Comparative evaluation of lignocellulosic biorefinery scenarios under a life-cycle assessment approach

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Abstract: The exploitation of lignocellulosic materials with the aim of producing high value-added products will potentially counteract concerns such as depletion of fossil resources or exponential population growth. The present study focuses on the assessment of an integrated process based on organosolv fractionation of residual beech woodchips, with the objective of implementing concepts such as circular economy or process integration. The life-cycle assessment (LCA) methodology and the eco-efficiency concept allow for a holistic analysis of sustainability in terms of the system's environmental approach.

The results show that the pre-treatment of biomass together with the energy demands of the process and enzyme production constitute the hotspots of the system. Analyzing the system by means of the eco-efficiency indicator demonstrates that broadening the multi-production spectrum of a biorefinery provides better results when production volume and processing steps fit environmental and techno-economical requirements. © 2018 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: bioethanol; biorefinery; eco-efficiency; furfural; life cycle assessment; lignocellulose

Introduction

The exploitation of lignocellulosic materials with the aim of producing high value-added products is a recent trend. Nowadays, the world faces major concerns such as the depletion of fossil resources, increasing greenhouse gas emissions, and exponential population growth. The premise is therefore to exploit alternative resources, which, in one way or another, would positively affect aspects such as environmental sustainability or circular economies.

According to recent forecasts, the market share of bio-based chemicals is projected to increase from 2% to 22% by 2025.¹ According to this estimate, an increase in large-scale bio-based facilities may be expected in the near future, as can be well perceived from current research trends. First-generation biorefineries derive biofuel and co-products mainly from crops or other agricultural raw materials; unfortunately, the use of food crops may generate problems such as rising food prices, net energy losses to greenhouse gas emissions, or changes in land use.² The recovery of residual biomass, which is not primarily intended for human consumption, avoids the ongoing food versus fuel predicament. European statistics (2016) show that ethanol from lignocellulosic feedstock represents a 5% share, whereas crop-based feedstocks such as wheat, corn, sugars and other cereals represent 32%, 31%, 24% and 8% respectively.³
The objective of this study is the assessment of a well-integrated process, based on organosolv fractionation of residual woodchips incorporated into a second generation biorefinery or lignocellulosic biorefinery (LCB). Lignocellulosic feedstock is a promising alternative to starch or sucrose containing materials (first-generation biorefineries). Most of the renewable ethanol market is based on feedstocks such as maize, wheat, sugar beet, and other cereals. However, the lignocellulosic raw materials present favorable results in terms of the output/input energy ratio, lower costs and high ethanol yields, which, together with their high availability in locations with temperate and tropical climates, make this raw material potentially advantageous. Lignocellulosic biomass may come from forest and wood residues, municipal solid waste, paper waste, or crop residues, hence its ready availability in multiple climates, as many different types of lignocelluloses are available to users almost anywhere. Considering the breadth of sources for lignocellulosic materials, it is considered to be one of the most abundant raw materials at low prices and limited environmental burdens. It has been estimated that it is feasible to produce bioethanol from lignocelluloses in a range of 442–491 billion liters per year. In comparison, world bioethanol production has been estimated at 95 billion liters in 2015. This demonstrates the high potential for almost completely replacing the production of first-generation biofuels with second-generation biomass sources, for the sake of minimizing the environmental impacts.

It has been demonstrated that one of the critical points in relation to the biorefining process of wood-based raw material is the pre-treatment stage. In fact, it is one of the processing steps with the greatest costs in biorefinery facilities. In the last decade, several technologies have been reported in literature covering a wide range of categories: physical, biological, chemical, and physico-chemical pre-treatments. The intended purpose of pre-treatment technologies is the efficient fractionation of lignocellulose into its basic components: cellulose, lignin, and hemicellulose. After efficient fractionation, the resulting streams should contain high value-added compounds in concentrations that make purification or recovery economically feasible.

Some pre-treatment alternatives include wet oxidation, steam explosion, dilute acid pre-treatment, ionic liquid pre-treatment, ozonolysis, biological pre-treatment, or organosolv digestion. As previously stated, this study is focused on an LCB that uses organosolv digestion as the fractionation technique. Authors such as Viel or Laure have demonstrated the economic viability of organosolv as a fractionation technique in wood biorefineries.

Industrially, some companies have adopted the approach of demonstrating the viability of the biorefining process through pilot and demo-scale implementation. Lignol Innovations in Canada has installed a plant facility (Lignol Biorefinery Technology) with a capacity of 100 metric t/day of dry wood. The demonstration plant constitutes an integrated biorefinery producing ethanol and other added value products such as lignin and furfural, xylose, or acetic acid. The lignol pre-treatment step is an ethanol-based organosolv fractionation.

Compagnie Industrielle de la Matière Végétale (CIMV), in France, has developed laboratory and pilot facilities, adequate for processing wheat straw or other agricultural residues as feedstock. Organosolv fractionation using acetic and formic acids allows relatively mild conditions for the pre-treatment of the feedstocks (atmospheric pressure and maximum temperature of 110 °C).

Abengoa Bioenergy New Technologies (ABNT) has developed a demonstration plant in Spain with a capacity to process 70 t/day of feedstock. The plant processes wheat straw along with other agricultural residues. One of the main features is the use of enzymatic hydrolysis together with steam explosion as the biomass pre-treatment method.

The Fraunhofer-Zentrum für Chemisch-Biotechnologische Prozesse (Fraunhofer CBP) in Germany has developed a pilot-scale facility that processes up to 70 kg of dry hardwood per batch. The pre-treatment of wood is performed with ethanol based organosolv fractionation and the main products obtained are glucose, lignin and xylose.

Analyzing different case studies, it can be concluded that the viability of second-generation biorefineries on a commercial scale is based on a few pillars. On the one hand, economic and technical feasibility: the facility must produce benefits in an efficient way and they must be technologically achievable. In the case of lignocellulosic biorefineries, the multi-product approach is favorable in this respect. On the other hand, if the plant is versatile, the availability of feedstock is not a constraint for production. Under this assumption, the objective must be to design biorefineries with the capacity to process multiple types of raw materials.

Nowadays, the objective is to exploit alternative resources, which would have a positive impact on environmental sustainability and circular economy. Accordingly, the process must show satisfactory environmental performance. The purpose of this study is, therefore, to assess the environmental sustainability of a large-scale simulated biorefinery. Life-cycle assessment (LCA) is the methodology applied in this study for the evaluation of environmental impacts associated with the process value chain.
The state of the art with regard to LCB proves that the concept of biorefining is not a novelty in itself. However, the aim of this report is to go beyond general considerations and address the real sustainability of intensive biomass exploitation through LCB. Some authors\(^1\) suggest that a biorefining facility will probably not be limited to the production of just one high value-added bioproduct. Therefore, the aim of this study is to address a simple hypothesis. If the production scope of a lignocellulosic biorefinery is broadened, is sustainability really improved?

Two illustrative cases have been identified to address the research question. Firstly, the so-called Biorefinery 1.0 was considered as a somewhat conventional biorefinery. This facility pre-treats and converts wood into basic products such as glucose, hemicellulose, and lignin, which do not undergo additional processing. The second case study, Biorefinery 2.0, is a somewhat more advanced facility. Consideration was given to the possibility of further conversion to more specialized and higher value-added bioproducts, such as furfural and bioethanol. For the scenarios considered here, material balances will be performed to obtain inventory data based on the project design of an organosolv facility reported by Kautto et al.\(^2\) These data will be used to perform an environmental evaluation and eco-efficiency assessment to benchmark alternative biorefinery configurations.

## Materials and methods

### Goal and scope

The function of the system under study (LCB) is the use of lignocellulosic biomass to produce bio-products with marketable added value. The aim of the environmental study, performed in accordance with the LCA methodology, is to determine the process subsystems that significantly affect the overall environmental performance of the system. Hence, it is expected that the result of the study will identify the process hotspots in the biorefinery and their root cause.

The functional unit considered was the processing of 1 t h\(^{-1}\) of hardwood chips in the biorefinery facility. It seems consistent to select a feedstock-based functional unit, as the process is characterized by its multiple-output nature. On the other hand, one of the objectives of this study is to benchmark three main plant schemes, Biorefinery 1.0, Biorefinery 2.0 and Biorefinery 2.5, with increasing number of produced bioproducts. Bearing in mind that each biorefinery has distinct outputs, the selection of the raw material input as a functional unit ensures consistency throughout the study.

The production scheme was assessed through a cradle-to-gate approach. It is a perspective that allows us to consider the processes from the production of feedstock up to the plant gate – that is, the products obtained, ready for the market.

### Overview of production system

This section is intended to provide a generic description of the production system. To address the research question, several plant configurations were considered using case studies. The subsystems described below do not necessarily belong to all the case studies. The specificities of the system boundaries regarding each case study are defined below.

The generic system comprises all the process units involved in the ethanol organosolv pulping process, as well as the downstream units for the valorization of pulp and liquor, respectively. The feedstock for the process, as already mentioned, is residual beech woodchips supplied by a sawmill. The plant under assessment has a capacity to process 83.3 t h\(^{-1}\) of dry wood.

The foreground system includes process units that are the direct subject of the present study. To provide meaningful results, the system under study is divided into nine subsystems (SS) described below: SS0.Feedstock, SS1.Organosolv pulping, SS2.Solvent recovery, SS3.Hemicellulose conditioning, SS4.Enzymatic hydrolysis, SS5.Cogeneration unit, SS6.Fermentation to ethanol, SS7.Acetic acid recovery, SS8.Furfural recovery. Figure 1 is a block diagram of the plant, identifying the system boundaries, subsystems and main inputs and outputs. Note that the figure addresses the most complete view of the LCB, including all possible subsystems considered in this study. Specific boundaries of every case study are reported in Table 1.

### SS0. Feedstock

This subsystem comprises forest activities for wood exploitation, sawmill activities, and chipping. These process sections and subsystems are implemented within the main subsystem. Feedstock production data have been adapted from other studies. SS0.1 includes activities ranging from soil preparation (use of fertilizers) to wood extraction.\(^3\) SS0.2 includes the sawmilling activities carried out to produce three main products: sawn timber, bark chips, and residual wood.\(^4\) Residual wood is the feedstock considered for the purpose of this study. The pre-processing of residual wood to prepare the feedstock for organosolv pulping is considered as SS0.3. Pre-processing activities include chopping of wood as...
physical pre-treatment to obtain woodchips of a suitable size for further processing. All the environmental burdens derived from this subsystem were allocated to this residual wood. Figure 2 depicts the general system configuration considered for SS0.

**SS1. Organosolv pulping**

The process is based on the digestion of wood chips with ethanol (50% v/v) and 1.25% sulfuric acid at 180 °C for 60 min. The pulp is washed with water and ethanol solution and pumped through a screen to the enzymatic hydrolysis stage (SS4). The liquor is further hydrolyzed to obtain sugar monomers. Heat and a fraction of ethanol are recovered prior to SS2 operations.

**SS2. Solvent recovery**

The SS1 liquor is diluted to an ethanol concentration of 15% (v/v) and cooled to 50 °C to promote lignin precipitation. After lignin precipitation, ethanol is recovered by distillation and recycled to SS1.

**SS3. Hemicellulose conditioning**

After solvent recovery, the liquor (sugar solution) is sent to a four-effect evaporation train. Low molecular weight soluble...
lignin (LMW) is easily separated after evaporation and has no added value so it is burned in the boiler (SS5). The aqueous stream is further subjected to liquid-liquid extraction with furfural, to separate the residual LMW lignin and other organic residues. Lastly, the addition of ammonia allows the pH to be adjusted to 5 before fermentation in SS6.22

SS4. Enzymatic hydrolysis
Conversion to glucose from cellulose and hemicellulose is feasible through the use of an enzyme cocktail, mainly cellulase with a minor percentage of hemicellulases, allowing a partial conversion of unreacted hemicellulose to hemicellulosic sugars. This process takes place in an enzymatic reactor at 48 °C with a residence time of 84 h.22 On-site enzyme production is included in this subsystem.26,27

SS5. Electricity and heat cogeneration
This process needs significant energy input. Thus, the operation of a boiler is considered to meet the demands of steam and electricity, using biogas, WWT sludge, bark, and all the organic waste from the different subsystems. In this way, it is possible to valorize the different waste streams. The contribution of natural gas as an external energy source is also considered necessary to balance energy demand.22

SS6. Fermentation to ethanol
The streams from the enzymatic hydrolysis and the diluted hemicellulosic sugar are used as culture medium for the fermentation stage, using Zymomonas mobilis as microorganism. In addition, corn liquor and diammonium phosphate are added as nutrient sources. After obtaining a sufficient volume of inoculum, the main fermenter of the process is operated with culture medium with a composition similar to that of the inoculum train.22

SS7. Acetic acid recovery
It is possible to recover the fraction of acids (acetic and formic) from the condensates obtained in the evaporator train (SS3). For this purpose, a liquid-liquid extraction (in a mixer-settler column) with trioctylphosphine oxide (TOPO) in undecane is used. Undecane and TOPO are recovered and reused within the system in a closed circuit. It was considered, however, that a makeup of 1% for each chemical was necessary due to possible losses. This subsystem also includes three distillation columns with intermediate decanting steps to separate the acetic acid (at the bottom of the third column) at 97% purity.22

SS8. Furfural recovery
As a lateral extraction of the distillation columns used for ethanol recovery (SS2), a furfural stream is recovered. The side-draw from the distillation columns is further separated in a decanter, where the aqueous phase is recycled to SS2. Part of the recovered furfural is used as extraction solvent to recover LMW lignin in SS3; the rest of the recovered furfural can be commercialized.22

The background system consists of processes that indirectly influence the system and contribute to environmental impacts. The background systems include the chemical production of ethanol, sulfuric acid, and ammonia as well as transport.

Definition of the system boundaries
Alternative approaches were assessed, departing from the system layout described above. Based on the general outline presented above, several hypothetical case studies have been considered. The case studies differ in terms of the downstream options considered and the final products obtained. Table 1 provides a summary of the schemes considered.

The simplest scenario that was considered is a biorefinery with the function of producing the most basic chemicals that are feasible to be obtained with minimum downstream processing. Biorefinery 1.0 produces glucose, hemicellulose, and lignin, with a disposition similar to that studied by Laure et al.16 The system boundaries are reduced to six subsystems presented in Fig. 3.

Biorefinery 2.0 was assessed as shown in Fig. 4. The aim of this biorefinery is to produce bioethanol, furfural, and lignin. This involves the inclusion of the processing steps in subsystems 6 and 7 for fermentation to ethanol and furfural recovery. Under the scope of Biorefinery 2.0, two distinct scenarios have been proposed for discussion:

- Furfural recovery methods (scenarios 2.1–2.4). In Biorefinery 2.0, furfural was recovered through distillation.22 However, the recovery of furfural exclusively by distillation is an energy-consuming process. Furfural is the precursor of multiple furan-based biochemicals and biofuels that could eventually lead to substitution of the petroleum based counterparts. It is listed as one of the top 30 biomass derived platform compounds by the US Department of Energy.28

Improving the efficiency of furfural recovery may be a significant aspect given its importance in the market. Nhien et al.29 have proposed an alternative arrangement for the recovery of furfural obtained from
lignocellulosic biomass. The process implements a two-step recovery system, combining extraction and distillation. Liquid-liquid extraction with three different solvents (toluene, benzene, and butyl chloride) results in two streams: an extract, containing most of the furfural in the feed stream, and a raffinate. The extract is then introduced into a distillation column to separate furfural and the solvent, which is recycled.

- Acetic acid co-production (scenario 2.5). Acetic acid is usually produced in bulk fermentation. The production of acetic acid has not been considered in the Biorefinery 2.0 case study, in view of the very low amount produced from such a common chemical. An additional scenario has therefore been considered to allow discussion about the adequacy of implementing acetic acid recovery onto the biorefinery route (Fig. 1). The objective is to assess whether the co-production of acetic acid (in Biorefinery 2.5) provides advantageous results considering its revenues and environmental factors.

**Life-cycle inventory**

The life-cycle inventory (LCI) is the compilation of the dataset for this assessment. In this study, basic process data, material balances as well as the biochemical

| Case study         | Description                        | Products                  | Subsystems included       |
|--------------------|------------------------------------|---------------------------|---------------------------|
| Biorefinery 1.0    | Basic biorefinery                  | Glucose, lignin, hemicellulose | SS0–SS5                  |
| Biorefinery 2.0    | Advanced biorefinery               | Ethanol, furfural, lignin | SS0–SS6 and SS8           |
| Scenario 2.1       | Distillation for furfural recovery | Ethanol, furfural, lignin | SS0–SS6 and SS8           |
| Scenario 2.2       | Hybrid extraction-distillation with benzene for furfural recovery | Ethanol, furfural, lignin | SS0–SS6 and SS8           |
| Scenario 2.3       | Hybrid extraction-distillation with toluene for furfural recovery | Ethanol, furfural, lignin | SS0–SS6 and SS8           |
| Scenario 2.4       | Hybrid extraction-distillation with butyl chloride for furfural recovery | Ethanol, furfural, lignin | SS0–SS6 and SS8           |
| Scenario 2.5       | Implementation of acetic acid coproduction | Ethanol, furfural, lignin, acetic acid | SS0–SS8                  |

Figure 3. System boundaries of the lignocellulosic biorefinery for the production of glucose, hemicellulose and lignin. Subsystems (SS) and system boundaries defined for Biorefinery 1.0.
production route considered, have been adapted from the simulation of an organosolv process for bioethanol production. Foreground data consists therefore of peer-reviewed literature sources (secondary data). The background system components (transport, chemicals, water) have been detailed through the Ecoinvent® database. A summary of data sources considered for inventory collection is presented in Table 2. Tables 3 and 4 display the inventories of the foreground systems considered throughout the life cycle assessment.

Methods

The ReCiPe 1.12 hierarchist method was used for the selection of characterization factors. Impact categories at midpoint level were studied. SimaPro 8.02 software was used for the computational implementation of the inventories.

Although all categories of the ReCiPe method were studied, environmental results are presented in terms of the following impact categories: climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), freshwater ecotoxicity (FET), marine ecotoxicity (MET), and fossil depletion (FD). In analyzing the results of standardization, the impact categories mentioned above are the most representative of European values.

Allocation

According to the considered disposition of SS0, multiple products are obtained as output of the subsystem (Fig. 2). However, not all wood products are used as input of the organosolv pulping subsystem (SS1). When assessing the environmental impacts of SS0, the resulting impacts are associated with all products leaving the subsystem and not just one. Subsystem 0 includes sawn timber, bark chips, and woodchips as outputs. As only woodchips are used
as raw material in subsequent subsystems, they are only responsible for their corresponding fraction of the overall impacts. The allocation of impacts to residual woodchips has therefore been applied.

Volumetric allocation could be considered as a viable option, allocating impacts to co-products in proportion to the produced volume of each product; volumetric allocation factors are 51% for sawn timber, 13% for bark chips, and 36% for residual woodchips.

However, even if all products from SS0 are marketable, they do not have the same economic value. Considering the reference market prices of products from sawmills the allocation factors are modified to 77% for sawn timber, 14% for bark and 9% for woodchips. Nowadays, residual wood is not as valuable for other applications, as can be seen through the calculated economic allocation factors. The second allocation method better reflects the purpose of finding a niche market for the residual fraction of a sawmill. It should be noted that the economic allocation has been considered for SS0.1 and SS0.2, but not for SS0.3, since this subsystem only treats residual wood to obtain woodchips.

**Assumptions and limitations**

The results presented in this study may show some uncertainty arising from assumptions made due to data gaps. The following are the hypotheses considered throughout the evaluation as the best possible approximation:

- Transport of woodchips from SS0 to SS1 is the only transport process included. The transport distance has been considered as 100 km, and impacts derived from transport have been assigned to SS1. Lorry freight (16–32 metric tons) was the selected mode of transport. Transport losses of 5% have been considered, with a resulting tonne-kilometre (tkm) value of 105 tkm.
- One of the distinctive characteristics of the system considered here is the cogeneration unit (SS5). Cogeneration provides energy and steam to the entire system through the burning of natural gas and process residues in a dual boiler. When a subsystem consumes electricity or uses utilities, these are supplied entirely through the cogeneration subsystem. This means that the impacts assigned to SS5 can be divided between subsystems that consume energy. This is relevant for the sake of result interpretation. The boiler produces energy for the plant. In turn, when any process unit uses the energy produced by the boiler, the impacts of energy consumption are the corresponding fraction of the environmental impacts derived from energy production (e.g. combustion emissions). If the energy produced in SS5 were to be accounted within the energy consumer subsystem, the impacts of that energy would be duplicated (counted once in SS5 and again in the consumer subsystem).
- No infrastructure process was considered in the assessment to assure uniformity of conditions across all subsystems.

| Table 3. Inventory for feedstock related activities. Inventory is presented with economic allocation to SS0.1 and SS0.2. |
|---------------------------------------------------------------|
| **SS0.1 Forest activities** |
| **Inputs from technosphere** |
| Diesel | 1.03 kg |
| N-mineral fertilizer | 0.15 kg |
| **Outputs to environment** |
| N₂ | 13.54 g |
| NH₃ | 1.85 g |
| NOₓ | 2.50 g |
| **SS0.2 Sawmill** |
| **Inputs from process** |
| Roundwood from SS0.1 | 0.71 m³ |
| **Inputs from technosphere** |
| Water | 244.38 kg |
| Lubricating oil | 0.09 kg |
| Steel (packaging) | 0.11 kg |
| Polyethylene (HDPE) | 0.16 kg |
| Inorganic chemicals (pretreatment) | 22.11 g |
| Organic chemicals (solvent) | 0.66 g |
| Electricity | 19.18 kwh |
| **Outputs to environment** |
| Heat | 422.63 MJ |
| CO₂ | 30.76 kg |
| CO | 15.67 g |
| NOₓ | 34.79 g |
| Particulates | 14.98 g |
| SO₂ | 0.82 g |
| Municipal solid waste | 1.50 kg |
| **Outputs to technosphere** |
| Bark chips | 0.10 m³ |
| Sawn timber | 0.41 m³ |
| **SS0.3 Chipping** |
| **Inputs from process** |
| Residual wood from SS0.1 | 1.28 m³ |
| **Inputs from technosphere** |
| Electricity | 2.30 kwh |
| **Outputs to SS1** |
| Residual wood chips | 1.25 m³ |
subsystems, as no reliable data is available for all equipment considered. On the other hand, environmental impacts per process unit, from the installation, construction, decommissioning, infrastructure, machinery, etc., have been considered negligible during the lifetime of a biorefinery facility. This has been a common practice in other biorefinery life-cycle assessment studies. 33,35–38

The cogeneration unit of the plant supplies electricity to SS1, SS2, SS3, SS4 (except for on-site enzyme production), SS6, SS7, SS8. Among these subsystems,

### Table 4. Global inventory for the lignocellulosic biorefinery considering all possible subsystems for the functional unit (1 t h⁻¹ dry wood chips).

| Subsystem                | Inputs from technosphere | Outputs to technosphere |
|--------------------------|--------------------------|-------------------------|
| **SS1 Pulping**          |                          |                         |
| Water (pulping)          | 3.72 t                   |                         |
| Water (washing)          | 4.56 t                   |                         |
| Sulfuric acid            | 1.01 × 10⁻² t            |                         |
| Ethanol (pulping)        | 3.74 t                   |                         |
| Transport, freight, lorry (16–32 metric ton) | 105 tkm                  |                         |
| High pressure steam      | 1.97 GJ                  |                         |
| Electricity (pulping)    | 7.80 × 10⁻² MWh          |                         |
| **SS2 Solvent recovery** |                          |                         |
| Water (dilution)         | 1.02 t                   |                         |
| Natural gas              | 0.05 × 10⁻³ t            |                         |
| Low pressure steam       | 0.77 GJ                  |                         |
| Electricity              | 6.00 × 10⁻² MWh          |                         |
| **SS3 Hemicellulose conditioning** |                    |                         |
| Furfural (makeup)        | 1.92 × 10⁻³ t            |                         |
| Ammonia                  | 6.24 × 10⁻³ t            |                         |
| Low pressure steam       | 0.06 t                   |                         |
| High pressure steam      | 0.21 GJ                  |                         |
| Lignin                   | 0.16 t                   |                         |
| **SS4 Enzymatic hydrolysis** |                      |                         |
| Enzyme (cellulase)       | 7.80 × 10⁻³ t            |                         |
| Electricity              | 2.04 × 10⁻² MWh          |                         |
| Low-pressure steam       | 9.12 × 10⁻² GJ           |                         |
| **SS5. Cogeneration unit** |                          |                         |
| Corn steep liquor        | 4.53 kg                  |                         |
| Ammonia                  | 0.61 kg                  |                         |
| Water                    | 577.74 kg                |                         |
| Nutrients                | 2.48 kg                  |                         |
| Heat                     | 37.90 MJ                 |                         |
| Electricity              | 81.84 MJ                 |                         |
| **SS6. Fermentation to bioethanol** |                |                         |
| Water                    | 0.21 t                   |                         |
| Diammonium phosphate     | 0.16 × 10⁻³ t            |                         |
| Corn steep liquor        | 1.27 × 10⁻² t            |                         |
| Low pressure steam       | 1.74 GJ                  |                         |
| Electricity              | 8.40 × 10⁻³ MWh          |                         |
| **SS7. Acetic acid recovery** |                      |                         |
| Low pressure steam       | 0.39 GJ                  |                         |
| Electricity              | 3.48 × 10⁻² MWh          |                         |
| TOPO                     | 3.32 kg                  |                         |
| Undecane                 | 11.93 kg                 |                         |
| **SS8. Furfural recovery** |                          |                         |
| Low pressure steam       | 2.40 × 10⁻³ GJ           |                         |
| Electricity              | 2.40 × 10⁻² MWh          |                         |
SS1 is the main electricity and steam consumer with a percentage of demand with respect to the total around 35%. Subsystem 0 includes off-site activities ranging from forestry to wood pre-treatment; electricity demands for SS0 are retrieved directly from the grid.

**Results**

The relative contributions to the environmental burdens in each of the selected impact categories are presented below for each alternative studied. The contribution of each process subsystem to each category is shown, allowing the critical points of the process to be discerned.

**Environmental performance of Biorefinery 1.0**

The characterization results of Biorefinery 1.0 are shown in Fig. 5. Analyzing the complete set of environmental results, SS1 can be appointed as the most burdening subsystem; however, there was no major difference with respect to SS4 (enzymatic hydrolysis) or SS5 (cogeneration unit). Nevertheless, SS1 is the largest energy and steam consumer, therefore, it is indirectly responsible for a significant fraction of environmental impacts associated to SS5.

The feedstock subsystem (SS0) presented a considerably uniform distribution of environmental impacts across all categories, with contributions always below 23%. Freshwater eutrophication (23%), marine eutrophication (19%) and climate change (18%) were the groups most affected by wood preparation activities. SS0 contributions were mostly appointed to SS0.2 (sawmill activities). Sawmill activities require high electricity consumption due to the use of machinery; electricity for SS0 is retrieved directly from the grid and not from the cogeneration unit. Other burdens were derived from the use of lubricant oil for maintenance, plastics for packaging and chemicals for finishing operations.

Photochemical oxidant formation was the most impacted category in the organosolv pulping subsystem with a share of 43%. This is mainly due to emissions of volatile organic compounds from road transport of woodchips to the site. The organosolv pulping subsystem (SS1) presented the largest contributions to ozone depletion, terrestrial acidification, and human toxicity, with values of 38%, 27%, and 34% respectively. SS1 was the second major contributor to climate change with 22%. Factors from SS1 responsible of CC were mainly emissions from road transport of woodchips.

Solvent recovery and hemicellulose conditioning (SS2 and SS3) did not contribute significantly to the overall environmental impact of the system. Solvent recovery (SS2) caused contributions to impact categories, ranging from 1% to 13%. Hemicellulose conditioning presented slightly higher values, ranging from 5% to 16%. In general, the contributions to the environmental profile were not significant.

The environmental impacts of SS4 were the result of enzyme production. For this subsystem, eutrophication categories (freshwater and marine) were the most impacted, together with marine ecotoxicity. Surprisingly, the contributions of this subsystem are very comparable to the organosolv pre-treatment. However, it should be noted that the cogeneration unit does not supply the heat.
and electricity demands, as the on-site cellulase production unit is not present in the plant originally considered. Enzyme production is the only input process into SS4.

For climate change, freshwater ecotoxicity and fossil depletion, SS5 was the most burdensome subsystem, with a maximum relative contribution of 40% allocated to fossil depletion. Although SS5 partly uses process residues to burn, it also needs a fresh supply of natural gas to meet the energetic demands of the plant. On the other hand, CO2 emissions from the boiler also contribute to the overall results.

**Environmental performance of Biorefinery 2.0**

Figure 6 depicts the characterization results of Biorefinery 2.0. The results show the impacts for the subsystems in the advanced biorefinery, producing bioethanol, furfural and lignin. Although the furfural recovery subsystem (SS8) was included in the analysis, it showed no environmental impacts. The only input of the furfural recovery subsystem is energy supplied by SS5. Although SS8 did not have direct environmental burdens in any category, one must assume that, indirectly, part of the burdens assigned to SS5 were in fact due to energy consumption in SS8. In general, the environmental profile of the plant has not been greatly affected by the addition of more downstream processing units.

The feedstock subsystem (SS0) presented the same results as in Biorefinery 1.0 with very slight changes and contributions always below 22%. Freshwater eutrophication (22%), marine eutrophication (17%), and climate change (17%) were the most impacted groups.

For SS1 the profile was once again quite similar to Biorefinery 1.0. Photochemical oxidant formation was the most impacted category in the organosolv pulping subsystem with a share of 39%. Ozone depletion (37%) and human toxicity (33%) categories contributed to SS1 total impacts with values close to POF. SS1 also contributed to emissions due to the use of chemicals (ethanol and sulfuric acid). Organosolv pulping was the greatest contributor among the subsystems in 4 out of 10 impact categories.

Solvent recovery and hemicellulose conditioning (SS2 and SS3) did not greatly contribute to the overall results. Solvent recovery made contributions to impact categories ranging from 2% to 12%. Hemicellulose conditioning presented slightly higher values ranging from 5% to 15%.

Enzymatic hydrolysis (SS4) contributed to overall impacts with significant values. The same reasoning as Biorefinery 1.0 can be used. Although the results are comparable to the organosolv pulping subsystem, organosolv does not include its impact contributions due to the consumption of electricity, heat, and steam. Cellulose production is a highly energy-intensive fermentation process, which, together with the carbon source consumption, contributes to the overall results in SS4. Both eutrophication categories presented relevant contributions to the total results (46% and 28% for FE and ME respectively) mainly due to water consumption in the fermentation process.

The largest contribution to the fossil depletion category originated in the cogeneration unit (44%), specifically due to the use of natural gas as fuel. The cogeneration subsystem was the main contributor to climate change (33%).

Finally, the fermentation subsystem contributed slightly to the overall environmental results. Contributions to
terrestrial acidification (17%) and marine eutrophication (13%) were the major impacts caused by SS6. Overall, the fermentation subsystem was not very significant for the sum of the total impacts. The environmental profile of the plant was not significantly altered due to the ethanol fermentation subsystem.

**Environmental performance of Biorefinery 2.0 with acetic acid co-production**

No significant overall differences were found when analyzing Biorefinery 2.0 and Biorefinery 2.0 with the co-production of acetic acid (Fig. 7). The environmental profile of the overlapping subsystems was maintained, and the only difference was the incorporation of environmental impacts due to SS7.

SS7 for acetic acid co-production presents the major contributions to ozone depletion (39%) followed by considerable impacts to fossil depletion (23%) and photochemical oxidant formation (15%). All contributions to every impact category from SS7 originate from the use of chemicals (TOPO and undecane).

**Comparative assessment of Biorefineries**

Comparative assessments for every biorefinery scenario displayed reasonable results (Fig. 8). Increasing complexity of biorefineries showed a proportional increase in the environmental impacts for each category. Biorefinery 2.0 with acetic acid co-production (scenario 2.1) displayed the greatest burdens for all impact categories. In contrast, the simplest scenario (Biorefinery 1.0) displayed the lowest environmental impacts overall.

According to expectations, when the biorefinery increased its downstream processing steps, the amount of equipment, inputs from technosphere, emissions, etc., the environmental impacts were greater. However, this comparative analysis alone is not sufficient to assess whether one scenario is more environmentally efficient than another. As the function of every biorefinery changed for each scenario, the facilities were not considered comparable and therefore further analysis should be performed.

**Comparative assessment of furfural recovery methods**

The comparative assessment for the recovery of furfural with four different alternatives (scenarios 2.1, 2.2, 2.3 and 2.4) is illustrated in Fig. 9. Seven out of ten categories presented higher impacts when considering only distillation. Only climate change, ozone depletion and fossil depletion displayed the hybrid extraction process with toluene as the most unfavorable scenario. These categories (CC, OD and FD) were the most impacted because the hybrid alternative uses fossil-based extractants for separation.

The extraction-distillation hybrid (for all the solvents studied) presented a better environmental performance than the purification process through distillation, mainly because it consumed less energy. The results showed that the use of benzene for extraction in the hybrid process was the best case scenario among the alternatives studied. In general, the hybrid separation is more efficient, technologically feasible and environmentally friendly.

**Discussion**

**Eco-efficiency assessment of the considered scenarios**

From the above discussion one might assume that the most environmentally sustainable LCB is Biorefinery...
1.0. However, the research question is not fully answered through the concluding remarks in the results section. The objective of this study was to perform a holistic sustainability assessment of a biorefinery and to conclude whether a more complex biorefinery would be more sustainable than a simplistic one. In the case of this LCA study, it was found that comparing the three scenarios with only environmental impacts in mind was not fair and did not meet the objective of determining the best case scenario. Generally speaking, if one scenario involves the use of more resources (chemicals, energy) than another, it is consistent that it results in more environmental impacts. However, the only quantification of environmental impacts does not take into account whether one scenario produces two bioproducts and another scenario produces three bioproducts, or the volume of production. For the sake of simplification, it was decided that the determination of potential revenues from each scenario would better describe the latter concern.

In accordance with ISO 14045, the concept of eco-efficiency acknowledges the consideration of environmental factors along with the value of the system to stakeholders. Considering the monetary benefit of each LCB scenario in parallel to the environmental indicators, a comparative evaluation of the environmental performance of integrated biorefineries is given. Other studies have concluded the imminent need to integrate issues related to environmental impacts and economic profitability in order to simultaneously evaluate processes and technologies. Quantitative evaluation of the different provisions across both perspectives is highly profitable for stakeholders and companies.

Figure 8. Comparative environmental profiles (in %) for Biorefinery 1.0, Biorefinery 2.0 and Biorefinery 2.0 with acetic acid co-production.

Figure 9. Comparative environmental profiles (in %) for furfural recovery methods: exclusive distillation and hybrid distillation-extraction with benzene, butyl chloride, and toluene.
Environmental impact versus revenue was the selected indicator of sustainability because it allows the objectives of economic growth and environmental protection to be tackled. The monetary benefit of each biorefinery according to product sales prices (Table 5) was the selected indicator for the assessment of eco-efficiency. When the emission factor is presented per unitary benefit potentially achieved by the biorefinery, the outcome of the assessment is different. In fact, the eco-efficiency indicator is a reliable tool to make comparable two systems which are not. Biorefinery 2.0 attains lower emissions per unitary benefit than Biorefinery 1.0. The eco-efficiency indicator (Table 6) for each impact category is lower for Biorefinery 2.0 in all cases except for ozone depletion and terrestrial acidification. Conversely, Biorefinery 2.5 (which includes acetic acid coproduction) does not follow the same trend and is less environmentally sustainable.

The objectives for optimizing eco-efficiency in a biorefinery are to minimize environmental impacts and maximize economic benefits. Figure 10 is the representation of the eco-efficiency indicator used in this study combining economic benefits with CO₂ emissions. The biorefineries evaluated are solutions to the optimization problem; however, the best case scenario is achieved when the solutions fall in the Q3 quarter of the graph. The virtual division of the eco-efficiency graph (Fig. 10) into four quadrants allows a biorefinery scenario to be qualitatively categorized according to the area of the graph in which it falls. Depending on its environmental impact and revenues, a scenario could be environmentally optimal (Q4, Q3), maximize the potential benefits of plant revenues (Q3, Q2), or accomplish both objectives (Q3) or neither of them (Q1) to a greater or lesser extent. The aim is to have a visual comparison tool to define quickly how a scenario behaves in relation to both the values of kg CO₂ equivalent and revenue.

When the expansion of the biorefinery is specifically performed for specialty bio-products, the biorefinery is more sustainable. However, the production of bulk chemicals such as acetic acid in this type of facility is not as environmentally sustainable, especially when the production volume is very small. The suggestion resulting from the results of the study would therefore be to broaden the multi-production spectrum of the biorefinery only when the production volume and the type of product are reasonable. From an environmental point of view, an integrated biorefinery is sustainable when the intensification of resource demand is not useless, for instance if the yield for the different products is not satisfactory or the final goods do not meet specifications.

Although social life-cycle assessment is not the objective of the present study, and is beyond the scope of the study, it is indeed interesting to address the current views on the three pillars of sustainability as defined by the Brundtland Report in 1987. The idea of sustainable development is a concept that considers the fact that economic progress is certainly bound to whether environmental and social concerns are fulfilled. All three perceptions should therefore be balanced to achieve the best possible production system (e.g. biorefineries). Social life-cycle assessment and other assessments regarding social indicators are still in their first steps towards the acquisition of a robust and reliable methodology commonly applied to case studies. The novelty of these type of studies makes it far more difficult to find reports of social analysis on lignocellulosic biorefineries, as they have not yet evolved into large-scale facilities. Some studies have addressed social issues of interest to biorefineries, recognizing, in particular, the relevance of the selection of social indicators. Valente et al., have considered the implications of the use of some social indicators on bioethanol lignocellulosic biorefineries. Categories such as health and safety, community infrastructure, governance, human and labor rights and decent work have been considered with respect to the conclusions that the simple interpretation of social outcomes is far from a reality. Health and safety and labor rights and decent work conditions were the categories of utmost importance. Generally speaking, socio-economic indicators are more commonly used than exclusively social indicators to determine social sustainability in biorefineries, as presented by the work of Palmeros Parada et al. Bearing these statements in mind, it can be argued that social conclusions may not have as many direct impacts on the design of biorefinery processes but have more repercussion, for instance, on the corporate values, vision, and strategy of a company.

There is a wide range of options on the road to the selection of indicators for environmental assessment. When social and economic issues are added, even more alternatives emerge. In any case, the selection of categories of indicators should be consistent with the objective of the evaluation. ISO 14045 establishes the combination indicator groups to

### Table 5. Market selling prices of biorefinery products.

| Product           | Average market selling price (€/t) |
|-------------------|-----------------------------------|
| Glucose           | 355.0 ±26,41                      |
| Lignin            | 530.6 ±23,46                      |
| Hemicellulose     | 105.4 ±47,49                      |
| Bioethanol        | 830.5 ±50,54                      |
| Furfural          | 865.3 ±56,60                      |
| Acetic acid       | 834.2 ±61,64                      |
be used to determine the eco-efficiency of a product or process. In general, the environmental impact and value of the system are the general concepts analyzed. Within the value of the system, different indicators can be considered, including, among others, the functional performance of products, monetary value of products, aesthetics, and market studies.39

### Acetic acid co-production

If the sustainability of a biorefinery is variable, then, what biorefinery products should be produced? In the case of acetic acid co-production, for instance, its recovery from the biorefinery route includes the use of TOPO and undecane, chemicals that, although recycled, have high environmental impacts. The recovery of acetic acid is therefore not sustainable. In fact, the average production of acetic acid in bulk is a feasible process of fermentation,69 avoiding the use of TOPO and undecane as well as petrochemical production options.

The production of acetic acid through an LCB increases potential revenues as demonstrated in this assessment and in agreement to other studies.61,70 However, the negative environmental consequences shift the overall eco-efficiency indicator towards the Q2 quarter (Fig. 10), where revenues are high but so are CO₂ emissions contributing to climate change.

### Furfural recovery

One of the outcomes of this study is the need not only to integrate the co-production of various bioproducts but also to optimize existing processes in the biorefinery route. An example would be the recovery of furfural. Recovery of furfural through less energy-intensive methods reduces global environmental impacts (Fig. 9), which, in fact, improves the eco-efficiency indicator. For the same production volume of furfural, fewer overall impacts are obtained for the benzene extraction-distillation alternative (Scenario 2.2).

This seems relevant in relation to fluctuations of furfural market prices.55 If the process is not fully optimized, a slight variation in the furfural price may change the eco-efficiency indicator towards the Q4 quarter (Fig. 10) where overall benefits are not relevant.

### Enzyme production

The enzymatic hydrolysis considered in the present system under study presents relevant impacts with respect to the biorefinery as a whole. It seems quite unlikely as the impacts of SS4 are derived from on-site enzyme production. Furthermore, enzyme dosage for hydrolysis does not constitute a significant amount. However, environmental results are aligned with the cost of enzyme production. Other studies have demonstrated the implications that enzyme production has on total costs and emissions for the production of lignocellulosic ethanol.71 The further integration of enzyme production into the biorefinery is

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### Table 6. Eco-efficiency indicator, calculated for every impact category considered in the study and for every biorefinery scenario.

| Eco-efficiency indicator | Biorefinery 1.0 | Biorefinery 2.0 | Biorefinery 2.5 |
|--------------------------|----------------|----------------|----------------|
| CC (kg CO₂ eq/€)         | 0.47           | 0.42           | 0.45           |
| OD (kg CFC-11 eq/€)      | 5.34 × 10⁻⁸    | 7.64 × 10⁻⁸    | 4.38 × 10⁻⁸    |
| TA (kg SO₂ eq/€)         | 2.32 × 10⁻³    | 2.41 × 10⁻³    | 2.62 × 10⁻³    |
| FE (kg P eq/€)           | 9.85 × 10⁻⁵    | 8.32 × 10⁻⁵    | 8.42 × 10⁻⁵    |
| ME (kg N eq/€)           | 5.81 × 10⁻⁵    | 5.52 × 10⁻⁵    | 5.91 × 10⁻⁵    |
| HT (kg 1,4-DB eq/€)      | 1.26 × 10⁻³    | 1.13 × 10⁻³    | 0.097          |
| POF (kg NMVOC/€)         | 3.04 × 10⁻³    | 1.13 × 10⁻³    | 1.30 × 10⁻³    |
| FET (kg 1,4-DB eq/€)     | 3.04 × 10⁻³    | 2.64 × 10⁻³    | 2.75 × 10⁻³    |
| MET (kg 1,4-DB eq/€)     | 2.62 × 10⁻³    | 2.19 × 10⁻³    | 2.23 × 10⁻³    |
| FD (kg oil eq/€)         | 0.24           | 0.22           | 0.28           |

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**Figure 10.** Climate change and monetary benefit per functional unit (1 t dry wood h⁻¹).
expected to result in a reduction of the total impacts aiming for a scenario in which total environmental burdens can be reduced. As in other studies enzyme production technologies significantly affect environmental impacts and LCA results may be sensitive to changes in this subsystem.

Conclusions

Biorefining systems have been studied with the aim of reducing environmental burdens. However, the topic of biorefineries is extensive and varied. Comparison of results with other studies is troublesome. The introduction of eco-efficiency and exemplification through different biorefining scenarios is therefore a stepping stone for the optimization of bioproduction.

Data on integrated biorefineries producing multiple bio-based products are scarce. The evaluation of facilities with primary data should provide an interesting background on the best configurations towards sustainability of biorefineries. On the other hand, if data availability is not a constraint, future research should focus on the assessment of a wider range of biorefinery scenarios.

Finally, regarding the system under study, optimization of LCB hotspots should focus on further integration of enzyme production, optimization of technologies for the manufacture of high value added bioproducts, and the optimization of the organosolv pre-treatment process. It would be advantageous, as well, to study possibilities of further energy optimization to achieve full integration of the plant.

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