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Life cycle assessment of bioethanol from corn stover from soil phytoremediation

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Abstract

Bioethanol is the most widely used biofuel in the world. Bioethanol production from biomass is a way to reduce crude oil consumption and the environmental pollution. This work aims to evaluate the potential environmental impacts of bioethanol production from corn stover obtained from phytoremediation, comparing four different acids (Sulfuric, Nitric, Hydrochloric and Acetic acids) to perform the biomass pre-treatment. The study follows a life cycle thinking perspective, accounting for all the life cycle stages from corn stover grinding, to biomass pre-treatment, enzymatic hydrolysis, fermentation, filtration and ethanol distillation, on a "gate-to-gate" approach. The life cycle inventory was developed using mainly primary data from laboratorial experiments, and complemented whenever necessary with information from literature and from the Ecoinvent V3.0 database available in the SimaPro 8.0.2 software. For the environmental impact assessment, the ILCD Midpoint 2011 methodology was used. Results show that in general, the sulfuric and hydrochloric acids have a better environmental performance than the acetic and nitric acids. Also, results show that pre-treatment, followed by enzymatic hydrolysis are the process steps with the highest relative contribution to the potential environmental impacts. Thus, an improvement analysis should focus on these process steps, for example to reduce fossil energy consumption by implementing renewable energy sources.

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Keywords: Acid pre-treatment; Agriculture residues; Bioethanol; Enzymatic hydrolysis; Life cycle Assessment; Lignocellulosic biomass

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1. Introduction

Bioethanol is currently the most widely used liquid biofuel for gasoline engine vehicles worldwide [1,2]. It can be produced from renewable biomass sources such as agriculture wastes (e.g. rice straw, wheat straw, corn stover and bagasse) and it is considered one of the most promising biofuels, aiming to reduce the greenhouse gas tailpipe emissions and thus, the climate change impacts [3,4]. One possible renewable source for bioethanol production is corn stover, which consists of the leaves, stalks, and cobs of maize (corn) plants left in a field after harvest. This way it is possible to give another end use for this agriculture waste, using it as a raw material on the biofuels industry, instead of sending it to final deposition, and promoting a more circular economy. However, before implementing this solution on an industrial scale, it is necessary to carry out economic and environmental evaluations.

With regard to the bioethanol environmental performance, the assessment must follow a life cycle thinking (LCT) approach. To produce bioethanol from corn stover, the biomass must be first reduced to smaller particles, by grinding, and then, be pretreated to remove lignin from biomass preserving the hemicellulose, reducing the cellulose crystallinity and increasing the porosity of the material [5], allowing the entry of enzymes, minimizing the hydrolysis time and reducing the required amount of enzyme [6,7]. After pre-treatment, biomass is submitted to enzymatic hydrolysis in which the cellulose and hemicelluloses are converted into simple sugars, and then, to fermentation by yeasts to bioethanol. Finally, the obtained broth is filtered and the liquid part is distilled to recover ethanol [2,8].

According to Ferreira et al. [9] enzymatic hydrolysis is carried out at low temperatures and has lower energy consumption than acid hydrolysis. Belkacemi and Hamoudi [8] refers that to obtain a sugar conversion of 90% of the corn stover, enzymatic hydrolysis must be carried out at a temperature of 30 °C and pH 5. The glucose in the hydrolyzed broth is then fermented by *Saccharomyces cerevisiae*, obtaining up to 4 g/L of ethanol [10]. Hence, this work aims to evaluate the potential environmental impacts of bioethanol production from corn stover cultivated in soil contaminated with metals aiming at its phytoremediation, following a Life Cycle Assessment (LCA) methodology [11]. The study is based on laboratory data obtained experimentally [12] aiming at the optimization of the pre-treatment and enzymatic hydrolysis steps of bioethanol production from corn stover derived from contaminate soil phytoremediation.

2. Methods

In this study, the potential environmental impacts of bioethanol production from corn stover are evaluated, following the LCA methodology, on a gate-to-gate approach, comparing different acids to perform the pre-treatment of the lignocellulosic biomass.

LCA is a structured, comprehensive and objective methodology to quantify all emissions and resources used in a product or service life cycle, and to evaluate its potential environmental impacts [13]. An LCA study considers all the life cycle stages of a product, from the extraction of raw materials, through production, transportation and use, until the end of life (final disposal or recycling). Currently, it is consensually considered as the most adequate tool to support the definition of environmental strategies and/or policies, and to support decision making, concerning changes in the current production and consumption patterns, clearly unsustainable in the medium to long terms. The LCA methodology is internationally standardized by ISO 14040 [14] and ISO 14044 [15] and it consists of four phases: (i) Goal and scope definition; (ii) Inventory analysis; (iii) Environmental impacts assessment and (iv) Interpretation.

2.1. Goal and scope definition

Study goal

This study aims to evaluate the potential environmental impacts associated with bioethanol production from corn stover, focusing on the comparison of four different acids to perform the biomass pre-treatment: Sulfuric acid (H_2SO_4), Nitric acid (HNO_3), Hydrochloric acid (HCl), Acetic acid (CH_3COOH).

Functional unit

The functional unit selected for this study is the production of 1 L of bioethanol. It takes into account the literature LCA studies in the area, in particular related to the production of bioethanol from lignocellulosic materials.

Study scope and assumptions

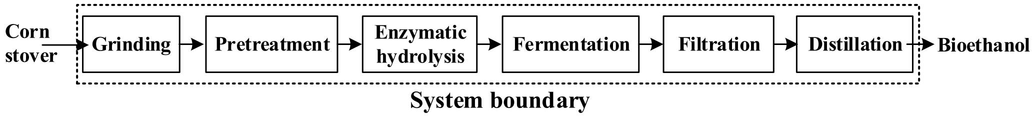

Fig. 1. Study system boundary of bioethanol production from corn stover.

The life cycle steps considered for the study are: grinding of the corn stover, acid pre-treatment, enzymatic hydrolysis, fermentation, filtration, and distillation, as shown in Fig. 1 of the study system boundary. The corn sow and growth and the bioethanol consumption are out of this study scope. For the defined life cycle steps, all material, energy and water inputs and emissions for air, soil and water were taken into account. The generation of energy (electricity or fuel), and the production of the auxiliary materials used in the process were also taken into account.

First, corn stover is grinded to reduce the size of the biomass particles, using a 1500 W Fritsch electric mill. For the pre-treatment step, 20 g of the previously ground biomass is added to each of 4 glass reagent bottles, containing each 150 ml of a different acid (H_2SO_4, HNO_3, HCl and CH_3COOH), aiming to identify which is the best acid to perform the biomass pre-treatment. Then, the glass reagent bottles are placed into a thermostatic water bath at 85 °C, for 48 h, with constant stirring. For the enzymatic hydrolysis step, it is necessary to set up the pH to 5 in each assay, using a 40% sodium hydroxide titrating solution. Then, 2 mL of each enzyme, *Accellerase* and *Ultraflo*, are added to each glass reagent bottle. After homogenization, the assays are placed into a thermostatic water bath, at 50 °C with constant stirring for 13 h. For the fermentation stage, the yeast is previously prepared by diluting 40 g of *Saccharomyces cerevisiae* in 200 mL of deionized water. Then, 25 mL of this enzyme solution is added to each of the 4 glass reagent bottles and they remain in a thermostatic water bath at 37 °C, for 11 days, with constant stirring.

Finally, the mixture in the assays is filtered, the resulting sludge is treated as a solid residue and the liquid component is a liquor that will be distilled, using a rotary evaporator, at a temperature of 60 °C and a pressure of 120 mbar.

2.2. Inventory analysis and data sources

Inventory data, including materials, water and energy were mainly obtained from laboratorial experiments [12]. Electricity consumption was estimated considering thermodynamic principles and the power of the equipment used for the thermostatic bath with agitation, time and temperature of operation. The water consumption corresponds to the volume needed for the assays in the bath, based on the equipment's capacity. Experimental data was complemented with information from the EcoInvent V3.0, such as for obtaining the Portuguese energy mix for electricity production and the transportation of materials from the source to the laboratory. Some auxiliary materials such as acids and bases used in the experiments were defined by EcoInvent. Other information is from the literature. The corn stover used in the study was cultivated in Estarreja soil, in Portugal, where the plants were used for soil phytoremediation. The auxiliary materials used in the process come from Lisbon. So the consumption of diesel in the transportation of materials to the laboratory is estimated considering the distance from suppliers and the average diesel consumption of the means of transport used. Cut-off criteria and allocation of energy and material consumption as well as emissions were not defined. Table 1 synthetizes the inventory data for the production of 1 L of bioethanol from corn stover.

2.3. Environmental impact evaluation

According to the inventory data and the expected environmental impacts, the following impact categories were selected for this study [16]:

- CC - Climate change (kg CO_2 eq/FU)
- OD - Ozone depletion (kg CFC-11 eq/FU)
- POF - Photochemical ozone formation (kg NMVOC eq/FU)
- AP - Acidification potential (kg NH_3 eq/FU)

Table 1. Inventory data for producing 1 L of bioethanol from corn stover.

Process	Inputs	Amount	Unit
Grinding	Electricity	0.050	kWh/L ethanol
Pre-treatment	Corn stover	0.200	kg/L ethanol
	Sulfuric acid	0.150	dm^3/L ethanol
	Nitric acid	0.150	dm^3/L ethanol
	Hydrochloric acid	0.150	dm^3/L ethanol
	Acetic Acid	0.150	dm^3/L ethanol
	Electricity	0.734	kWh/L ethanol
	Water	0.200	dm^3/L ethanol
	Diesel	0.0426	dm^3/L ethanol
Enzymatic hydrolysis	Sodium Hydroxide (40%)	0.020	dm^3/L ethanol
	Accellerase enzyme	0.002	dm^3/L ethanol
	Ultraflo enzyme	0.002	dm^3/L ethanol
	Electricity	0.306	kWh/L ethanol
	Water	20.000	dm^3/L ethanol
	Diesel	0.0425	dm^3/L ethanol
Fermentation Filtration Distillation	*Saccharomyces cerevisiae*	0.040	kg/L ethanol
	Deionized water	0.200	dm^3/L ethanol
	Electricity (bath + rotary evaporator)	0.550	kWh/L ethanol
	Water	20.000	dm^3/L ethanol
	Diesel	0.0425	dm^3/L ethanol

- EP - Eutrophication potential (kg PO_4^{3-} eq/FU)
- EC - Ecotoxicity (kg 1,4 DB eq/FU)
- WRD - Water resource depletion (m^3 water/FU)
- FRD - Fossil resource depletion (kg Sb eq/FU)

This is an attributive study, since the environmental impacts are evaluated based on an existing process for bioethanol production from corn stover. The potential environmental impacts were estimated using the ILCD Midpoint 2011 methodology, using the SimaPro 8.0.2 software. This method was developed by the European Commission in 2011, in order to reconcile the various existing LCA methods [17].

3. Results and discussion

Four scenarios were defined for the biomass pre-treatment stage, each one using a different acid (Sulfuric acid, Nitric acid, Hydrochloric acid, Acetic acid), and keeping the remaining stages unchanged. Fig. 2 shows the overall results for each of the four acids analyzed. Please note that the results were scale-up to fit in the same graphic, and the units were not included (please see Section 2.3) to allow a better results visualization. As shown in Fig. 2, H_2SO_4 contributes less than the other acids to the total potential environmental impact, in nearly all impact categories, except for FRD in which the contributions of HNO3 and CH_3COOH are higher and for AP in which the contribution of HNO_3 is higher.

The HNO_3 is the acid with the higher contribution to the total environmental impacts, except for WRD in which the contribution of HCl is higher, and for OD in which the contributions of HCl and CH_3COOH are higher. The HCl contribution to the total environmental impacts is higher than the other acids for the EC category and, it is second highest, after CH_3COOH, in the OD category. The CH_3COOH contribution to the total environmental impacts is higher than the other acids in the OD category. It is the second highest, after HNO_3 in CC, POF, EP and FRW, and it is the second highest, after HCL, in the OD, EC and WRD categories.

In general, it is observed that sulfuric acid and hydrochloric acid have a better environmental performance than the acetic and nitric acids. This is due to the fact that the production processes of the first acids are already well optimized at the industrial level with minimized environmental impacts.

Fig. 3 shows the relative contribution of each life cycle step (grinding, pre-treatment, enzymatic hydrolysis and fermentation) to the potential environmental impacts, due to the acid's pre-treatment influence. It can be seen that the pre-treatment step, followed by the enzymatic hydrolysis, have the highest relative contribution to the potential

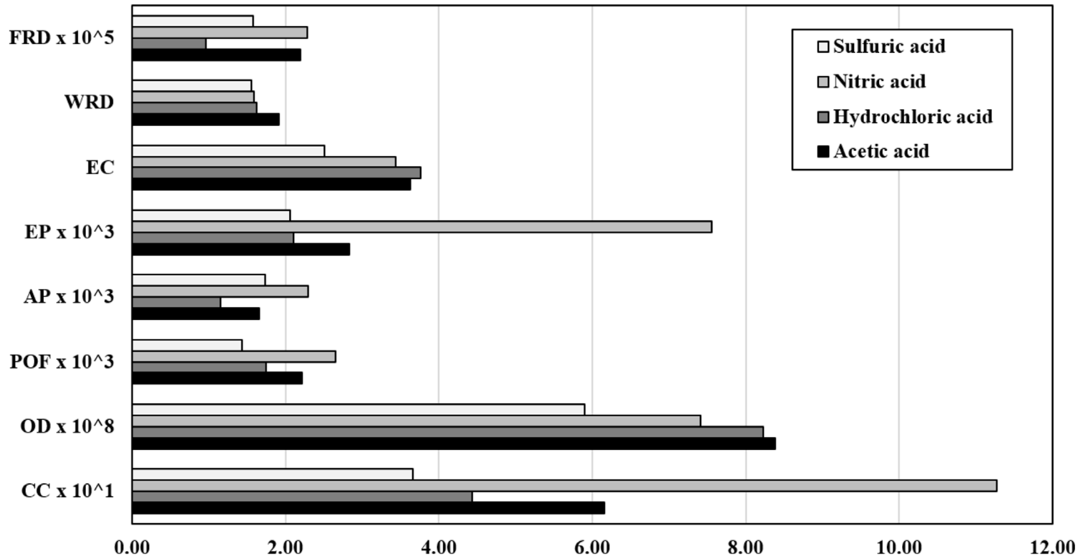

Fig. 2. Total potential environmental impacts of corn stover bioethanol, comparing four acids used for the biomass pre-treatment: sulfuric, nitric, hydrochloric, and acetic acids (environmental indicators units can be found in Section 2.3)

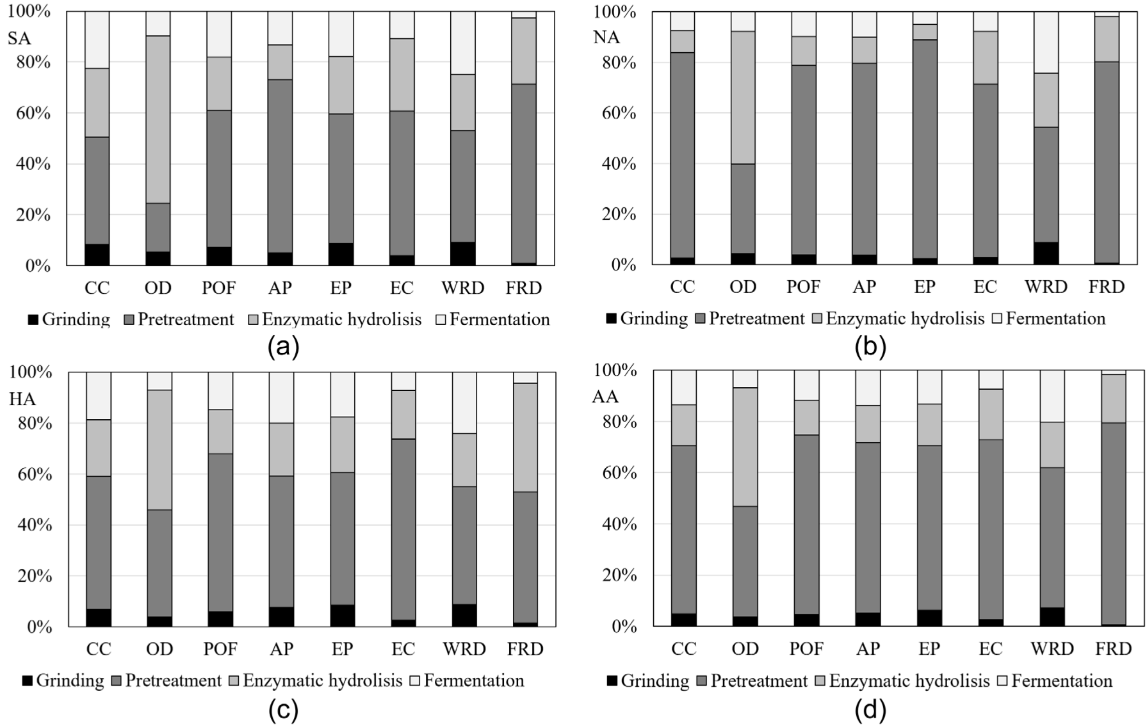

Fig. 3. Relative contribution of each life cycle step (grinding, pre-treatment, enzymatic hydrolysis and fermentation) to the potential environmental impacts, due to the pre-treatment acid's influence: (a) sulfuric acid (SA), (b) nitric acid (NA), (c) hydrochloric acid (HA), (d) acetic acid (AA).

environmental impacts. This means that one needs to focus on these process steps for an analysis of improvements. After analyzing possible improvements to the bioethanol production process, it is recommended to reduce fossil energy consumption, through the implementation of renewable energy sources, in particular photovoltaics, and also, to look for closer suppliers to reduce diesel consumption in the transportation of the auxiliary materials for the bioethanol production process.

4. Conclusion

In this work, bioethanol production from corn stover was evaluated from an environmental point of view on a life cycle thinking perspective. The pre-treatment, followed by enzymatic hydrolysis, are the process steps with the highest contribution to the potential environmental impacts. Four acids are compared to perform the pre-treatment of corn stover, showing that it is preferable to use sulfuric or hydrochloric acid to perform that operation, since they have lower contributions to the potential environmental impacts, as the industrial production of these acids is already well established and optimized for minimizing the environmental impacts. Nitric followed by acetic acid presents the highest Climate Change impacts. The use of renewable energy for grinding or enzymatic hydrolysis has the potential to reduce the Fossil Resources Depletion.

CRediT authorship contribution statement

Teresa M. Mata: Investigation, Formal analysis, Validation, Writing – review & editing, Writing – original draft. **Sara Rodrigues:** Investigation, Formal analysis, Writing – review & editing. **Nídia S. Caetano:** Writing – review & editing, Project administration, Funding acquisition. **António A. Martins:** Investigation, Formal analysis, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Demirbaş A. Bioethanol from cellulosic materials: A renewable motor fuel from biomass. Energy Sources 2005;27:327–37. http://dx.doi.org/10.1080/00908310390266643.
[2] Sarkar N, Ghosh SK, Bannerjee S, Aikat K. Bioethanol production from agricultural wastes: An overview. Renew Energy 2012;37:19–27. http://dx.doi.org/10.1016/j.renene.2011.06.045.
[3] Kim S, Dale BE. Environmental aspects of ethanol derived from no-tilled corn grain: Nonrenewable energy consumption and greenhouse gas emissions. Biomass Bioenergy 2005;28:475–89. http://dx.doi.org/10.1016/j.biombioe.2004.11.005.
[4] Kim S, Dale BE. Global potential bioethanol production from wasted crops and crop residues. Biomass Bioenergy 2004;26:361–75. http://dx.doi.org/10.1016/j.biombioe.2003.08.002.
[5] Chen M, Zhao J, Xia L. Enzymatic hydrolysis of maize straw polysaccharides for the production of reducing sugars. Carbohydr Polym 2008;71:411–5. http://dx.doi.org/10.1016/j.carbpol.2007.06.011.
[6] Hakeem KR, Jawaid M, Rashid U. Biomass and bioenergy: Applications. Biomass Bioenergy Appl 2015;1–397. http://dx.doi.org/10.1007/978-3-319-07578-5.
[7] Sánchez ÓJ, Cardona CA. Trends in biotechnological production of fuel ethanol from different feedstocks. Bioresour Technol 2008;99:5270–95. http://dx.doi.org/10.1016/j.biortech.2007.11.013.
[8] Belkacemi K, Hamoudi S. Enzymatic hydrolysis of dissolved corn stalk hemicelluloses: Reaction kinetics and modeling. J Chem Technol Biotechnol 2003;78:802–8. http://dx.doi.org/10.1002/jctb.865.
[9] Ferreira S, Duarte AP, Ribeiro MHL, Queiroz JA, Domingues FC. Response surface optimization of enzymatic hydrolysis of cistus ladanifer and Cytisus striatus for bioethanol production. Biochem Eng J 2009;45:192–200. http://dx.doi.org/10.1016/j.bej.2009.03.012.

[10] Moniruzzaman M. Alcohol fermentation of enzymatic hydrolysate of exploded rice straw by Pichia stipitis. World J Microbiol Biotechnol 1995;11:646–8. http://dx.doi.org/10.1007/BF00361008.
[11] Mata TM, Martins AA, Neto B, Martins ML, Salcedo RLR, Costa CAV. Lca tool for sustainability evaluations in the pharmaceutical industry. Chem Eng Trans 2012. http://dx.doi.org/10.3303/CET1226044.
[12] Santos MH. Bioethanol production from corn stover used in phytoremediation of heavy metal contaminated soils (Produção de bioetanol a partir de resíduos de plantas usadas em fitoremediação de solos contaminados com metais pesados) (in Portuguese). Instituto Superior de Enegenharia do Porto; 2019.
[13] Rodrigues V, Martins AA, Nunes MI, Quintas A, Mata TM, Caetano NS. LCA of constructing an industrial building: Focus on embodied carbon and energy. In: Energy procedia. 2018, http://dx.doi.org/10.1016/j.egypro.2018.10.018.
[14] ISO 14040. Environmental management — life cycle assessment — principles and framework. International Organization for Standardization; 2006.
[15] ISO 14044. Environmental management — life cycle assessment — requirements and guidelines. International Organization for Standardization; 2006.
[16] Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of bioethanol production from wheat straw. Biomass Bioenergy 2012;47:9–19. http://dx.doi.org/10.1016/j.biombioe.2012.10.017.
[17] European Union. Characterisation factors of the ILCD recommended life cycle impact assessment methods. European Commission - Joint Research Centre - Institute for Environment and Sustainability; 2012.