Evaluation of a lignocellulosic biorefinery based on organosolv pulping under a life-cycle assessment approach

S. Bello*, C. Ríos, G. Feijoo, M.T. Moreira

Department of Chemical Engineering, University of Santiago de Compostela, Santiago de Compostela, 15782, Spain

*Corresponding author: sara.bello.ould-amer@usc.es

Abstract

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

The results show that the pre-treatment of biomass together with the energy demand of the process and enzyme production constitute the hotspots of the system. Analyzing the system by means of the ecoefficiency indicator demonstrates that, broadening the multi-production spectrum of a biorefinery, provides better results when production volume and processing steps are reasonable.

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

Abbreviations

LCA	Life Cycle Assessment
LCB	Lignocellulosic Biorefinery
SS	Subsystem
WWT	Wastewater treatment
TOPO	Trioctylphosphine oxide
HDPE	High density polyethylene
CC	Climate change
OD	Ozone depletion
TA	Terrestrial acidification
FE	Freshwater eutrophication
ME	Marine eutrophication
HT	Human toxicity
POF	Photochemical oxidant formation
FET	Freshwater ecotoxicity
MET	Marine ecotoxicity
FD	Fossil depletion
ISO	International Organization for Standardization

1. Introduction

The exploitation of lignocellulosic materials with the aim of producing high added value products, is a trend that has been ventured in recent years. Nowadays, the world faces major concerns such as depletion of fossil resources, increasing greenhouse gas emissions or the exponential growth of population. Therefore, the premise is to exploit alternative resources, which, in one or another way would positively impact on aspects such as environmental sustainability or circular economy.

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 what is expected for the near future, as can be well perceived through 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, while 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 cost and high ethanol yields, which together with their high availability in locations with temperate and tropical climates, make this raw material potentially advantageous.[4]

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 pretreatment 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.[5]

Some pretreatment alternatives include wet oxidation,[6] steam explosion,[7] dilute acid pretreatment,[8] ionic liquid pretreatment,[9] ozonolysis,[10] biological pretreatment[11] or organosolv digestion. As previously stated, this study is focused on a LCB that uses organosolv digestion as the fractionation technique. Authors such as Viel[12] or Laure[13] 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[14], has installed a plant facility (Lignol Biorefinery Technology) with a capacity of 100 metric tons/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.

CIMV (Compagnie Industrielle de la Matière Végétale), 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[15] 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 also developed a demonstration plant in Spain with a capacity to process 70 t/d 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[16].

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 pretreatment of wood is performed with ethanol based organosolv fractionation and the main products obtained are glucose, lignin and xylose[13].

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 be technologically achievable. In the case of lignocellulosic biorefineries, the multi-product approach is favorable to this first premise. On the other hand, if the plant is versatile, the availability of feedstock is not a constraint for production. Therefore, 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. The process must therefore 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[17].

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[18] 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 achieves the pretreatment and conversion of wood into basic products such as glucose, hemicellulose and lignin that do not undergo additional processing. The second case study, Biorefinery 2.0, conveys 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 considered scenarios, material balances will be performed to obtain inventory data based on the project design of an organosolv facility reported by Kautto et al.[19] These data will be used to perform an environmental and economic evaluation to benchmark alternative biorefinery configurations.

2. Materials and methods

2.1 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 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 two plant schemes. 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.

2.2 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 through the conception of 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 in Section 2.3.

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 of 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 of dry wood.

The foreground system includes process units that are the direct object of the present study. To provide meaningful results in terms of the process sections that will be inferred in more environmental loads, 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. Fig.1

depicts 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 Section 2.3.

-FIGURE 1-

SS0.Feedstock 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.[20] SS0.2 includes the sawmilling activities carried out to produce three main products: sawn timber, bark chips and residual wood.[21] 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.[22] All the environmental burdens derived from this subsystem were allocated to this residual wood. Fig. 2 depicts the general system configuration considered for SS0.

-FIGURE 2-

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.[19]

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.[19]

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 to adjust pH to 5 before fermentation in SS6.[19]

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 and a residence time of 84 hours.[19] On-site enzyme production is included in this subsystem.[23,24]

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.[19]

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.[19]

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 triocyphosphine oxide (TOPO) in undecane is used. Undecane and TOPO are used in a closed circuit, however, for the purpose of LCA, 1% loses are considered in the circuit. This subsystem includes, as well, three distillation columns with intermediate decanting steps to separate the acetic acid (at the bottom of the third column) at 97% purity.[19]

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.[19]

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.

2.3 Definition of the system boundaries

Alternative approaches were assessed parting from the system layout described above. Based on the general outline presented in Section 2.2, 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.

<TABLE1>

The simplest considered scenario is a biorefinery with the function of producing the most basic chemicals 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.[13] 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.

i. Furfural recovery methods (scenarios 2.1-2.4). In Biorefinery 2.0, furfural was recovered through distillation.[19] 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.[25] Improving the efficiency of furfural recovery may be a significant aspect given its importance in the market. Nhien et al.[26] 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 was then introduced into a distillation column to separate furfural and the solvent, which was recycled.

ii. 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. Therefore, an additional scenario has 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 provides advantageous results considering economic and environmental factors.

-FIGURE 3-

-FIGURE 4-

2.4 Life cycle inventory

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 production route considered have been adapted from the simulation of an organosolv process for bioethanol production.[19] 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.

<TABLE2>

<TABLE3>

<TABLE4>

2.5 Method

The ReCiPe 1.12 hierarchist method[27] 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 above-mentioned impact categories are the most representative of European values.[28–30]

2.6 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). The total environmental impacts do not fully correspond to the residual woodchips used as raw material. Therefore, allocation of impacts to residual woodchips has been applied.

Mass 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[31] 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.

2.7 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.

i. 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 tonne-kilometre.

ii. One of the distinctive characteristics of the considered system 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. Although a subsystem may not present any direct contribution to impacts, strictly speaking, a fraction of the SS5 impacts would be caused indirectly by the subsystem's energy and/or steam consumption.

iii. No infrastructure process was considered in the assessment to assure uniformity of conditions across all subsystems.

iv. 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, 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.

3. Results

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

3.1 Environmental performance of Biorefinery 1.0

The characterization results of Biorefinery 1.0 are shown in Figure 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 directly retrieved 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 demand of the plant. On the other hand, CO_2 emissions from the boiler also contribute to the overall results.

-FIGURE 5_Use Color-

3.2 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. As mentioned in Section 2.7, although SS8 did not have direct environmental burdens to any category, one must assume that indirectly, part of the burdens assigned to SS5, were in fact due to energetic 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. Cellulase production is a highly energy-intensive fermentation process, which, together with the carbon source consumption contribute 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 was 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.

-FIGURE 6_Use Color-

3.3 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).

-FIGURE 7_Use Color-

3.4 Comparative assessment of Biorefineries

Comparative assessments for every biorefinery scenario displayed reasonable results (Fig. 8). The increasing complexity of biorefineries showed a proportional increase of 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 number of equipments, 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. Since the function of every biorefinery changed for each scenario, the facilities were not considered comparable and therefore further analysis should be performed.

-FIGURE 8_Use Color-

3.5 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 consumes 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.

-FIGURE 9-Use Color-

4. Discussion

4.1 Eco-efficiency assessment of the considered scenarios

As reported through Sections 3.1 to 3.4, one would assume that the most environmentally sustainable LCB is Biorefinery 1.0. However, the research question is not fully answered through the concluding remarks on the results section. The objective of this study was to perform the holistic sustainability assessment of a Biorefinery and to conclude whether a more complex biorefinery would be more sustainable than a simplistic one.

In accordance with ISO 14045,[32] the concept of eco-efficiency acknowledges the consideration of environmental factors along with the value of the system to stakeholders. Considering the economic benefit of each LCB scenario in parallel to the environmental indicators, an in-depth assessment of the concept of sustainability of integrated biorefineries is clearly 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.[33]

The monetary benefit of each biorefinery according to product sales prices (Table 5) was the selected economic 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.

<TABLE5>

<TABLE6>

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 CO_2 emissions. The set of 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.

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. Therefore, the suggestion resulting from the results of the study would 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 counterproductive.

-FIGURE 10-Use Color-

4.2 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. Therefore, the recovery of acetic acid is not sustainable. In fact, the average production of acetic acid in bulk is a feasible process of fermentation,[34] avoiding the use of TOPO and undecane as well as petrochemical production options.

The production of acetic acid through a LCB increases potential revenues as demonstrated in this assessment and in agreement to other studies.[35,36] However, the negative environmental consequences shift the overall eco-efficiency indicator towards the Q2 quarter (Fig. 10), where economic benefits are high, but so are CO_2 emissions also contribute to climate change.

4.3 Furfural recovery

One of the outcomes of this study is the need not only to integrate the co-production of various bioproducts but to also 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 ecoefficiency 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.[37] 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.

4.4 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.[38] The further integration of enzyme production into the biorefinery is 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[39] enzyme production technologies significantly affect environmental impacts and LCA results may be sensitive to changes in this subsystem.

5. Conclusions

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

Data on integrated biorefineries producing multiple bio-based products is 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 pretreatment process. It would be advantageous, as well, to study possibilities of further energy optimization to achieve full integration of the plant.

Acknowledgements

This research was supported by the Spanish Government (Ministry of Economy and Competitiveness) through the ERA-IB2 project 2G-Enzymes (PCIN-2015-031) and the European project STARProBio (Grant Agreement Number 727740). The authors belong to the Galician Competitive Research Group GRC2013-032 and to the CRETUS Strategic Partnership (AGRUP2015/02). All these programmes are co-funded by FEDER (EU).

References

1. Biddy MJ, Scarlata C, Kinchin C., Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential. *NREL Tech Rep* (2016).
2. Menon V, Rao M., Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Prog Energy Combust Sci* **38**(4):522–50 (2012).
3. ePURE. European renewable ethanol-key figures 2016. http://epure.org/media/ 1610 /2016-industry-statistics.pdf [accessed 15 Nov 2017]
4. Sánchez ÓJ, Cardona CA., Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresour Technol* **99**(13):5270–95 (2008).

5. Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al., Features of promising technologies for pretreatment of lignocellulosic biomass. B*ioresour Technol* **96**(6):673–86 (2005).

6. Martín C, Klinke HB, Thomsen AB., Wet oxidation as a pretreatment method for enhancing the enzymatic convertibility of sugarcane bagasse. *Enzyme Microb Technol* **40**(3):426–32 (2007).

7. Jacquet N, Maniet G, Vanderghem C, Delvigne F, Richel A., Application of Steam Explosion as Pretreatment on Lignocellulosic Material: A Review. *Ind Eng Chem Res* **54**(10):2593–8 (2015).

8. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, et al., Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. *NREL Tech Rep*. (2011).

9. Brandt A, Ray MJ, To TQ, Leak DJ, Murphy RJ, Welton T., Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures. *Green Chem* **13**(9):2489 (2011).

10. Travaini R, Martín-Juárez J, Lorenzo-Hernando A, Bolado-Rodríguez S., Ozonolysis: An advantageous pretreatment for lignocellulosic biomass revisited. *Bioresour Technol* **199**:2–12 (2016).

11. Sindhu R, Binod P, Pandey A., Biological pretreatment of lignocellulosic biomass - An overview. *Bioresour Technol* **199**:76–82 (2016).

12. Viell J, Harwardt A, Seiler J, Marquardt W., Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study. *Bioresour Technol* **150**:89–97 (2013).

13. Laure S, Leschinsky M, Fröhling M, Schultmann F, Unkelbach G., Assessment of an Organosolv Lignocellulose Biorefinery Concept Based on a Material Flow Analysis of a Pilot Plant. *Cellul Chem Technol* **48**:793–8 (2014).

14. Arato C, Pye EK, Gjennestad G., The Lignol Approach to Biorefining of Woody Biomass to Produce Ethanol and Chemicals. *Appl Biochem and Biotechnol* **121**:871–82 (2005).

15. Snelders J, Dornez E, Benjelloun-Mlayah B, Huijgen WJJ, de Wild PJ, Gosselink RJA, et al., Biorefining of wheat straw using an acetic and formic acid based organosolv fractionation process. *Bioresour Technol* **156**:275–82 (2014).

16. De Wild PJ, Huijgen WJJ, Gosselink RJA., Lignin pyrolysis for profitable lignocellulosic biorefineries. *Biofuels, Bioprod Biorefining* **8**(5):645–57 (2014).

17. ISO14040. ISO 14040-Environmental management - Life Cycle Assessment - Principles and Framework (2006).

18. Boisen A, Christensen TB, Fu W, Gorbanev YY, Hansen TS, Jensen JS, et al., Process integration for the conversion of glucose to 2,5-furandicarboxylic acid. *Chem Eng Res Des* **87**(9):1318–27 (2009).

19. Kautto J, Realff MJ, Ragauskas AJ., Design and simulation of an organosolv process for bioethanol production. *Biomass Convers Biorefinery* **3**(3):199–212 (2013).

20. González-García S, Bonnesoeur V, Pizzi A, Feijoo G, Moreira MT., Comparing environmental impacts of different forest management scenarios for maritime pine biomass production in France. *J Clean Prod* **64**:356–67 (2014).

21. Werner F, Althaus HJ, Künniger T, Richter K, Jungbluth N., Life inventories of wood as fuel and construction material. Final report ecoinvent data v2.0 No.9. Dübendorf, CH (2007).

22. Laschi A, Marchi E, González-García S., Environmental performance of wood pellets' production through life cycle analysis. *Energy* **103**:469–80 (2016).

23. Heinzle E, Biwer AP, Cooney CL., *Development of Sustainable Bioprocesses: Modelling and Assessment*. John Wiley and Sons, Ltd, England (2006).

24. Dunn JB, Mueller S, Wang M, Han J., Energy consumption and greenhouse gas emissions from enzyme and yeast manufacture for corn and cellulosic ethanol production. *Biotechnol Lett* **34**(12):2259–63 (2012).

25. Werpy T, Petersen G., Top Value Added Chemicals from Biomass Volume I — Results of Screening for Potential Candidates from Sugars and Synthesis Gas Top Value Added Chemicals From Biomass (2004).

26. Nhien LC, Long NVD, Kim S, Lee M., Techno-economic assessment of hybrid extraction and distillation processes for furfural production from lignocellulosic biomass. *Biotechnol Biofuels* **10**(1):81 (2017).

27. Goedkoop M, Heijungs R, Huijbregts M, Schryver A De, Struijs J, Zelm R Van., ReCiPe 2008, A Life Cycle Impact Assessment Method Which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level. University of Leiden, Radboud University Nijmegen, RIVM, Bilthoven, Amersfoort, Netherlands (2009).

28. González-García S, Gullón B, Rivas S, Feijoo G, Moreira MT., Environmental performance of biomass refining into high-added value compounds. *J Clean Prod* **120**:170–80 (2016).

29. González-García S, Luo L, Moreira MT, Feijoo G, Huppes G., Life cycle assessment of flax shives derived second generation ethanol fueled automobiles in Spain. *Renew Sustain Energy Rev* **13**(8):1922–33 (2009).

30. Uihlein A, Schebek L., Environmental impacts of a lignocellulose feedstock biorefinery system: An assessment. *Biomass and Bioenergy* **33**(5):793–802 (2009).

31. Lundmark R. Consequence Analysis of Changing Market Conditions for the Swedish Sawmill Industry. (2006).

32. ISO 14045. ISO 14045:2012 - Environmental management - Eco-efficiency assessment of product systems-Principles, requirements and guidelines. (2012).

33. Gavrilescu M., Biorefinery Systems: An Overview. In: *Bioenergy Research: Advances and Applications*, pp. 219–41 (2014).

34. Dodds DR, Gross R a., Chemicals from Biomass. *Science* **318**:1250–1251 (2007).

35. Zhang YHP, Ding SY, Mielenz JR, Cui JB, Elander RT, Laser M, et al., Fractionating recalcitrant lignocellulose at modest reaction conditions. *Biotechnol Bioeng* **97**(2):214–23 (2007).

36. Zhu Y, Jones S., Techno-economic Analysis for the Thermochemical Conversion of Lignocellulosic Biomass to Ethanol via Acetic Acid Synthesis. US Department of Energy (2009).

37. Brentzel ZJ, Barnett KJ, Huang K, Maravelias CT, Dumesic JA, Huber GW., Chemicals from Biomass: Combining Ring-Opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural. *ChemSusChem* **10**(7):1351–5 (2017).

38. Olofsson J, Barta Z, Börjesson P, Wallberg O., Integrating enzyme fermentation in lignocellulosic ethanol production: life-cycle assessment and techno-economic analysis. *Biotechnol Biofuels* **10**(1):51 (2017).

39. Singh A, Pant D, Korres NE, Nizami A-S, Prasad S, Murphy JD., Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: Challenges and perspectives. *Bioresour Technol* **101**(13):5003–12 (2010).

40. Klein-Marcuschamer D, Oleskowicz-Popiel P, Simmons BA, Blanch HW., The challenge of enzyme cost in the production of lignocellulosic biofuels. *Biotechnol Bioeng* **109**(4):1083–7 (2012).

41. Budzinski M, Nitzsche R., Comparative economic and environmental assessment of four beech wood based biorefinery concepts. *Bioresour Technol* **216**:613–21 (2016).

42. Budzinski M, Nitzsche R., Comparative economic and environmental assessment of four beech wood based biorefinery concepts. *Bioresour Technol* **216**:613–21 (2016).

43. Zhao X, Siming Li RW, Liu D., Organosolv fractionating pre-treatment of lignocellulosic biomass for efficient enzymatic saccharification: chemistry, kinetics, and substrate structures. *Biofuels, Bioprod Biorefining* **11**(3):567–90 (2017).

44. Nitzsche R, Budzinski M, Gröngröft A., Techno-economic assessment of a wood-based biorefinery concept for the production of polymer-grade ethylene, organosolv lignin and fuel. *Bioresour Technol* **200**:928–39 (2016).

45. Hodásová L, Jablonsky M, Skulcova A, Haz A., Lignin , potential products and their market value. *Wood Res* **60**(6):973–86 (2015).

46. Qureshi N, Hodge DB, Vertes A., *Biorefineries: Integrated Biochemical Processes for Liquid Biofuels,* Amsterdam, pp. 73-100 (2014).

47. Persson T, Nordin AK, Zacchi G, Jönsson AS., Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce. In: *Applied Biochemistry and Biotechnology*, pp. 741–52 (2007).

48. Li Z, Xiao H, Jiang W, Jiang Y, Yang S., Improvement of solvent production from xylose mother liquor by engineering the xylose metabolic pathway in Clostridium acetobutylicum EA 2018. *Appl Biochem Biotechnol* **171**(3):555–68 (2013).

49. Joelsson E, Erdei B, Galbe M, Wallberg O., Techno-economic evaluation of integrated first- and second-generation ethanol production from grain and straw. *Biotechnol Biofuels* **9**(1):1 (2016).

50. Bechara R, Gomez A, Saint-Antonin V, Schweitzer JM, Maréchal F., Methodology for the optimal design of an integrated first and second generation ethanol production plant combined with power cogeneration. *Bioresour Technol* **214**:441–9 (2016).

51. Rodrigues Gurgel da Silva A, Errico M, Rong BG., Techno-economic analysis of organosolv pretreatment process from lignocellulosic biomass. *Clean Technol Environ Policy* 1–12 (2017).

52. Macrelli S, Galbe M, Wallberg O., Effects of production and market factors on ethanol profitability for an integrated first and second generation ethanol plant using the whole sugarcane as feedstock. *Biotechnol Biofuels* **7**(1):26 (2014).

53. Frankó B, Galbe M, Wallberg O., Bioethanol production from forestry residues: A comparative techno-economic analysis. *Appl Energy* **184**:727–36 (2016).

54. Kaylen M, Dyne DL Van, Choi Y, Blase M., Economics feasibility of production ethanol from lignocellulosic feedstocks. *Bioresour Technol* **72**:19–32 (2000).

55. Moncada J, Cardona CA, Higuita JC, Vélez JJ, López-Suarez FE., Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural

in Colombia: Experimental, techno-economic and environmental assessments. *Chem Eng Sci* **140**:309–18 (2016).

56. Win DT., Furfural – Gold from Garbage. *Assumpt Univ J Technol* **8**(4):185–90 (2005).

57. Machado G, Leon S, Santos F, Lourega R, Dullius J, Mollmann ME, et al., Literature Review on Furfural Production from Lignocellulosic Biomass. *Nat Resour* **7**(3):115–29 (2016).

58. Huang K, Brentzel ZJ, Barnett KJ, Dumesic JA, Huber GW, Maravelias CT., Conversion of Furfural to 1,5-Pentanediol: Process Synthesis and Analysis. *ACS Sustain Chem Eng* **5**(6):4699–706 (2017).

59. Straathof AJJ, Bampouli A., Potential of commodity chemicals to become bio-based according to maximum yields and petrochemical prices. *Biofuels, Bioprod Biorefining* **11**(5):798–810 (2017).

60. Himmelblau DM, Riggs JB., *Basic Principles and Calculations in Chemical Engineering*. Prentice Hall, USA, (2004).

61. ICIS. Indicative chemical prices A-Z. https://www.icis.com/chemicals/channel-info-chemicals-a-z/ [accessed 29 December 2017]

Tables

Table 1: Studied scenarios and specification of boundaries

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 co-production	ethanol, furfural, lignin, acetic acid	SS0-SS8

Table 2: Summary of data sources

Subsystem	Bibliographic source
SS0. Feedstock	
SS0.1 Forest activities	20
SS0.2 Sawmill	21
SS0.3 Chipping	22
SS1. Organosolv pulping	19
SS2. Solvent recovery	19
SS3. Hemicellulose conditioning	19
SS4. Enzymatic hydrolysis	19
Enzyme production	23, 24
SS5. Cogeneration unit	19
SS6. Fermentation to ethanol	19
SS7. Acetic acid recovery	19
SS8. Furfural recovery	19

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		
N_2	13.54	g
NH_3	1.85	g
NO_x	2.50	g
SS0.2 Sawmill		
Inputs from process		
Roundwood from SS0.1	0.71	m^3
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
CO_2	30.76	kg
CO	15.67	g
NO_x	34.79	g
Particulates	14.98	g
SO_2	0.82	g
Municipal solid waste	1.50	kg
Outputs to technosphere		
Bark chips	0.10	m^3
Sawn timber	0.41	m^3
SS0.3 Chipping		
Inputs from process		
Residual wood from SS0.1	1.28	m^3
Inputs from technosphere		
Electricity	2.30	kwh
Outputs to SS1		
Residual wood chips	1.25	m^3

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

SS1 Pulping		
Inputs from technosphere		
Water (pulping)	3.72	t
Water (washing)	4.56	t
Sulfuric acid	$1.01\cdot10^{-2}$	t
Ethanol (pulping)	3.74	t
Transport, freight, lorry (16-32 metric ton)	105	tkm
High pressure steam	1.97	GJ
Electricity (pulping)	$7.80\cdot10^{-2}$	MWh

SS2 Solvent recovery		
Inputs from technosphere		
Water (dilution)	1.02	t
Natural gas	$5.40\cdot10^{-3}$	t
Low pressure steam	0.77	GJ
Electricity	$6.00\cdot10^{-2}$	MWh
Outputs to technosphere		
Lignin	0.16	t

SS3 Hemicellulose conditioning		
Inputs from technosphere		
Furfural (makeup)	$1.92\cdot10^{-3}$	t
Ammonia	$6.24\cdot10^{-3}$	t
Low pressure steam	0.36	t
High pressure steam	0.21	GJ

SS4 Enzymatic hydrolysis		
Inputs from technosphere		
Enzyme (cellulase)	$7.80\cdot10^{-3}$	t
Electricity	$2.04\cdot10^{-2}$	MWh
Low pressure steam	$9.12\cdot10^{-2}$	GJ
Cellulase production (7.8 kg)		
Inputs from technosphere		
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
Outputs to environment		
N_2	$2.16\cdot10^{3}$	kg
O_2	$6.56\cdot10^{3}$	kg
CO_2	$1.10\cdot10^{3}$	kg

SS5. Cogeneration unit		
Inputs from technosphere		
Water	0.68	t
Sludge (from WWT)	$5.78\cdot10^{-2}$	t
Biogas (from WWT)	$4.27\cdot10^{-2}$	t
Natural gas	$2.26\cdot10^{-2}$	t
Outputs to environment		
CO_2	6.84	kg
Water (vapor)	108.84	kg

SS6. Fermentation to bioethanol		
Inputs from technosphere		
Water	0.21	t
Diammonium phosphate	$1.68\cdot10^{-3}$	t
Corn steep liquor	$1.27\cdot10^{-2}$	t
Low pressure steam	1.74	GJ
Electricity	$8.40\cdot10^{-3}$	MWh
Outputs to technosphere		
Bioethanol	0.24	t
Water	0.37	t
Outputs to environment		
CO_2	218.77	kg
O_2	1.44	kg
Wastewater	0.0034	m^3

SS7. Acetic acid recovery		
Inputs from technosphere		
Low pressure steam	0.39	GJ
Electricity	$3.48\cdot10^{-2}$	MWh
TOPO	3.32	kg
Undecane	11.93	kg
Outputs to technosphere		
Acetic acid	$1.56\cdot10^{-2}$	t
Outputs to environment		
TOPO	3.32	kg
Undecane	11.93	kg

SS8. Furfural recovery		
Inputs from technosphere		
Low pressure steam	$2.40\cdot10^{-3}$	GJ
Electricity	$2.40\cdot10^{-2}$	MWh
Outputs to technosphere		
Furfural	$5.28\cdot10^{-3}$	t

Table 5: Market selling prices of products obtained in the biorefinery configurations

Product	**Average market selling price (€/t)**
Glucose	355.0 [23,40]
Lignin	530.6 [41–45]
Hemicellulose	105.4 [46–48]
Bioethanol	830.5[49–53]
Furfural	865.3 [37,54–58]
Acetic acid	834.2 [36,59–61]

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 CO_2 eq/€)	0.47	0.42	0.45
OD (kg CFC-11 eq/€)	$5.34\cdot10^{-8}$	$7.64\cdot10^{-8}$	$4.38\cdot10^{-8}$
TA (kg SO_2 eq/€)	$2.32\cdot10^{-3}$	$2.41\cdot10^{-3}$	$2.62\cdot10^{-3}$
FE (kg P eq/€)	$9.85\cdot10^{-5}$	$8.32\cdot10^{-5}$	$8.42\cdot10^{-5}$
ME (kg N eq/€)	$5.81\cdot10^{-5}$	$5.52\cdot10^{-5}$	$5.91\cdot10^{-5}$
HT (kg 1,4-DB eq/€)	$1.26\cdot10^{-3}$	$1.13\cdot10^{-3}$	0.097
POF (kg NMVOC/€)	$3.04\cdot10^{-3}$	$1.13\cdot10^{-3}$	$1.30\cdot10^{-3}$
FET (kg 1,4-DB eq/€)	$3.04\cdot10^{-3}$	$2.64\cdot10^{-3}$	$2.75\cdot10^{-3}$
MET (kg 1,4-DB eq/€)	$2.62\cdot10^{-3}$	$2.19\cdot10^{-3}$	$2.23\cdot10^{-3}$
FD (kg oil eq/€)	0.24	0.22	0.28

Figure 1

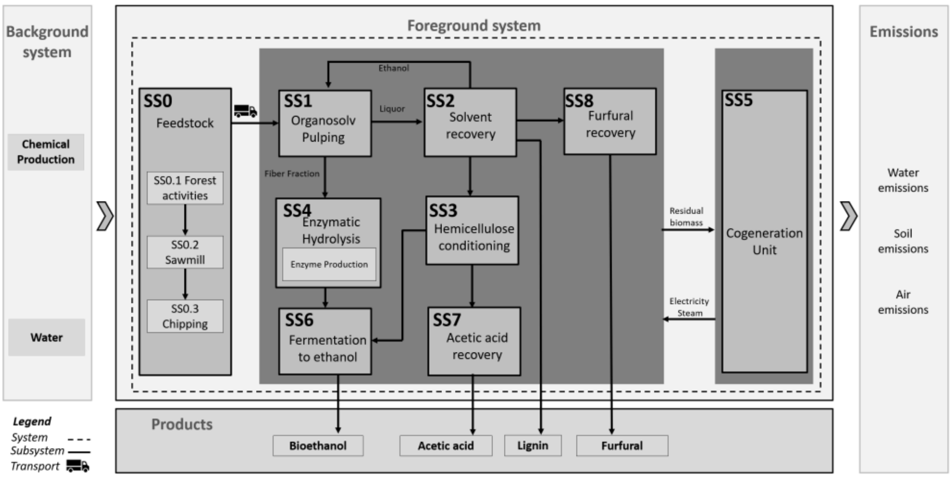

Background system
Chemical Production
Water
Foreground system
SS0
Feedstock
SS0.1 Forest activities
SS0.2 Sawmill
SS0.3 Chipping
Ethanol
SS1
Organosolv Pulping
Liquor
SS2
Solvent recovery
SS8
Furfural recovery
Fiber Fraction
SS4
Enzymatic Hydrolysis
Enzyme Production
SS3
Hemicellulose conditioning
SS6
Fermentation to ethanol
SS7
Acetic acid recovery
Residual biomass
Electricity Steam
SS5
Cogeneration Unit
Emissions
Water emissions
Soil emissions
Air emissions
Products
Bioethanol
Acetic acid
Lignin
Furfural
Legend
System
Subsystem
Transport

Figure 2

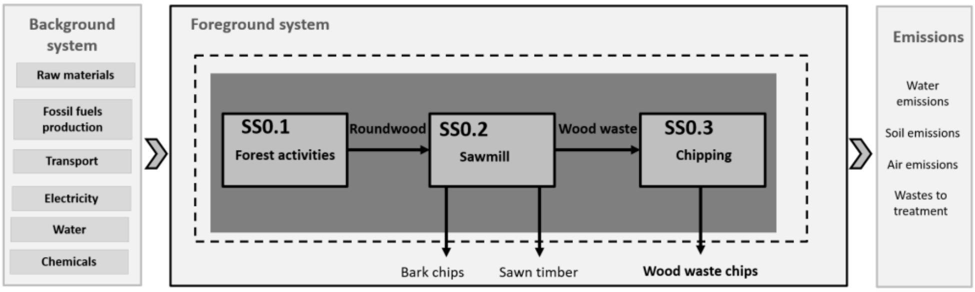

Background system
Raw materials
Fossil fuels production
Transport
Electricity
Water
Chemicals
Foreground system
SS0.1
Forest activities
Roundwood
SS0.2
Sawmill
Wood waste
SS0.3
Chipping
Bark chips
Sawn timber
Wood waste chips
Emissions
Water emissions
Soil emissions
Air emissions
Wastes to treatment

Figure 3

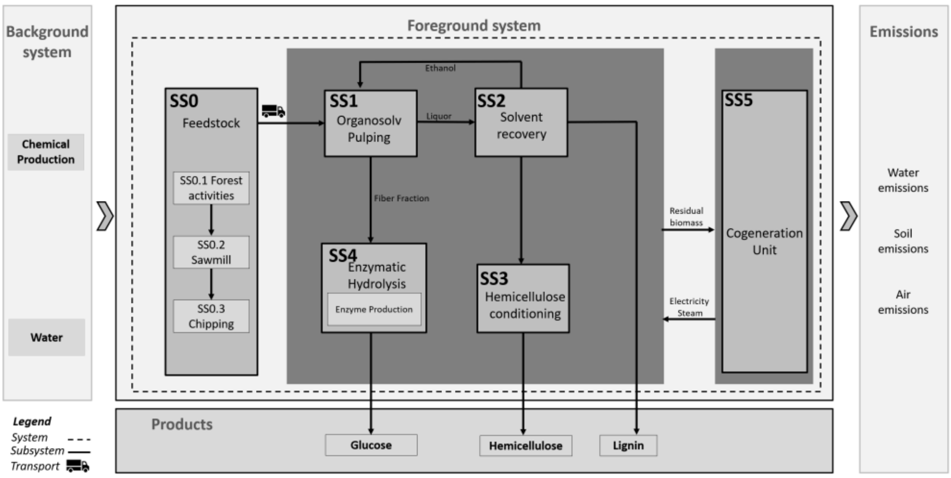

Background system
Chemical Production
Water
Foreground system
SS0
Feedstock
SS0.1 Forest activities
SS0.2 Sawmill
SS0.3 Chipping
SS1
Organosolv Pulping
Ethanol
Liquor
SS2
Solvent recovery
Fiber Fraction
SS4
Enzymatic Hydrolysis
Enzyme Production
SS3
Hemicellulose conditioning
Residual biomass
Electricity Steam
SS5
Cogeneration Unit
Emissions
Water emissions
Soil emissions
Air emissions
Products
Glucose
Hemicellulose
Lignin
Legend
System
Subsystem
Transport

Figure 4

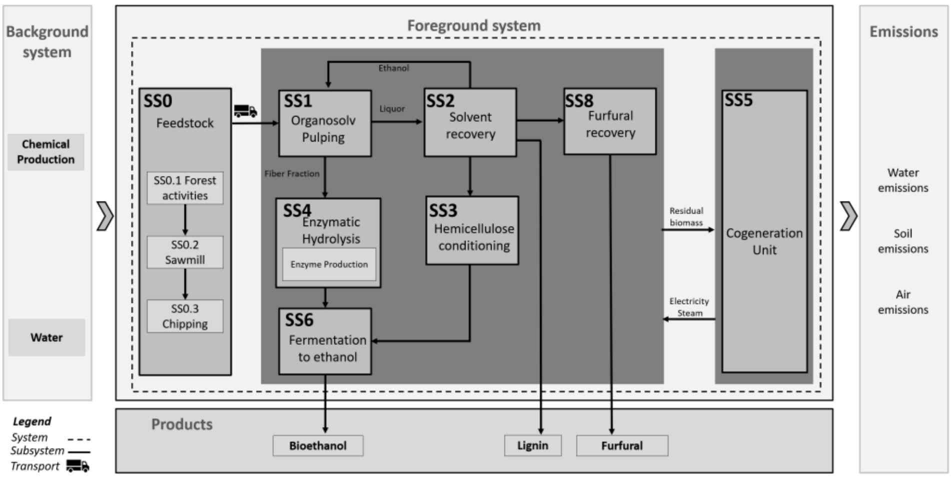
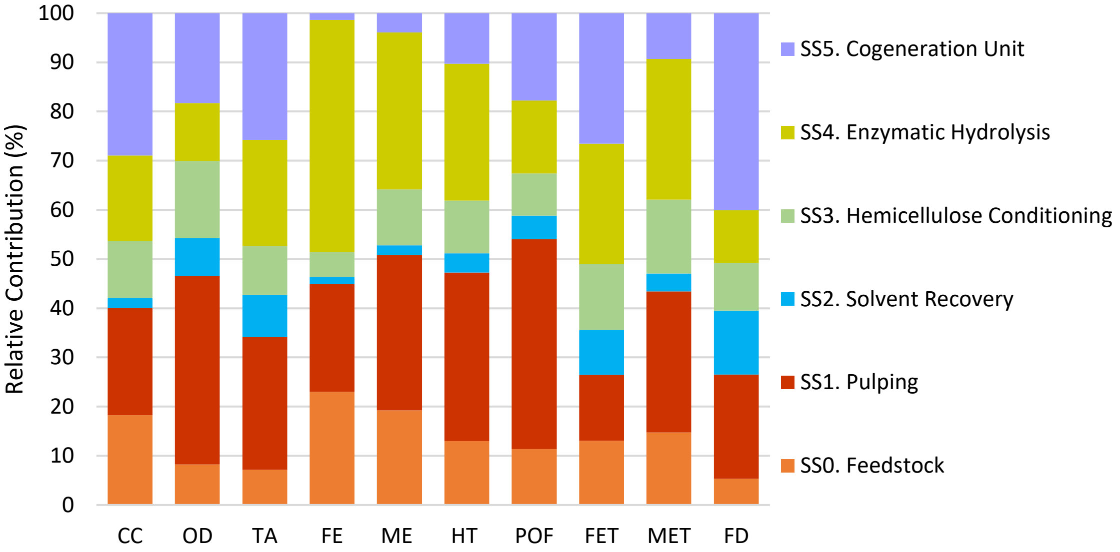

Background system
Chemical Production
Water
Foreground system
SS0
Feedstock
SS0.1 Forest activities
SS0.2 Sawmill
SS0.3 Chipping
Ethanol
SS1
Organosolv Pulping
Liquor
SS2
Solvent recovery
SS8
Furfural recovery
Fiber Fraction
SS4
Enzymatic Hydrolysis
Enzyme Production
SS3
Hemicellulose conditioning
SS6
Fermentation to ethanol
Residual biomass
Electricity Steam
SS5
Cogeneration Unit
Emissions
Water emissions
Soil emissions
Air emissions
Products
Bioethanol
Lignin
Furfural
Legend
System
Subsystem
Transport

Figure 5


Relative Contribution (%)
100
90
80
70
60
50
40
30
20
10
0
CC
OD
TA
FE
ME
HT
POF
FET
MET
FD
SS5. Cogeneration Unit
SS4. Enzymatic Hydrolysis
SS3. Hemicellulose Conditioning
SS2. Solvent Recovery
SS1. Pulping
SS0. Feedstock

1 **Figure 6**

2

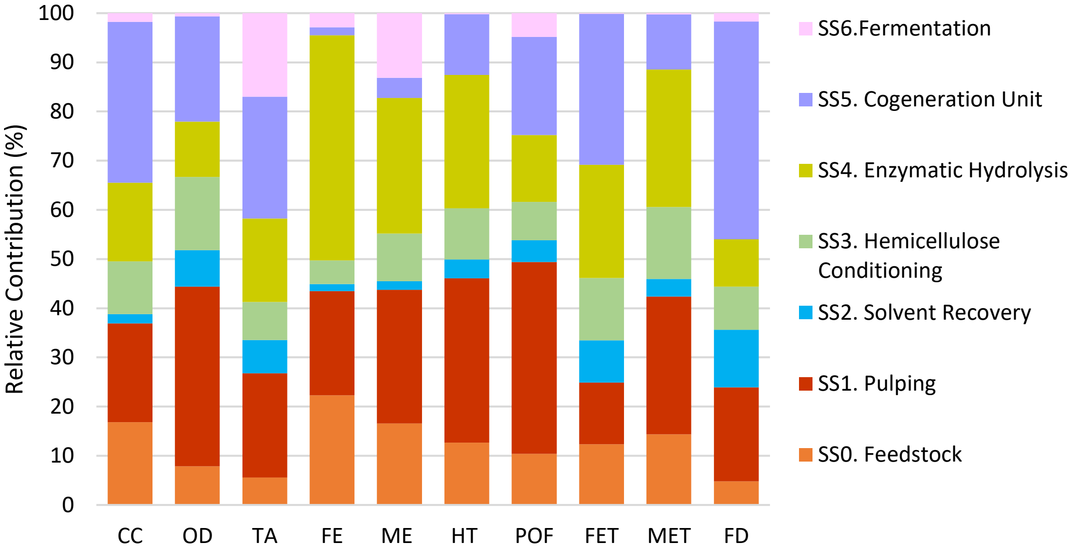
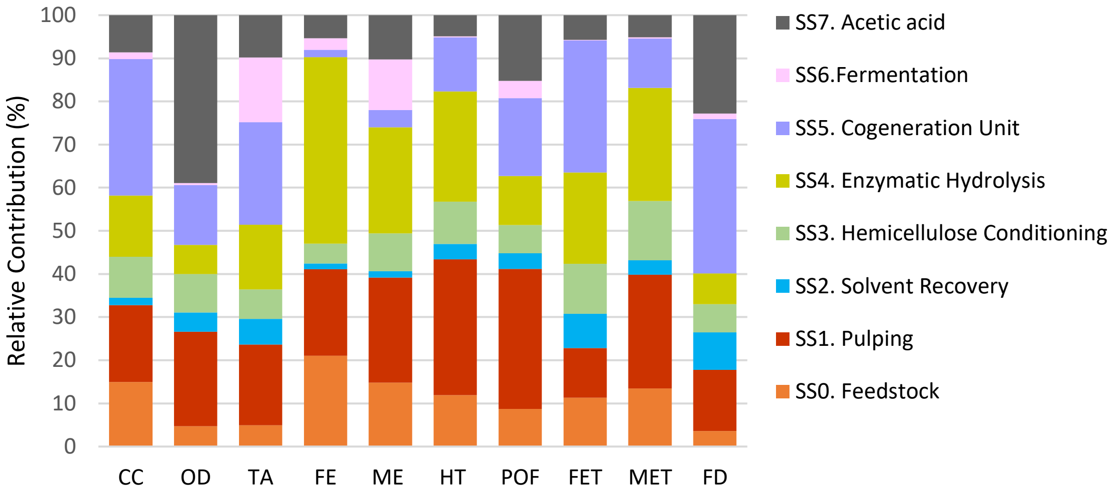

Relative Contribution (%)
100
90
80
70
60
50
40
30
20
10
0
CC
OD
TA
FE
ME
HT
POF
FET
MET
FD
SS6.Fermentation
SS5. Cogeneration Unit
SS4. Enzymatic Hydrolysis
SS3. Hemicellulose Conditioning
SS2. Solvent Recovery
SS1. Pulping
SS0. Feedstock

Figure 7



100
90
80
70
60
50
40
30
20
10
0
Relative Contribution (%)
CC
OD
TA
FE
ME
HT
POF
FET
MET
FD
SS7. Acetic acid
SS6.Fermentation
SS5. Cogeneration Unit
SS4. Enzymatic Hydrolysis
SS3. Hemicellulose Conditioning
SS2. Solvent Recovery
SS1. Pulping
SS0. Feedstock

Figure 8

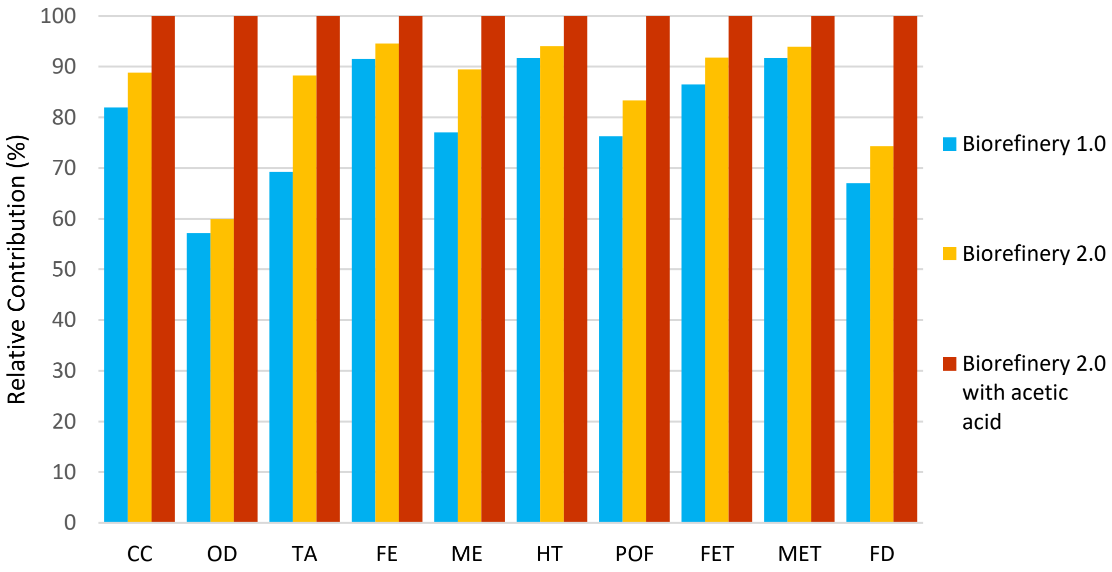

Relative Contribution (%)
100
90
80
70
60
50
40
30
20
10
0
CC
OD
TA
FE
ME
HT
POF
FET
MET
FD
Biorefinery 1.0
Biorefinery 2.0
Biorefinery 2.0 with acetic acid

Figure 9

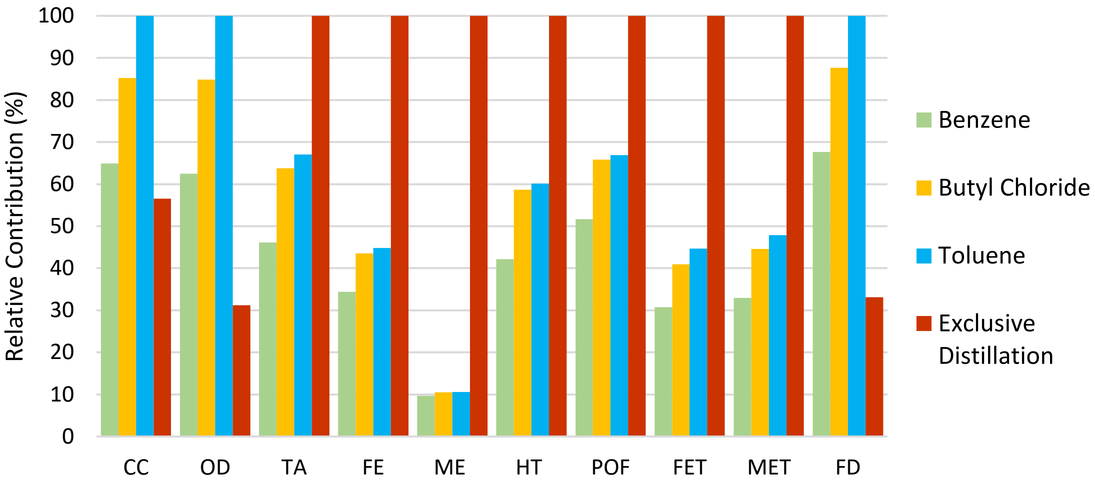

Relative Contribution (%)
100
90
80
70
60
50
40
30
20
10
0
CC
OD
TA
FE
ME
HT
POF
FET
MET
FD
Benzene
Butyl Chloride
Toluene
Exclusive Distillation

Figure 10

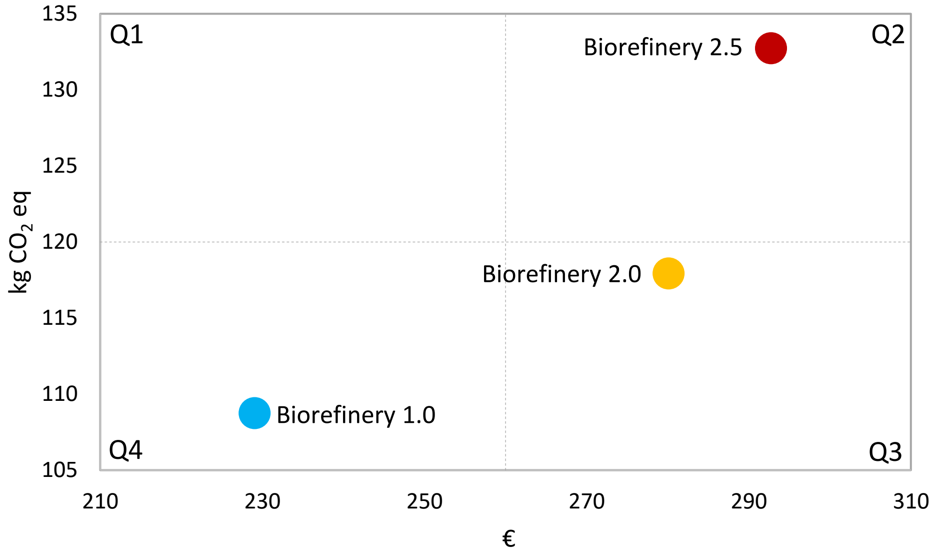

135
130
125
120
115
110
105
kg CO_2 eq
Q1
Q2
Q3
Q4
Biorefinery 2.5
Biorefinery 2.0
Biorefinery 1.0
210
230
250
270
290
310
€

Figure captions

Figure 1 System boundaries of the lignocellulosic biorefinery for the production of bioethanol, acetic acid, lignin and furfural. Subsystems (SS) are defined with reference to process units in the plant.

Figure 2 General system configuration SS0. Feedstock

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

Figure 4 System boundaries of the lignocellulosic biorefinery for the production of bioethanol, lignin and furfural. Subsystems (SS) and system boundaries defined for Biorefinery 2.0

Figure 5 Relative contributions (in %) per subsystem in the overall production process of the Biorefinery 1.0

Figure 6 Relative contributions (in %) per subsystem in the overall production process of the Biorefinery 2.0

Figure 7 Relative contributions (in %) per subsystem in the overall production process of the Biorefinery 2.0 with co-production of acetic acid

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

Figure 10 Climate change and monetary benefit per functional unit (1 t dry wood /h)