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SIMULATION AND SUSTAINABLE ENGINEERING ANALYSIS OF CELLULOSE PRODUCTION VIA IONIC LIQUIDS

SIMULACIÓN Y ANÁLISIS DE SOSTENIBILIDAD DE PROCESOS EN LA PRODUCCIÓN DE CELULOSA EMPLEANDO LÍQUIDOS IÓNICOS

C.A. Vásquez[1]*, M. Marulanda[1], M. Sánchez[1], J.C. Cruz[2]

[1]Departament of Chemical Engineering, Universidad de Antioquia, Calle 67 # 53-108. PC: 1226, Medellín, Antioquia, Colombia.
[2]Departament of Biomedical Engineering, Universidad de los Andes, Carrera 1 # 18 A 12, PC: 111711, Bogotá, Cundinamarca, Colombia.

Abstract

As one of the main agricultural producers in Latin America, Colombia generates important amounts of biomass residues that are currently discarded or incorporated into composting processes. Here, we propose a new process for the transformation of these residues into cellulose, which can be potentially used as a source for the manufacture of high-added value products. The process was designed and simulated in ASPEN PLUS® where the 1-ethyl-3methylimidazolium acetate (EmimAoC) ionic liquid was used as solvent medium for the delignification of the biomass within the cellulose extraction process. The sustainability potential of the newly designed process was estimated by implementing the approach developed by Fan and Zhang (2012a), which allowed us to demonstrate higher profitability, lower energy consumption and environmental impacts, when compared with the Acetosolv process. Here, we selected this process for benchmarking purposes due to lower environmental impacts with respect to the well-established Organosolv and Kraft processes.

Keywords: simulation, ionic liquid, cellulose, sustainable, Acetosolv.

Resumen

Como uno de los principales productores agrícolas en América Latina, Colombia genera importantes cantidades de residuos de biomasa que actualmente se descartan o incorporan a los procesos de compostaje. Aquí, proponemos un nuevo proceso para la transformación de estos residuos en celulosa, la cual puede potencialmente usarse para la fabricación de productos de alto valor agregado. El proceso fue diseñado y simulado en ASPEN PLUS® donde se empleó el líquido iónico 1-ethyl-3methylimidazolium acetate (EmimAoC) como medio solvente para la delignificación de la biomasa en el proceso de obtención de celulosa. El potencial de sostenibilidad del proceso recientemente diseñado se estimó mediante la implementación del enfoque desarrollado por Fan y Zhang (2012a) lo que nos permitió demostrar una mayor rentabilidad, menor consumo de energía e impactos ambientales, en comparación con el proceso Acetosolv. Aquí, seleccionamos este proceso para propósitos de comparación debido el menor nivel de impacto ambiental cuando se compara con los bien establecidos procesos Organosolv y Kraft.

Palabras clave: simulación, líquidos iónicos, celulosa, sostenibilidad, Acetosolv.

1 Introduction

Cellulose is glucose polymer present in plants, non-soluble in water and with an important structural function. It has a high molecular weight (3000 glucose units) and its chains have no ramifications. One important characteristic are the β (1-4) bonds between its glucose units. It has an arrangement in which the hydroxyls generate strong intermolecular bonds, acquiring crystalline properties (Ponce-Reyes *et al*., 2014). The relatively high structural stability and axial rigidity of cellulose fibers has been mainly attributed to the inter- and intra- molecular hydrogen bonding among the pendant hydroxyls along the backbone

(Poletto, *et al.*, 2013).

Despite the linearity of cellulose chains, dissolution in polar solvents for oligomers with more than 10 units is challenging. This has been attributed to the limited ability of these solvents to disrupt the interchain hydrogen bonding network. Also, polar solvents promote interchain hydrophobic interactions that further limit solvation processes (Olsson and Westman, 2013).

The presence of polar and non-polar regions has served as the basis for putting forward the notion that cellulose solubility can be promoted in amphipathic solvents. A family of amphipathic solvents known as ionic liquids has been proposed as an attractive alternative for this purpose (Olsson and Westman, 2013). In this regard, it has been demonstrated that ionic liquids are capable of disrupting the interchain hydrogen network of cellulose by forming an electron transfer complex with the pendant hydroxyls. In this case, the Oxygen atoms act as electron donors while the Hydrogen atoms as acceptors. At the same time, the cation in the ionic liquid (IL) accepts electrons while the anion serves as donor. This promotes a charge separation once the IL and cellulose are put in contact that ultimately leads to dissolution (Feng and Chen, 2008).

Cellulose has been conventionally produced via chemical delignification in the kraft, viscose and soda processes. In all cases, biomass digestion is accomplished in aqueous media with the aid of sodium hydroxide, sodium sulfide, carbon sulfide and some chlorinated compounds. Typically, processes are conducted at temperatures of about 383.15 K and pressures of about 0.55 MPa. After digestion, cellulose is obtained along with lignin, byproducts and excess reagents. These processes are highly intensive in the use of water and produce sulfur compounds that are discharged to the atmosphere and wastewaters with high contents of acids and bases (Ott, *et al.*, 1954). Other methodologies for obtaining cellulose includes conventional chemical methods such as acid hydrolysis, chlorination, alkaline extraction and bleaching (Bolio-López *et al.*, 2011).

Even though ionic liquids were first synthesized at the beginning of the 20th century, only until recently they have attracted attention for applications in catalysis, organic synthesis and analytical methods. In addition to their ability to solubilize complex macromolecules, ionic liquids offer high thermal stability, low flammability, negligible vapor pressure and reusability. As a result, over the past few years they have been considered as potential candidates for green applications. This notion has boosted a number of initiatives where they can be incorporated as solvents into sustainable process for the extraction of natural polymers (Olsson and Westman, 2013). In the particular case of cellulose, numerous research reports have confirmed that some ionic liquids are suitable for the extraction of cellulose (Gericke *et al.*, 2012; Lindman *et al.*, 2010; Freire *et al.* 2011).

The IL cation and anion based ILs are a sub class of non-volatile solvents with unique solvating properties. The cellulose dissolution results from the solvent ability to eliminate the inter-and intra-molecular hydrogen bonding network present in biomass molecules. As this network is disrupted by interactions with the IL anion, other anions are able to establish interactions with the cellulose. This also explains why protic polar solvents such as water and methanol can be used to precipitate cellulose from IL solutions (Xu *et al.*, 2013). The potential of ILs such as 1-butyl-3methyl-imidazolium acetate (BmimAoC), 1-butyl-3methyl-imidazolium chloride, (BmimCl), 1-ethyl-3methylimidazolium acetate (EmimAoC) in the dissolution of different biomass sources has been recently explored at the laboratory scale regard, The IL EmimAoC has attracted considerable attention for biomass processing due to the ability of the imidazolium group to dissolve cellulose with higher efficiencies than other ILs. For instances, Ang, *et al* (2011) confirmed the ability of an imidazolium-based IL in dissolving the cellulose of, rice husks after 10 hours of contact. These findings led to the notion that EmimAoC could be employed for the development of novel cellulose large-scale production processes with higher yields and potentially reduced environmental impacts.

To estimate this potential, the advantages and disadvantages of alternative methods with respect to the conventional ones have been recently explored by a number of research groups. For instance, Espinoza-Acosta *et al.* (2014), demonstrated that ILS are able to facilitate the release of lignin with purities superior to those achieved via alkaline processing. As a result, they put forward the idea that ILs might be considered as excellent candidates for the fractionation of lignocellulose biomass and subsequent cellulose production. This has been mainly attributed to the ease for cellulose precipitation and the possibility of recycling of IL several times. The inability to recycle the extraction solvents has been considered as one of the main drawbacks of the Organosolv process for the pretreatment of cellulosic biomass (Espinoza-Acosta *et al.*, 2014). Wu *et al.* (Wu *et al.*, 2011)

showed that at the laboratory scale, EmimAoC can be reused up to ten times during the pretreatment of various lignocellulosic biomasses. This study, also concluded that acetate based ILs are effective for the reduction of the recalcitrance of corn stove, switchgrass and hardwood. As a result, these findings strongly support the idea that incorporating ILs into biomass transformation process is environmentally beneficial mainly due to a significant reduction in the amount of IL required for the extraction purposes.

According to Hou *et al*. (2017), ILs might even have the potential to enable the operation of complete biorefineries. Their analyses demonstrated the suitability of ILs to enable process schemes that range from pretreatment biomass to, recovery and reincorporation of them back to the process. They also emphasize the need for rational and holistic tools to simultaneously analyze the impact of process changes on critical technical, economic and environmental parameters.

Sustainability analyses have gained considerable attention for estimating, in a holistic manner, the technical and economic impacts of incorporating changes to processes (Fan *et al*., 2007). One of the most robust methodologies for sustainability analysis was put forward by Fan *et al*. (2007) and is based on the comprehensive estimation of consumed exergy, profit potential and Life Cycle Assessment (LCA) indexes (Fan and Zhang, 2012b). According to this approach, the exergy analysis is crucial to unequivocally determine process energy losses. The profit potential is estimated as the difference of income by sales of the product (ζ_p) and the cost of feedstocks (ζ_r). Sustainable processes should have a positive profit potential, i.e., $\zeta_p - \zeta_r = \Delta\zeta_i > 0$ (Fan and Zhang, 2012b). LCA analyses are conducted by evaluating the environmental impacts on ecosystems, human health and natural resources. LCA is also well suited for estimating the environmental burden of products throughout their entire life cycle. This approach comprises various stages including the extraction of raw materials, use, transformation, and final disposition and recycle of the obtained product (de Brujin *et al*., 2002). This complete analysis is also known as "cradle to grave"; however, when information is scarce the preferred approach is the "gate to gate" analysis where only stages required for the transformation of feedstocks into terminated products are analyzed (Fan and Zhang, 2012b).

Acetosolv is a variant of the Organosolv process in which the catalyst was replaced by concentrated acetic acid. This process is a sulfur- and chloride-free alternative for the production of cellulose pulp, biofuels and paper (Vila and Parajo, 2003). Moreover, it has been reported that replenishment flows of catalysts and acids are quite low. For these reasons, the Acetosolv process was selected as a benchmark for our studies. This work aims at evaluating the sustainability potential of the ionic liquid 1-ethyl-3-metilimidazolium acetate (EmimAoC) as solvent for extraction in the cellulose production process. Here we implemented the sustainability engineering analysis proposed by Fan and Zhang (2012b). The impact analyses for the process involving the EmimAoC ionic liquid were compared with those of the Acetosolv process, published by Vila and Parajo (2003) (2003).

2 Methods

Colombia is a major global producer of coffee, banana and flowers. According to the Colombian National Institute of Agriculture (ICA), for 2014 the flower crops approached a cultivated area of about 7,000 hectares. This roughly corresponds to approximately 65,000 tons/year of residues, which are mainly composed of stems (Escalante *et al*., 2010). Composition of stem residues is 39.3% cellulose, 34.9% hemicellulose and 13.5% lignin (López *et al*., 2005). This suggests that the cellulose available from these residues approaches 25.000 tons/year, which can be potentially used for the production of high-added value products. Despite this potential, thus far residues are mainly incorporated into composting processes.

A cellulose derivative of interest due to high added value is microcellulose. This versatile product finds applications in pharmaceuticals, cosmetics, paints and food and beverages. In accordance with The Food and Agriculture Organization of the United Nations (FAO and Organization, 2017), microcellulose is a particulate (10% of the material < 5 microns) purified, partially depolymerized (degree of polymerization < 400) cellulose material prepared by treating alpha-cellulose (obtained as a pulp from fibrous plant material) with mineral acids. The world annual production of microcellulose is about 100,000 tons, which represents near 2 - 3% of dissolving pulp and 0.08% of paper pulp annually produced worldwide. Although several methods have been proposed for the production of microcellulose, most common processes involve hydrolysis of dissolved paper pulp via chemical, enzymatic or hydrothermal processes or their combination. Microcellulose can be

manufactured from all celluloses derived from several natural sources including among many others, rice hulls, bleached kraft bagasse pulp, oil palm residue, esparto grass, and cotton linters (Vanhatalo *et al.*, 2014).

2.1 Simulation of the Acetosolv process in ASPEN PLUS®

For benchmarking purposes, the Acetosolv process was also implemented in ASPEN PLUS® by incorporating the data reported by Vila and Parajo (Vila and Parajo, 2003). Fig 1 shows the layout process which starts by delignification of lignocellulosic biomass in a hydrolysis reactor where this biomass is mixed with concentrated hydrochloric and acetic acid at 413.15 K and 0.28 MPa. This hydrolysis results in cellulose pulp, pulp liquors, and wastewater. The obtained pulp liquors are directed to a recovery unit where fractions catalysts and solvent are recycled. Furfural, xylose, hydrophobic and hydrophilic compounds are then separated from the mixture in subsequent stages. Additional process details can be consulted elsewhere (Vila and Parajo, 2003). Mass and energy balances obtained in ASPEN PLUS® simulations of the Acetosolv process recreated the data obtained by Villa and Parajo (Vila and Parajo, 2003) with an accuracy of ±2% (Supplementary Table 2). This allowed to confidently proceed with the simulations of our own process.

2.2 Design and simulation of a process for the production of cellulose from flower residues via EmimAoC as extracting solvent

In this work, a process was designed by directly scaling up the laboratory results of da Costa *et al.* (2013). They used wheat straw residues as a source of cellulose in their work. According to Khan and Mubeen (2012) the composition of wheat straw residues is 33.7 - 40.0% cellulose, 21.0 - 26.0% hemicellulose and 11.0 - 22.9% lignin. Wheat straw residues are close enough in composition to those of flower stems to confidently extent the applicability of da Costas *et al.* process for the extraction of cellulose from floricultural residues.

The design and simulation of the micro cellulose production was developed with ASPEN PLUS®, for which The National Renewable Energy Laboratory (NREL) compiled the required properties for the simulation of chemical processes involving cellulose, hemicellulose or lignin (Wooley and Putsche, 1996). However, they needed to be incorporated in ASPEN PLUS® prior to running simulations. Thermodynamic parameters of ionic liquids are not available in ASPEN PLUS® databases either. This information was collected from Abdulwahab, 2013. Table 1 summarizes some of the most relevant thermodynamic parameters for cellulose, xylose, lignin (Wooley and Putsche, 1996) and for ionic liquid EmimAoC (Abdulwahab, 2013).

Fig. 1. Acetosolv process for the manufacturing of cellulose from wood. Adapted from Vila and Parajo (2003).
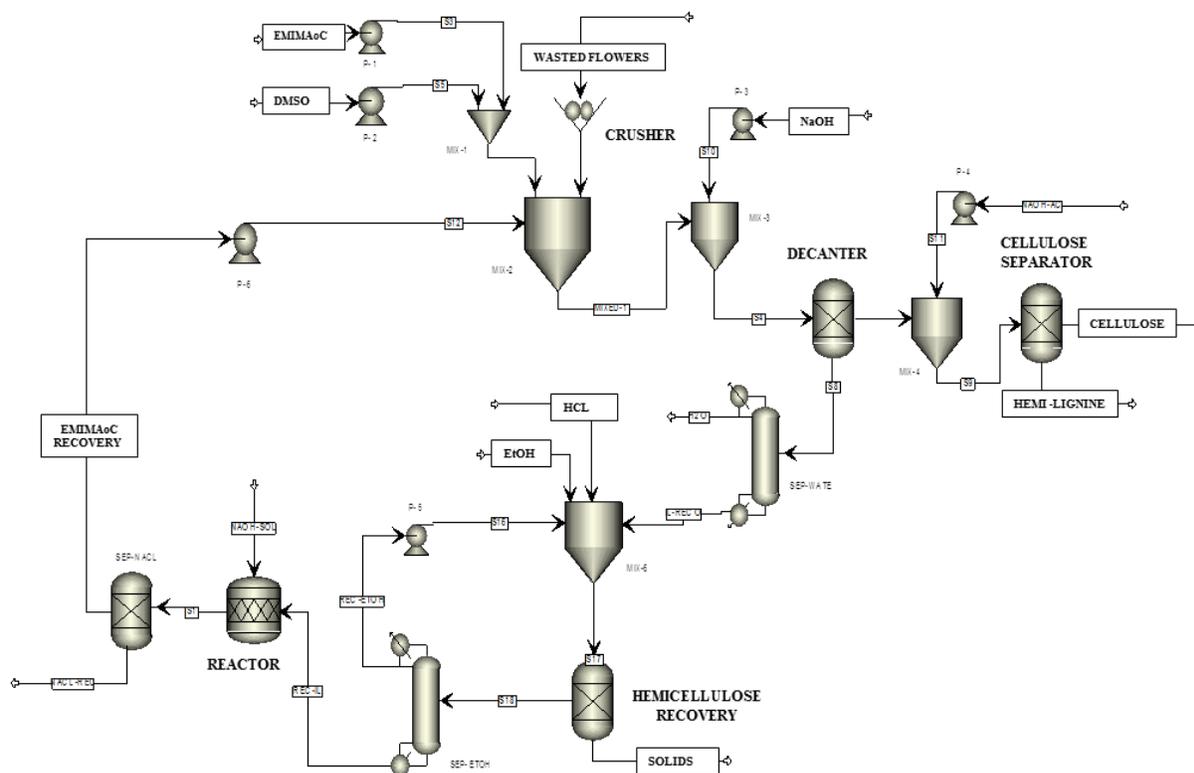
Fig. 2. Process for the manufacturing of cellulose from agricultural flower residues via EmimAoC

Table 1. Summary of some of the most relevant thermodynamic parameters for cellulose, xylose, lignin and ionic liquid 1-ethyl-3methylimidazolium acetate (EmimAoC).

Component	M [kg/kmol]	Tb [K]	Tc [K]	Pc [MPa]	Vc [cm^3/mol]	Density [g/cm^3]	ΔHform [J/kmol]
Cellulose	162.14	255.37	n/a	n/a	n/a	1.5	-976,362.00
Xylose	150.13	575.3	n/a	n/a	n/a	1.52	-762,416.00
Lignin	122.49	397.24	n/a	n/a	n/a	n/a	-74,944.00
EmimAoC	170.21	578.8	807.1	2.92	544	1.04	n/a

Fig. 2 shows the layout of the proposed process, which starts with dissolution of flower residues in EmimAoC at 373.15 K and 0.1 MPa. Dimethylsulfoxide (DMSO) is then added to the mixture to assure a viscosity low enough for processing (da Costa Lopes *et al.*, 2013). The aqueous mixture obtained is mainly composed by EmimAoC/DMSO/hemicellulose/lignin. Solids in acidic EmimAoC are then precipitated by adding ethanol, which is later recovered in a distillation unit. Cellulose is separated from EmimAoC by adding

sodium hydroxide, which is neutralized and separated later on as sodium chloride. The process was designed by directly scaling up the laboratory results of da Costa *et al*. (2013).

The solvent mixture (EmimAoC/DMSO) is recycled to the process where is mixed with fresh biomass. Process simulation was implemented in ASPEN PLUS® using the NRTL-ELEC (Non Random Two Liquids - Electrolytes) thermodynamic model. This is an extension of the widely used NRTL model (Song and Chen, 2009), which has

proven effective for systems based on electrolytes and partially miscible phases for benchmarking purposes, the acetosolv process was also implemented in ASPEN PLUS® by incorporating the data reported by Vila and Parajo (2003). Briefly, the process starts by delignification of lignocellulosic biomass in a hydrolysis reactor where this biomass is mixed with concentrated hydrochloric and acetic acid at 413.15K and 0.28 MPa. This hydrolysis results in cellulose pulp, pulp liquors and wastewater. The obtained pulp liquors are directed to a recovery unit where fractions catalysts and solvents are recycled. Furfural, xylose, hydrophobic and hydrophilic compounds are then separated from the mixture in subsequents stages. Additional process details can be consulted elsewhere (Vila and Parajo, 2003).

2.3 Sustainable engineering analysis

2.3.1 Profit potential analysis (Δζ)

For the process studied here, a Functional Unit (FU) of 1.0 kg of produced cellulose was defined. Conversely, both feedstocks and LCA indexes were normalized to this FU.

Profit potential for designed process and the benchmark were calculated from consumed feedstocks and their market prices. For recycled materials such as catalysts, solvents and ionic liquids, contribution to profit potential is estimated from returned mass flows. Processes were oriented toward the production of 20-micron cellulose, taking a market price of 60.00 US$/kg. Eq. (1) shows the expression to estimate the profit potential of processes.

$$\Delta\zeta i = \sum(\gamma\zeta)products - \sum(\gamma\zeta)reagents \quad (1)$$

Where ζ is the cost/kg of the material of interest and γ is the amount of the material in kg. Table 2 summarizes costs for feedstocks employed in the designed process and the benchmark.

Table 2. Summary of costs for feedstocks employed in the designed process and the benchmark.

Feedstock	Cost ($ US/kg)
Wood sawdust	0.13
Flower residues	0.13
Hydrochloric acid	1
Acetic acid	1.63
Sodium hydroxide	0.7
Dimethyl sulfoxide	413.3
Ethanol	1.5
EmimAoC	645

2.3.2 Exergy analysis (X)

2.3.2.1 Chemical exergy (X_i^{CH})

The chemical exergy of a mixture is the maximum useful work that can be obtained when this mixture is carried through a reversible process from the conditions of temperature, pressure, and standard chemical potential of the environment (T_0, P_0, μ_0) to the of the dead state (T_{oo}, P_{oo}, μ_{oo}) (Romero and Linares, 2014). Here we calculated the specific chemical exergy X_i^{CH} of a compound i from the relationship between its standard chemical exergy X_i^0 and the corresponding molar mass (of i compound) as follows:

$$X_i^{CH} = \frac{X_i^0}{M_i} \quad (2)$$

Where: X_i^0 is the standard chemical exergy in kJ/kmol of i compound and M_i is the molar mass of the compound i in kg/kmol.

For substances with complex chemical structures, such biomass, chemical exergy can be estimated from semi-empirical correlations as a function of elemental composition (Szargut, *et al.*, 1988; Fan and Zhang, 2012a). Accordingly, Eq. 3 was implemented to estimate the chemical exergy of biomass components (Fan and Zhang, 2012a).

$$X^{CH} = 8177.79(C) + 27892.63(H) + 3173.66(O)$$
$$+0.15(0)[7837.667(C)+33888.889(H)-4236.1(O)] \quad (3)$$

Where: C, H y O are the mass fractions of carbon, hydrogen and oxygen, respectively.

In the case of complex electrolytes such as ionic liquids, information of standard exergies is rather scarce; however, according to Szargut (2005) chemical exergy of this type of compounds can be estimated from the standard chemical exergies of each functional group present in the molecule. Accordingly, the chemical exergy of the ionic liquid i (X_{IL}^{CH}) can be estimated by contribution of groups j via Eq. 4:

$$X_{IL}^{CH} = \sum\left(n_j \sum X_{CH,j}^0\right) \quad (4)$$

Where $X_{CH,j}^0$ is the standard chemical exergy in kJ/kmol of functional group j and n_j is the number of repetitions of functional group j in the molecule i (Szargut, 2005).

2.3.2.2 Physical exergy (X_{ph}) and Flow exergy (X_f)

Physical exergy (kJ/kg) is the work that can be obtained when a substance is subjected to a change in its pressure and temperature through a reversible process. This occurs from initial conditions to those of a reference state. Physical exergy can be calculated from Eq.(5) (Cornelissen, 1997):

$$X^{PH} = H - H_0 - T_0(S - S_0) \qquad (5)$$

Where: H is enthalpy and S is entropy

All the equipment and processing units for cellulose production involved inputs and outputs of mass and; therefore, were defined as open systems. In such cases, it is necessary to estimate the flow exergy (X^f), which is associated with the boundary work in excess of the surrounding and can be calculated from the physical and chemical exergies as shown in Eq. (6) (Szargut, *et al.*, 1988):

$$X^f = \gamma_i(X_i^{PH} + X_i^{CH}) \qquad (6)$$

Where γ is the mass flow in kg/h of compound i.

2.3.2.3 Exergy change (ΔX) and destroyed exergy (X_D)

The change in the exergy of a system is zero if the state of the system or surroundings remain unchanged during process. For open systems, where conditions vary for inlets and outlets, the change in process exergy can be determined as follows:

$$\Delta X = \sum_{out} X_i^f - \sum_{in} X_i^f \qquad (7)$$

Where, X_i^f is the flow exergy of the i component in the inlets (in) and outlets (out).

Flow exergy was calculated from chemical and physical exergies, which in turn were estimated via standard chemical exergies for pure substances or semiempirical correlations and group contribution methods for more complicated structures (Fan & Zhang, 2012a; Szargut *et al.*, 1988).

According to the principle of decreasing exergy, when a process takes place, the exergy for such system is always destroyed. Eq. (8) allows calculation of destroyed exergy (X_D) as a function of exergy for inlets and outlets and the external energy supplied to the system (Cengel and Boles, 2002):

$$X_D = \sum_{out} X_i^f + P_{in} - \sum_{in} X_i^f \qquad (8)$$

Where, P_{in} is the external energy supplied to the system. Eq. (9) is useful to calculate the total exergy destroyed ($X_{DT,i}$) for both the benchmark and the designed process by the summation of the destroyed exergies for each j:

$$X_{DT,i} = \sum X_{D,j} \qquad (9)$$

More details on the conceptual basis of each of the parameters associated with exergy destroyed (X_D) can be consulted elsewhere (Romero & Linares, 2014; Fan & Zhang, 2012a; Szargut *et al.*, 1988; Szargut, 2005; Cengel & Boles, 2002).

2.3.3 Life Cycle Impact Assessment - LCIA Indexes

In this study a life cycle assessment is performed to determine the environmental performance of cellulose production via Acetosolv and EmimAoC-based processes starting from agricultural residues. The cellulose production chain studied requires flower residues as main feedstock for the EmimAoC-based process and wood for the benchmark Acetosolv process. Both processes comprise three main unit operations, namely preprocessing via solvent treatment, reaction and cellulose separation and recovery.

Here we implemented the "gate to gate" LCIA indexes by considering that transport of substances was the same for all analyzed unit operations. Table 3 shows the expressions to estimate potential impacts for the studied processes. In Table 3, equations (10) to (15) represent the weighing factors for the evaluated potential impacts while B_j is the amount of required resource j per FU. The human toxicity impact and the aquatic toxicity (Eq. 16 - 17) are estimated by the summation of the individual impacts on air (A), water (W) and soil (S). Further details on the LCIA analysis can be reviewed elsewhere (Fan & Zhang, 2012a,b; de Brujin *et al.*, 2002; Szargut *et al.*, 1988; Gloria *et al.*, 2007). Table 3 summarizes the equations of potential index for LCIA analysis.

The normalization and weighting are crucial in comparative LCIA analysis to provide decision support in the face of uncertain environmental parameters. This approach is useful to evaluate areas where one process alternative shows a better performance compared others. In problems of comparative technology assessment, characterized results alone seldom result in a definitive environmental choice, thereby leaving decision-makers to conform complex environmental tradeoffs.

Table 3. Definition of potential index for LCIA analysis.

Potential Impact	Units	Assessment	Equation
Resource Depletion (E_1)	[MJ/kg oil eq./m^3]	$\sum_{j=1}^{j} \frac{B_j}{ec_{1,j}}$	(10)
Global Warming GWP 100 years (E_2)	[kgCO$_2$ eq./kg]	$\sum_{j=1}^{j} ec_{2,j} B_j$	(11)
Ozone Depletion ODP (E_3)	[kg CFC-11 eq./kg]	$\sum_{j=1}^{j} ec_{3,j} B_j$	(12)
Acidification AP (E_4)	[(kg SO$_2$ eq./kg]	$\sum_{j=1}^{j} ec_{4,j} B_j$	(13)
Eutrophication EP (E_5)	[kg PO$_4$ eq./kg]	$\sum_{j=1}^{j} ec_{5,j} B_j$	(14)
Photochemical Smog (E_6)	[kg NMVOC eq./kg]	$\sum_{j=1}^{j} ec_{6,j} B_j$	(15)
Human Toxicity* (E_7)	[kg 1,4-DCB eq./kg]	$\sum_{j=1}^{j} A + \sum_{j=1}^{j} W + \sum_{j=1}^{j} S$	(16)
Aquatic Toxicity (E_8)	[kg 1,4-DCB eq./kg]	$\sum_{j=1}^{j} ec_{8,jA} B_{jA}$	(17)

* Where, $A = ec_{7,jA} B_{jA}$; $W = ec_{c7,jW} B_{jW}$; $S = ec_{7,js} B_{js}$

Eqs. (10) to (15) represent the weighing factors for the evaluated potential impacts while B_j is the amount of required resource j per FU.

The human toxicity impact is estimated by the summation of the individual impacts on air (A), water (W) and soil (S). Further details on the LCIA analysis can be reviewed elsewhere (Fan & Zhang, 2012b; de Brujin *et al.*, 2002; Fan & Zhang, 2012a; Szargut *et al.*, 1988; Gloria *et al.*, 2007).

This is a critical and challenging issue in sustainability analysis because the tradeoffs exit regardless of the completeness of characterization factors of LCI databases. Typically, LCIA methods rely on external normalization, references, which refer to large scale communities such as Europe, USA or even the world. In contrast, internal normalization references rely on an internal baseline such as the largest or smallest process (Prado, *et al.*, 2018). In this work, we employed an external normalization approach for the LCIA analysis where the reference factors were those reported by the Environmental Protection Agency - U.S. EPA - (Bare, 2012; EPA, 2014). The normalized impact i ($E_{N,i}$) was determined as follows (de Brujin, *et al.*, 2002; L. T. Fan, 2012):

$$E_{N,i} = \frac{E_i}{W_i} \qquad (10)$$

Where, W_i is relative normalization factor for each E_i impact.

To compare between product systems and across impact categories, externally normalized results must be weighted. This provides the basis for aggregation to a single score. The weighting in LCIA reflects therefore the relative importance of each impact category and enables the ranking of alternatives. From Eq. (19) and using the weighting factors reported by National Institute of Standardizations and Technology - NIST-, the weighted potential impact i ($E_{p,i}$) was determined as follows (Gloria, *et al.*, 2007):

$$E_{p,i} = F_p \cdot E_{N,i} \qquad (11)$$

Where, F_P is the weight factor for each impact i

3 Results and discussions

Table 4 summarizes the results for the standard chemical exergy (X_i^0) and the specific chemical exergy X_i^{CH} of each compound. Table 5 summarizes the results for both profit potential and exergy destroyed for the designed process and the benchmark. Compared with the acetosolv process, the EmimAoC process is approximately 45% more profitable. This can be attributed to the low replenishment flows of EmimAoC to the process. This finding is surprisingly attractive from the economic viewpoint if we take into consideration the elevated cost of EmimAoC compared with the low-cost feedstocks required for the Acetosolv process.

Exergy destroyed for the EmimAoC process is about 32 times lower than that of the Acetosolv process. Despite the considerable number of separation and recovery units, the process exhibits an exceedingly low energy investment mainly due to the remarkable solvent power of EmimAoC. The energy and economic attributes make the EmimAoC quite attractive for further large-scale studies. Table 6 shows the LCIA index per FU for both processes while Table 7 shows the LCIA index potentials normalized and weighted per FU for both processes. Normalization is crucial to make direct comparisons between the different impact categories as they are originally calculated on a different unit basis.

Table 4. Results for standard chemical exergy (X^0) and specific chemical exergy (X_i^{CH}) for each compound.

Component	Chemical Formula	Molar mass (kg/kmole)	Standard Chemical Exergy (X0) (kJ/kmole)	Specific Chemical Exergy (XiCH) (kJ/kg)
Water (liq)	H_2O	18.01	0.9	49.95
Steam water	H_2O	18.01	9.5	527.33
Acetic acid	$C_2H_4O_2$	60.05	907.2	15106.68
Carbon dioxide	CO_2	49	19.48	397.47
Chloride acid	HCl	36.46	84.5	2317.54
Sulfoxide dimethyl	C_2H_6OS	78.13	2040.51	26116.85
Xylose	$C_5H_{10}O_5$	150.13	n/a	15511.19
Lignin	$C_9H_{10}O_2$	150.17	n/a	30590.58
Cellulose	$C_6H_{10}O_5$	162.14	n/a	17005.97
Hemicellulose	$C_5H_8O_4$	132.11	n/a	17343.3
Acetil groups	$C_9H_{12}O_6$	216.19	n/a	18850.25
EmimAoC	$C_8H_{14}N_2O_2$	170.21	n/a	4963.66
NVDS*	$C_5H_8O_4$	132,11	n/a	17343,30
OCSP**	$C_5H_8O_4$	132,11	n/a	17343,30

*NVDS = nonvolatile dissolved solids

**OCSP = other compounds in the solid phase

Table 5. Results for both profit potential and exergy destroyed for designed process and the benchmark.

Profit Potential (U$ D/kg cellulose)		Destroyed Exergies (kW/kg cellulose)	
Acetosolv	Flower Residues	Acetosolv	Flower Residues
30.78	44.79	15.61	0.5

Table 6. Results of LCIA index per FU (kg-weighted/kg cellulose) for both process.

Environmental Impact	Units	Results	
		Acetosolv	*Flower Residues*
Resource Depletion (E_1)	[MJ/kg oil eq./m^3]	7.65×10^{-3}	9.10×10^{-3}
Global Warming (E_2)	*[kgCO$_2$ eq./kg]*	32.45	4.92×10^{-4}
Ozone Depletion (E_3)	*[kg CFC-11 eq./kg]*	0	0
Acidification (E_4)	*[(kg SO$_2$ eq./kg]*	10.62	8.88×10^{-4}
Eutrophication (E_5)	*[kg PO$_4$ eq./kg]*	0	0
Photochemical Smog (E_6)	*[kg NMVOC eq./kg]*	1.88	5.18×10^{-3}
Human Toxicity (E_7)	*[kg 1,4-DCB eq./kg]*	0	0
Aquatic Toxicity (E_8)	*[Kg 1,4-DCB eq./kg]*	25.33	8.84×10^{-4}

The weighted and normalized factors can be can be reviewed elsewhere (Gloria, *et al.*, 2007). In general, ozone layer (E_3), eutrophication (E_5) and human toxicity (E_7) impacts contributed to a greater extent than non-renewable resources (E_1), global warming (E_2), acidification (E_4), photochemical oxidation (E_6) and aquatic toxicity (E_8) impacts.

Fig. 3 shows a comparison of the potential LCIA index weighted per FU for the designed process and the benchmark. Compared with the EmimAoC process, the Acetosolv process shows significantly higher environmental impacts in global warming (E_2), acidification (E_4), photochemical smog (E_6) and aquatic toxicity (E_8). This can be attributed to emissions of CO_2 and hydrochloric acid.

Table 7. Results of LCIA indexes weighted per FU (kg-weighted/kg cellulose) for both process

Environmental Impact	Normalized index (kg-weighted/kg cellulose)	
	Acetosolv	*Flower Residues*
Resource Depletion (E_1)	2.96×10^4	3.35×10^{-4}
Global Warming (E_2)	4.2×10^2	1.65×10^{-5}
Ozone Depletion (E_3)	0	0
Acidification (E_4)	2.26×10^3	4.47×10^{-7}
Eutrophication (E_5)	0	0
Photochemical Smog (E_6)	8.58×10^4	8.25×10^{-6}
Human Toxicity (E_7)	0	0
Aquatic Toxicity (E_8)	1.08×10^{-5}	$3.78 \times 10^{-1}0$

Table 8. Normalized results of LCIA indexes per FU (kg-weighted/kg cellulose) for different delignification and cellulose production processes.

	NORMALIZED LCIA INDEXES PER FU							
Process	Resource Depletion (E_1) [MJ/kg oil eq./m^3]	Global Warming (E_2) [kgCO$_2$ eq./kg]	Ozone Depletion (E_3) [kg CFC-11 eq./kg]	Acidification (E_4) [(kg SO$_2$ eq./kg]	Eutrophication (E_5) [kg PO$_4$ eq./kg]	Photochemical Smog (E_6) [kg NMVOC eq./kg]	Human Toxicity (E_7) [kg 1,4-DCB eq./kg]	Aquatic Toxicity (E_8) [Kg 1,4-DCB eq./kg]
Organosolv[a]	-	9.23	-	0.025	5.3×10^{-2}	-	-	-
Paper production from bagasse[b]	17.82	729.81	1.5×10^{-4}	3.43	0.71	0.37	242.14	57.31
Cellulose dissolution in BmimCl[c]	9.1×10^{-3}	3.7	7.7x10-8	9.4×10^{-3}	1.8×10^{-3}	1.1×10^{-3}	2.2×10^{-1}	1.2×10^{-1}

References
a. (Prasad et al. 2016)
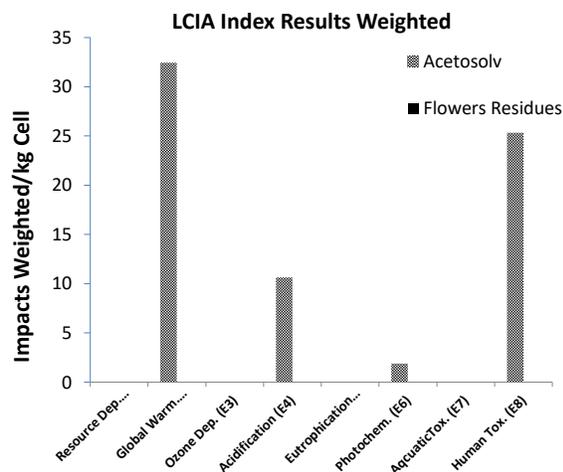b. (Poopak & Agamuthu 2011)
c. (Righi et al. 2011)

Fig. 3. Comparison of potential LCIA impacts weighted per FU (kg /kg cellulose) and relative contributions of potential LCIA impacts.
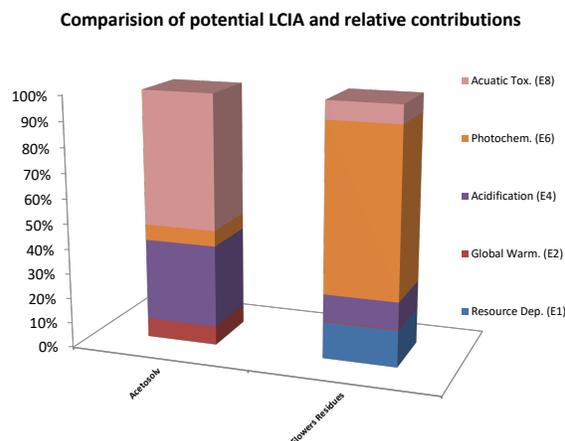

Fig. 4. Comparison of normalized potential LCIA and their relative contributions.

Fig. 4 shows the relative contributions of selected LCIA index for the EmimAoC and the benchmark processes. Impacts for the EmimAoC process are dominated by photochemical smog with about 65% percent of the contribution. This can be explained by the contributions to resource depletion (13.0%), acidification (10.0%) and aquatic toxicity (8.0%), which in turn are due to extensive use of organic compounds in the process.

The global warming potential of this process is negligible. For the Acetosolv process, major impacts are aquatic toxicity (60.0%) and acidification (25.0%) due to the required solvents and acid catalysts. Photochemical smog and global warming are next in importance mainly due to the needed organic compounds.

To have an idea of the order of magnitude and robustness of our LCIA analyses, in table 8, the obtained indexes were compared with those of Righi *et al* (2011) for the dissolution of cellulose in the ionic liquid BmimCl as well as those of Prasad *et al* (2016)

(Prasad *et al.*, 2016) for the Organosolv process, and Poopak & Agamuthu (2011) (Poopak and Agamuthu, 2011) for the production of paper from bagasse. A direct comparison with the data by Righi *et al* (2011) demonstrates that resource depletion (E_1) and ozone depletion (E_3) are similar to those calculated by us while global warming (E_2), acidification (E_4), photochemical smog (E_6) and aquatic toxicity (E_8) differed by several orders of magnitude. The difference of 4 orders of magnitude for the E_2 is most likely due to the higher energetic demand to achieve a complete dissolution of cellulose in BmimCl, which is not case for our process that avoids heating and cooling operations.

Conclusions

It was demonstrated that the methodology for estimating the potential of sustainability and its holistic approach that simultaneously considers the economic, energy and environmental implications of the processes represents a powerful tool for the study and selection of process alternatives that are being developed and under competition.

This work evaluated the sustainability potential of a newly designed process for the production of cellulose that relies on residual local agricultural biomass and incorporates the ionic liquid 1-ethyl-3-metilimidazolium acetate (EmimAoC) as main extraction solvent. This was accomplished by simulating the process and subsequently implementing the sustainable engineering analysis methodology developed by Fan and Zhang (2012a). This approach allowed us to quantitatively compare the new process with the low-impact and profitable process acetosolv, in light of the simultaneous evaluation of energy consumption, economic feasibility, and environmental and human toxicity impacts. With respect to the benchmark, our findings strongly suggest that the proposed process provides a route for approximately 45% increase in profitability, a 32 fold reduction in energy consumption, and almost negligible environmental impact.

This was mainly attributed to the greener production scheme of EmimAoC as well as its potential to be recycled several times back into the process. Despite these attractive benefits, it is important to experimentally confirm the thermal and chemical stability of EmimAoC after several recycles as this factor is key to assure the sustainability of the proposed process.

Nomenclature

AGU	glycosidic anhydride units
B_j	amount of required resource j per FU
CFC - 11	trichlorofluoromethane
DCB	1,4 dichlorobenzene
DMSO	dimethyl sulfoxide
DP	degree of polimerization
eci,j	factor of effect of the potential i generated by the emissions of compound j
Ei	potential impact on the enviromental i
ELEC-NRTL	electrolytes non-random two liquid
EmimAoC	1-etil-3-metil imidazolium
E_N	normalized impact
E_p	weighted potential impact
FAO	Food and Agriculture Organization of the United Nations
F_p	weight factor
H formation	solid heat of formation, J/kmol
ICA	Colombian National Institute of Agriculture
IL	ionic liquid
LCA	life cycle assessment
M	molecular weight, kg/kmol
MCC	microcristaline cellulose
nj	number of repetitions of the functional group j
NREL	National Renewable Energy Laboratory
NMVOC	Non methane volatile organic compounds
P	pressure, MPa
Pc	critic pressure, MPa
P_0	reference pressure, MPa
P_{oo}	surroundings pressure dead state, K
Sm	mix entropy
T	temperature, K
Tc	critic temperature, K

T_0	reference temperature, K
T_{oo}	surroundings temperature dead state, K
UF	functional unit
V	volume, cm^3
Vc	critic volume, cm^3/mol
W_i	relative normalization factor
X	exergy, kJ/kg
X_i^{CH}	specific chemical exergy of component i, kJ/kg
X_D	destroyed exergy, kW/kg
X_{DT}	total destroyed exergy, kW/kg
X^f	exergy flow, kJ/kg
X_i^0	standard chemical exergy of the component i, kJ/kg
$X_{CH,j}^0$	standard chemical exergy of functional group j, kJ/kg
X_i^{PH}	physical exergy, kJ/kg

Greek symbols

ζ	feedstock and products, US$/kg
γ	mass flow, kg/h
μ_{oo}	chemical potential of the dead state

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