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Are Eucalyptus Harvest Residues a Truly Burden-Free Biomass Source for Bioenergy? A Deeper Look into Biorefinery Process Design and Life Cycle Assessment

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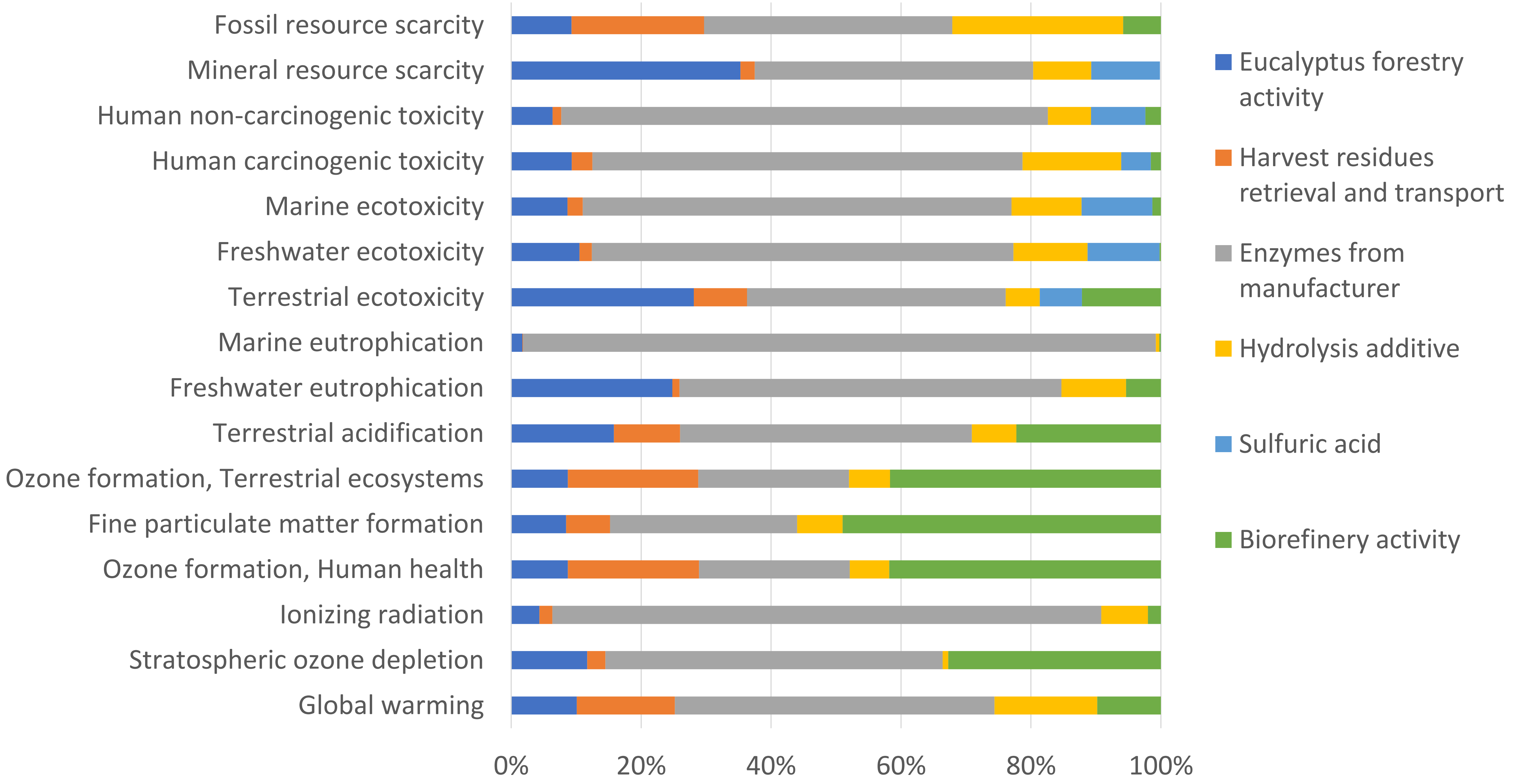
Graphical Abstract

Environmental profile of bioethanol production from Eucalyptus Forest Residues in Brazil



Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRediT author statement

Guilherme Pessoa Nogueira: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization; **Marcelle C. McManus:** Methodology, Supervision, Writing - Review & Editing; **David J. Leak:** Supervision, Writing - Review & Editing, Project administration, Funding acquisition; **Telma Teixeira Franco:** Writing - Review & Editing, Project administration, Funding acquisition; **Marina Oliveira de Souza Dias:** Conceptualization, Methodology, Supervision, Writing - Review & Editing; **Carla Kazue Nakao Cavaliero:** Conceptualization, Methodology, Supervision, Writing - Review & Editing.

Are Eucalyptus Harvest Residues a Truly Burden-Free Biomass Source for Bioenergy? A Deeper Look into Biorefinery Process Design and Life Cycle Assessment

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Highlights

- **Biodigestion and energy integration improved electricity production in 105%;**
- **Hydrous and anhydrous ethanol production generate 31.5 and 35.5 g CO_{eq}.MJ^{-1}, each;**
- **Forestry activities and retrieval operations are environmentally relevant;**

- **Enzymes are the main environmental bottleneck in most of the impact categories;**
- **The inventories for enzymes available are not consistent and lack transparency.**

Abstract

With the advent of RenovaBio, Brazil has cast a new light towards the life cycle of cellulosic ethanol. Once considered a resource intensive alternative pathway to achieve the same biofuel, second-generation approaches can now provide an economic advantage due to their potentially lower carbon footprint. The exploration of lignocellulosic harvest residues to this end can be beneficial, since productivity can be increased while not expanding cultivated areas. Eucalyptus forest residues are an example, result of logging and harvest procedures, being a low-cost and readily available biomass. Through an integrated biorefinery process simulation and a Life Cycle Assessment of the coproduction of ethanol and electricity, it was analyzed whether forestry burden is truly relevant when exploring this material, identifying technical and environmental bottlenecks. The biorefinery design implementation of anaerobic digestion and energy integration allowed a productivity boost 20% for ethanol and 115% for electricity. With a 80 km collection radius, an annual production capacity of 30.3 ML could be achieved in the Campinas region. Enzymes were identified as the main environmental hotspot, but inconsistent published datasets and lack of transparency lead to inconclusive results regarding this input. While the burden associated with the lignocellulosic feedstock is relevant in most impact categories, the main bottleneck resides within the biorefinery itself, with chemicals related to pretreatment and hydrolysis, boiler emissions and water consumption. Nevertheless, eucalyptus harvest residues cannot be considered a burden-free resource, since additional operations such as retrieval and transportation cannot be dismissed and often surpasses the impact potential of the aforementioned forestry activities.

Keywords

- **Cellulosic ethanol**
- **Life Cycle Assessment**
- **Biorefinery design**
- **Eucalyptus**
- **Harvest residues**

1. Introduction

Mitigating climate change is a global challenge. In order to limit temperature rise to 1.5 ºC, carbon emissions would need to be reduced in 7.6% every year until 2030. In 2018, however, greenhouse gases emissions (GHG) reached an record of 51.8 Gt of CO_{2eq} (Watts et al., 2021). A paradigm shift towards the economy decarbonization, thus, is urgent and bioenergy generation plays an important role to this solution in the short and medium terms (IEA, 2020).

Encompassing the production of electricity, liquid biofuels, biogas and hydrogen, bioenergy's suitability for this task relies heavily on land-use governance and optimal use of biomass. Which implies expanding exploration for different biomass sources, such as dedicated cellulosic crops and agro-forestry residues (Rogelj et al., 2018), and maximizing its valorization (Moncada et al., 2016). Significant advances were made regarding the industrial feasibility and scale-up of cellulosic ethanol, reducing costs progressively and moving towards the biorefinery concept (Kumar et al., 2020; Lugani et al., 2020).

Waste biomass have an intrinsic advantage, under the life-cycle perspective, when used for biofuel production, since agricultural environmental burden is diminished or even dismissed entirely (Demichelis et al., 2020). This provides an extra margin in reducing GHG emissions, in substitution fossil fuels, and can even be translated into economical perks, such as in Brazil, with RenovaBio (Grassi and Pereira, 2019).

1.1. Brazilian Drivers for Low Carbon Fuels

In 2019, 45.4% of GHG emissions of the Brazilian energy sector were attributed to transportation (EPE, 2020). This is addressed in the Brazilian intended National Determined Contributions (iNDC) for COP 21, in which the sustainable bioenergy share of energy grid is to be increased to 18%, by ramping up supply of advanced biofuels, with a focus on ethanol and biodiesel, by 2030 (CGEE, 2017). Surprisingly, this target has already been met by the sugarcane sector alone, according to the National Energy Balance (BEN), with bioethanol demand rising 15.5% in 2019, compared to the previous year. While a promising scenario, ethanol's fossil counterpart gasoline still represents 55% of the energy used in light vehicles in Brazil, and 25.3% of the transportation sector total energy demand (EPE, 2020).

This scenario is expected to further improve with RenovaBio, a national policy approved in 2018 developed to foster biofuel production and demand. In this program, biofuel producers are rewarded based on their products' life-cycle. Production chains that rely less on fossil-derived inputs and emit less GHG, while also maximizing productivity and efficiency, will receive better grades. Then, by comparison with their fossil counterparts, carbon certificates (CBios) are given, that are to be acquired by fuel distributors, in order to commercialize fossil fuels (CGEE, 2017; Grassi and Pereira, 2019).

Furthermore, by translating environmental benefits into economic advantages, RenovaBio could boost demand for cellulosic biofuels (second-generation, or 2G), since they represent a potential reduction in GHG emissions when compared to first generation (1G) biofuels (CGEE, 2017; Wiloso et al., 2012). On the other hand, such biofuels may present a significant environmental burden in other impact categories, such as terrestrial acidification, eutrophication of water bodies, ecotoxicity and human health, on a regional scale. The Life Cycle Assessment (LCA) tool addresses such categories, identifying critical hotspots in process design of bioenergy and other renewables operations, stimulating progress towards more environmentally friendly solutions (Borrion et al., 2012; Cavalett et al., 2013; Huijbregts et al., 2017; McManus and Taylor, 2015).

1.2. Brazilian bioethanol industry

The Brazilian ethanol industry relies heavily on sugarcane, which is processed on 1G mills for both ethanol and electricity production, by using bagasse as fuel. As the main lignocellulosic residues available, sugarcane bagasse rapidly became the focus for research and process development regarding 2G solutions. Scale-up, however, has proved to be challenging, since the overall technology readiness level was overestimated by both government and private-sector investors. This led to a slow and resource-intensive learning curve, that could have been avoided by adopting a step-wise approach (Dias et al., 2015, 2012; Lynd, 2017).

Cellulosic ethanol in Brazil also lacks diversification of feedstock, crucial to bring flexibility, both in operation and material availability during sugarcane off-season (CGEE, 2010; Ghatak, 2011; Moncada et al., 2016). Eucalyptus is widely cultivated in Brazil, with São Paulo state being the country’s second biggest producer (17.5%) in 2019, with 1.22 Mha of planted area, with an average productivity of 35.3 $m^3.year^{-1}.ha^{-1}$ (IBÁ, 2020). Its harvesting, however, generates a plethora of lignocellulosic residues, such as bark, branches, logs, and leaves. These Eucalyptus Forest Residues (EFR), may account for up to 25% of the total aerial biomass and be considered a low-cost alternative feedstock (Dias, 2014; Mariano, 2015).

As opposed to bagasse, EFR are available on field and play an important role in soil protection and maintenance on eucalyptus forests. By covering the soil, EFR assure nutrient recycling, water retention and erosion avoidance, all of which contribute to soil quality and the forest overall biomass yield (Foelkel, 2007; Hernández et al., 2016; Souza et al., 2016). This could inhibit the exploitation of EFR as a feedstock. However, studies indicate that a fraction of these residues can be retrieved with little to no detriment to soil protection, and could even be replaced by industrial residues from the pulp and paper business (Hernández et al., 2016; Pincelli et al., 2017). Therefore, if they can be collected with minimal environmental and economic burden, these residues may provide a viable feedstock for biofuel production.

In this study we have explored EFR as a lignocellulosic feedstock for ethanol production, with electricity cogeneration, by evaluating its technical feasibility, process bottlenecks and potential scale within the context of São Paulo state. Following this, we estimated the potential environmental impacts associated with this product portfolio, by means of LCA, highlighting the main hotspots found and suggesting where design choices should be made to improve the biorefinery environmental profile.

2. Material and methods

This work is divided into two main parts: (a) process design and simulation, where literature process data is assembled into a coherent biorefinery process design, in which bottlenecks and scale potential can be identified; and (b) Life Cycle Assessment (LCA), where the main biorefinery products are analyzed from a life cycle perspective, to unravel environmental hotspots in the process configuration and its inputs and outputs.

2.1. Process design and simulation

Three scenarios were built in Aspen Plus v10, following the simulation methodology introduced by Dias (2011), Humbird et al. (2011) and Morais et al. (2016). The core design (Figure 1) consists of an independent cellulosic ethanol biorefinery, composed of five process units:

i. 2G processing: EFR is fed into the process, going through a two step pretreatment (dilute acid, followed by steam explosion), and then through a pre-saccharification and simultaneous saccharification and fermentation (PSSF). This unit is described in more detail in section 2.1.2 and is depicted in Figure 2;
ii. Purification: the wine obtained from the PSSF is purified by distillation into hydrous ethanol (HE), with 93% purity (wt.);
iii. Dehydration: half of the resulting HE production is further dehydrated into anhydrous ethanol (AE), with 99.5% purity (wt.) by extractive distillation with monoethylene glycol;
iv. Anaerobic digestion (AD): fed by the pentose liquor, generated in 2G processing; and by the vinasse from Purification and Dehydration. The mixture is, then, digested anaerobically into biogas;
v. Cogeneration: fueled by biogas and the ligneous solid residue from the PSSF, this unit generates steam and electricity to meet the process energy demand, with the surplus being available as part of the product portfolio.

Each of the three biorefinery scenarios is defined by incremental improvements on the process design:

1. Base scenario: in this first option, the AD unit is absent. Therefore, cogeneration uses the ligneous residue and 17% of the EFR inlet as fuel, in order to meet the biorefinery energy requirements;
2. Biodigestion: AD is now implemented. All of the EFR inlet is fed into the 2G processing unit. Biogas supplements the ligneous solid as fuel in the boiler;
3. Biodigestion + Heat Integration: in this, an energy integration arrangement was implemented on the dilute acid reactor inlet, in order to

reduce the equipment’s steam demand (Figure 3). The AD unit operates as described in the previous scenario.

2.1.1. Process data selection:

The adopted composition for EFR (in weight, dry basis) was 40.2% cellulose, 15.7% hemicellulose, 2.4% acetyl groups, 27.0% lignin, 13.2% extractives and 1.4% ash (Canettieri et al., 2007). Guidelines provided in the literature for the insertion of components on Aspen were followed (Morais et al., 2016). Since gallic acid is the most abundant component amongst the eucalyptus wood extractives, this chemical was used to represent this fraction (Esteves et al., 2008). Following the same logic, calcium oxide was used to represent ash (Neiva et al., 2018).

Data source selection for process performance followed the criteria list: (i) feedstock should consist of at least one of the EFR fractions, but preferably as the mixture found *in-situ* after eucalyptus harvest; (ii) data should present continuous and coherent figures for pretreatment, enzymatic hydrolysis, and fermentation; (iii) process information should be complete enough to perform a mass balance; (iv) experiments should have been performed, preferably, at pilot scale; (v) the final ethanol titer in the fermentation should be higher than 4% (wt.).

The work by McIntosh et al. (2017, 2016, 2012) met these criteria, in which eucalyptus thinnings are used as feedstock. This source presents pilot-scale process data, including pretreatment, enzymatic hydrolysis and fermentation. This work also introduces specific process design choices and optimization to achieve economically feasible ethanol titers, such as high solids loading, simultaneous hydrolysis and fermentation (SSF), and use of additives to reduce enzyme loading.

While being a type of EFR, thinnings are not harvest residues, since they are generated during forest maintenance operations. Macroscopically, however, thinnings present a similar proportion of bark, leaves and ligneous material when compared to harvest EFR. Thinnings present 74% of ligneous material (wood and branches) (McIntosh et al., 2016), whereas EFR, 75% (Pincelli et al., 2017). The same applies to their lignocellulosic composition (Canettieri et al., 2007; McIntosh et al., 2017). Therefore it was assumed that the process had a similar performance if fed by EFR in the place of eucalyptus thinnings. The main inputs are summarized on Table 1.

2.1.2. 2G processing unit

The 2G processing unit (Figure 2) is responsible for processing EFR into wine, rich in ethanol. First, the EFR undergoes a two-step pretreatment, consisting of a reaction with dilute sulfuric acid, and then steam explosion. In both steps, the pretreated solid is washed in diffusers with water, and the resulting pentose liquor collected.

This pretreated solid transfers to the PSSF, where a pre-saccharification (PS) reactor partially hydrolyses the EFR, and then the SSF reactor finishes the hydrolysis along with the fermentation. This approach gives a smaller overall residence time, when compared to the more conventional separate hydrolysis and fermentation (SHF). PSSF is also more suitable for high solids loadings, which facilitates higher ethanol titers to be achieved (Manfredi et al., 2018).

Also, the PSSF unit uses polyethylene glycol (PEG) as an additive, to improve enzyme activity and reduce its loading. PEG acts by reducing the affinity between lignin and enzyme, increasing its availability to process cellulose. While its effects are clear, a more thorough explanation of this phenomenon is pending (McIntosh et al., 2017).

2.2. Life Cycle Assessment (LCA)

In this section, the three main biorefinery products (HE, AE and electricity) were analyzed individually. The adopted system boundary (Figure 4) consisted of: (a) forestry activity, including agrochemicals application and machinery operations; (b) EFR retrieval options; (c) biomass transportation to biorefinery; and, finally, (d) the biorefinery process itself. All of these were described in the Life Cycle Inventory (LCI) with foreground data.

In order to identify bottlenecks and benefits within the production chain, the cradle-to-gate approach was selected. The defined functional units (FU) were kilowatt-hour (kWh) for electricity and kilograms (kg) for ethanol. LCI construction and Life Cycle Impact Assessment (LCIA) calculations were performed on SimaPro 9.0, using ReCiPe 2016 midpoint. ReCiPe 2016 embodies characterization factors and a normalization methodology that are representative on a global scale, with both midpoint and endpoint indicators (Huijbregts et al., 2017).

The main source for background data was EcoInvent 3.5 (Wernet et al., 2016), incorporated in SimaPro 9.0. For attributional studies, such as this, two datasets are available: Allocation at Point of Substitution (APOS) and Cut-Off. Using the APOS method means that by-products from waste treatment and recyclable materials are not burden-free, as opposed to Cut-Off. In this study, EFR are considered as by-products from the eucalyptus harvest, with the consequent attributed burden. Therefore, APOS is the most consistent choice with this decision, and was used in this work.

For background data, “market for” flows from EcoInvent were used. Market activities on EcoInvent comprise different transformation processes that lead to the same product, with their respective market share. Transportation and trade are included in the unit processes, also accounting losses (EcoInvent, 2020). When available, inventories designed for Brazil (BR) were used, but those selected for background data were, mainly, either Global (GLO) or Rest of the World (RoW).

Regionalized data from the literature was used to describe eucalyptus forestry activities (Silva, 2012; Silva et al., 2015, 2013). On these, the forest yields 290 m³.ha^{-1} of wood, which correspond to 137.5 ton.ha^{-1}. 25% of the total biomass production is assumed to comprise EFR (Dias, 2014), and, from this fraction, 75% corresponds to the ligneous residue that can be retrieved as the biorefinery feedstock, which corresponds to the woody, or ligneous, fraction of these residues (Pincelli et al., 2017). Mass allocation was established between wood and the EFR amount that is actually retrieved. The remaining 25%, consisting of leaves and loose bark, were recommended to be left as soil coverage and considered burden-free.

ISO 14040 guidelines suggest, when possible, system expansion as the best approach to avoid allocation procedures between co-products (ABNT, 2009). Thus, expansions were carried on the units related to biomass cultivation and biorefinery processing. Biomass cultivation was expanded into: seedling production; soil preparation; seedling planting; forest maintenance; and harvest. Biorefinery processing considered each unit process independently; more on this in section 2.2.2.

The benchmarking used inventories from the Brazilian Biorenewables Laboratory (Cavalett et al., 2012; Chagas et al., 2015) to model a 1G sugarcane mill on SimaPro. 1G corn ethanol was modelled using the default LCI available on EcoInvent 3.5. For the Brazilian electricity generation mix inventory, the original dataset from EcoInvent was updated with 2019 numbers (EPE, 2020).

2.2.1. EFR retrieval options and transportation

Two retrieval options were considered: (i) loose forwarding with chipping at the roadside (LFCR), where EFR is forwarded to the roadside and chipped with portable machinery, and chips are then transported from the field to the biorefinery; and (ii) balling with chipping at biorefinery (BCB), where EFR is forwarded and bundled with a modified forwarder on-site, bales are then transported to the biorefinery, where they are dismantled, chipped and fed into the process. The EFR retrieval rate was considered to be 75%, as suggested by Pincelli et al. (2017). This fraction corresponds to ligneous material, in form of branches and residual wood. These options were adapted from an LCA study, focused on EFR use as fuel (Dias, 2014). After being compared to each other for 1 ton of EFR delivered to the biorefinery, the retrieval option which had the best environmental profile was chosen for the subsequent steps in the LCA.

2.2.2. Simulation data adaptation

In order to represent the biorefinery in a disaggregated form on the LCI, the system was expanded into five unit processes, following the core process design hierarchy blocks (Figure 1). The chosen simulation scenario was “Biodigestion + Heat Integration” to be adapted into the LCI, since it includes the two suggested design improvements. The 2G processing unit incorporates a large selection of products and inputs, so it was further expanded into: (a) pretreatment; and (b) hydrolysis and fermentation. This allows a better attribution of inputs such as chemicals for pretreatment, enzymes for hydrolysis, and consumption of utilities.

Even with the two aforementioned expansions, allocation procedures still need to be defined. For the Cogeneration, energy allocation was chosen, since both steam and electricity applications are mainly for energy purposes. For the AD unit, no allocation is needed, since no burden was attributed to wastewater and biogas is the sole product. For the other units, mass allocation would be a suitable choice. But water dilution, present in a number of flows such as vinasse and C5 liquor, tends to distort the streams’ importance in the overall process’ context.

An allocation procedure based on mass organic content was then introduced, since the organic fraction of each flow is the actual product of interest from biomass fractioning. Complementary data was used to describe the boiler emissions on Cogeneration, since Aspen does not calculate emissions such as particulates, nitrogen oxides and carbon monoxide. This way, the carbon dioxide flows from Aspen were maintained and the others calculated (Table 2), following the proportion from reported profiles for bagasse burning (Chagas et al., 2015).

3. Results and discussion

In this section, the main findings related to the biorefinery process design, including exploration of potential improvements in terms of energy optimization and product yield are presented. The scale up potential, considering regional biomass availability has been evaluated and, through the LCA, environmental hotspots present in the design, and strategies to minimize then, have been identified and discussed.

3.1. Process design and simulation

By simulating the three scenarios, both design options (AD and HI) brought improvements in outputs related to energy balance, such as steam consumption and fuel availability. This directly impacted the overall biorefinery ethanol productivity per biomass unit and surplus generation of electricity (Table 3). In the base scenario, part of the EFR input was used as fuel in the cogeneration unit. By implementing the AD unit, biogas, by itself, was able to replace this demand, and even improve the electricity surplus. So, with AD supplying the process energy needs, all EFR could be directed to ethanol production.

The highest demand for steam occurred in the dilute acid reactor. This operation requires a mass proportion of 6:1 (water:biomass), with the input being heated from room temperature to 180 ºC, with a significant pressure build-up. By introducing the proposed heat integration layout, the steam demand on the equipment could be reduced by 65% and the electricity surplus increased by 39%. The third scenario, used as reference for the LCA, produces an ethanol yield of 230.5 L.ton^{-1} (comprising hydrous and anhydrous). This sum is comparable to the reported by (McIntosh et al., 2017)), and translates to a 78% of the total theoretical ethanol obtainable from the EFR cellulose fraction.

A common concern in fermentation is the ethanol titer in the wine. High concentrations are more likely to be achieved by using high solids loading, and by adopting a fermentation configuration that promotes hydrolytic enzyme activity by simultaneous generation and use of glucose in the medium, such as PSSF. A rule of thumb sets this target at 4% (wt.), to achieve economically feasible ethanol purification (Manfredi et al., 2018). With the two proposed process design choices on the “Biodigestion + Heat Integration” scenario, an ethanol titer of 6.8% (wt.) was obtained.

3.2. Potential scale and collection radius

In order to estimate the potential scale for a biorefinery simulated on the third scenario, the Administrative Region of Campinas (ARC), on São Paulo state, was selected. According to the literature, this region has an eucalyptus planted area of 31,482 ha, which corresponds to around 3.3% of the eucalyptus forests in the state (Romero et al., 2019).

By considering an average EFR production of 7.05 ton.ha^{-1}.year^{-1} (Dias, 2014; Silva, 2012), and an allowed retrieval of 75% (Pincelli et al., 2017), the available amount of EFR would be 166,462.1 ton.year^{-1}, in the ARC. By assuming the biorefinery to be located in the centre (by mass) of the total eucalyptus culture area, as proposed by Romero et al. (2019), a collection radius of 160 km would be necessary to cover all eucalyptus forests in the region.

This would allow an annual production of 34.1 ML of ethanol, comprising AE and HE, which correspond to 1.84% of the ethanol demand in this region. Decreasing collection radius by half (80 km), however, still allows a 89% coverage of all eucalyptus area, slightly reducing ethanol production to 30.3 ML.year^{-1} (1.64% of the ARC's demand). Increasing the collection radius beyond 80 km only accesses 0.5% more culture area per km, at most.

For comparison purposes, around 24% of Brazilian 1G sugarcane mills have a yearly crushing capacity of up to 1 million tonnes of sugarcane, which corresponds to a productivity of around 80 ML.year^{-1} of ethanol (Klein et al., 2019). Operational 2G plants, such as Raízen's Costa Pinto mill, in Brazil, and Clariant's SunLiquid® plant, in Romania, have a nominal capacity of 40 ML.year^{-1} (CGEE, 2017), and 63.4 ML.year^{-1} (Lask et al., 2019), respectively.

While the EFR biorefinery does not match the smallest of the cited examples, further research is recommended towards prospection of more suitable regions, with denser concentration of eucalyptus forests than the ARC. This could be within São Paulo state or elsewhere in Brazil, such as Minas Gerais and Mato Grosso do Sul, both prominent states in eucalyptus production (IBÁ, 2020). Moreover, the wood yield per hectare, and the proportion of wood and EFR adopted in this study are literature-based, and could be further refined to reflect the reality of companies in the pulp and paper industry.

Regarding the co-production of electricity, a surplus of 101 GWh.year^{-1} could be generated alongside with the aforementioned ethanol capacity, with the maximum collection radius (160 km). With 80 km, this surplus decreases to 89.5 GWh.year^{-1}. These would meet 0.39% and 0.35% of the ARC electricity demand, respectively (Romero et al., 2019).

3.3. Life Cycle Assessment

The LCA results comprise: comparative analysis between two retrieval options for EFR; the LCIA of the final biorefinery scenario, exploring the main hotspots; a closer look into the data availability on enzyme production; and, finally, a benchmark of this LCIA with literature data.

3.3.1. EFR Retrieval options

BCB is perceived to be the best alternative from an economic perspective, since balling makes EFR denser, promoting easier transportation (Dias, 2014). From an environmental perspective, on the other hand, BCB has a higher impact in every category when compared to LFCR (Figure 5). This is due to the bundling process itself, that requires a modified forwarder, with extra fuel consumption. This suggests that the additional impact from bundling exceeds the advantages that it promotes in terms of transportation (Dias, 2014). No other LCA study has been found comparing EFR retrieval options.

By comparison, BCB's global warming potential (GWP) is 14% higher than that for LFCR. Among the other categories, the impacts for LFCR are 17% lower on the two related to ozone formation and 20% lower in fossil resource scarcity. On the five prominent categories after normalization (marine, terrestrial and freshwater ecotoxicities; and carcinogenic and non-carcinogenic human toxicities), the two retrieval options differ by less than 3%. Nonetheless, with the overall best LCIA results, LFCR was chosen as the retrieval option for the next steps of the LCA.

3.3.2. LCIA of biorefinery products

The LCIA for the biorefinery main products is compiled in Table 4. HE had a GWP of 0.79 kg $CO_{2\ eq}.kg^{-1}$, with enzymes being the major contributor (49%), even with the adopted process design incorporating measures to reduce enzyme dosage in the PSSF, by using polyethylene glycol (PEG) as an additive (McIntosh et al., 2017). This persisted throughout the remaining categories, with enzymes making the largest contribution to the impact factors (Figure 6).

By normalizing the LCIA output of HE (Figure 7), the same five categories emerge: related to ecotoxicity (marine, freshwater and terrestrial) and to human toxicity (carcinogenic and non-carcinogenic). Of these, the supply of enzymes represents more than 60% of the potential impact, with the exception of terrestrial toxicity, where the share is of 40% and the recovery of EFR has a stronger influence (28%) than in the other highlighted categories.

A further important aspect to analyze is the contribution of additional retrieval operations, necessary for the adoption of EFR as a biorefinery feedstock. On HE's LCIA, EFR retrieval had a stronger influence on fossil resource scarcity (20.4%), and a smaller on marine eutrophication (0.1%). In the highlighted categories after normalization, this contribution is less than 8.2% and always smaller than that from eucalyptus forestry activities.

A large contribution in impact categories such as GWP, ozone formation and fine particulate matter formation is attributed to “others”. This share includes elementary flows that occur within the biorefinery process, especially concerning emissions from the cogeneration unit. However, none of the impact categories where this share is prominent are highlighted by the normalization.

AE, on the other hand, has a higher impact than HE in every category (Table 4). This difference can be attributed to the extra energy demand (steam) to perform the separation, and to the use of monoethylene glycol (MEG) as the entrainer for overcoming the water-ethanol azeotrope.

Electricity generation had a GWP of 0.18 kg $CO_{2\ eq}$/kWh, with enzyme input also being a major contributor (40%). The same applies to the remaining categories, with a similar profile of process contributions (Figure 8). Compared to HE's LCIA, however, it is possible to acknowledge the direct contribution of the co-generation unit's emissions, which are especially significant on ozone and fine particulate formation. Proceeding with normalization, the same five categories emerge, related to ecotoxicity and human toxicity. Similarly to HE, enzyme input, PEG and EFR are the identified hotspots in these impact categories.

3.3.3. Exploring data options for enzymes

The use of enzymes surfaced as an important hotspot in the overall LCA, for all biorefinery products, but including enzyme consumption in the LCA of cellulosic ethanol is not a common practice (Gilpin and Andrae, 2017). The main reason is the lack of reliable and transparent data, since process details are often associated with bureaucracy (Jegannathan and Nielsen, 2013), even though promoting enzymes as an environmentally clean solution is of interest to their suppliers (Novozymes, 2020).

For the sake of consistency, this work used the enzyme inventory from EcoInvent 3.5. In this, a generic cocktail and process are described, with adapted regionalization and average values for manufacturing (Valsasina, 2018). On this dataset, 1 kg of enzymes gives a GWP of 7.2 kg CO_{2eq}, including manufacturing and transportation.

In the explored process design, however, a non-generic enzyme cocktail is used: namely Novozymes' Cellic CTec 2 (McIntosh et al., 2017). On the database USLCI, also available on SimaPro, three datasets from Novozymes cocktail portfolio: Celluclast, Liquozyme, and Spirizyme. While these are not Cellic CTec 2, a comparison can still be drawn to the EcoInvent inventory.

With the USLCI datasets, the GWP for 1 kg of enzymes ranges from 1.2 to 4.4 kg CO_{2eq} and the overall performance is better in every impact category, when compared to Ecoinvent (Figure 9). Novozymes published a cradle-to-gate study for a larger selection of their cocktail portfolio, in which the GWP for these three enzymes sat within the interval of 1 to 10 kg CO_{2eq} per kg of enzymes (Nielsen et al., 2007). However, it is not clear, though, from either the USLCI datasets or the aforementioned study, what process parameters and inputs were used to manufacture these enzymes, with only simple process flowsheets being provided, along with LCIs with only elementary flows.

As an alternative to importing from enzyme manufacturers, onsite production could also be considered. This approach was used in technoeconomic studies of cellulosic ethanol in order to better evaluate the true costs associated with this input (Davis et al., 2015; Humbird et al., 2011). By using part of the raw material as feedstock for enzyme production, the literature suggests a range of GWP between 7.9 and 10.6 kg CO_{2eq} per kg of enzymes (Gilpin and Andrae, 2017), which is actually higher than the GWP from EcoInvent’s dataset.

While the economic advantages of onsite production may be clear, the environmental benefits of doing so are still unclear. This approach requires to diversion of biomass from ethanol production to a different process of microbial cultivation. Moreover, this biomass needs to be pretreated, which may increase equipment sizing and energy demand on pretreatment, and compromise the maximum processing capacity of the biorefinery, as a whole.

3.3.4. LCIA benchmarking

To better evaluate the EFR ethanol environmental profile, a benchmark with two standard processes was performed (Figure 10): sugarcane 1G ethanol, largely adopted in Brazil; and 1G corn ethanol, from the United States. In general, EFR ethanol underperforms either of the two references in all categories, except for stratospheric ozone formation and terrestrial acidification. EFR ethanol outperforms 1G corn ethanol in GWP, freshwater and marine eutrophication, human carcinogenic toxicity, and mineral and fossil resource scarcities. It is important to note, however, that the EFR ethanol LCIA impacts are mostly due to enzyme usage, as pointed out in section 3.3.2.

Looking at the literature, no LCA studies for ethanol production from eucalyptus harvest residues were found in any of the databases, either as a mixture or as one of its fractions, i.e. from bark, stumps, leaves and such. While this limits the options for benchmarking, comparisons can be drawn with ethanol produced from eucalyptus wood and other forest residual biomass.

Jonker et al. (2019) explored the potential for chemicals and fuel production from eucalyptus, which included bioethanol. The reported greenhouse gas (GHG) emissions ranges from 0.1 to 0.2 $kgCO_{2eq}^{-1}$ per kg of fuel, calculated in a cradle-to-gate approach, regionalized for Brazil. While accounted in the technoeconomic assessment, it is not clear whether enzymes were included in the LCI. Eucalyptus biomass cultivation, on the other hand, was attributed as the main hotspot, contributing around 80% of the biofuel's GWP.

Considering the share attributed to forestry activities on EFR hydrous ethanol GWP (10.1%), this would correspond to 0.08 $kgCO_{2eq}.kg_{ethanol}^{-1}$, or 0.2 $kgCO_{2eq}.kg_{ethanol}^{-1}$, if EFR retrieval solutions are also accounted. These figures sit within the mentioned GWP range (Jonker et al., 2019), which suggests this variance is the result of the process data inserted in the LCI.

Liang et al. (2017) explored the use of conifer harvest residues as the raw material for ethanol production. The study included enzymes in the LCI, using the USLCI dataset mentioned on section 3.3.3. The resulting ethanol GWP was 0.67 $kgCO_{2eq}$ per kg and, while relevant, enzymes weren't the main bottleneck, with other units being mentioned, such as AD and co-generation. This set was regionalized for the USA and the residual biomass was considered burden-free from forestry activities.

By considering EFR hydrous ethanol as burden-free from forest activities, but still including EFR retrieval and transport, its GWP would be of 0.71 $kgCO_{2eq}.kg_{ethanol}^{-1}$. While this is closer to the conifer residues, the enzyme contribution to EFR ethanol GWP is 49.2%, whereas the adopted enzyme LCI in the reference (Liang et al., 2017) was half of this value.

Finally, comparing EFR electricity, with bioelectricity from sugarcane bagasse and the national production mix, a similar situation occurs (Figure 11). EFR electricity, as a coproduct, does not outperform the references in any of the categories. However, it has a lower contribution to stratospheric ozone depletion, compared to sugarcane bagasse bioelectricity; and, also, in ionizing radiation, compared to the national mix. It is important to note, however, that 46% of Brazilian electricity generation is of renewable origin.

4. Conclusions and future prospects

Design alternatives investigated in the independent biorefinery for the production of cellulosic ethanol and electricity from eucalyptus forest residues (EFR), such as anaerobic digestion and energy integration, can benefit the overall energy balance and, hence, both ethanol and electricity productivity. With these, direct use of EFR as fuel in the boiler is dismissed, and a larger production scale is attainable, with similar capacity to operational second-generation plant examples such as Clariant and Raízen.

In the biorefinery's main products LCA, important environmental hotspots were identified. A significant share of the potential impacts is embedded into EFR as the feedstock, carrying burden from both the eucalyptus forestry activities and EFR's retrieval and transportation. Additional operations required for EFR to be available as a feedstock in the biorefinery, are as or more relevant than the biomass associated burden from forestry activities. So, while most public policies, including RenovaBio, consider harvest residues to be burden-free, the true bottleneck does not reside in this stage of the products’ life cycle.

The biorefinery process, on the other hand, was identified as being the major contributor to the potential environmental impact for all three main products, with enzymes being the most prominent contributor. Data quality and clarity regarding enzymes LCIs contained discrepancies and was oversimplified, limiting this study’s conclusions relevant to this input. Initiatives to reduce enzyme loading, however, such as the use of PEG (polyethylene glycol) as an additive, can be effective in impact mitigation and are encouraged.

Compared to 1G sugarcane ethanol and corn ethanol, EFR ethanol appears to be a viable solution in terms of GWP, considering that both references are already able to mitigate carbon emissions when replacing gasoline. EFR electricity, on the other hand, had a larger GWP than both sugarcane bagasse bioelectricity and the Brazilian production mix, with the same hotspots as previously mentioned for ethanol.

Since enzyme use came to be such an important aspect in the LCA, it is of interest to further investigate the effects of using different datasets and process configurations, such as on-site production, in the biorefinery environmental impact profile profile.

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Table captions

Table 1 – Input data for the biorefinery simulation, in the second generation ethanol processing unit

Table 2 - Emission profile in the cogeneration block

Table 3 – Productivity data for each configuration, considering incremental implementation of process improvements (biodigestion and heat integration)

Table 4 – Environmental impact profile for the biorefinery main products

Figure captions

Figure 1 – Biorefinery process units flowsheet

Figure 2 – Biorefinery process unit "2G processing" flowsheet

Figure 3 – Proposed heat integration in the dilute acid pretreatment

Figure 4 – Boundary definition for the Life Cycle Assessment

Figure 5 – Comparative impact assessment between retrieval options: loose forwarding with chipping at the roadside (LFCR), and balling with chipping at biorefinery (BCB)

Figure 6 – Environmental impact assessment for hydrous ethanol (HE), with process contributions

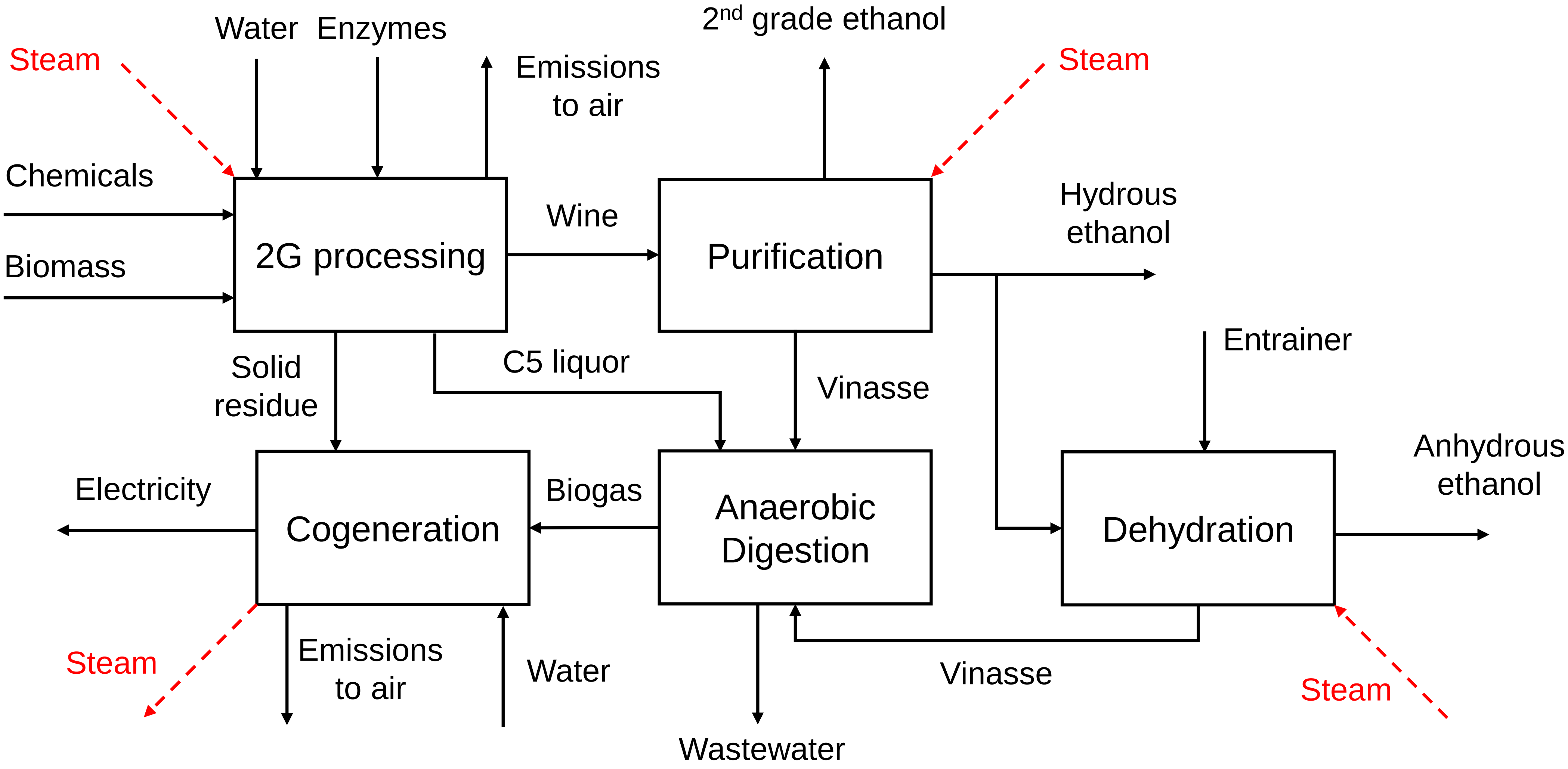
Figure 7 – Normalized impact assessment for hydrous ethanol (HE), with process contributions

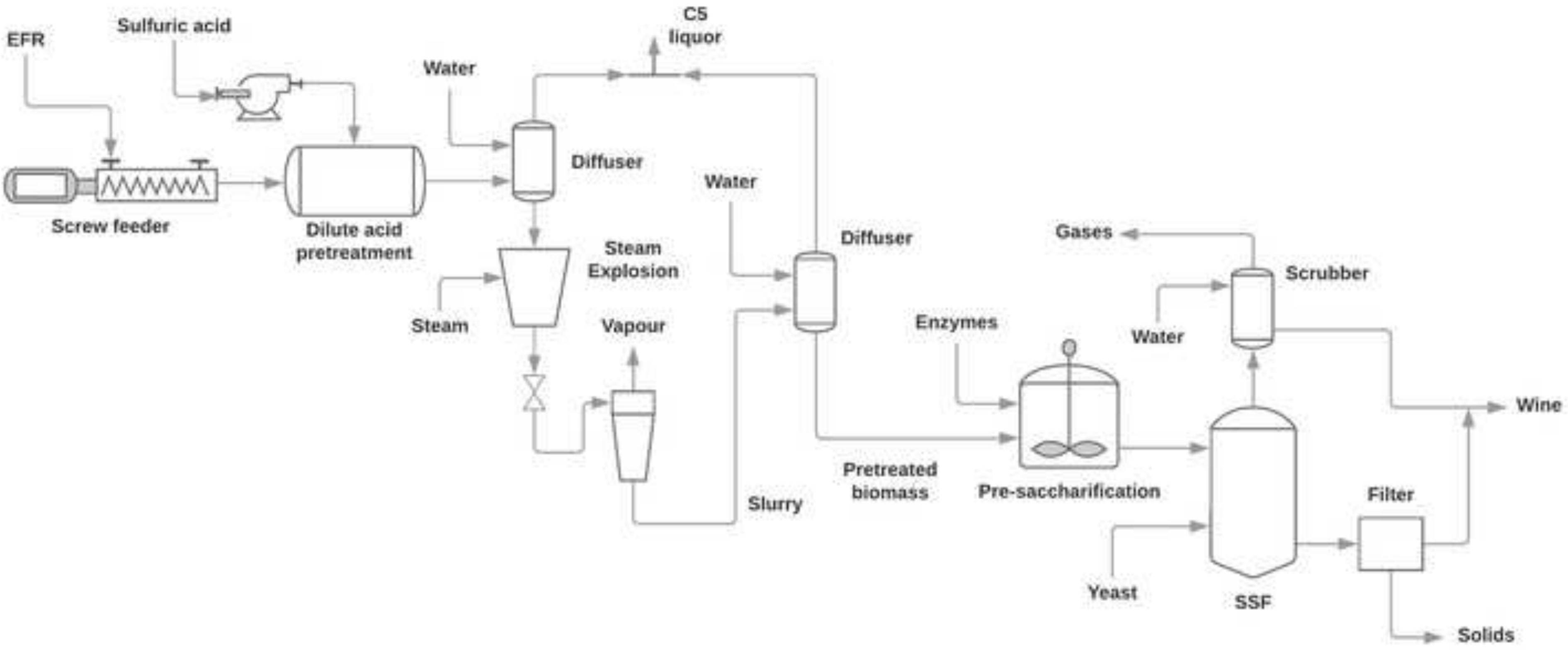
Figure 8 - Environmental impact assessment for electricity, with process contributions

Figure 9 – Comparative environmental impact assessment of enzymes, using different available databases

Figure 10 – Anhydrous ethanol (AE) environmental impact benchmarking, comparison between Eucalyptus Forest Residues (EFR) and first generation (1G) counterparts

Figure 11 – Electricity environmental impact benchmarking, comparison between Eucalyptus Forest Residues (EFR) with sugarcane bagasse and national mix


Steam
Water
Enzymes
Emissions to air
2nd grade ethanol
Steam
Chemicals
Biomass
2G processing
Wine
Purification
Hydrous ethanol
Solid residue
C5 liquor
Vinasse
Entrainer
Anhydrous ethanol
Electricity
Cogeneration
Biogas
Anaerobic Digestion
Dehydration
Steam
Emissions to air
Water
Vinasse
Steam
Wastewater


EFR
Sulfuric acid
Screw feeder
Dilute acid pretreatment
Water
Diffuser
C5 liquor
Steam Explosion
Steam
Vapour
Water
Diffuser
Slurry
Pretreated biomass
Enzymes
Pre-saccharification
Gases
Scrubber
Water
Wine
SSF
Yeast
Filter
Solids

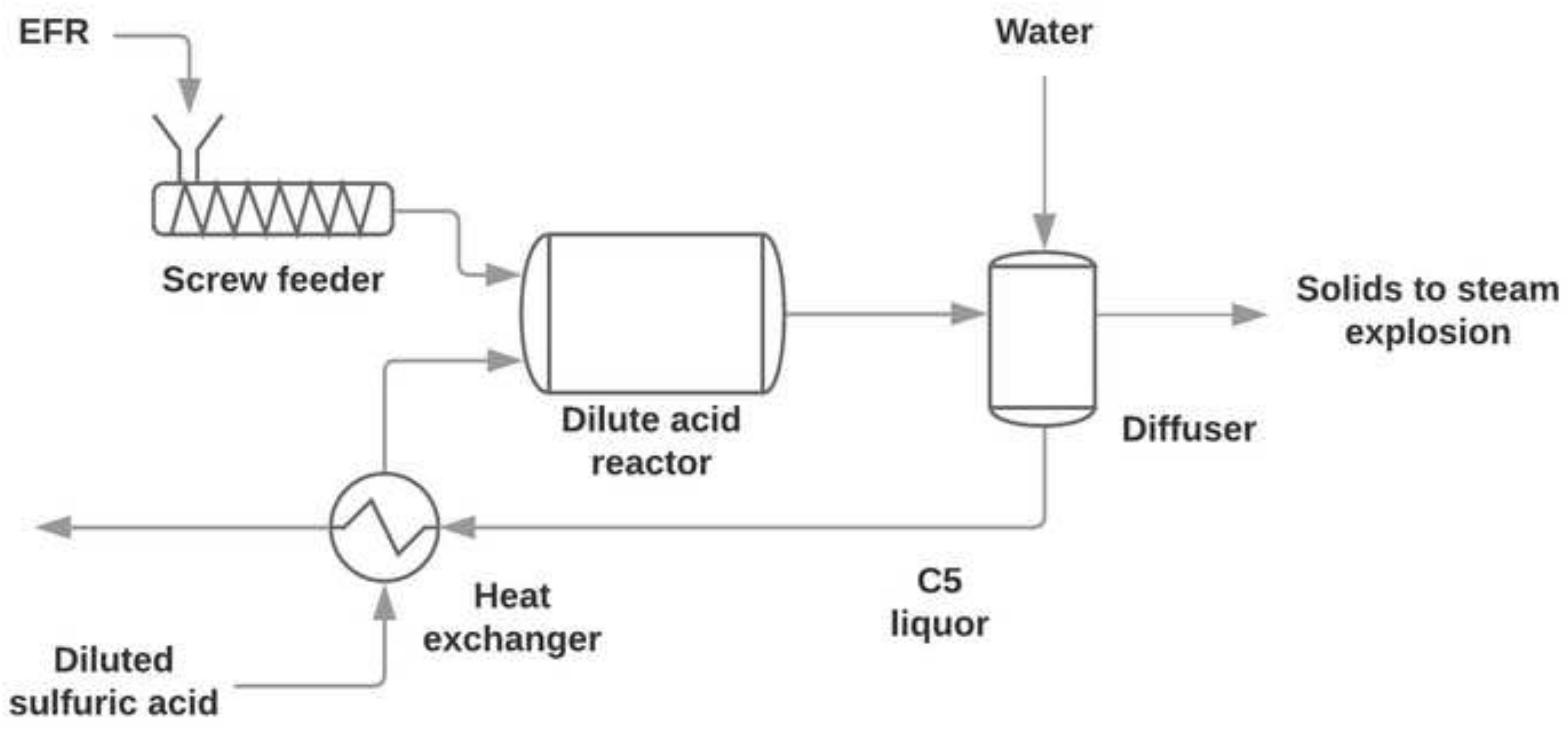
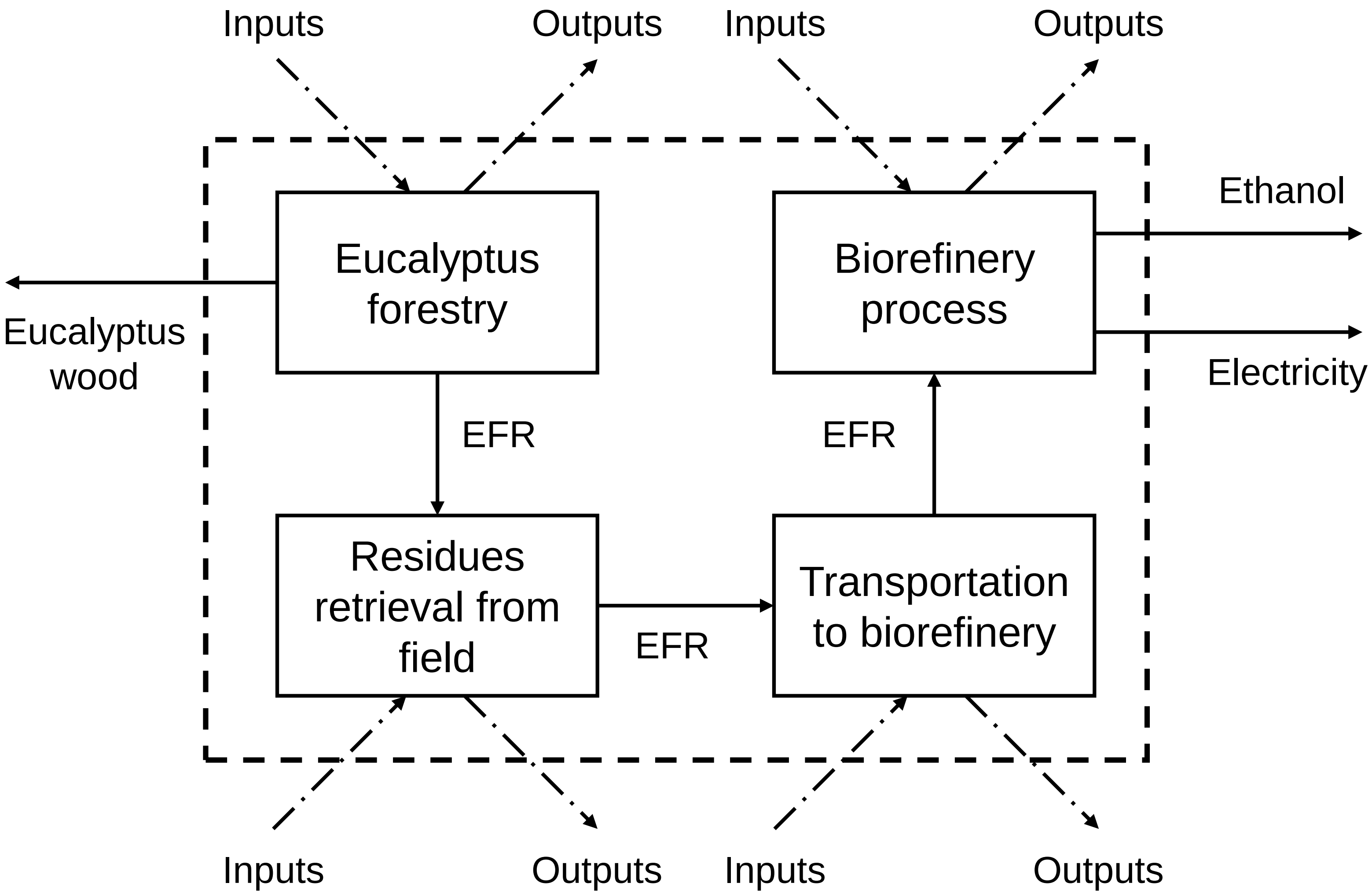
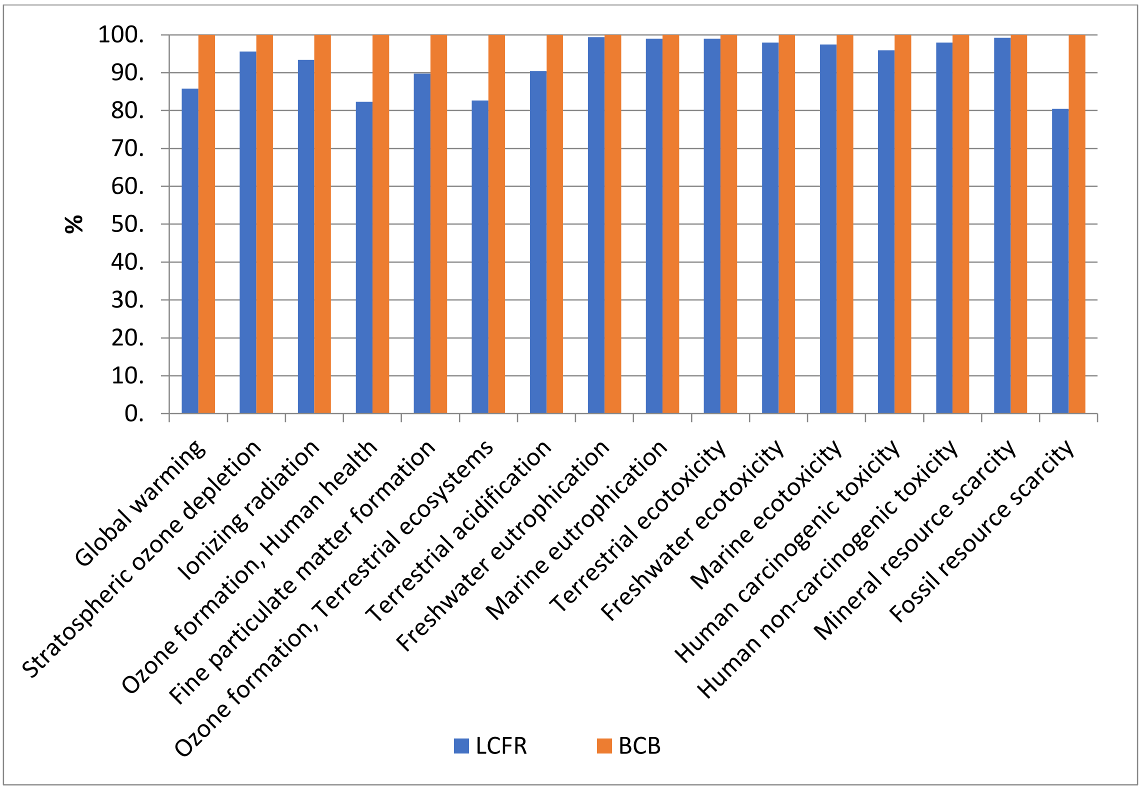
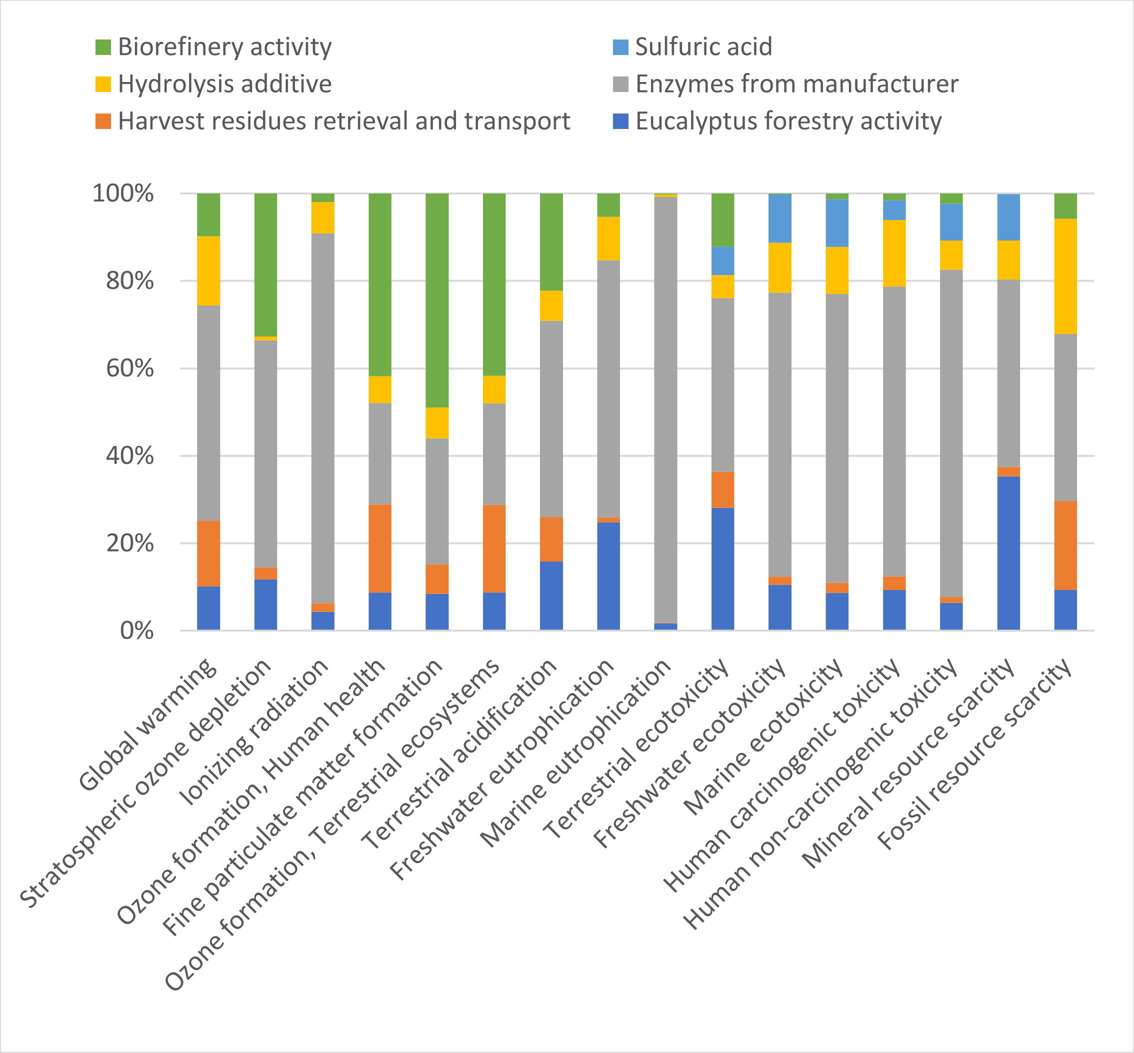
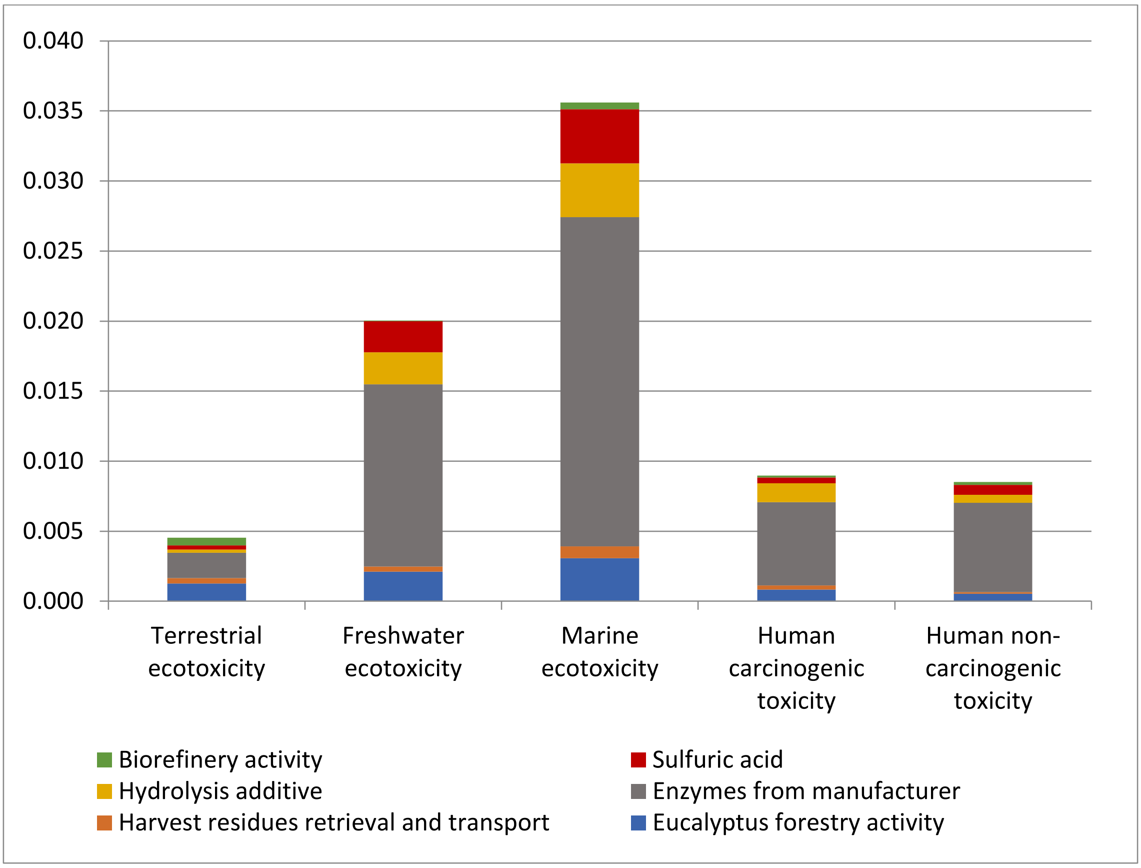

EFR
Water
Screw feeder
Solids to steam explosion
Dilute acid reactor
Diffuser
Heat exchanger
C5 liquor
Diluted sulfuric acid

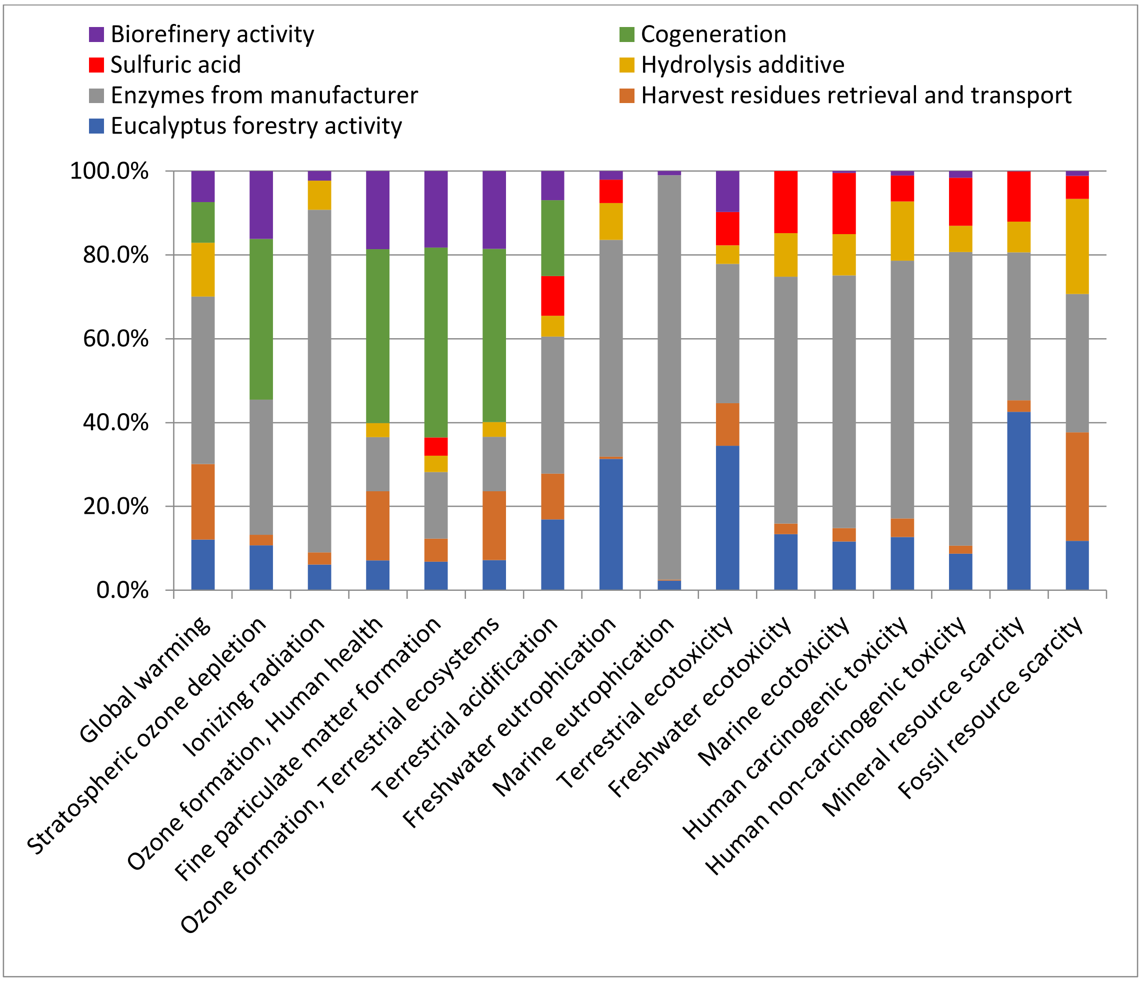
Figure 4 (color)




%
100.
90.
80.
70.
60.
50.
40.
30.
20.
10.
0.
Global warming
Stratospheric ozone depletion
Ionizing radiation
Ozone formation, Human health
Fine particulate matter formation
Ozone formation, Terrestrial ecosystems
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Mineral resource scarcity
Fossil resource scarcity
LCFR
BCB


Biorefinery activity
Hydrolysis additive
Harvest residues retrieval and transport
Sulfuric acid
Enzymes from manufacturer
Eucalyptus forestry activity
100%
80%
60%
40%
20%
0%
Global warming
Stratospheric ozone depletion
Ionizing radiation
Ozone formation, Human health
Fine particulate matter formation
Ozone formation, Terrestrial ecosystems
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Mineral resource scarcity
Fossil resource scarcity


0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Biorefinery activity
Sulfuric acid
Hydrolysis additive
Enzymes from manufacturer
Harvest residues retrieval and transport
Eucalyptus forestry activity


Biorefinery activity
Cogeneration
Sulfuric acid
Hydrolysis additive
Enzymes from manufacturer
Harvest residues retrieval and transport
Eucalyptus forestry activity
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Global warming
Stratospheric ozone depletion
Ionizing radiation
Ozone formation, Human health
Fine particulate matter formation
Ozone formation, Terrestrial ecosystems
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Mineral resource scarcity
Fossil resource scarcity

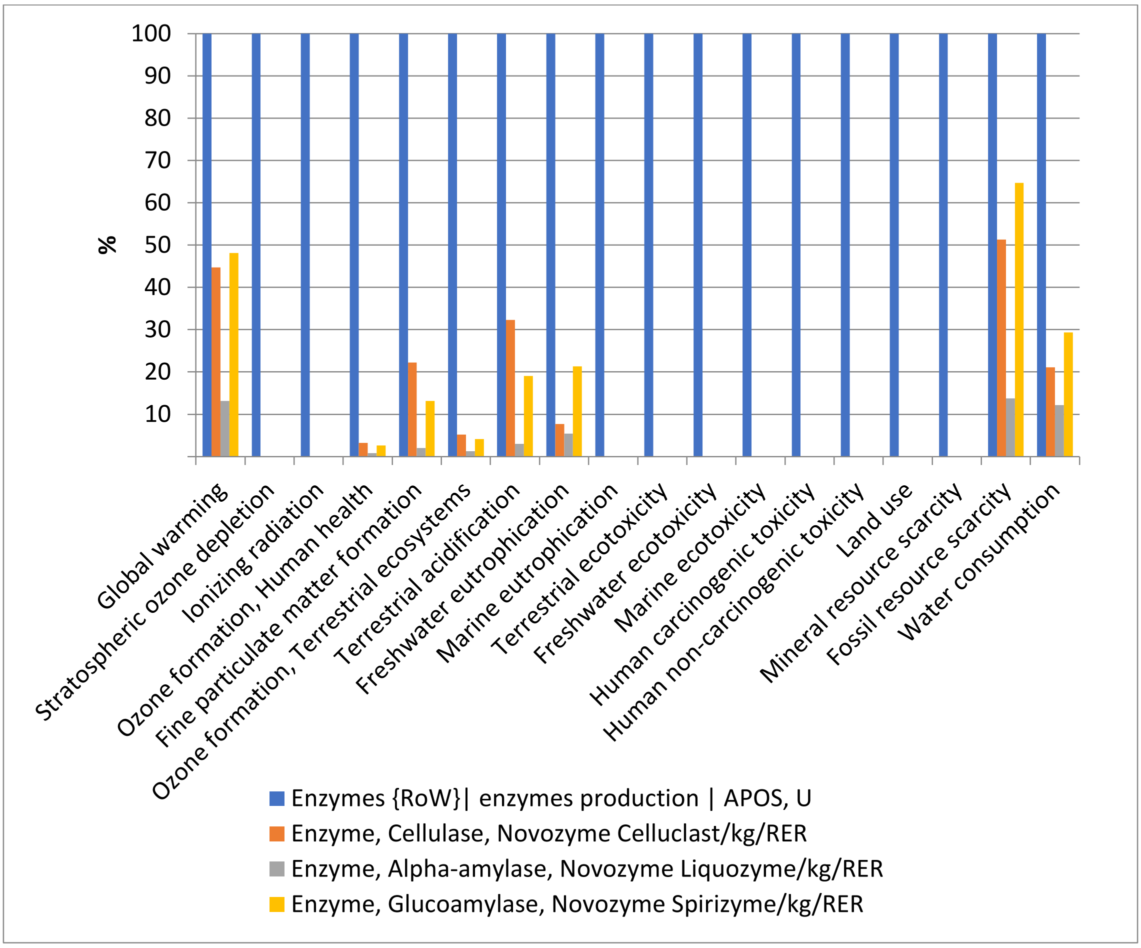
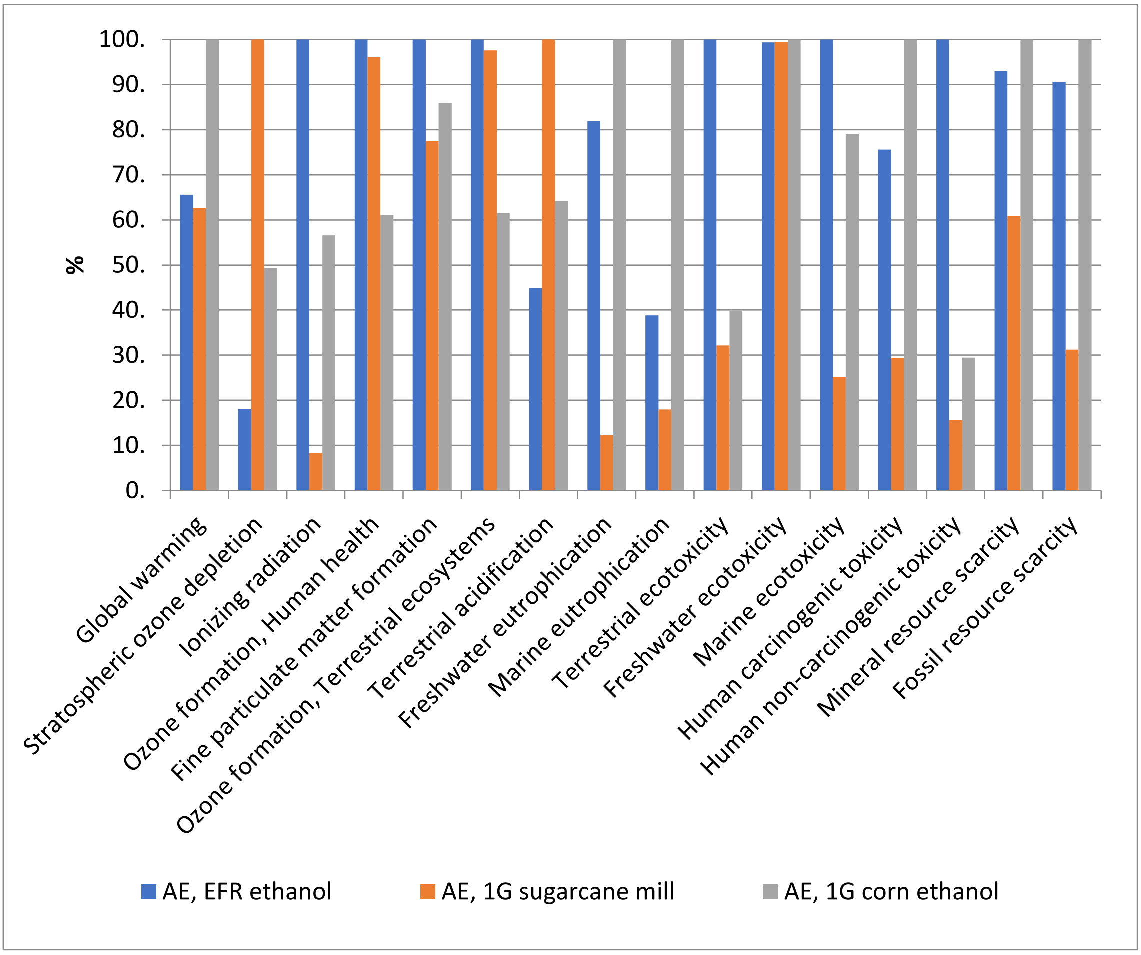

100
90
80
70
60
50
40
30
20
10
%
Global warming
Stratospheric ozone depletion
Ionizing radiation
Ozone formation, Human health
Fine particulate matter formation
Ozone formation, Terrestrial ecosystems
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Land use
Mineral resource scarcity
Fossil resource scarcity
Water consumption
Enzymes {RoW}| enzymes production | APOS, U
Enzyme, Cellulase, Novozyme Celluclast/kg/RER
Enzyme, Alpha-amylase, Novozyme Liquozyme/kg/RER
Enzyme, Glucoamylase, Novozyme Spirizyme/kg/RER

Figure 10 (color)



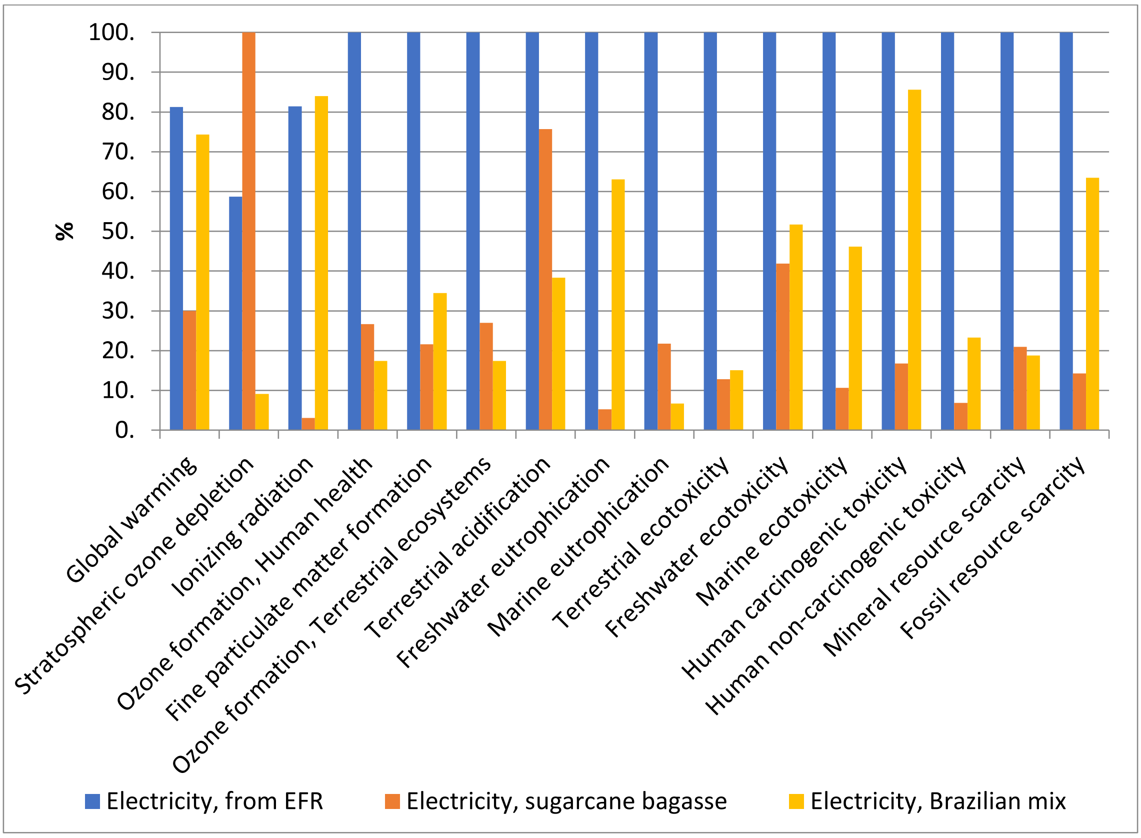

100.
90.
80.
70.
60.
50.
40.
30.
20.
10.
0.
%
Global warming
Stratospheric ozone depletion
Ionizing radiation
Ozone formation, Human health
Fine particulate matter formation
Ozone formation, Terrestrial ecosystems
Terrestrial acidification
Freshwater eutrophication
Marine eutrophication
Terrestrial ecotoxicity
Freshwater ecotoxicity
Marine ecotoxicity
Human carcinogenic toxicity
Human non-carcinogenic toxicity
Mineral resource scarcity
Fossil resource scarcity
Electricity, from EFR
Electricity, sugarcane bagasse
Electricity, Brazilian mix

Table 1 – Input data for the biorefinery simulation, in the second generation ethanol processing unit

Parameter	**Value**	**Reference**
Pretreatment - Dilute acid		
Solids loading (w/w)	14.2%	(McIntosh et al., 2017)
Temperature	180 °C	(McIntosh et al., 2017)
Sulfuric acid proportion to solids loading (w/w)	2.4%	(McIntosh et al., 2017)
Pretreatment - Steam explosion		
Temperature	185 °C	(McIntosh et al., 2017)
Residence time	15 min	(McIntosh et al., 2017)
Pretreatment - Global performance		
Cellulose conversion to glucose	5%	(McIntosh et al., 2016)
Cellulose conversion to celluoligosaccharides	5,6%	Assumption[a]
Cellulose conversion to HMF	0,6%	(McIntosh et al., 2016)
Hemicellulose conversion to xylose	74%	(McIntosh et al., 2016)
Hemicellulose conversion to xyloligosaccharides	10.1%	Assumption[a]
Hemicellulose conversion to furfural	11.4%	(McIntosh et al., 2016)
Lignin solubilization	8.7%	(McIntosh et al., 2016)
Acetyl groups conversion to acetic acid	100%	(McIntosh et al., 2016)
Pre-saccharification reactor		
Solids loading (w/w)	20%	(McIntosh et al., 2017)
Enzyme proportion to cellulose (w/w)	4.65%	(McIntosh et al., 2017)
Temperature	50 °C	(McIntosh et al., 2017)
Residence time	24 h	(McIntosh et al., 2017)
Cellulose conversion to glucose	73.3%	(McIntosh et al., 2017)
Hemicellulose conversion to xylose	100%	Assumption[a]
SSF reactor		
Yeast proportion to cellulose	3.6%	(McIntosh et al., 2017)
PEG proportion to cellulose	5.41%	(McIntosh et al., 2017)
Cellulose conversion to glucose	51.38%	(McIntosh et al., 2017)

[a] assumptions to close mass balance

Table 2 - Emission profile in the cogeneration block

Substance	**Unit**	**Amount**[*]
Carbon dioxide (biogenic)	kg	1043,5
Carbon monoxide (biogenic)	g	820,65
Nitrogen oxides	g	816,89
Dinitrogen monoxide	g	45,13
Sulfur oxides	g	43,82
Methane (biogenic)	g	338,27
Volatile organic compounds	g	57,09
Particulates, >2,5µm and <10µm	g	925,81
Particulates, <2,5µm	g	462,59

[*] Emissions per ton of eucalyptus forest residues processed in the biorefinery

Table 3 – Productivity data for each configuration, considering incremental implementation of process improvements (biodigestion and heat integration)

	Base case	**Biodigestion**	**Biod. + Heat Int.**
Hydrous eth. (L.ton^{-1} [a])	97.6	117.2	117.2
Anhydrous eth. (L.ton^{-1} [a])	94.4	113.3	113.3
Electricity (kWh.ton^{-1} [a])	280.9	433.9	604.3

[a] per ton of biomass (dry basis) fed to the biorefinery

Table 4 – Environmental impact profile for the biorefinery main products

Impact category	Unit	Anhydrous ethanol[1]	Hydrous Ethanol[1]	Electricity[2]
Global warming	kg $CO_{2\ eq}$	3.55E-02	3.15E-02	1.84E-01
Stratospheric ozone depletion	kg $CFC_{11\ eq}$	1.38E-07	1.20E-07	9.10E-07
Ionizing radiation	kBq Co-60 eq	3.96E-03	3.61E-03	1.78E-02
Ozone formation, Human health	kg $NO_{x\ eq}$	1.98E-04	1.69E-04	1.42E-03
Fine particulate matter formation	kg $PM_{2.5\ eq}$	1.22E-04	1.04E-04	8.81E-04
Ozone formation, Terrestrial ecosystems	kg $NO_{x\ eq}$	2.02E-04	1.73E-04	1.44E-03
Terrestrial acidification	kg $SO_{2\ eq}$	2.37E-04	2.10E-04	1.37E-03
Freshwater eutrophication	kg P_{eq}	1.98E-05	1.78E-05	1.00E-04
Marine eutrophication	kg N_{eq}	1.86E-05	1.72E-05	8.23E-05
Terrestrial ecotoxicity	kg 1,4-DCB	2.14E-01	1.93E-01	1.10E+00
Freshwater ecotoxicity	kg 1,4-DCB	1.14E-03	1.03E-03	5.44E-03
Marine ecotoxicity	kg 1,4-DCB	1.70E-03	1.53E-03	8.05E-03
Human carcinogenic toxicity	kg 1,4-DCB	1.15E-03	1.04E-03	5.35E-03
Human non-carcinogenic toxicity	kg 1,4-DCB	5.73E-02	5.22E-02	2.67E-01
Mineral resource scarcity	kg Cu_{eq}	1.65E-04	1.47E-04	8.79E-04
Fossil resource scarcity	kg oil_{eq}	1.14E-02	1.01E-02	5.55E-02

Functional units are [1] 1 MJ, [2] 1 kWh