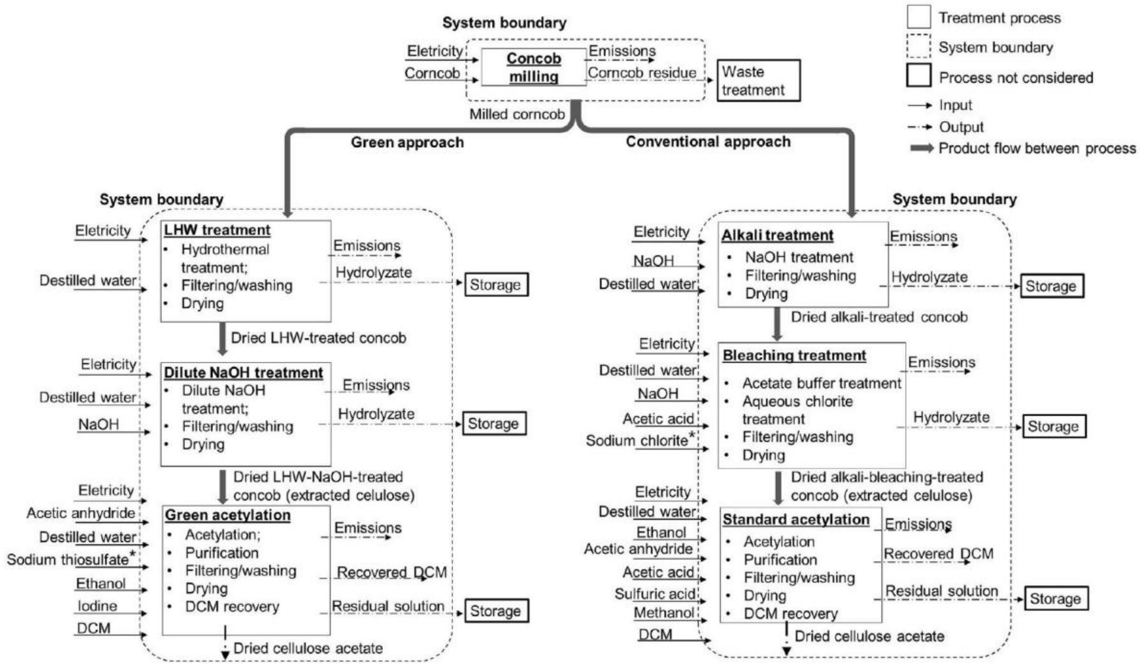

Fig. 1. Flow chart of product systems: Left branch - modeled green approach scenario; right branch - modeled conventional approach scenario. Inputs highlighted with an asterisk do not exist in Ecoinvent database and had to be modeled in OpenLCA.

Table 1
Environmental impact categories and normalization references used. CFC: Chlorofluorcarbon, kBq: Kilobecquerel, NMVO: Non-Methane Volatile Organic Compounds; CTU: Comparative Toxicity Unit, e: Ecotoxicity, h: Human.

Impact category	Abbreviation	Method	Normalization reference	Unit
Non-toxicity related impact categories				
Global Warming Potential	GWP	IPCC 2013	8400	kg CO_2-eq/person
Stratospheric Ozone Depletion	ODP	CML 2001 (Guinée et al., 2002)	2.34×10^{-2}	kg CFC11-eq/person
Ionizing Radiation - Human Health	IR	ILCD 2016 (European Commission, 2012)	4.220	kBq-U-235-eq/person
Photochemical Ozone Formation	POF	ReCiPe (H) (Goedkoop et al., 2013)	40.6	kg-NMVO-eq/person

Freshwater Eutrophication	FE	ReCiPe (H) (Goedkoop et al., 2013)	0.734	kg P-eq/person
Marine Eutrophication	ME	ReCiPe (H) (Goedkoop et al., 2013)	28.3	kg N-eq/person
Terrestrial Acidification	TA	ILCD 2016 (European Commission, 2012)	55.5	Mol H+-eq/person
Terrestrial Eutrophication	TE	ILCD 2016 (European Commission, 2012)	177	Mol N-eq/person
Particulate Matter	PM	Selected LCI results (Hischier et al., 2010)	2.76	kg $PM_{2.5}$ /person
Toxicity related impact categories				
Human toxicity, Cancer Effect	HTc	USEtox (Rosenbaum et al., 2008)	3.75×10^{-5}	CTUh/person
Human Toxicity, non-Cancer Effect	HTnc	USEtox (Rosenbaum et al., 2008)	4.75×10^{-4}	CTUh/person
Freshwater Ecotoxicity	ET	USEtox (Rosenbaum et al., 2008)	1.18×10^{4}	CTUe/person
Resource impact categories				
Depletion of Abiotic Resources - Fossil	Rf	Cumulative Exergy Demand (Hischier et al., 2010)	6.54×10^{4}	MJ-eq/person

of 2010. This limitation does not compromise the results (normalized impacts) since, at laboratory activity level, many chemical reagents are produced and supplied by foreigner companies. Moreover, in the absence of regional normalized factors it is preferable to use global factors, as some impact methods (such as CML 2002 and Usetox) present a global scope for the application of their impact categories. By using global values, it is also avoided an imbalance in normalization resulting from comparison with activities of different populations (Stranddorf et al., 2005).

Sensitivity analysis

The sensitivity of the modeled product systems (green approach and conventional approach) was performed via scenario analysis. It was first modeled a scenario named as "intermediate approach" in order to assess the effect of changing the alkali-bleaching pretreatment at the conventional approach by the combined green pretreatment. On impact categories, this change allows comparing the influence of the two main processes (pretreatment and acetylation) on both product systems.

Moreover, taking into account the different acetylation yields reported in literature as a result of the application of the standard acetylation (Bello et al., 2016; Das et al., 2014; Wan Daud and Djuned, 2015), improvements over the concerned technique, represented as a percentual increase in weight gain, were assumed. For this, all the process and parameters regarding the green pretreatment were kept unchanged and percentual increments of 10,20 and 30% were added upon the yield obtained experimentally for the standard acetylation (in the scope of the conventional approach). These changes gave rise to three scenarios with results presented as impact increment (in percentage) taking as baseline reference the green approach scenario. Through this, it is possible to assess the environmental viability of performing the green approach in face of possible variations in the standard acetylation yield.

Results

Cellulose extraction and chemical composition

The determined chemical composition of untreated corncob presented hemicellulose (47.32%), lignin (16.32%) and cellulose (36.35%) fractions similar to others in literature (Lee et al., 2014; Silvério et al., 2013). Remarkable changes on chemical composition of corncob were verified after the combined pretreatment. The LHW was performed to solubilize the hemicellulose, while the dilute- NaOH treatment was applied to remove lignin. The mass recovery after the combined pretreatment was around 38%. After the treatment, the cellulose, hemicellulose and lignin contents were 84.73,4.58 and 10.68%, respectively. These values indicate that the combined treatment applied worked properly to fractionate the cellulose from corncob, which was obtained as a fine, light gray and fluffy powder.

Cellulose acetate syntheses - degree of substitution and yield

The acetylation methods performed in this study differ from each other since the chemical reagents used and the reactions mechanisms are dissimilar. Briefly, the green acetylation runs as heterogeneous process in which, firstly, the iodine activates the carbonyl carbon of the acetic anhydride in the presence of an alcoholic group. Then, the acetic anhydride reacts with hydroxyl groups of cellulose and the esterification takes place, leading to the generation of acetic acid as a byproduct (Biswas et al., 2006; Das et al., 2014). Conversely, the standard acetylation occurs as a homogeneous process, through which H_2SO_4 acts as a catalyst helping to dissolve the cellulose pulp in the reaction media (acetic acid). Following, subsequent acetylation via displacement of hydroxyl with acetyl groups by acetic anhydride is triggered (Luo et al., 2013).

The applied synthesis methods gave different acetylation yields (calculated as dry weight percent gain), calculated as 60% for the green acetylation and 40% for the standard acetylation. These results are comparable with others yields derived from the acetylation of cellulose-rich biomasses, such as rice husk (66%) (Das et al., 2014), cotton stalk (48.5%) (Bello et al., 2016), cotton linters (54%) (Mostafa and Tayeb, 2018) and landscaping waste (45.6%) (Cao et al., 2018). These indicate that the optimization of the synthesis using iodine as catalyst in the presence of acetic anhydride, proposed by Das et al. (2014) for the acetylation of rice husk, also works out for the acetylation of corncob.

Fig. 2 shows the ^{1}H NMR spectra of CA synthesized from green (Fig. 2a) and standard (Fig. 2b) acetylation methods. Both spectra display typical resonances of CA chemical structures, with peaks in the region of $3.5 - 5.3$ppm related to the protons bonded to the seven ring protons of anhydroglucose (AGU) (indexes H1 to H6 in both graphs). The successful synthesis of CA by both methods was confirmed by the presence of peaks in the region $2.2 - 1.5$ppm, assigned to the methyl (CH_3) of acetyl groups. The peak around 2.49 and 3.3 are related to the protons of DMSO and residual water, respectively. The DS of CA samples were calculated based on methodology previously described (Biswas et al., 2006). Both

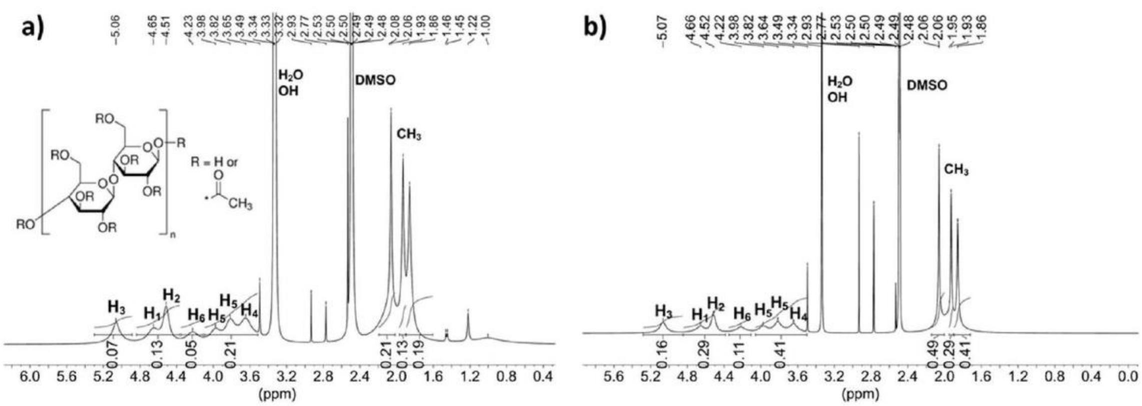

Fig. 2. ^{1}H NMR spectra of cellulose acetate synthesized by (a) green and (b) standard acetylation methods.

methodologies resulted in synthesized CA with high DS, namely 2.68 and 2.89 obtained by the green acetylation and by the standard acetylation, respectively. Cellulose acetate with DS varying from 2.5 to 3, synthesized from standard acetylation, or through few variations of this technique, was also obtained by Jo et al. (2016), Coletti et al. (2013), Candido et al. (2017) and Cao et al. (2018). By varying parameters of the green acetylation method, Das et al. (2014) synthesized cellulose acetate with DS ranging from 2.12 to 2.91. These results demonstrate that both methodologies originate CA with similar characteristics and in agreement with other studies.

Fourier transformed infrared analysis

By comparing the FTIR data of untreated and pretreated corncob (Fig. 3), a reduction in bands corresponding to lignin and hemicellulose is verified. The absence of peaks around 1598 cm^{-1}, 1513 cm^{-1} arises from the extraction of the $C = C$ bonds in aromatic ring stretching ascribed to lignin (These peaks are clearly identified in the FTIR spectrum of raw corncob, available in the

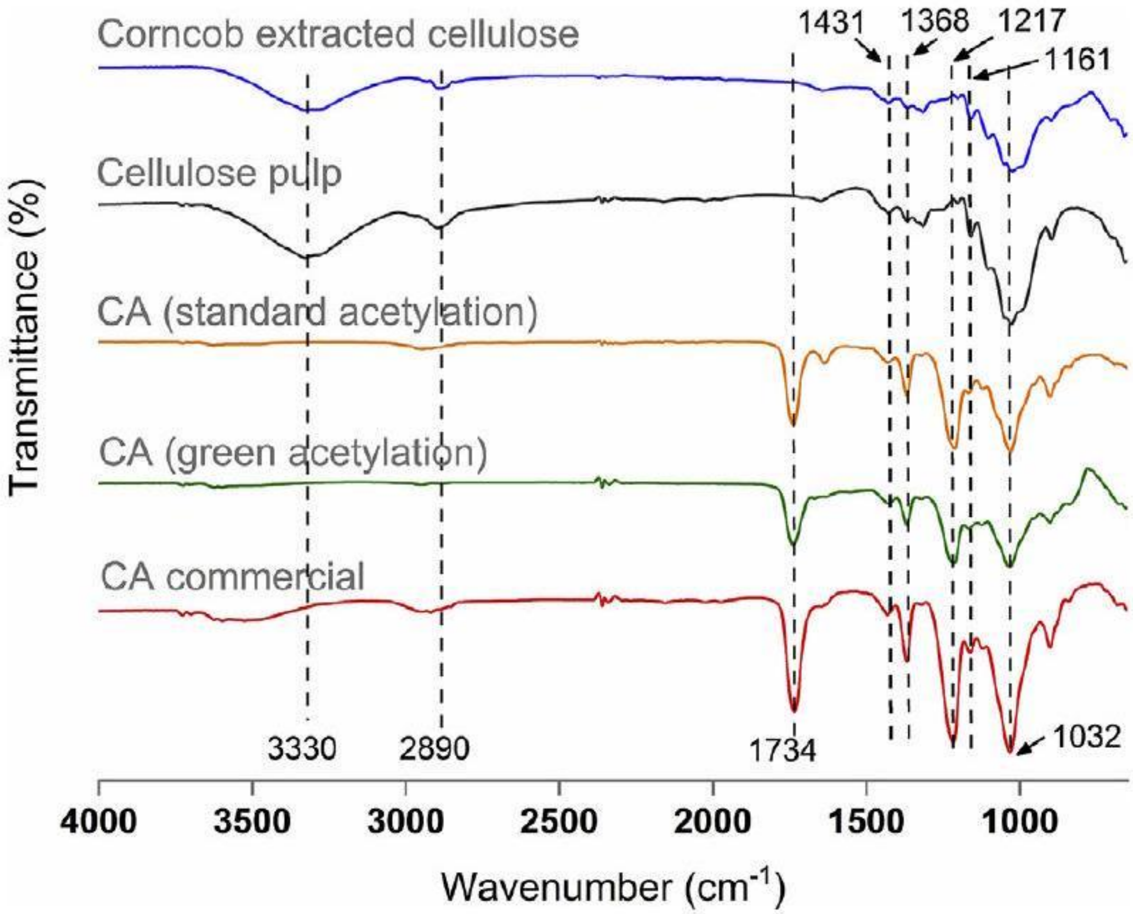

Fig. 3. FTIR spectra of cellulose pulp, commercial CA, extracted cellulose (LHW-dilute NaOH pretreatment) and CA synthesized by green and standard acetylation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

supplementary information C). Besides, the band at $1250\ \mathrm{cm}^{-1}$ was also reduced and can be related to $\mathrm{C-O}$ stretching in the aryl group of lignin and acetyl group in hemicellulose (Ma et al., 2015; Reddy et al., 2017). These results indicate the efficient removal of noncellulosic components by the combined pretreatment and the consequent purification of the cellulosic fraction.

The presence of absorbed peaks related to the cellulose chemical structure (clearly observed by comparing the FTIR curves of the pretreated sample with the pulp cellulose), along with the rising of new absorption peaks in acetylated samples (Fig. 3), namely $1734\ \mathrm{cm}^{-1}$, $1368\ \mathrm{cm}^{-1}$ and $1217\ \mathrm{cm}^{-1}$ related to $\mathrm{C=O}$ stretching of ester group, $\mathrm{C-H}$ in $\mathrm{O-(C=O)-CH_3}$ and $\mathrm{C-O}$ stretching of acetyl groups, respectively, confirm the successful acetylation of corncob extracted cellulose. Moreover, the reduced intensity of peaks assigned to -OH stretching also provides evidence of acetylation, since it results from the substitution of -OH groups in cellulose by acetyl groups. Lately, the definitive proof of the successful synthesis of cellulose acetate by both methods is taken from the comparative analysis (peak-by-peak) between the synthesized CA samples and the CA commercial. Furthermore, it is interesting to note that the peak at 1290, originated from C-H stretching, is more pronounced in the commercial CA curve. The higher absorbance at this wavelength indicates that the commercial CA has a lower degree of substitution than the synthesized CA samples, which corroborates with the other analysis and respective results. The absence of absorption peaks around $1700\ \mathrm{cm}^{-1}$ and $1760-1840\ \mathrm{cm}^{-1}$ indicates that the obtained synthesized CA are free of acetic acid and unreacted acetic anhydride (Chen et al., 2016; Das et al., 2014; Wan Daud and Djuned, 2015).

Thermogravimetric analysis

The TG and DTG curves of all samples are presented in Fig. 4a and *b*, respectively. In general, degradation reactions observed in all curves occurred in a single step and in a narrow temperature range, allowing to infer that all samples are composed mainly by a unique component. The onset (T_{onset}) and end (T_{end}) temperatures of both synthesized cellulose acetate samples are identical ($T_{onset} = 320°C$, $T_{end} = 366°C$), and their maximum weight loss rate (T_{max}) slightly differ, as shown in Fig. 4 and Table 2. Taking into to account the errors associated with measurement, these results clearly show that, notwithstanding the different acetylation techniques applied, the thermal stability of synthesized CA samples are very similar. Furthermore, T_{onset} and T_{max} of synthesized CA samples are slightly

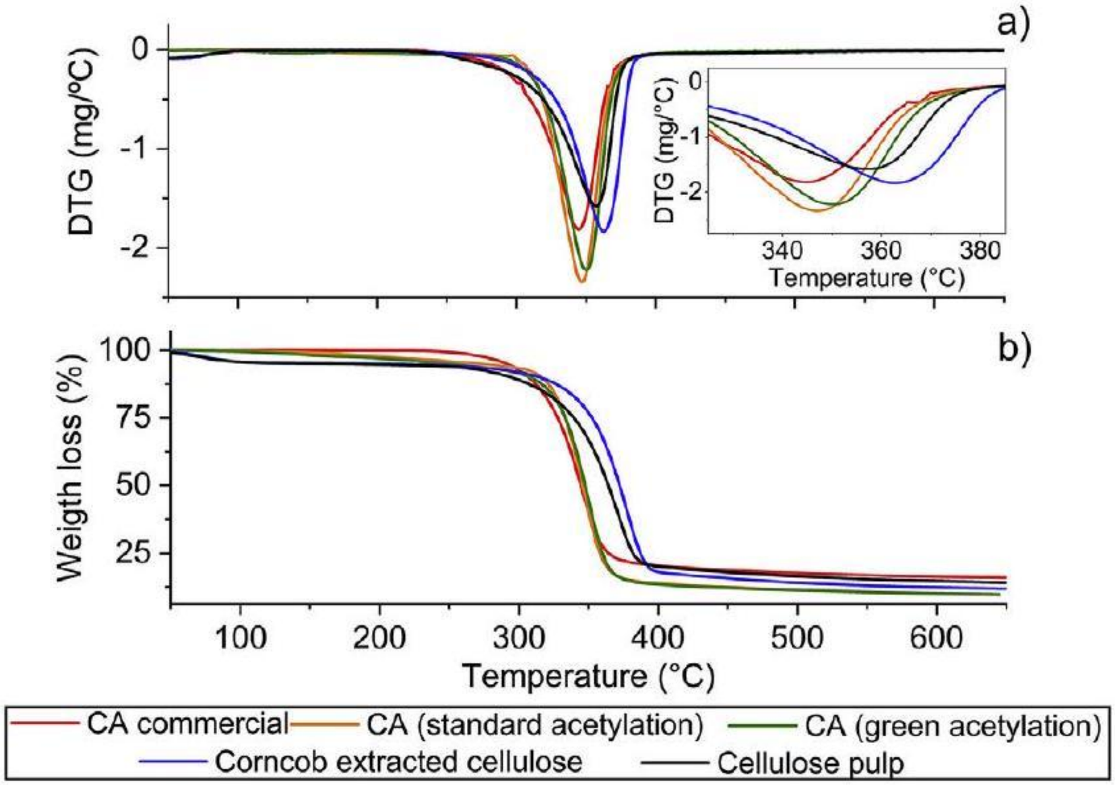

Fig. 4. (a) TG and (b) DTG (as well as inset plot in the graph 4b of DTG ranging from 330°C to 390°C) curves of cellulose pulp, commercial CA, extracted cellulose (LHWdilute NaOH pretreatment) and CA synthesized by green and standard acetylation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Thermogravimetric results for cellulose pulp, commercial CA, extracted cellulose (LHW-dilute NaOH pretreatment) and CA synthesized by green and standard acetylation. T_{onset} : onset temperature, T_{max} : temperature of maximum weight loss rate, T_{end} : end temperature.

Sample	DS	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)
CA commercial	2.4	310	345	361
CA (green acetylation)	2.68	320	350	366
CA (standard acetylation)	2.86	320	347	366
Cellulose pulp	0	327	357	383
Corncob extracted cellulose	0	242	363	392

higher than that of the commercial CA, probably due to their higher DS or to the origins of precursor materials. As evidenced by Cao et al. (2010) and Morgado and Frollini (2011), the thermal stability of CA samples increases as the DS value increases. This can be explained by the fact that, as DS increases, more acetyl groups are introduced onto the C2 and C3 carbons of the anhydroglucose unit (AGU), which require more energy when compared to the least sterically hindered group C_{6COOCH}, and increase the apparent activation energy for thermal decomposition, leading to an increase in thermal stability (Morgado and Frollini, 2011).

The most remarkable changes on thermal profiles are verified when comparing the extracted cellulose profile with the synthesized CA curves. The onset and end temperatures of the extracted cellulose ($T_{onset} = 294°C, T_{end} = 361°C$) are higher than those of CA obtained by both acetylation methods (Fig. 4 and Table 2). Likewise, the temperature of maximum weight loss rate related to the extracted cellulose ($363\,°C$) is higher than that of synthesized samples (CA green acetylation $-350°C$; CA standard acetylation $347°C$). These indicate that the thermal stability of the extracted cellulose decreased due to acetylation, which is in agreement with the literature (Cao et al., 2010; Yang et al., 2015).

The thermogravimetry analysis, along with the previous chemical characterization, were performed first and foremost to investigate the properties of cellulose acetate produced from both, green and standard acetylations, and assess their suitability to be compared via LCA, which was successfully confirmed. Upon reaching this target of the work, the next following two topics will be mostly dedicated to the elucidations about the potential application of the CA produced by the green approach as a film forming.

Scanning electron microscopy analysis

A cellulose acetate film was produced from CA samples synthesized by the green approach in order to demonstrate the potential of this material for industrial applications. SEM images of the raw corncob, LHW-NaOH pretreated corncob, as well as the cellulose acetate film surface and cross-section are presented in Fig. 5.

As a result of the combined green pretreatment, the compact structure of the corncob (Fig. 5a) was unpacked and fractionated into cellulosic fibers with irregular shape and size (Fig. 5b). After the acetylation of extracted cellulose and subsequent dissolution in dichloromethane and casting, the fibrous shape of the extracted cellulose (Fig. 5b) was turned into a film with a quite smooth, flat and homogeneous surface (Fig. 5c and d). The film was obtained as a circular shape as presented in Fig. 6b, with a thickness of approximately 0.025 mm . This indicates that the acetylation reaction successfully occurred, and reagents used could penetrate into the cellulosic fibers. The few porous and rough surface in the cross section and film surface may be attributed to the solvent evaporation process.

Dynamic mechanical analysis of cellulose acetate film

The viscoelastic behavior of the produced film was investigated by dynamic mechanical analysis (Fig. 6a). The acetylation reaction, as well as the cellulose acetate film prepared, are depicted in Fig. 6b. The viscoelastic properties of the film were characterized by the storage modulus (a measure of the material's ability to recover from deformation), the loss modulus (a measure of the material's ability to loses energy as heat) and the Tan δ or damping (an indicator of how efficiently the material loses energy to molecular rearrangement and internal friction). The behavior of E' and E'' in Fig. 6a is typical of amorphous thermoplastics, as no defined transition zones are identified, but rather a continuous decrease along the temperature range. This can be associated to the introduction of acetyl groups onto the AGU unity, which prevent the packaging of cellulose chains and the resultant polymer becomes more amorphous and less opaque (de Freitas et al., 2017). At lower temperatures, despite the presence of a secondary relaxation, the molecules are reasonable immobile and remain in energy elastic state, which was characterized by a drop in E' of about 0.8 GPa over the temperature range $40 - 138\ ^{\circ}\mathrm{C}$. This is followed by an intermediate state, the glass transition, characterized by a sharp drop in E' of about 0.8 GPa in a short temperature range $138 - 152^{\circ}\mathrm{C}$, and further by an entropy elastic state at elevated temperatures. For this class of material, the maximum operating temperature (i.e. the maximum temperature at which the material possesses the stiffness to resist deformation and the flexibility to not shatter under strain) is usually defined by the glass transition temperature ($\mathrm{T_g}$), which was found to be $140^{\circ}\mathrm{C}$, approximately, using the peak of Tan δ curve method. Similar $\mathrm{T_g}$ values of other cellulose acetate films were reported by de Freitas et al. (2017), Bao et al. (2015), Abdel-naby and Al-ghamdi (2014) and Számel et al. (2008). However, the $\mathrm{T_g}$ found may differ from others in literature since this property is intrinsically related to the DS, and higher DS leads to a lower T_g.

The E'' reaches the maximum dissipated energy at $136^{\circ}\mathrm{C}$, from which nonelastic deformation takes place. From this point until $160^{\circ}\mathrm{C}$ the storage modulus drops roughly one decade. A broad secondary peak in E'' is also verified at about $64^{\circ}\mathrm{C}$. In response there is a decrease in E' from $40^{\circ}\mathrm{C}$ to $100^{\circ}\mathrm{C}$, probably originated from the natural mobility of chains in response to temperature rising and relaxation transitions triggered by local mobility of chains plasticized with water (Startsev et al., 2017).

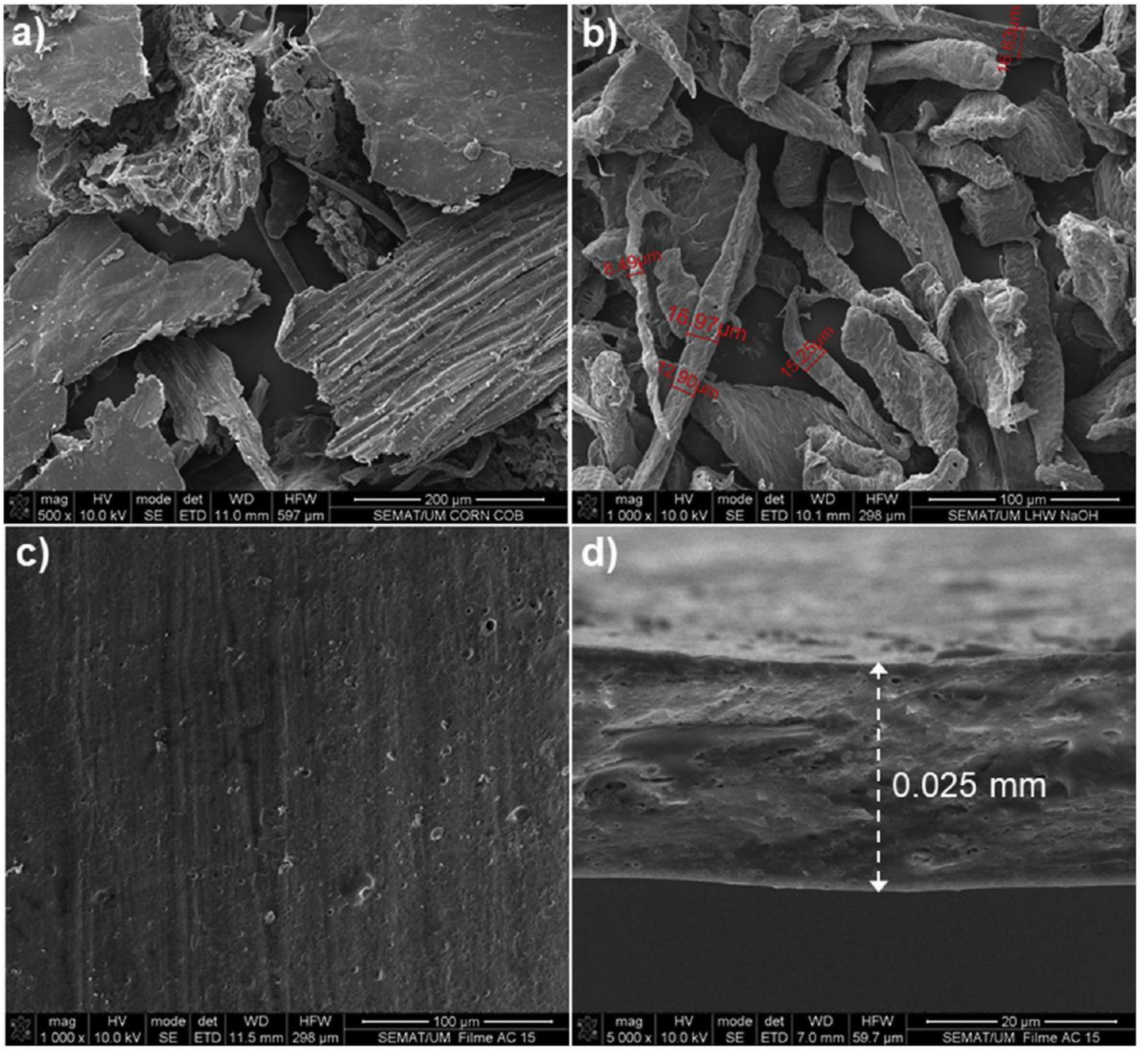

Fig. 5. SEM micrographs of (a) untreated corncob, (b) LHW-dilute NaOH pretreated corncob, as well as the (c) surface and (d) cross-section of the cellulose acetate film.

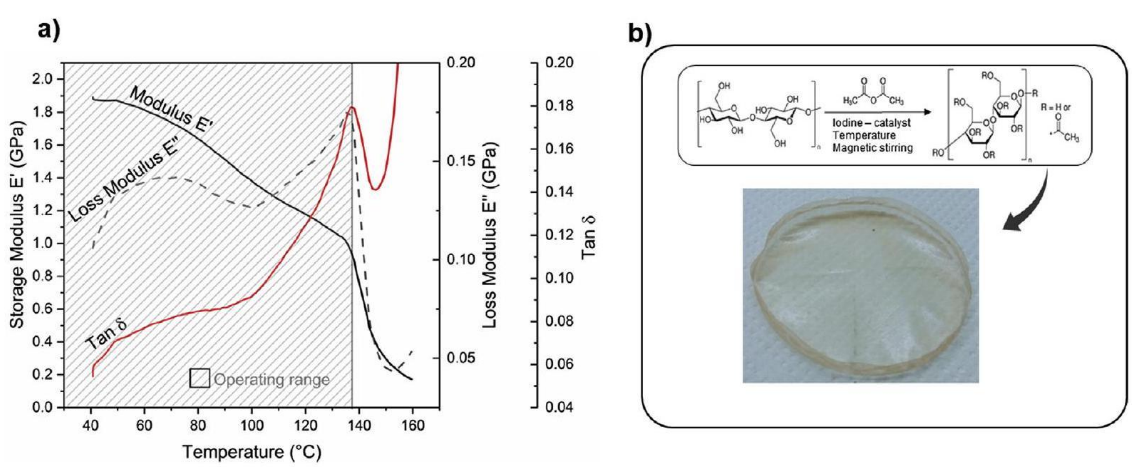

Fig. 6. (a) Dynamic mechanical analysis of cellulose acetate film produced and (b) the schematic representation of the green approach processing steps performed. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The storage modulus of the produced film, at $50^{\circ}\mathrm{C}$, is 1.88 GPa , which is higher than the E' value of a commercial one (1.58 GPa) with DS of 2.48, as reported by de Freitas et al. (2017). Furthermore, at a temperature close to $160^{\circ}\mathrm{C}$ the cellulose acetate film produced presents a rather significant E', with value around 178 MPa , demonstrating excellent processing conditions and high resistance. Despite the dynamic Young's modulus calculate from DMA is not exactly the same as Young's modulus (elastic modulus) resultant from the classic stress-strain curve, they are ideally equivalent so that their comparison does not commit the interpretation of results. From literature, commercial cellulose acetate is known to have elastic modulus varying from 600 to 3000 MPa , depending on the DS and the average molecular weight (Abdel-naby and Alghamdi, 2014). By applying Equation (2), at $40^{\circ}\mathrm{C}$ the E^{*} of the produced film is equivalent to 1.89 GPa , which is consistent with the previously mentioned range of values. The similar values of E' and E^{*} come from the prevailing elastic property of the film. Notwithstanding, at $40^{\circ}\mathrm{C}$ the material runs through an increase of the atomic vibration yet, which, in turn, may decrease the stress needed to produce a given strain. Thus, these results suggest that the cellulose acetate film produced via a green approach, using corncob residue as a material source, could be potentially used in value-added applications, such as packaging.

Life cycle assessment

The overall environmental impact categories of conventional and green approaches, considering the functional unit of 10 g of synthesized cellulose acetate, are compared in Fig. 7a. The LCA results show that, except for ET, the proposed green approach exhibited lower environmental impacts for all categories. This is the result of the lowest energy consumption and chemical throughout the green pretreatment and acetylation steps, which, in percentage terms, resonated in a reduction of impacts varying from 4% (fossil resources depletion) to 19% (ionizing radiation). The higher ET impact associated with the green approach were caused mainly by copper emissions involved in the production of acetic anhydride. In the green acetylation method this reagent is used in amount over four times greater than the amount deployed in the standard acetylation.

The acetylation processes were the main contributors to environmental impacts in both approaches, mainly due to their energydemanding characteristic and chemicals used. The following aspects/process were identified as having major influences on environmental impacts of conventional approach: electricity consumption (related to the standard acetylation process) > alkali and bleaching treatment (chemicals used and electricity consumption) > dichloromethane consumption (purification step) > ethanol consumption. The proportional contribution of individual processes associated with the green approach can be found in Fig. 7b. The overall impact analysis for this approach also shows that the electricity consumption related to the acetylation process is the main contributor to environmental burdens, followed by the chemicals used throughout the acetylation (being the ethanol and acetic anhydride consumption the most prominent contributors), dichloromethane consumption in the purification step and, lastly, the combined green pretreatment. The proportional impacts of corncob milling were also accounted, but its contribution to the global impacts was too low to be evidenced in Fig. 7b. As the precedence of aspects/process for both approaches were drawn up on the basis of an overall LCA analysis, they might slightly vary in some impact categories, though. By comparing both approaches within the order of precedence dictated by the process/aspects' contribution impacts, it is possible to verify that, not surprisingly, significant environmental savings could be achieved through the reduction on electricity and chemicals in the pretreatment stage. The effective savings provided by the green pretreatment are discussed in more detail further in the sensitivity analysis. Furthermore, it is interesting to note that the combined green pretreatment contributed more than 20% only for three impact categories, namely IR, FE and PM, (Fig. 7b). These categories are particularly affected by impacts related to energy generation, which coherently agree with the energy-demanding characteristic of the LHW treatment. Comparatively to the combined green pretreatment, the proportional contribution of the alkali-bleaching pretreatment on each impact categories is substantially greater. For the same impact categories referred previously (IR, FE an PM) the conventional pretreatment accounted roughly for 33%, 29% and 29% respectively of their total impacts.

Besides, in previous studies Boonterm et al. (2016) and Dedpakdee et al. (2015) have shown that, in comparison to hydrothermal treatments, concentrate NaOH pretreatment can lead to higher potential impacts on toxicity (HTc, HTnc and ET). Consistently with these findings, the dilute NaOH solution here applied reduced significantly impacts in the context of toxicity, and showed lower impacts on HTc, HTnc and ET than that of the LHW treatment by 43%, 42% and 43%, respectively. Moreover, within the framework of the conventional approach, the alkali-bleaching pretreatment had relevant influence over these ecotoxicity categories and affected the impacts on HTc and ET by 20% and 26%, respectively.

It is worth mentioning that, within the acetylation process are also computed the impacts related to the recovery of dichloromethane. At the laboratory scale level its recovery was possible and can represent an overriding strategy in view of environmental

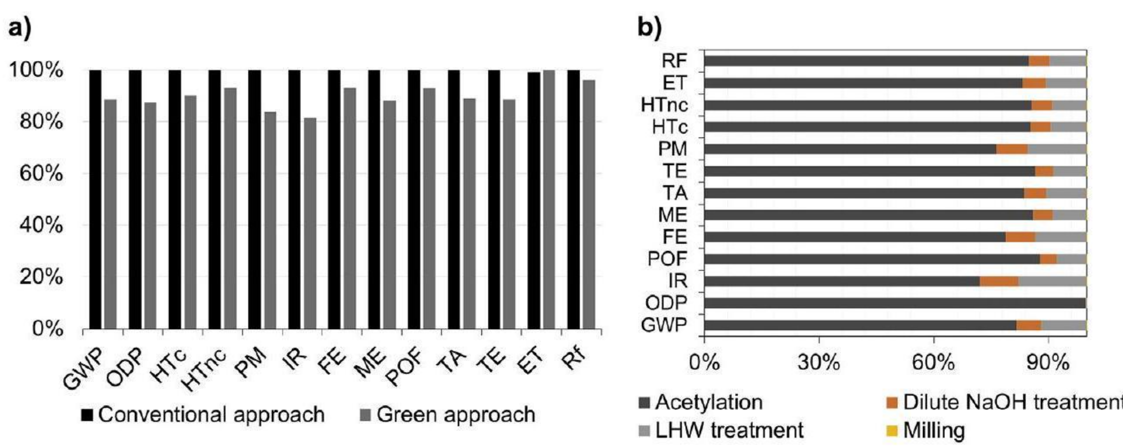

Fig. 7. (a) Potential environmental impacts of cellulose acetate synthesized by green and conventional approaches and (b) proportional contributions of green approach processing steps on each environmental impact category. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

gains. For instance, the primary consumption of dichloromethane leads to a significant impact share for ODP, HTc, GWP, ME and TE. Particularly for HTc and ODP, classified as some of the largest impact categories when expressed in person-equivalents (Fig. 8), the primary dichloromethane consumption contributed roughly with 33 and 98%, respectively, in both approaches. Assuming a recovery rate of dichloromethane at about 80% (estimated experimentally in laboratory) when performing the green approach processing, the savings for HTc could reach 27%. In addition, by using recovered dichloromethane ultimately reduces atmospheric emissions of carbon dioxide and methane originated from its production, which also substantially imparts environmental negative impacts on the GWP and POF. Therefore, the recovery and recyclability of dichloromethane is an effective way to reduce the environmental footprint of subsequent acetylation cycles.

By dividing the LCA results of each impact categories by their correspondent normalization reference, their characterized values are adjusted to a notionally common scale - person-equivalents (PE) - that means the fraction of the contribution to the concerned impact deriving from the average person in the reference geographical area. Thus, these normalized values can give information on impacts' magnitude and enable comparison of different impact categories. From Fig. 8, it is clear that the magnitude of HTc is much higher than that of the other categories. The main aspect enclosed to potential impacts over human toxicity (with carcinogenic effects) deals with the emission at long-term of chromium VI to groundwater, resulting from the landfilling of residual materials originated in dichloromethane and electricity production. In the conventional approach this impact is compounded by the effects associated with the pretreatment used. The large magnitude of impact also seen on freshwater eutrophication is mainly affected by the emission at long-term of phosphate resulting from the landfilling of residual material originated from fossil fuel energy production and chemicals production. Especially for the conventional approach, it is also resultant from the pretreatment step and chemicals used in the acetylation (namely acetic acid and anhydride acetic). Taking into account also the marked magnitude of HTnc, it is reasonable to infer that both processing approaches contributed the most to toxicity related impact categories. More precise information on this regard could be obtained by performing weighting, but this step is not in the scope of the study. By contrast, the lower magnitude of categories IR, ME and TE, in both approaches, are partially raised from the processing design and requirements in its core, as well as from the system boundary assumed, which ultimately limited the inputs and consequential outputs linked to the occurrence of environmental aspects with repercussion on such impacts.

Sensitivity analysis

A sensitivity analysis based on comparison of scenarios was

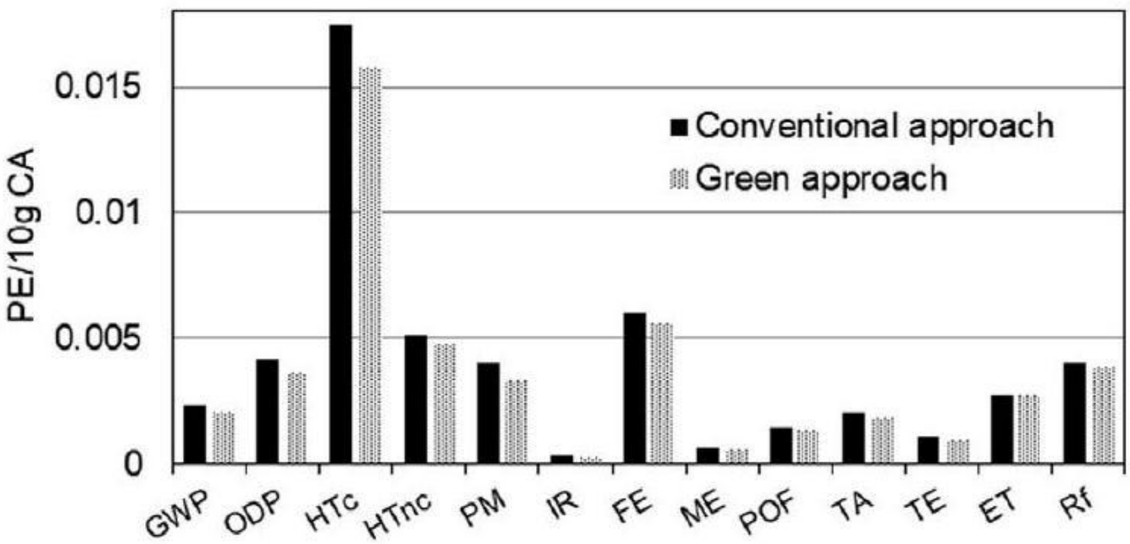

Fig. 8. Potential impact contribution in PE/10 g of cellulose acetate of the green and conventional approach.

conducted to investigate the specific contribution of acetylation and pretreatment process over the impact categories. For this, an additional scenario, referred to as intermediate approach, was modeled by setting up the combined green pretreatment preceding the standard acetylation. The following discussion will be carried out taking as reference the green approach impacts, since it sets a lower limit for all impact categories, except for ET. From Fig. 9 it is noticeable that the enlargement of impacts over ODP, TA, TE and Rf are independent of the pretreatment applied, indicating that they come almost entirely from the standard acetylation process. Conversely, the alkali-bleaching pretreatment step was the main contributor to increase the HTnc and FE impacts. For all other impact categories the extent of impacts is almost equally provided by both process (conventional pretreatment and standard acetylation), other than for a slightly superior contribution assigned to the standard acetylation. The findings drawn from this analysis support the previous discussion and makes clear that the application of green pretreatments is an obvious way to reduce negative environmental impacts, although its gains may not extend to all impact categories. Additional savings can be achieved by reducing the use of chemicals, as afforded by the green acetylation, or through recovery of solvents. Last, but certainly not least, reducing energy consumption might be the most effective way to reduce the environmental footprint of the concerned process. However, this has been reported to be a challenge when it comes to biomass valorization (Arvidsson et al., 2015; Boonterm et al., 2016; Prasad et al., 2016), and the most obvious way to manage this bottleneck seems to be the use of integrated renewable energy sources, as suggested by Yates and Barlow (2013).

The sensitivity of the LCA results regarding the overall advantages of the green approach in comparison to the conventional approach was also tested via a different perspective. As stated previously, the yield of green acetylation is 12.5% greater than that of standard acetylation. Considering that both approaches are assessed under the same functional unit, this yield gap has a direct influence on the amount of raw material (corncob) to be processed and consequently on the number of chemicals and electricity consumed, which means that the lower the yield, the greater the need for inputs. However, the yield of the standard acetylation is susceptible to optimization by slightly changing the reaction parameters, as reported by Bello et al. (2016). Thus, potential perspective scenarios for the conventional approach were modeled by varying its acetylation weight gain from 40 to 70%, and named as WG-40%, WG-50% and so on, as presented in Fig. 10. By conducting this assessment is possible to ascertain to what extent the green approach (baseline scenario) remains environmentally viable in face of a possible optimization of the standard acetylation

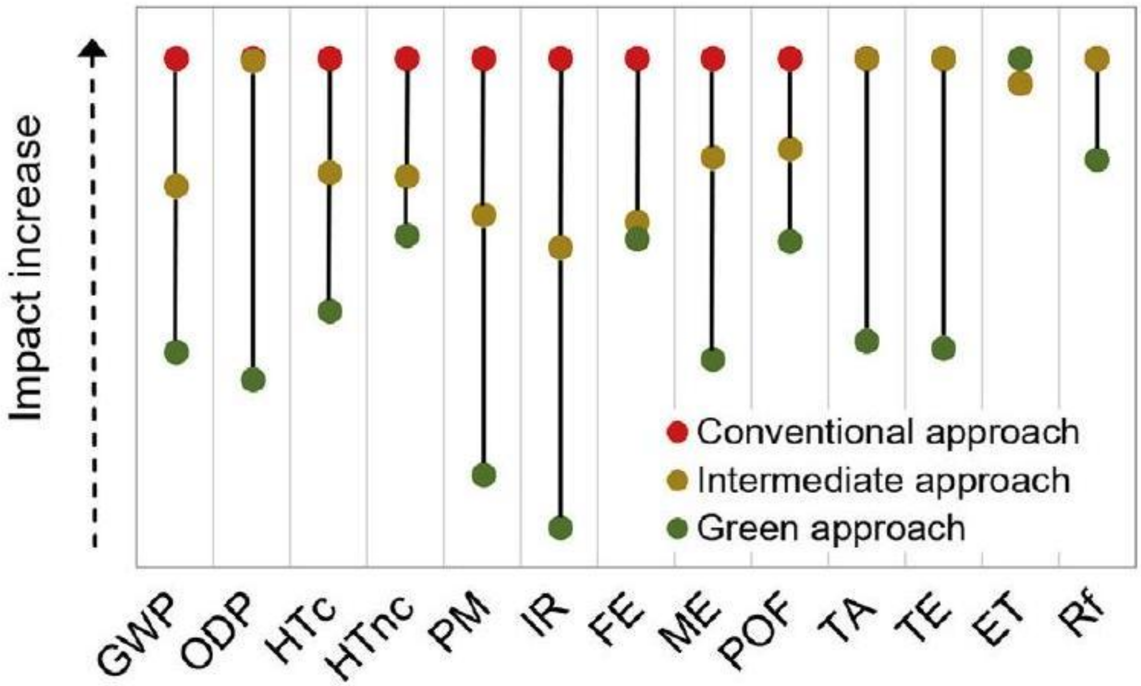

Fig. 9. Influence of pretreatments and acetylation techniques on environmental impacts. Comparison of reference scenarios with Modeled intermediate one constituted by LHW-dilute NaOH pretreatment and acetic acid acetylation process.

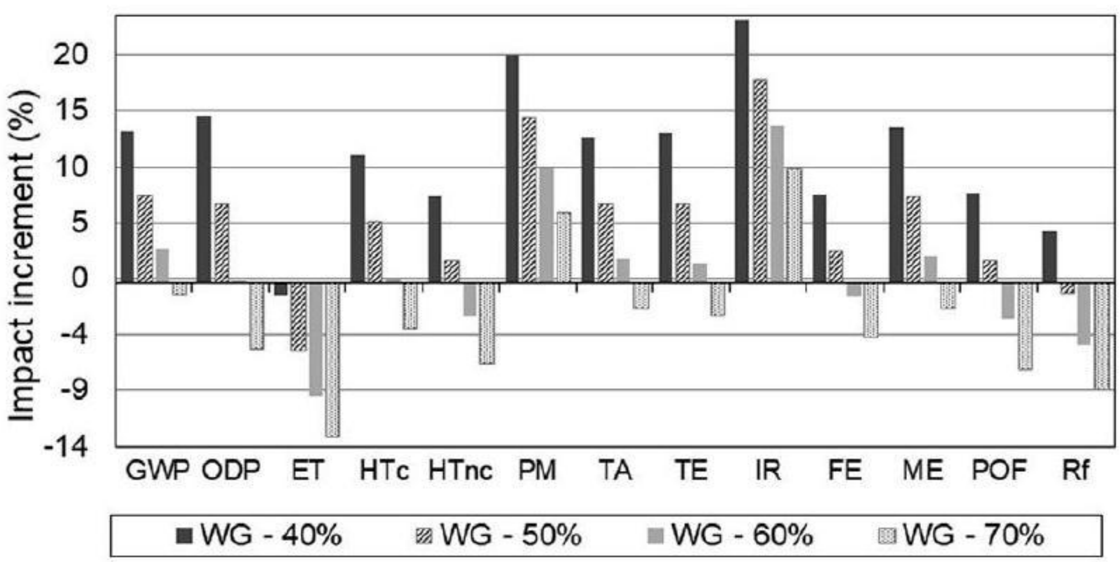

Fig. 10. Potential impact differences in all categories due to possible changes in the acetylation yield of the conventional approach. Impact increment was calculated taking as baseline scenario the green approach. WG means weight gain. processing.

The LCA sensitivity analysis for each impact category associated with all modeled scenarios is reported in Fig. 10. Taking as baseline scenario the green approach, by comparison, a positive impact increment indicates a negative environmental effect, while a negative impact increment indicates a positive effect. Results indicate that, although both processes have a quite similar environmental footprint in the assumption of same yield (WG-60%), the performance of the conventional approach only exhibits overall positive environmental effects for weight gains $\geq 70\%$. Along with the results previously discussed, this analysis clearly indicates that, in comparison to the standard acetylation synthesis, the key factors to lower the environmental impacts resulting from the green acetylation are the high yield obtained and not use acetic acid as reaction media. The attempts made in previous works to substitute the traditional catalyst H_2SO_4 by eco-friendly ones, could not be deeply investigated here since, based on the FU adopted, this chemical was used in little quantity which could have masked its pollution effects. Nevertheless, even with a weight gain of 70% the conventional approach still results in superior environmental burdens for IR and PM, and notwithstanding the prospective analysis, the green acetylation may also be subject of optimization, as shown by Das et al. (2014), who successfully varied the acetylation yield as a function of the acetylation time and iodine amount. It is also important to bear in mind that environmental impacts related to the green pretreatment would probably be reduced when scalingup this processing step, mainly due to the higher cellulosic fiber yielding produced per electricity consumed (Boonterm et al., 2016).

Conclusions

Cellulose was successfully extracted and cellulose acetate was synthesized from corncob by applying a green approach, constituted by a combined LHW-dilute NaOH pretreatment and iodinecatalyzed acetylation free of solvent. The outstanding physicochemical properties of the synthesized cellulose acetate endorse its use as a value-added product, which was proved by the preparation of a thin film with remarkable mechanical properties. The effective fractionation and cellulose extraction capacity of the pretreatment was confirmed via chemical composition analysis and backed up by the high DS (2.68) and yield (60%) obtained after the acetylation. Along with the high yield of acetylation, the less use of energy and chemical reagents associated with the green approach were key aspects within its environmental benefits. In comparison with a current conventional approach, the environmental sustainability of the proposed green route was confirmed through life cycle assessment. Overall LCA results revealed that the proposed green approach exhibited lower environmental impacts than the conventional approach for all categories, except for ET. Moreover, in both approaches the acetylation process accounted for the main share of impacts, which was in part due to the length of the process and the consequent amount of electricity required. In general, the most obvious way to improve even more the proposed processing design relies on the use of integrated renewable energy sources and recycling of solvents, namely DCM. Although there are few studies regarding these addressed subject for comparison purpose, the data used fulfilled the requirements of the LCA and the obtained outcome is reliable.

Acknowledgements

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