Use of Lignin Side-Streams from Biorefineries as Fuel or Co-product? Life Cycle Analysis of Bio-ethanol and Pulp Production Processes

Michela Secchi, Valentina Castellani, Marco Orlandi,* and Elena Collina

Increasing the profitability of lignin side-streams is a challenge in the scientific community. Lignin residue originates from black liquor and lignin cake, which are residues from pulp and bio-ethanol production. This paper presents a life cycle assessment study to investigate how pulp and bio-ethanol processes vary in their environmental performance when a fraction of lignin is removed and to identify the best alternative energy source. Fossil energy, natural gas, and cogeneration were evaluated as heat and power alternative sources. The results showed that lignin removal does not considerably affect the environmental performance of the baseline systems and does not generate a relevant risk of "burdens shifting." Natural gas was the best alternative of power source in a bio-ethanol system, whereas cogeneration showed better compatibility with pulp mills. For the analyzed systems, the necessary allocation distributed the impact contributions between the main products (bio-ethanol/pulp) and the co-products (lignin-cake/black liquor), counterbalancing the impact increase due to the introduction of the new heat, electricity supply, and additional treatment aimed at lignin extraction. Finally, sensitivity analyses confirmed the low influence on the results of the substitution ratio.

Keywords: Lignin; Side-streams valorization; Biorefinery; Life cycle assessment; Allocation criteria; Green chemistry; Industrial symbiosis

*Contact information: Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milano, Italy; *Corresponding author: marco.orlandi@unimib.it*

INTRODUCTION

Second generation bio-ethanol conversion and pulp production are both well-known technologies. There is an abundance of literature reviews dealing with these industry processes and their sustainability (Aresta *et al.* 2012; Aditiya *et al.* 2016). Many aspects, such as the choice of energy sources for pulp mills, the problem of competition in land use for food crops, or the energy profitability of bio-ethanol compared to traditional fuel sources, have been investigated from a life cycle perspective (Bai *et al.* 2010; Cherubini and Ulgiati 2010; Gaudreault *et al.* 2010; Naik *et al.* 2010; Cherubini and Strømman 2011; Fazio and Monti 2011; Aresta *et al.* 2012; Tonini *et al.* 2012).

One of the current challenges in the scientific community is the use of lignin residue coming from these activities (Sannigrahi *et al.* 2010; González-García *et al.* 2016). Lignin, the second most abundant polymer in nature, is the generic term for a large group of aromatic polymers resulting from the oxidative combinatorial coupling of 4-hydroxyphenylpropanoids (Boerjan 2005). Lignin is one of the main compounds present in black liquor and lignin cake, which are residues from pulp and bio-ethanol production processes. As aromatic structures are still present, they have sustainable and economic potential in bio-based chemicals and materials and in the energy sector; for these reasons, new lignin fates are being studied. After a necessary reduction in lignin molecular complexity, purification, or fractionation (Schmiedl *et al.* 2012; Zoia *et al*. 2017), the possible applications of lignin as a sustainable alternative to fossil feedstocks include phenolic and epoxy resins (Lora and Glasser 2002; Salanti *et al*. 2018), green composites (Thakur *et al.* 2014), and fillers or additives in tires (Frigerio *et al.* 2014; Barana *et al*. 2018). These applications could lead to the development and improvement of green chemistry and industrial symbiosis solutions, where the residual streams coming from the biorefinery are sent to other industries and transformed in higher value products. Industrial symbiosis is the clustering of activities to prevent by-products from becoming wastes (EC COM/2014/0398 final).

While only recently lignin extraction from lignin cake residue has been investigated (Argyropoulos 2014), the extraction from black liquor in pulp industry has been explored in the kraft process. One extraction method is the Lignoboost process (Tomani *et al.* 2011; Tomani 2013). This technology allows a highly purified lignin to be obtained, often used for combustion as an alternative fuel, alone or together with a common liquid fossil fuel, increasing the onsite energy production.

Within the Pro-Lignin "high-value products from lignin side-streams of modern biorefineries" project framework, lignin by-products from current biomass fractionating processes with distinct structural features, *e.g.*, softwood and hardwood kraft and steam-exploded lignin, were assessed with the aim of evaluating the potential valorization routes by also considering the environmental sustainability aspect. The final scope of the project was to improve the profitability of lignocellulosic-based bio-ethanol and pulp production processes by the upgrading of lignin side-streams to high-value products (dispersants, resins, adhesives, foams, and thermoplastics, *e.g.*, for coatings, wood products, composites, and construction materials).

The recovery of lignin as a by-product represents a case of industrial symbiosis because in the current production processes for pulp and bio-ethanol the streams containing lignin (black liquor and lignin cake, respectively) are not discarded as waste, but are used instead as an energy source. Therefore, the potential environmental gain coming from their reuse in other production processes has to be compared with the potential additional burdens coming from the substitution of lignin as a fuel in the original production process.

The present study is one of the outputs of the above-mentioned project, and it investigates how pulp and bio-ethanol processes vary in their environmental performance when lignin is removed from these closed loops where it is one of the main energy sources. Life cycle assessment (LCA) methodology, the most reliable tool to assess the environmental feasibility of eco-innovation strategies, was applied to the current production processes and to the alternative processes where lignin is removed and substituted by other energy sources. The study focused on the "burdens shifting" risk, namely reducing the environmental impact at one point in the life cycle while increasing it at another point. A critical issue addressed is the choice of allocation criteria, *i.e.*, how the environmental burdens arising from a production process are partitioned between products and co-products. In addition, a comparison among different energy sources helps to define the most environmentally friendly option for the substitution of lignin.
The goals of the study were as follows:

- to assess the possible risk of "burdens shifting" derived from lignin removal from pulp and bio-ethanol production process;

- to evaluate the influence of allocation criteria when lignin cake and black liquor become co-products respectively of bio-ethanol and pulp;
- to identify the best alternative to lignin energy source, from an environmental point of view.

The focus of the paper is entirely on the current bio-ethanol and pulp production processes and their modifications for lignin extraction and substitution as an energy source, independently from the use of lignin after its removal. The results may support the pulp and bio-ethanol industry in finding the best solution for the substitution of lignin as an energy source within the innovative production process.

EXPERIMENTAL

The production processes considered in the study are: bio-ethanol production (system 1); softwood (SW) pulp production (system 2); hardwood (HW) pulp production (system 3). For each of the analyzed systems, the study compares the LCA results of the pulp and bio-ethanol production systems in the baseline scenario (B1, B2, and B3), corresponding to the current closed-loop process, with the innovative scenarios where the lignin is partially removed from the production process as a co-product of bio-ethanol and paper (scenarios B1*, B2*, and B3*). The definition of removal scenarios considers several parameters that may influence the result, such as the energy source (or the mix of energy sources) used to replace lignin and the type of allocation applied to the system (*e.g.*, by mass, economic value, or energy content). Therefore, several removal scenarios are developed, assessed, and compared. Table 1 summarizes the options considered and all the scenarios assessed in the study.

The main assumptions tested in each scenario are illustrated in the section, Main Assumptions. Additionally, the Monte Carlo analysis was run to see the combined influence on the impact quantification of the uncertainty related to the various data inputs. This type of analysis makes it possible to calculate the range extent in the LCA actual results. In the Monte Carlo approach, the software builds the uncertainty distribution through a series of repeated calculations (in the present work 1000 times), by taking into account every time a random variable for each value within the uncertainty range related to the specific input data. Finally, two sensitivity analyses were performed to test the effect of the assumptions made on two parameters used in the systems modeling: the amount of lignin removed from the main system and the market price assumed for lignin as a co-product.

Table 1. List of the Evaluated Scenarios ^

Bio-ethanol scenarios	Lignin removal (%)	Allocation	Substituted type of energy	Energy source
B1 (Baseline)	0%	No	-	100% lignin cake
B1 * cogen + en	40%	Energy content	Electricity	60% lignin cake + 40% co-generation
B1 * cogen + m	40%	Mass	Electricity	60% lignin cake + 40% co-generation
B1 * gas + en	40%	Energy content	Electricity	60% lignin cake + 40% natural gas
B1 * gas + m	40%	Mass	Electricity	60% lignin cake + 40% natural gas
B1 * grid + en	40%	Energy content	Electricity	60% lignin cake + 40% grid electricity
B1 * grid + m	40%	Mass	Electricity	60% lignin cake + 40% grid electricity
Softwood pulp scenarios	**Lignin removal (%)**	**Allocation**	**Substituted type of energy**	**Energy source**
B2 (Baseline)	0%	No	-	100% black liquor
B2 * cogen + ec	50%	Economic	Heat	50% black liquor + 50% co-generation
	-	-	Electricity	100% co-generation
B2 * cogen + m	50%	Mass	Heat	50% black liquor + 50% co-generation
	-	-	Electricity	100% co-generation
B2 * fossil + ec	50%	Economic	Heat	50% black liquor + 50% fossil (heavy fuel oil)
B2 * fossil + m	50%	Mass	Heat	50% black liquor + 50% fossil (heavy fuel oil)
B2 * gas + ec	50%	Economic	Heat	50% black liquor + 50% natural gas
B2 * gas + m	50%	Mass	Heat	50% black liquor + 50% natural gas
Hardwood pulp scenarios	**Lignin removal (%)**	**Allocation**	**Substituted type of energy**	**Energy source**
B3 (Baseline)	0%	No	-	100% black liquor
B3 * cogen + ec	50%	Economic	Heat	50% black liquor + 50% co-generation
B3 * cogen + m	50%	Mass	Heat	50% black liquor + 50% co-generation
B3 * fossil + ec	50%	Economic	Heat	50% black liquor + 50% fossil (heavy fuel oil)
B3 * fossil + m	50%	Mass	Heat	50% black liquor + 50% fossil (heavy fuel oil)
B3 * gas + ec	50%	Economic	Heat	50% black liquor + 50% natural gas
B3 * gas + m	50%	Mass	Heat	50% black liquor + 50% natural gas

^ Abbreviations used to define the names of scenarios: Baseline = "B", co-generation = "cogen", natural gas = "gas", grid electricity = "grid", heavy fuel oil = "fossil", allocation by mass = "m", allocation by economic value = "ec", allocation by energy content = "en"

Scope Definition, System Boundaries, and Functional Unit of the Studied Systems

As defined in the ISO 14040 (2006) series, the first step in LCA is to define the general aspects on which the analysis is conducted: main scope, system boundaries, and functional unit.

The analysis was performed on 1 kg of final product (bio-ethanol or kraft pulp). This functional unit allows addressing the study on the production process and possible innovations thereof. The analysis is cradle-to-factory gate, which means that it focuses on the production stages of pulp and bio-ethanol supply chains, from the raw materials to the final product. According to its scope, the assessment does not consider product use and disposal stages but only the handling of the biomass input (cultivation and transport) and its treatments (water, energy, and chemicals input), energy recovery, waste, and emissions coming from the abovementioned life cycle stages. The discussion about possible uses of lignin and the development of future scenarios is out of the scope of this paper.

Main Assumptions

Allocation

The scope of the analysis included the lignin extraction stage and the whole production process. Therefore, the allocation rules were adopted to assign the respective share of impact to the products and co-products (bio-ethanol and lignin cake or pulp and black liquor).

Although ISO 14044 (2006) and the International Reference Life Cycle Data System (ILCD) Handbook (Institute for Environment and Sustainability 2010) recommend a system expansion, it is not possible to apply it to the present case studies. Lignin has a wide range of potential uses, but currently none of them is at the market stage. Hence, it is not possible to identify and model a single option of substitution to be included in the models. Moreover, the focus of the analysis is on bio-ethanol and pulp industries and on the effect of lignin removal (and substitution) on the environmental profile of the main products (bio-ethanol and pulp), independently of the final use of the lignin removed. This is reflected also by the functional unit chosen (*i.e.* 1 kg of main product).

Allocation can be a critical issue when dealing with the LCA of innovations (Hospido *et al.* 2010; Hetherington *et al.* 2014). In particular, the choice of the allocation approach could have a remarkable influence on the results, especially when dealing with biorefineries and their multifunctional products (Singh *et al.* 2010; Cherubini *et al.* 2011; Wang *et al.* 2011; Ahlgren *et al.* 2015; Karka *et al.* 2015; Sandin *et al.* 2015; Djomo *et al.* 2017). Therefore, different allocation approaches are evaluated and compared for the systems considered in this study. The assumptions used to define the allocation values for the products and co-products are described below.

For the bio-ethanol system, the mass allocation is the first choice, as suggested by ILCD Handbook (Institute for Environment and Sustainability 2010) and ISO 14044:2006, but also the energy content criterion has been evaluated. Mass allocation is performed according to De Bari *et al.* (2008): 3.6 kg of lignin cake are produced for 1 kg of bio-ethanol, therefore 28% of impact is allocated to bio-ethanol.

Energy allocation is performed according to the lignin cake energy content (9850 MJ/t) and 91.9% of the impacts is allocated to the bio-ethanol.

For a SW and HW pulp system, following the EPD Product Category Rules (EPD 2011) for the product basic organic chemicals, an economic allocation is applied based on market price. Because the potential fates of purified lignin could assume different economic values, depending on the material it could replace, economic allocation is performed according to following assumptions:

1. The prices of pulp and lignin are based on the literature data according to the best knowledge and judgment of the researchers.
2. The mean monthly price for wood pulp was calculated over the period of October 2013 to May 2015: 688 €/t (IndexMundi 2016).
3. As there is no list price for lignin and the price is dependent on source and quality of lignin as well as final product, it is not easy to select only one proper price for lignin. Therefore, the price range for lignin will be used to give the best and worst scenarios.
4. According to the public data available, a price range of 1000 €/t to 2000 €/t was selected for pure high quality kraft lignin to be used to replace high value compounds.
5. Reasoning for the selected price range is as follows:
    - According to Lake (2010) and Hodásová *et al.* (2015), lignin with 1500 USD/t price (1100 €/t) could still be a cost competitive alternative to replace phenol.
    - According to Nikishkina (2014), the market price of phenol 1500 USD/t is expected to increase in the future, justifying also the use of lignin prices higher than 1100 €/t.
    - Lake (2010) and Hodásová *et al.* (2015) report that lignin prices around 2000 USD/t (1500 €/t) could be tolerated in PU resins, whereas Nikishkina (2014) indicated market prices of 6000 USD/t to 8000 USD/t for epoxy resins. Therefore, we assumed that the epoxy resins could tolerate higher prices of 2000 €/t for the lignin raw material.
    - Even though lignin-based dispersants (such as lignosulfonates) are considered lower/medium value products, Higson (2011) gives price ranges of 250 £/t to 2000 £/t (310 €/ton to 2500 €/ton) for lignin and lignosulfonates in general. Furthermore, Hodásová *et al.* (2015) report that kraft lignin and lignosulphonates price starts from around 200 USD/t (about 184 €/t).
    - In Finland, given a margin, the assumed lignin price range could be of 1000 €/t to 2000 €/t, as calculated starting from the data above and in accordance to a personal communication from the companies involved in the Pro-Lignin project.

According to the assumptions, 65% of the impacts are allocated to pulp. A sensitivity analysis on this value was run for softwood pulp production.

In addition, a mass allocation is performed and compared to the economic allocation. According to average production data (44000 t/y of dried black liquor is produced for 181818 t/y pulp), 80.5% of impacts is allocated to pulp.

Amount of lignin removed

The amount of lignin that is removed from the main system (bio-ethanol or pulp production) should be a trade-off between the market value of lignin as a co-product and the cost of its substitution with other energy sources. Because there is currently no market for lignin, the amount of lignin assumed in the scenarios is based on estimations made by companies supporting the work within the Pro-Lignin project. According to these data (personal communication), the amount of lignin removed from the bio-ethanol production process is assumed to be 40%, whereas the amount of lignin removed from the pulp production process is 50%. A sensitivity analysis is run on the softwood pulp system, varying the amount of lignin removed from 50% to 30% (worst scenario, in case the cost of alternative energy sources would rise in the future).

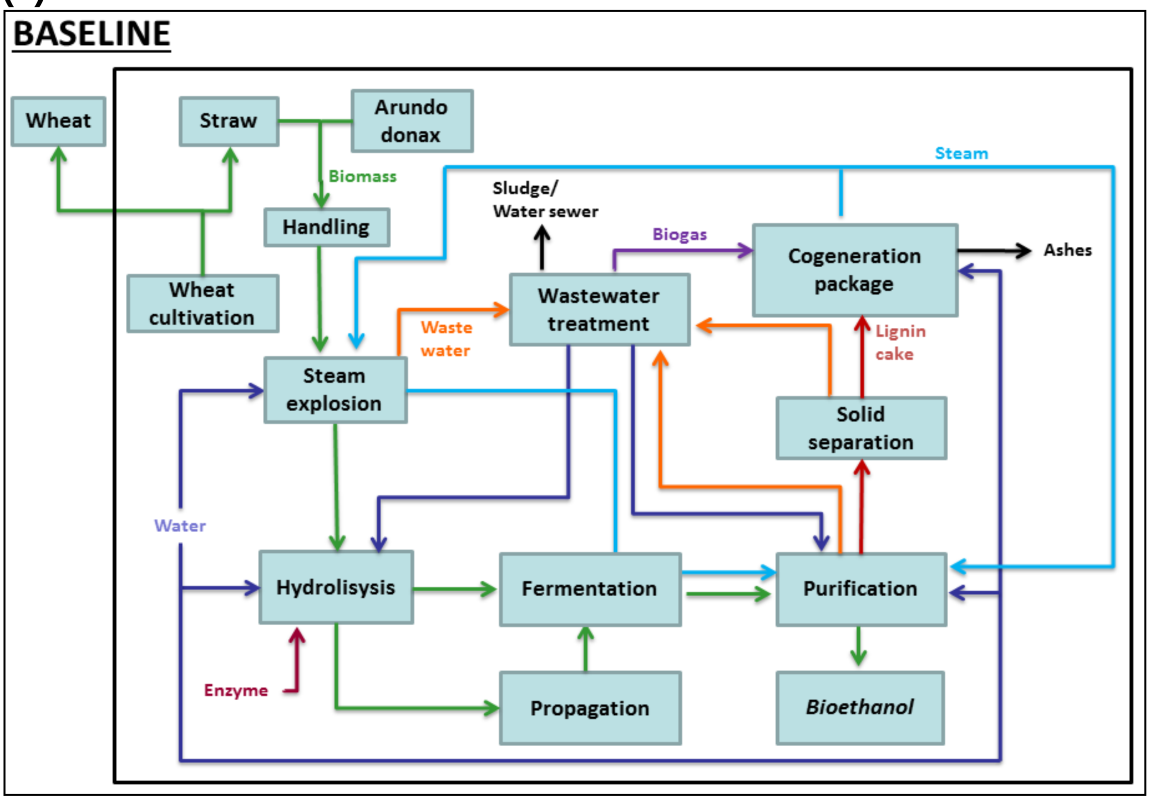
Life Cycle Inventories of the Production Processes

The inventories (LCI) are built with both primary data (*i.e.* directly collected at manufacturers) as well as secondary data, such as literature and ecoinvent libraries v. 2.2 (Frischknecht *et al*. 2007). The LCI data includes energy and water consumption, biomass cultivation, chemicals, air and water emissions, disposal, and wastewater treatments.

Bio-ethanol

The bio-ethanol plant is outlined in Fig. 1a. Figure 1b illustrates the same system where a partial lignin removal is taking place.

(a)



(b)

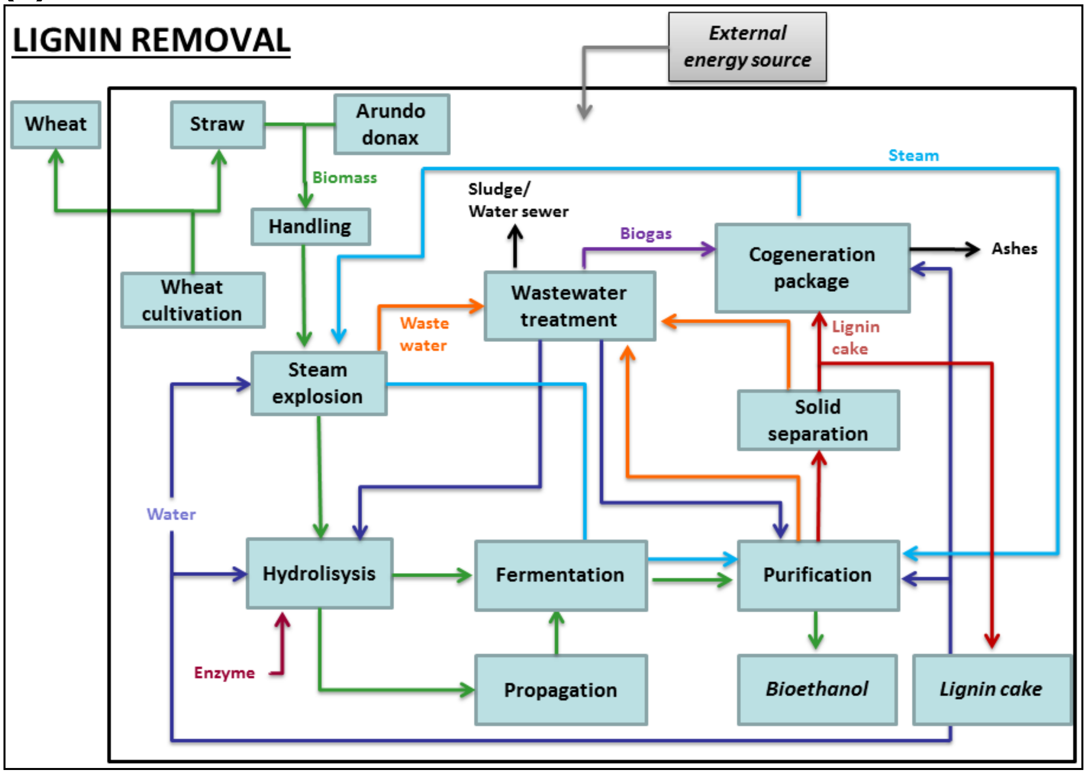


Fig. 1. System boundaries in bio-ethanol production. (a) Baseline scenario, (b) partial lignin removal scenario

Bio-ethanol production in this study is modelled according to an average plant located in Europe, using simultaneous saccharification and fermentation (SSF) technology. Bio-ethanol derives 50% from crop residues (wheat straw) and 50% from a perennial crop (*Arundo donax*). Further details about the production process are reported in the supplementary material (See Appendix).

To build the inventory, the ecoinvent (Frischknecht *et al.* 2007) process "ethanol, 95% in H_2O, from corn, at distillery" has been modified according to the study performed by De Bari *et al.* (2008) to model a second-generation production process, starting from 50% agricultural residues (wheat straw) and 50% perennial energy corps (*Arundo donax*).

The wheat straw dataset belongs to the Agrifootprint database (Durlinger *et al.* 2014) and derives from a multi-output process that describes the average yearly production of wheat grain and straw on a hectare of agricultural soil. Mass allocation based on dry matter content is adopted. Because no data about *Arundo donax* was available, *Miscanthus rhizome* was used as proxy for *Arundo donax* seeds, as they are both perennial energy crops and require similar raw materials and energy input (Fazio and Monti 2011; Salanti *et al.* 2012). The inventory for *Arundo donax* cultivation is built according to Monti *et al.* (2009) and is reported in Table 2. The functional unit of the process is 1 ha of cultivation and allows evaluating the perennial crop end use.

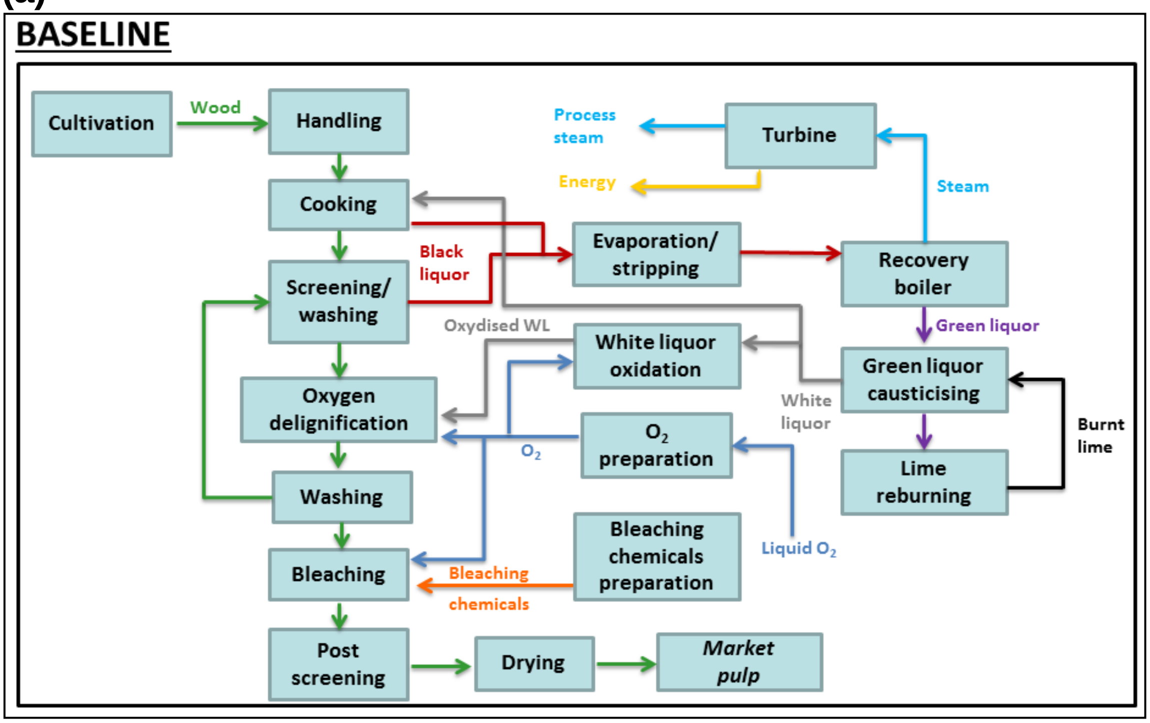
Table 2. LCI for Giant Reed (*Arundo donax*) Cultivation

Input	Unit	Amount	Source
Miscanthus rhizome, for planting	P	10000	Monti *et al*. (2009)
Tillage, ploughing	Ha	1	
Tillage, harrowing, by rotary harrow	Ha	1	
Phosphate fertilizer, as P_2O_5	kg	250	
Diesel	kg	107.1	
Ammonium nitrate, as N	kg	80	
Chopping, maize	Ha	1	
Water for irrigation	kg	30000	

Ecoinvent process data for *Miscanthus* considers the possible benefits derived from using it for phytoremediation, to adsorb heavy metals emissions to soil and water (*e.g.* copper and zinc) derived from the agricultural phase (Nemecek and Schnetzer 2011). Because it was not possible to verify whether the same can be assumed also for *Arundo donax* cultivation, emissions of copper, chromium, zinc, and nickel to soil were set to zero, and no avoided impact was inventoried. No additional drying process was included.

In the baseline bio-ethanol process, the lignin cake underwent combustion and supplied 10 kWh electricity to the system. According to expert judgment, the maximum amount of lignin-cake that can be removed without seriously affecting the system is 40%. This quantity corresponds to 4 kWh of electricity that need to be substituted by grid electricity, cogeneration, or natural gas in the alternative scenarios analysed.

(a)



(b)

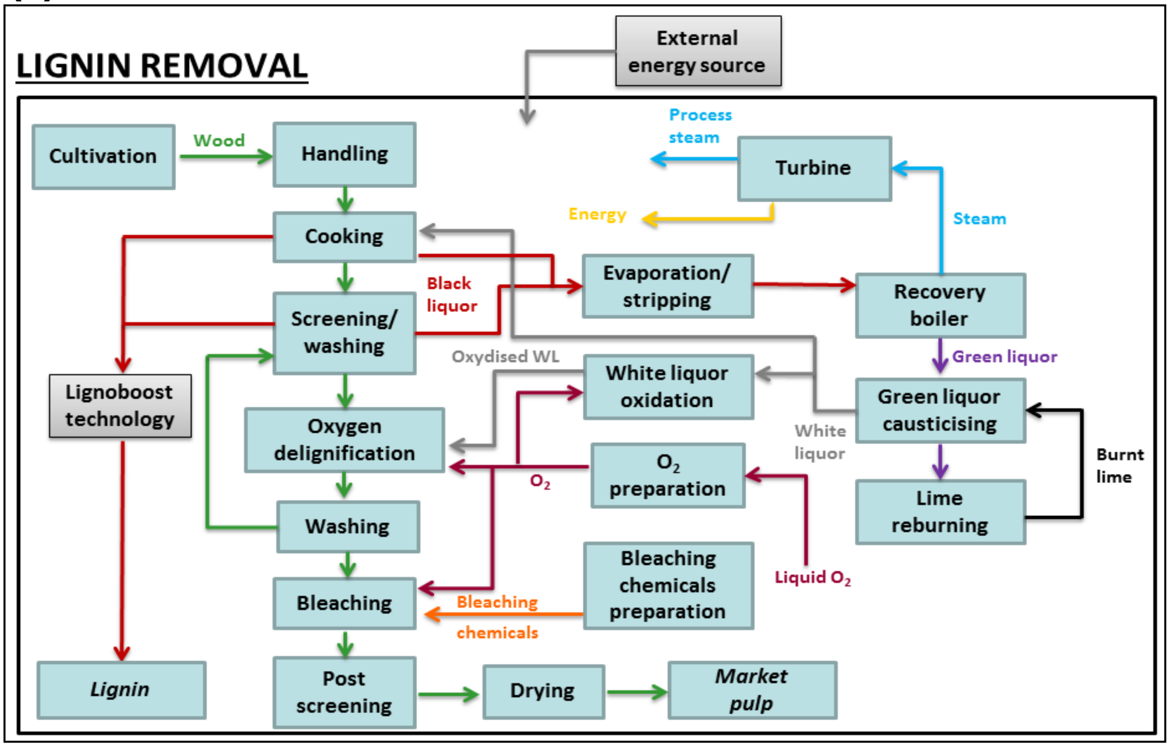


Fig. 2. System boundaries in softwood and hardwood pulp production (modified from: Suhr *et al.* 2015). (a) Baseline scenario, (b) partial lignin removal scenario

Pulp (SW and HW)

The pulp plant outline is shown in Fig. 2a. Figure 2b illustrates the same system in a situation of partial lignin removal.

For the softwood pulp production system (details in the supplementary material), the ecoinvent process "sulphite pulp, bleached, at plant" had been modified according to data provided by the one of the biggest pulp and paper companies in Europe, to better represent the situation. For this reason, water and limestone inputs and particulate emissions were changed, and an additional step of lignin extraction (Hannus *et al.* 2012) was modelled only in the alternative scenario.

LignoBoost technology was adopted only in softwood pulp mills to extract the wood component lignin from the black liquor. The process description is reported in the supplementary material, whereas in Table 3 the chemical inputs are reported, as calculated according to Hannus *et al.* (2012). Considering that 1 t of black liquor 30% DS (dry solids) contains 0.07 t of lignin 70% DS, a plant producing 4790 t/day of black liquor was taken as reference for calculations, and the final process has been modelled as reported in Table 3. Because of the lack of specific data about energy and water consumption, only chemical inputs are included in the inventory.

Table 3. LCI for 1 kg of Lignin Precipitated with LignoBoost Technology

1 kg of precipitated lignin	CO_2	0.34	kg
	H_2SO_4	0.062	kg

All data regarding pulp production from hardwood came entirely from a Brazilian company producing pulp and paper from eucalyptus fibers: their inputs were used to modify the ecoinvent dataset "sulphite pulp, bleached, at plant" (as shown in the supplementary material, Table S1) to better model the production process. Instead, for the softwood process the inventory stuck to the dataset retrieved in ecoinvent.

In both pulp production processes, the black liquor undergoes combustion to generate electricity and heat.

In hardwood pulp production systems, black liquor combustion supplies the entire energy requirement; in this case, 0.315 MJ of heat, *i.e.* 50% of black liquor, was substituted. Alternative energy sources analyzed were heavy fuel oil, cogeneration technology, and natural gas. Because of the lack of detailed information and the similarity of production technologies, the authors chose to model the black liquor removal by applying the same maximum fraction as in a softwood pulp mill (50%, see following paragraph).

For a softwood pulp mill, the authors supposed to remove 50% of the black liquor (maximum removable amount, information from well-acquired experience in a pulp and paper company), *i.e.* 5.4 MJ of heat. This amount can be alternatively supplied by heavy fuel oil, natural gas, or cogeneration technology. Only in the latter case, also 100% of electricity, *i.e.* 0.14 kWh, was replaced. The authors tested the effects of all these substitution options to identify the most environmentally friendly one.

A sensitivity analysis was performed to evaluate the influence of the substitution ratio on the results, evaluating a 30% hypothetical substitution rate.

RESULTS AND DISCUSSION

The life cycle inventory analysis (LCIA) was run by means of Simapro 8.0.3 software, using the ILCD impact assessment method v. 1.03 (Institute for Environment and Sustainability 2012).

Results are presented as single score calculations carried out with ILCD method, by applying ILCD normalization factors (Benini *et al*. 2014) and equal weighting among impact categories, to allow for an easier comparison among the scenarios.

Influence of Lignin Removal

In this section, a comparison between the baseline scenario and the alternative scenario where lignin was removed and replaced is presented for all production systems (bio-ethanol, SW pulp, and HW pulp). In the alternative scenarios, impacts were allocated to both the main product (bio-ethanol and pulp) and to the co-product (lignin). Results were presented for scenarios where the cogeneration technology was selected as the alternative energy source because this was the most probable option according to companies who operate in the two sectors involved.

In Figs. 3, 4, and 5 the baseline scenario for each supply chain was compared to the new one in which lignin was considered as a co-product and impacts were allocated according to the considered criteria, *i.e.* mass or energy content for bio-ethanol and mass or economic for pulp. What really changes throughout the two supply chains was the amount of lignin removed. In the bio-ethanol system, the removed fraction represented the 40% of lignin cake (which corresponds to 4 kWh of electricity), and in the pulp systems, the removed fraction represented 50% of black liquor (namely, 5.4 MJ of heat for SW pulp and 0.315 MJ for HW pulp).

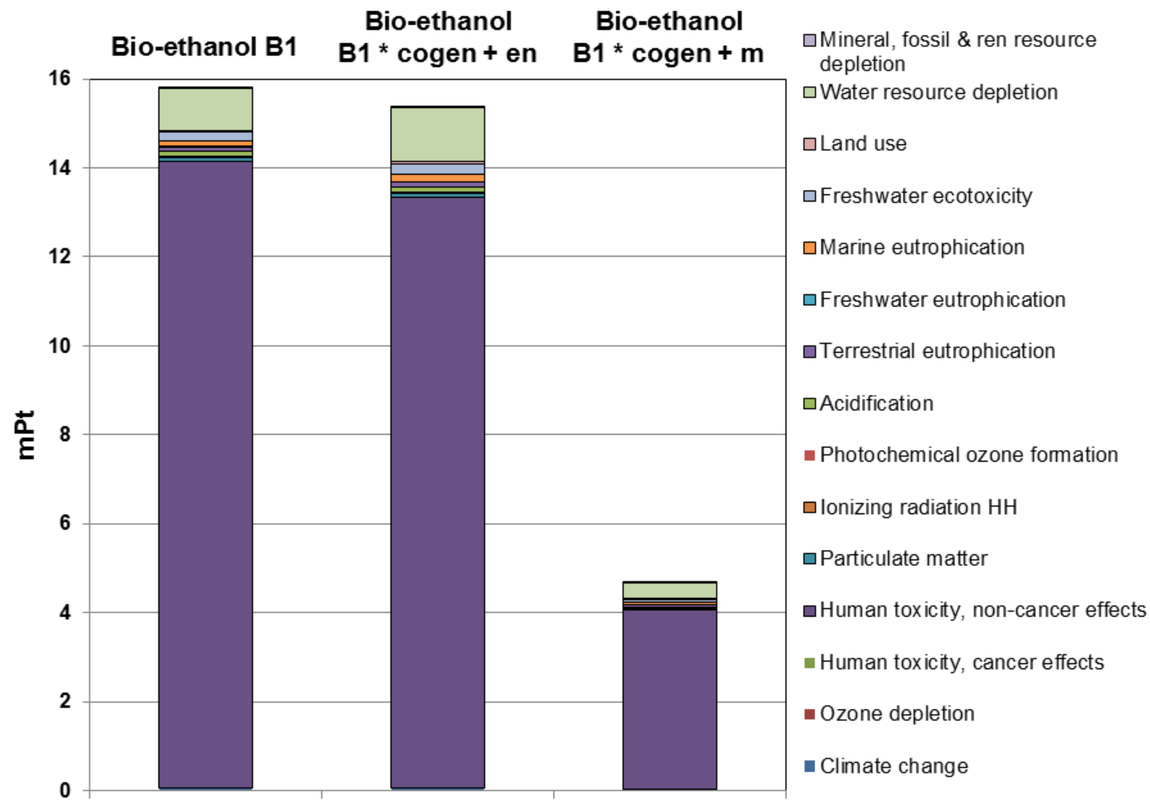


Fig. 3. Bio-ethanol system: baseline *vs.* lignin removal (energy [B1 * cogen + en] and mass [B1 * cogen + m] allocation); Lignin substitution with cogeneration, single score

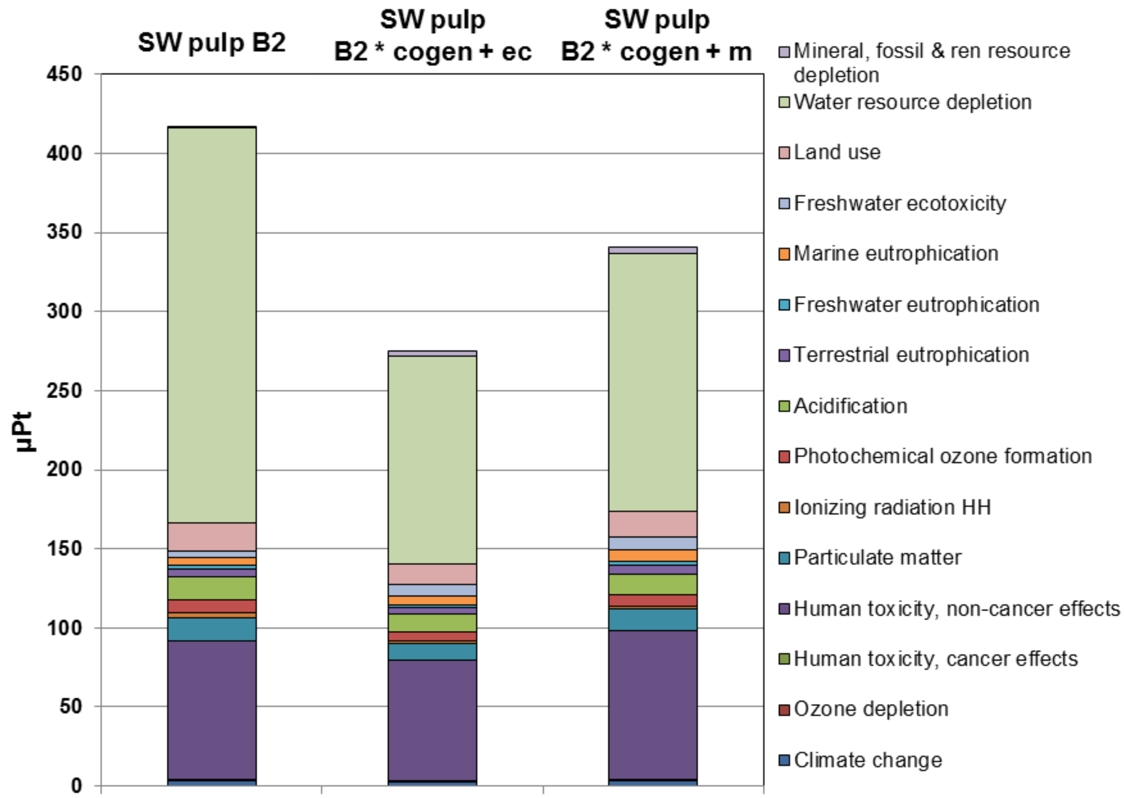


Fig. 4. SW pulp system: baseline *vs.* lignin removal (economic [B2 * cogen + ec] and mass [B2 * cogen + m] allocation); Lignin substitution with cogeneration, single score

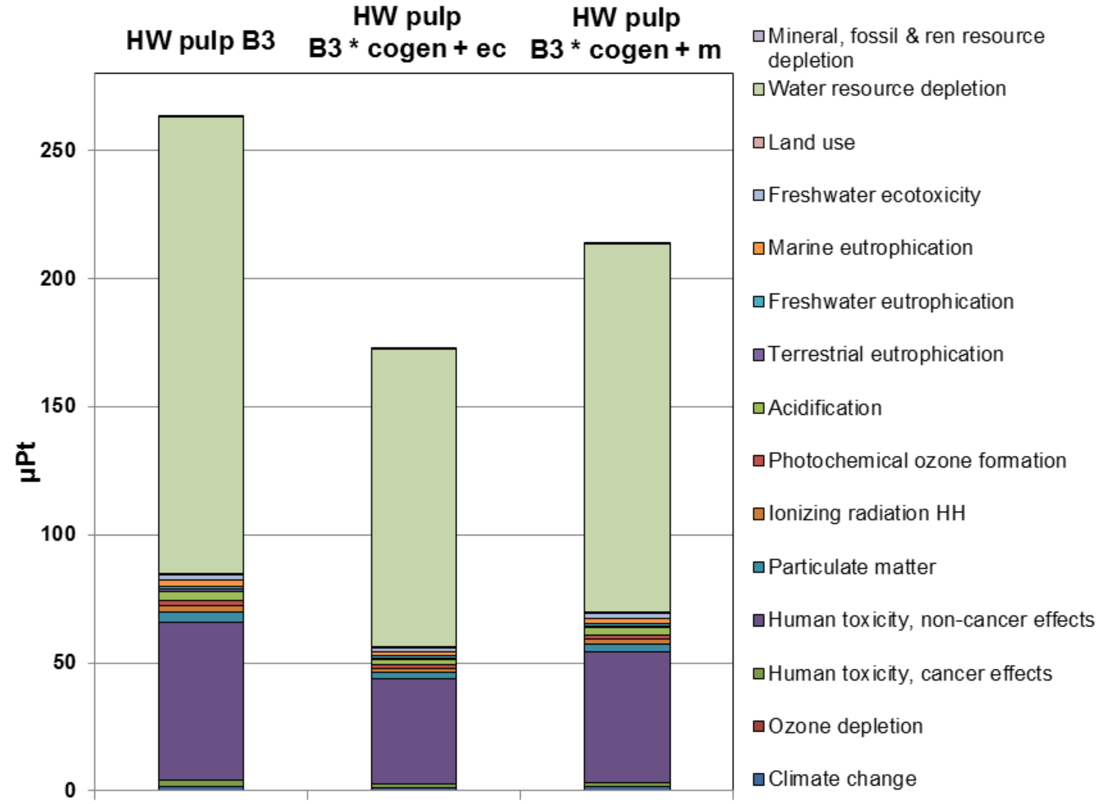


Fig. 5. HW pulp system: baseline vs. lignin removal (economic [B3 * cogen + ec] and mass [B3 * cogen + m] allocation); Lignin substitution with cogeneration, single score

A characterization analysis of all the systems is reported in the supplementary material (Fig. S1 to S6). In all evaluated systems, the incidence of allocation was evident. In the bio-ethanol scenario, by allocating impacts according to the energy content, the related contributions increased considerably because the fraction of the impact that attributed to the main product (bio-ethanol) changed from 28% to 91.9%. This means that the removal of lignin from the bio-ethanol production process led to a decrease of the impacts related to the bio-ethanol, even if other energy sources were introduced. The adoption of a mass allocation of impacts emphasized this decrease: the contribution of bio-ethanol production was 65% lower to the baseline, despite the added impact due to the introduction of the new energy source.

Concerning SW pulp, when allocating impacts according to the mass or to the market value, the major contribution is generally assigned to the main product (pulp), with the exception of eutrophication-related categories and resource depletion impact categories, where the choice of an economic allocation returns a less sustainable result related to the lignin removal. Focusing on mass allocation, the main difference to the market value criterion consists in a general impact increase, except for the human toxicity non-cancer effect, where the economically allocated contribution of pulp was higher. It is important to highlight that the allocation systems include two more elements with regard to the baseline: (i) cogeneration energy, which supplies 100% of grid electricity (namely, 0.14 kWh), and (ii) an extra step for the treatment of removed lignin (Lignoboost technology). Even if the Lignoboost step implies additional environmental burdens, the economic allocation allows for an average 20% pulp impact decrease. The only exception is the impact category mineral, fossil, and renewable resource depletion: for this indicator the production step of sulfuric acid, used in the Lignoboost treatment, contributes to 50% of the impact (see Fig. S4). The eutrophication categories presented an impact increase as well; this is due to the pesticides for biomass cultivation step in co-generation technology.

In the HW pulp baseline, results of allocation are similar to the softwood pulp outcome, namely a general decrease of the impact due to pulp production, compared to the baseline scenario. By allocating according to the market value, the impact of pulp decreased to a limited extent by 34%, whereas following the mass criterion, the pulp contribution decreased by 20%. Black liquor combustion showed a moderate impact (Fig. S5), and the introduction of the new energy source did not generate remarkable changes in contribution results, except for the land use category where the cogeneration contribution was influenced by the biomass agricultural stage (land transformation to arable) and plant installation (land occupation and transformation).

Influence of Energy Source

In the following step of the analysis, the effects of the lignin replacement by three different energy sources are compared (Fig. 6, 7, and 8). In the bio-ethanol scenarios, the evaluated energy options to substitute the fraction of electricity originally generated by lignin combustion (*i.e.* 4 kWh) were natural gas, cogeneration technology, or grid electricity. In the pulp scenarios, the options for substituting the fraction of heat originally produced by black liquor combustion (*i.e.* 5.4 MJ for SW pulp and 0.315 MJ for HW pulp) were cogeneration technology, fossil fuels (heavy fuel oil), and natural gas. To stress the differences among the energy sources in terms of impacts, results report one allocation criterion: mass for bio-ethanol and market value for pulp.

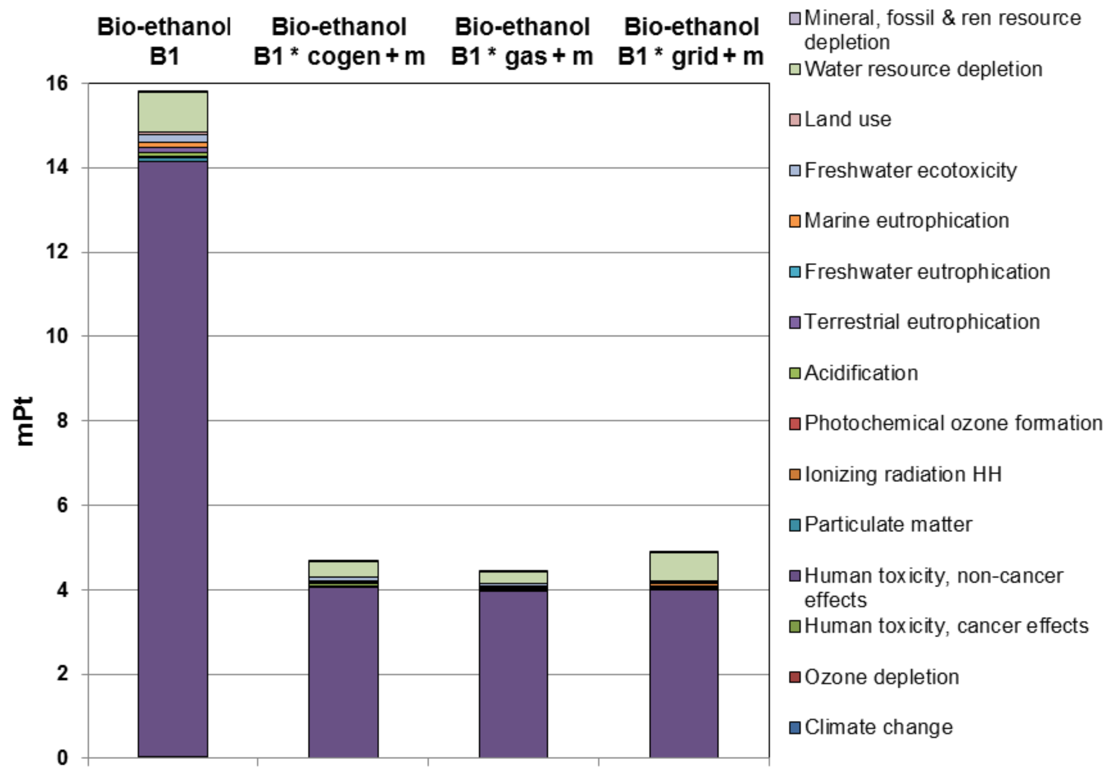


Fig. 6. Bio-ethanol: comparison of different energy sources (cogeneration = B1 * cogen + m; natural gas = B1 * gas + m; grid electricity = B1 * grid + m) (mass allocation, single score)

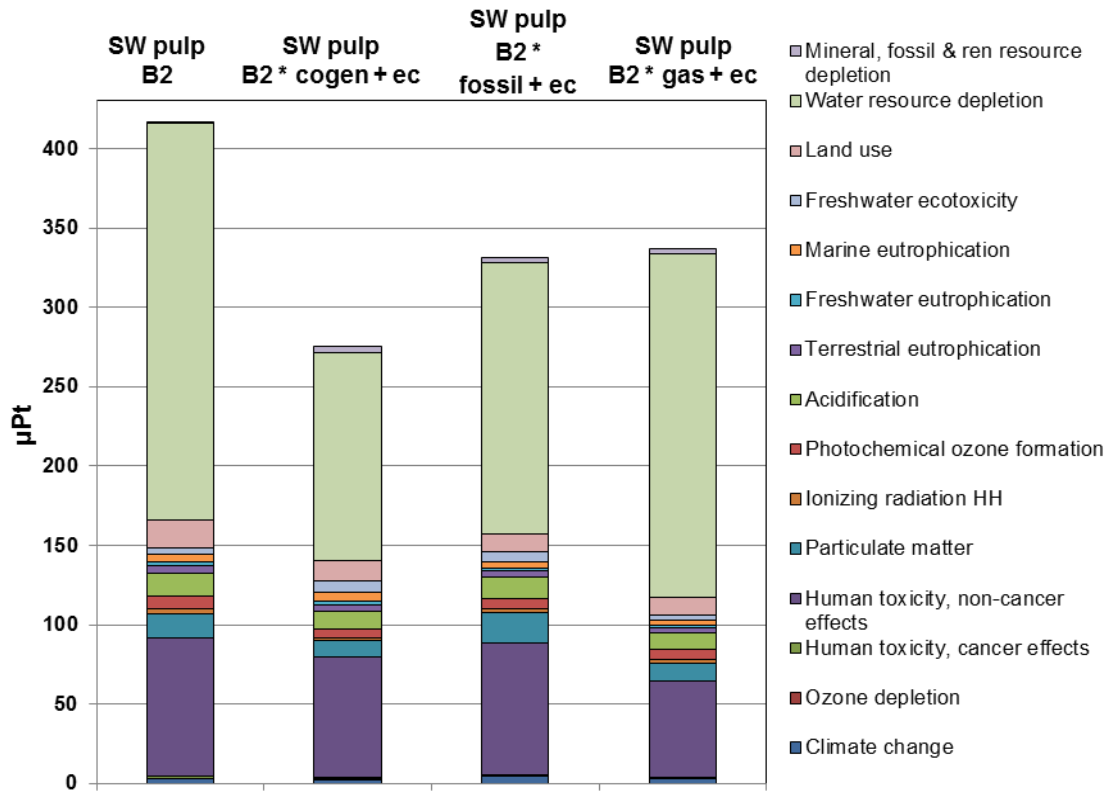


Fig. 7. SW pulp: comparison of different energy sources (cogeneration = B2 * cogen + ec; heavy fuel oil = B2 * fossil + ec; natural gas = B2 * gas + ec) (economic allocation, single score)

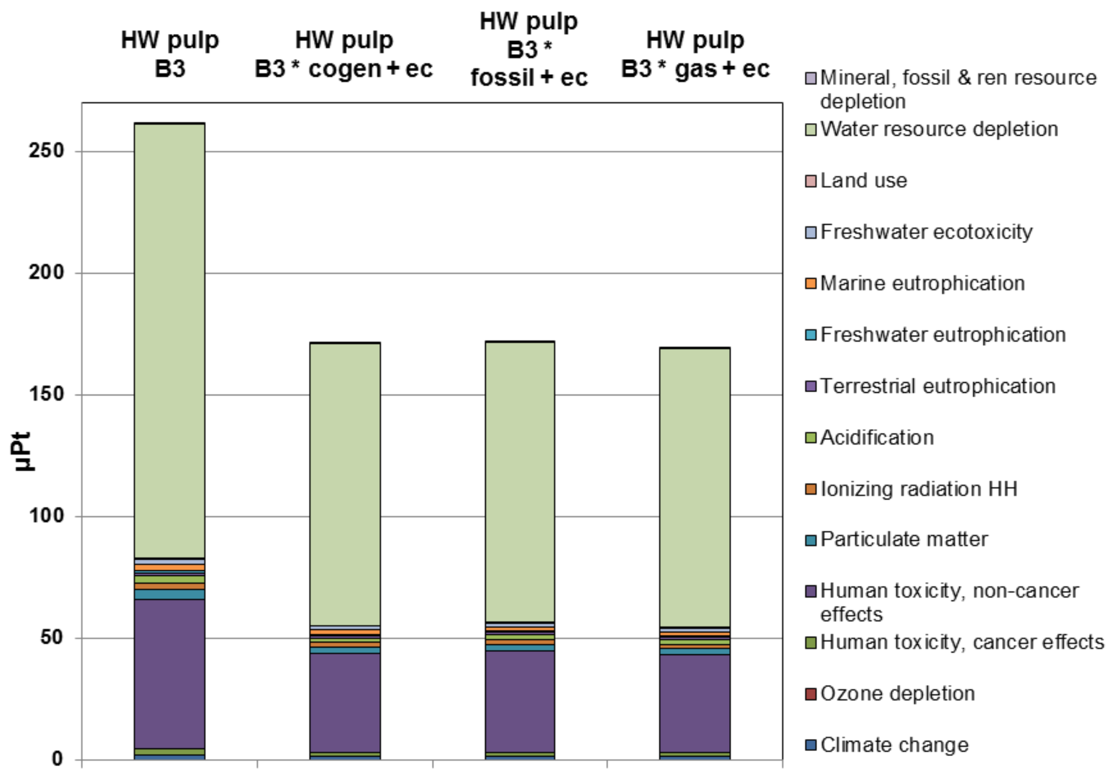


Fig. 8. HW pulp: comparison of different energy sources (cogeneration = B3 * cogen + ec; heavy fuel oil = B3 * fossil + ec; natural gas = B3 * gas + ec) (economic allocation, single score)

Starting from the bio-ethanol system, it is possible to notice that the removal and substitution of lignin as an energy source does not imply additional environmental burden compared to the baseline situation, independently from the energy source chosen for substitution. Human toxicity non-cancer and water depletion continue to be the indicators contributing the most to the overall impact. This could be due to the allocation. Replacing the lignin cake with natural gas leads to the most relevant impact decreased (about 70%), showing a negative influence in ozone depletion. On the other hand, cogeneration and grid electricity options show a 65% impact decrease, although the latter returns a more remarkable contribution in water resource depletion, caused by the large fraction of hydropower in the energy country mix.

Concerning the softwood system, in most of the categories, the baseline scenario presented the greatest impact, but in the case of lignin substitution with fossil fuel, the contribution to the overall impact of climate change, particulate matter, terrestrial, marine eutrophication, and mineral, fossil, and renewable resource depletion increased. The benefit coming from this option was low, showing its maximum in ionizing radiation and water resource depletion. On the other hand, when natural gas was introduced to replace 50% of heat from black liquor combustion, a moderate reduction of the overall impact occurred (-15%). According to this choice, the contribution of water depletion remained considerably high, similarly to the baseline situation. The cogeneration technology option showed the best performance, leading to the most considerable total contribution decrease (-20%) when compared to the baseline. It was important to highlight that even in this case of the cogeneration substitution, 100% of electricity, *i.e.* 0.14 kWh, was replaced.

The hardwood pulp system presented slightly different results when compared to the softwood pulp scenario. Benefits coming from the three possible substitutions are quite comparable. Every option leads to a 32% to 35% impact decrease. Cogeneration contribution was higher in land use, while the heavy fuel oil option showed its greater impact in ozone depletion and particulate matter. On the other hand, when replacing 50% of black liquor with natural gas, there were no meaningful contributions, but a general 35% improvement in every impact category.

Monte Carlo analyses were run to evaluate the robustness of the results obtained. For bio-ethanol production (Fig. S7), cogeneration substitution presented the best performance in most of the investigated categories, which confirmed the previous outcome. The same result occurred also for the SW pulp scenario, where the moderately better performance of cogeneration solution when compared to the natural gas substitution was confirmed (Fig. S8). For the HW pulp system, the Monte Carlo analysis (Fig. S9) did not show relevant differences between cogeneration and natural gas solutions.

Other Scenarios

In addition to the scenarios illustrated so far, the remaining possible combinations of allocation criteria and energy substitution were assessed, with the aim of obtaining a complete and meaningful overview.

In Fig. 9, 10, and 11 the additional comparison results were reported. The models behind these results were the same used in the previous section with different allocation criteria.

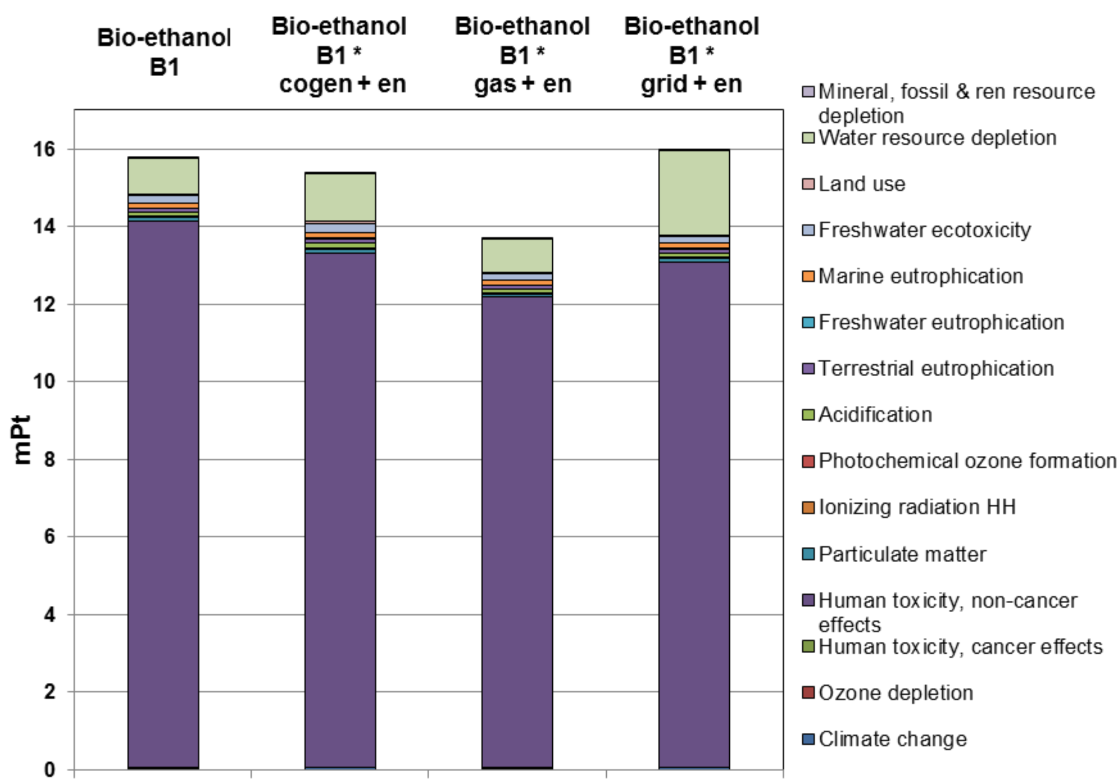


Fig. 9. Bio-ethanol: comparison of different energy sources (cogeneration = B1 * cogen + en; natural gas = B1 * gas + en; grid electricity = B1 * grid + en) (energy allocation, single score)

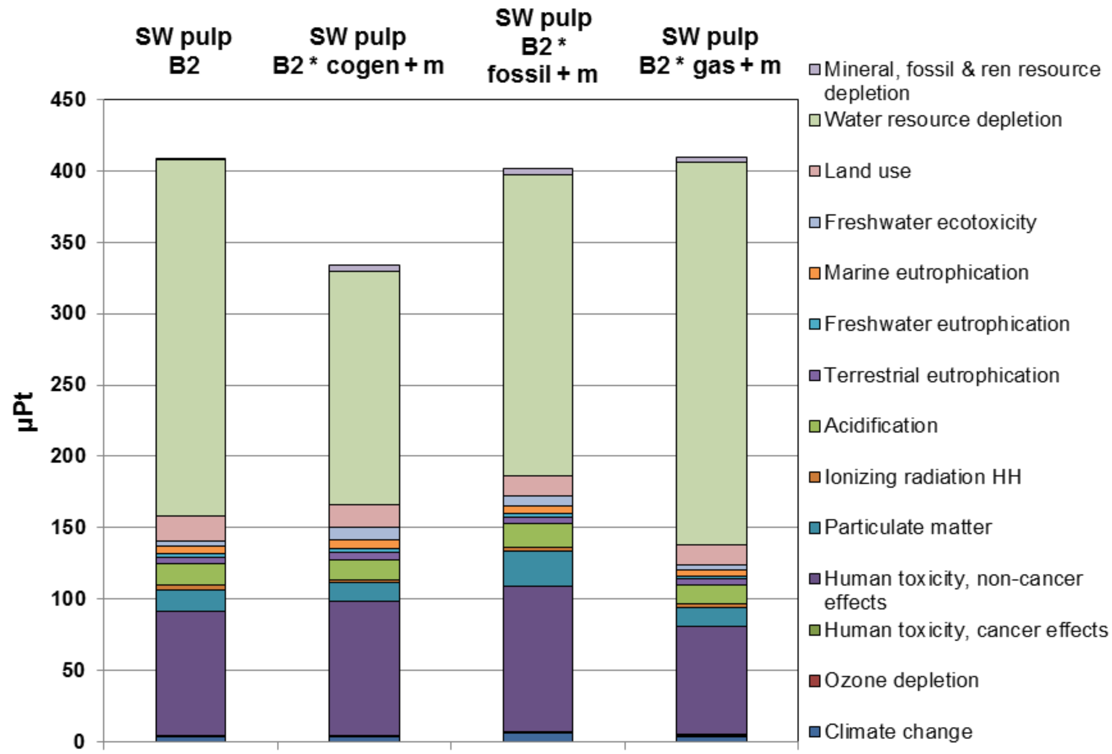


Fig. 10. SW pulp: comparison of different energy sources (cogeneration = B2 * cogen + m; heavy fuel oil = B2 * fossil + m; natural gas = B2 * gas + m) (mass allocation, single score)

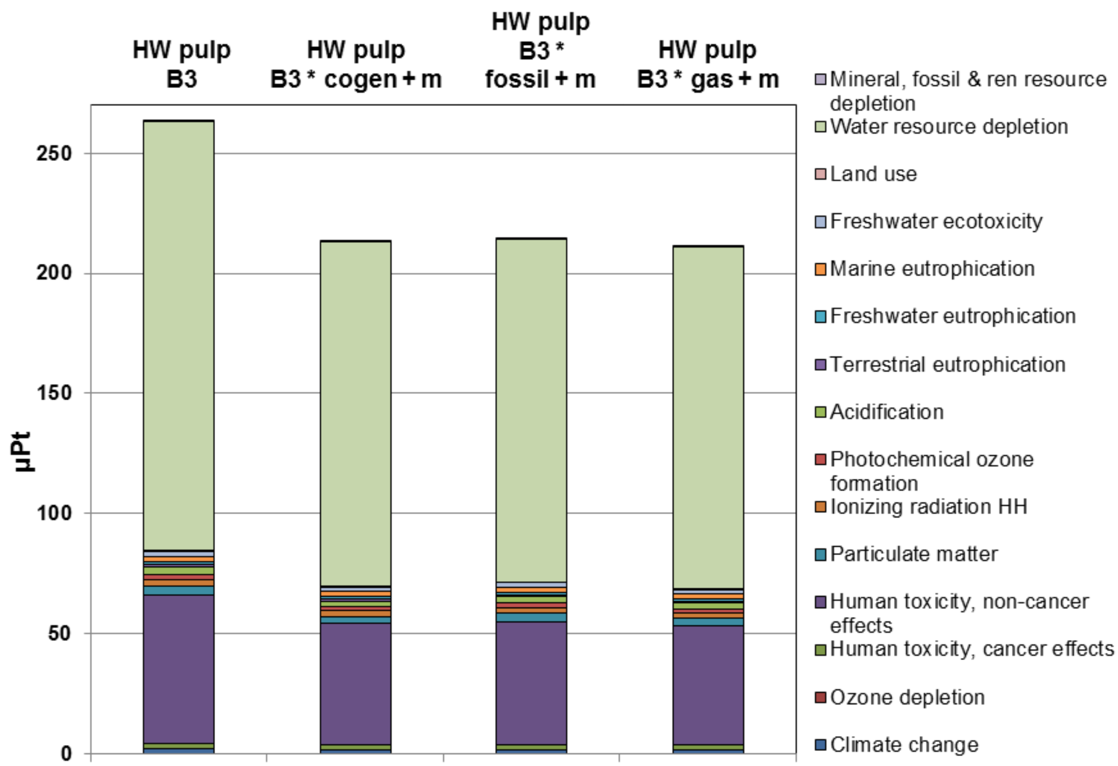


Fig. 11: HW pulp: comparison of different energy sources (cogeneration = B3 * cogen + m; heavy fuel oil = B3 * fossil + m; natural gas = B3 * gas + m) (mass allocation, single score)

When using the alternative allocation criteria, results presented a few considerable differences with respect to the previous ones, especially for bio-ethanol and softwood pulp systems. The use of grid electricity combined with energy allocation modified the environmental profile of the bio-ethanol scenario, which slightly increased the overall impact of bio-ethanol production. In fact, the possible benefits derived from the allocation (see Fig. 3a) were canceled by the additional electricity external source and strongly influenced by the hydropower in the grid mix.

Softwood pulp showed a similar outcome. The combination of mass allocation and energy substitution emphasized the differences between the energy options. For example, natural gas slightly increased the overall impact of pulp production compared to the baseline, where cogeneration was coupled with the contribution of lignin as an energy source. On the other hand, the impact decrease due to the cogeneration adoption was still evident.

Sensitivity Analyses

There are uncertainties in hypothetical scenarios. Because of this, it was important to test the incidence of the assumptions made in the LCI phase. For this reason, two sensitivity analyses were performed on:

- Removed lignin amount
- Lignin market price

For every analysis, the most impacting option for each category was taken as a reference (*i.e.* its impact was scaled up to 100%) and the others were expressed as percentage with reference to this one.

At a laboratory scale, lignin coming from softwood black liquor appeared to be the most suitable to be re-used in other industries. Therefore, softwood pulp production with cogeneration substitution was taken as a reference system for these analyses.

Removed lignin amount

A scenario in which cogeneration technology replaced 30% of the heat derived from black liquor combustion (3.24 MJ) and 100% of grid electricity (0.14 kWh) was compared to the baseline and was the first option presented in the study (50% of black liquor removed and replaced).

Removing a different amount of lignin did not considerably affect the previous outcome (Fig. S10). Impacts related to the new option presented a 1% to 10% decrease range with regard to the previous one (the minimum value was in human toxicity-cancer effects while the maximum was marine eutrophication). In most cases, the allocated impact did not exceed the baseline one (except for eutrophication and resource depletion-related categories where pesticides in co-generation and sulfuric acid influences were still evident). This means that lignin removal in softwood pulp production lead to a possible improvement, regardless of the amount subtracted.

Lignin market price

Because there is no defined price list for lignin and the price is very much dependent on source and quality of lignin as well as the final product, it was not easy to select a proper price. Therefore, for the analysis the authors chose to operate with an average value (1500 €/t) based on a price range for lignin, used to model the best and worst scenarios. The authors ran a sensitivity analysis based on the maximum (2000 €/t) and the minimum (1000 €/t) market prices (Fig. S11). The prices refer to high quality kraft lignin from softwood.

Results vary according to the lignin price selected. By choosing the maximum price, for example, the 58% of contribution was allocated to the pulp production, therefore a general impact decrease can be observed. If the economic allocation was based on the lignin minimum price, pulp production contributes for 74% and an overall increase of impact was shown in this case. The only exception was the human toxicity non-cancer effect, in which the average price allocation presented the greater impact.

CONCLUSIONS

1. From an environmental point of view, one of the possible difficulties affecting the sustainability of lignin recovery and re-use could be the modification of the current baseline production closed loop, in both pulp and bio-ethanol systems. Altering these systems could lead to a “burdens shifting” risk. The outcome of the study indicates that the risk of environmental burden shifting is rather low. In fact, results generally highlight that lignin removal from bio-ethanol and pulp systems does not remarkably affect the environmental performance of the baseline scenario in most of the cases analyzed.
2. For both systems, the choice of the allocation rule is quite critical. If part of lignin cake and black liquor is removed and replaced with another energy source, the necessary allocation distributes the contributions to the main product and co-product. This leads

to a mitigation of the possible impact increase due to (i) the introduction of the new heat or electricity supply and (ii) the residue treatment aimed to extract the lignin content from black liquor and lignin cake. For bio-ethanol production, impacts related to the co-product (lignin cake) allocated by the mass are lower with regard to the bio-ethanol. The fraction of impacts varies when the energy content is the reference: in that case, allocation assigns a greater percentage of impacts to the main product, although this increase affects the results to a limited extent. On the other hand, impacts related to pulp are higher when allocated according to the market value of co-products, while the mass criterion assigns a lower contribution. An additional sensitivity analysis confirms these results also when the maximum and minimum price of lignin-derived co-products are used for the allocation.

3. When focusing on the energy substitution, results show some differences between bio-ethanol and pulp systems. Co-generation seems to be the best choice for both the pulp systems, and natural gas appears to be the best alternative as a power source when the bio-ethanol scenario is analyzed. Co-generation presents critical impacts related to the land use that affect the improvement derived from a renewable energy source: these criticalities make this energy source comparable to the grid electricity performance. On the other hand, pulp mills show a relevant environmental benefit by adopting cogeneration technology as an alternative heat and power source. Both softwood and hardwood mills obtain a remarkable advantage from the substitution, also when the 100% of electricity supply is replaced as well (*i.e.* in softwood mill). The additional sensitivity analysis carried out on the amount of lignin removed from the systems supports this outcome: results indicate that this parameter does not seriously influence the environmental performances.

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APPENDIX

Life Cycle Inventories

Ethanol production

Ethanol production from lignocellulosic biomass comprises the following main steps: biomass cultivation (wheat and *Arundo donax*), pretreatment (steam explosion), enzymatic hydrolysis of cellulose and hemicellulose to glucose, sugar fermentation, recovery, purification of the ethanol to meet fuel specifications, and separation of the solid containing lignin residue, *i.e.*, lignin cake (Alvira *et al.* 2010). Steam explosion is a hydrothermal pretreatment in which the biomass is subjected to pressurized steam for a time ranging from seconds to several minutes. The aim of the pretreatment is to break down the lignin-carbohydrate bonds and disrupt the crystalline structure of cellulose for enhancing the enzymes accessibility to the cellulose during the hydrolysis step (Mosier *et al.* 2005).

Softwood pulp production

Kraft pulping treatment involved the heating of wood chips in an aqueous solution of sodium hydroxide and sodium sulfide from approximately 70 °C to a cooking temperature (about 170 °C), followed by a 1 h to 2 h cooking period. During this treatment, lignin was extensively degraded, and the degradation products are dissolved. Carbohydrates, in particular hemicelluloses, underwent partial degradation and dissolution. Extractives were removed (Gierer 1980). In this plant, the bleaching part of cellulosic fibers was performed by molecular oxygen, which was one of the most environmentally friendly bleaching technologies, was also included (Pavan *et al*. 2006).

LignoBoost process

LignoBoost technology was composed of the following steps: (i) lignin precipitation by acidification of the black liquor with CO_2 and dewatering; (ii) lignin suspension and pH adjustment by sulphuric acid (H_2SO_4) addition; (iii) dewatering; (iv) washing water addition; and (v) dewatering and drying of the lignin cake produced and separation of lignin from washing water.

Table S1: LCI for Hardwood Pulp and Paper Baseline

Input	**Unit**	**Amount**	**Source**
Raw materials and energy			
Water	m3	0.027	Company
Hardwood	m3	0.003	
Chlorine dioxide	kg	0.010	
Hydrogen peroxide 50% in H2O	kg	0.012	
Sulphuric acid	kg	0.030	
Sodium chlorate	kg	0.021	
Sodium hydroxide 50% in H2O	kg	0.038	
Oxygen	kg	0.020	
Energy from biomass (black liquor, bark, etc.)	MJ	0.630	
Heavy fuel oil	MJ	0.238	

Transports	km	120	
Emissions			
Nitrogen oxides	kg	0.0001	Company
Sulfur dioxide	kg	1.86E-05	
Particulates	kg	0.0001	
Adsorbable Organic Halogen	kg	4.8E-05	
Biological Oxygen Demand	kg	0.0002	
Chemical Oxygen Demand	kg	0.006	
Sulfate	kg	0.039	
Nitrogen	kg	0.0001	
Phosphorus	kg	4.20E-06	
Waste			
Landfilled (wood ash mixture, green liquor, solid waste, sludge, ash from paper production sludge)	kg	0.107	Company
To incineration (plastic, paper, textiles, wood untreated, steel)	kg	0.012	
Incineration			
Disposal, plastics	kg	0.008	Ecoinvent
Disposal, paper	kg	0.002	
Disposal, textiles	kg	0.0008	
Disposal, wood untreated	kg	0.0004	
Disposal, steel	kg	0.0008	
Landfill			
Disposal, wood ash mixture	kg	0.073	Company
Disposal, green liquor dregs	kg	0.006	
Disposal, municipal solid waste	kg	0.006	
Disposal, sludge	kg	0.017	
Disposal, ash	kg	0.005	

Bio-ethanol Production Characterization Analysis

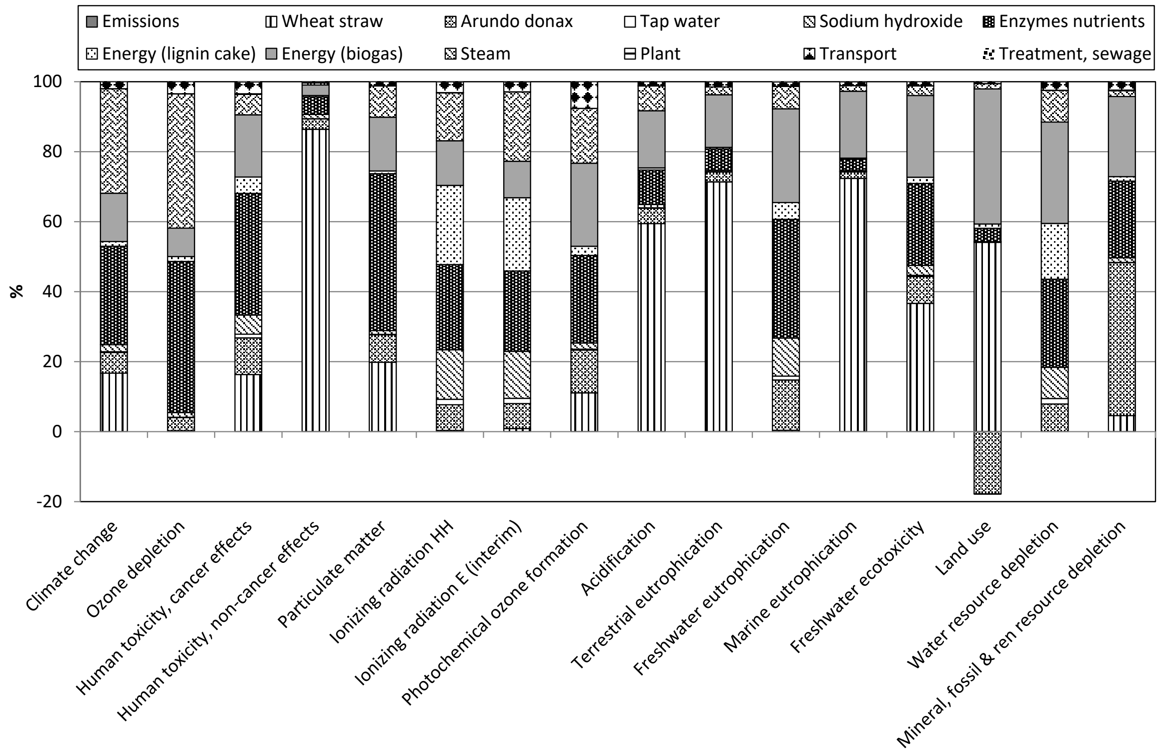

Fig. S1: Bio-ethanol production characterization, baseline

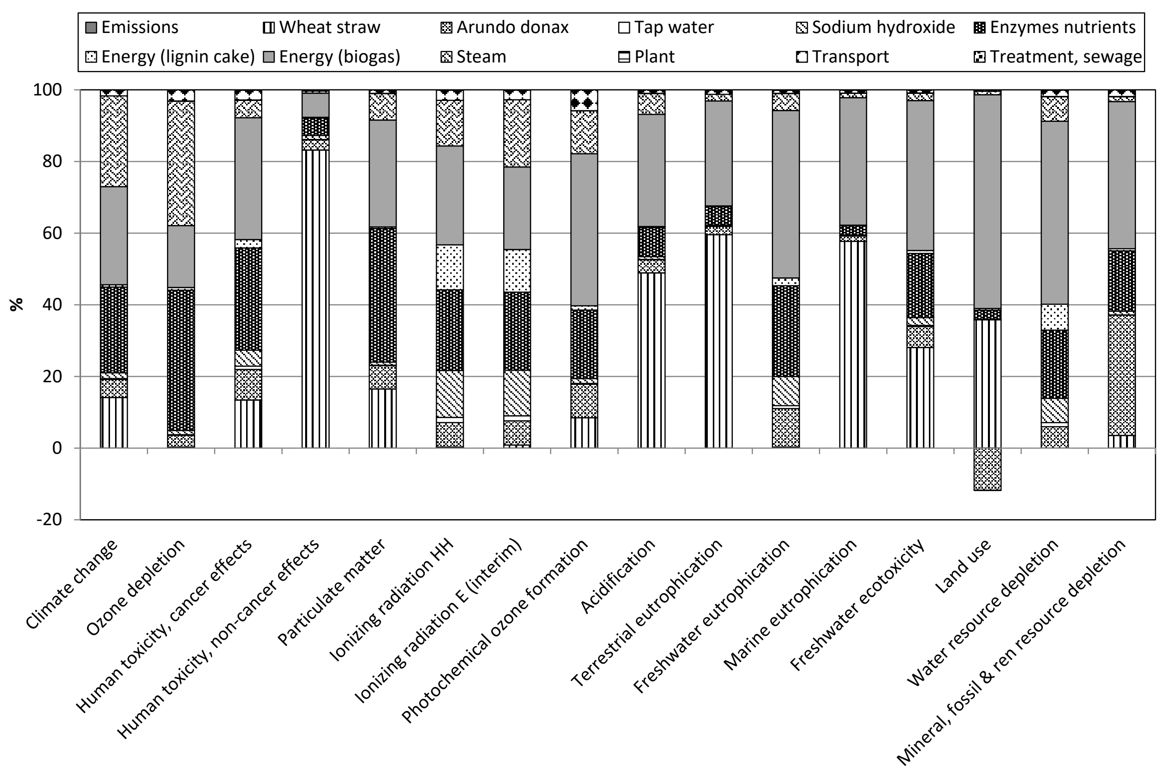

Fig. S2: Bio-ethanol production characterization, cogeneration substitution

Softwood Pulp Production Characterization Analysis

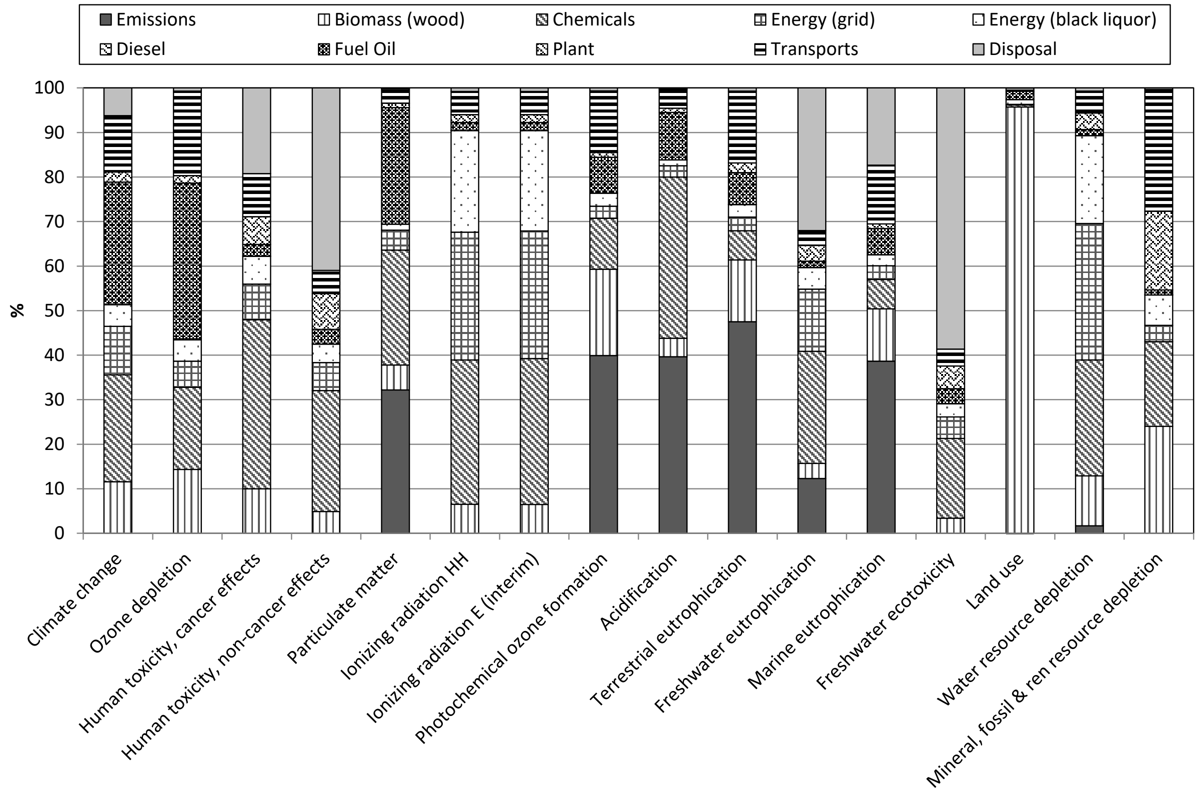

Fig. S3: Softwood pulp production characterization, baseline

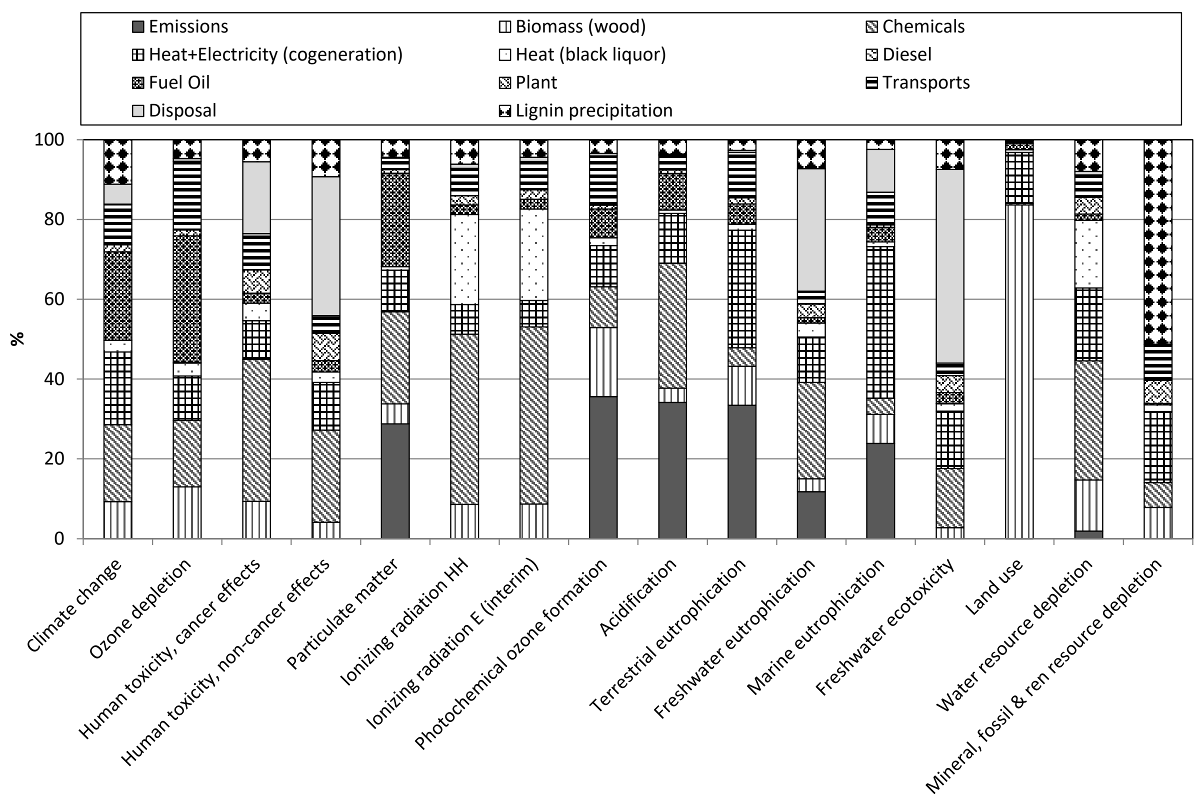

Fig. S4: Softwood pulp production characterization, cogeneration substitution

Hardwood Pulp Production Characterization Analysis

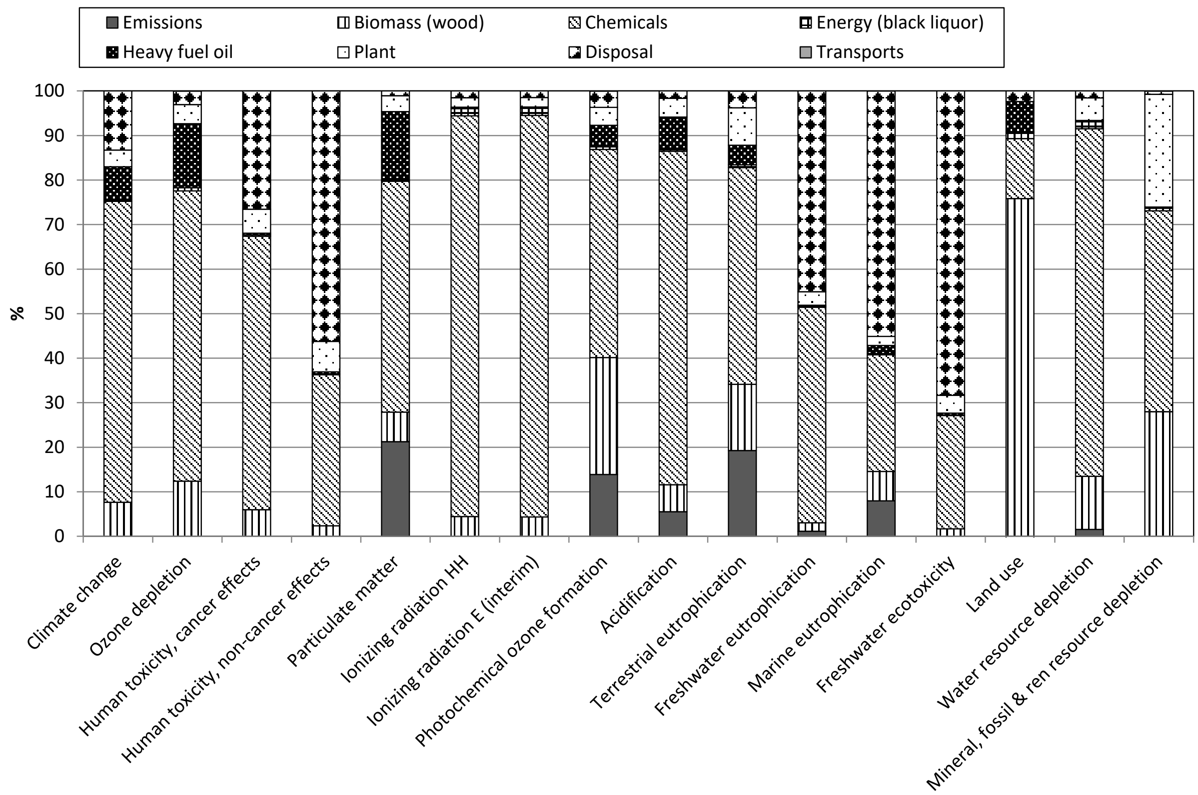

Fig. S5: Hardwood pulp production characterization, baseline

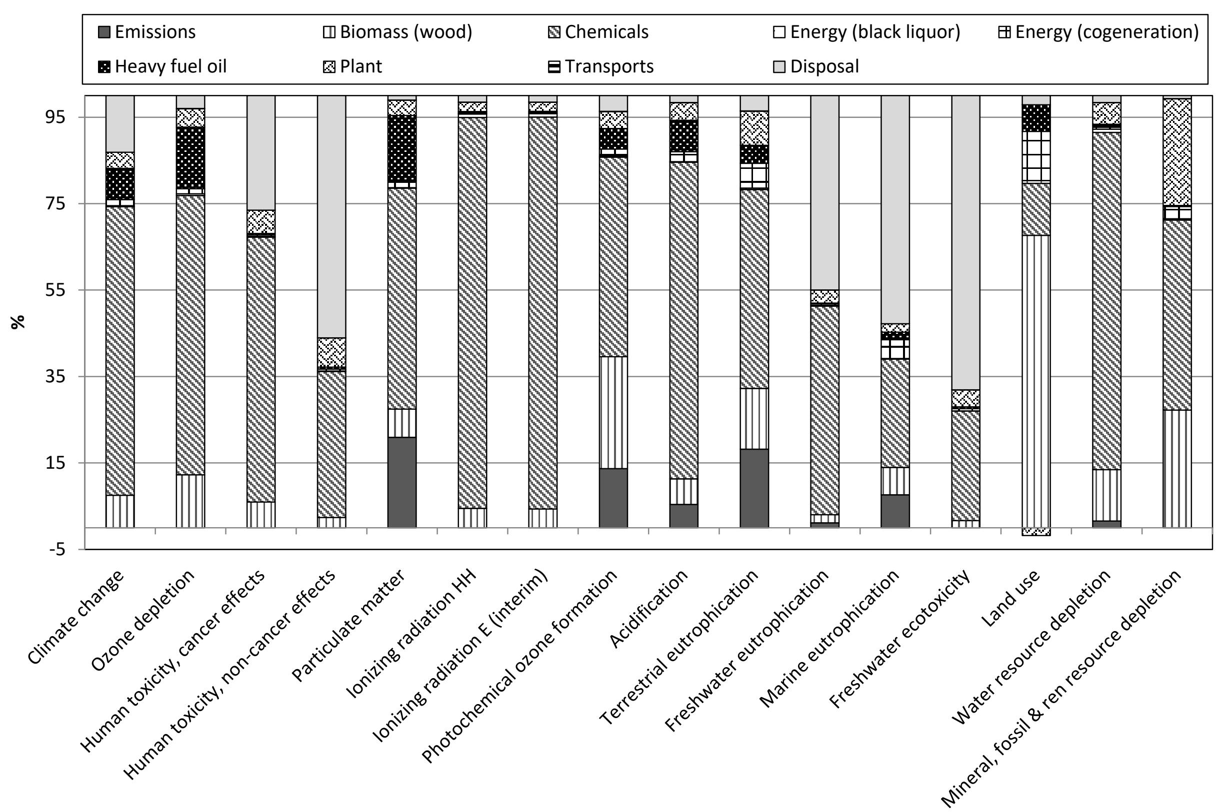

Fig. S6: Hardwood pulp production characterization, cogeneration substitution

Monte Carlo Analyses

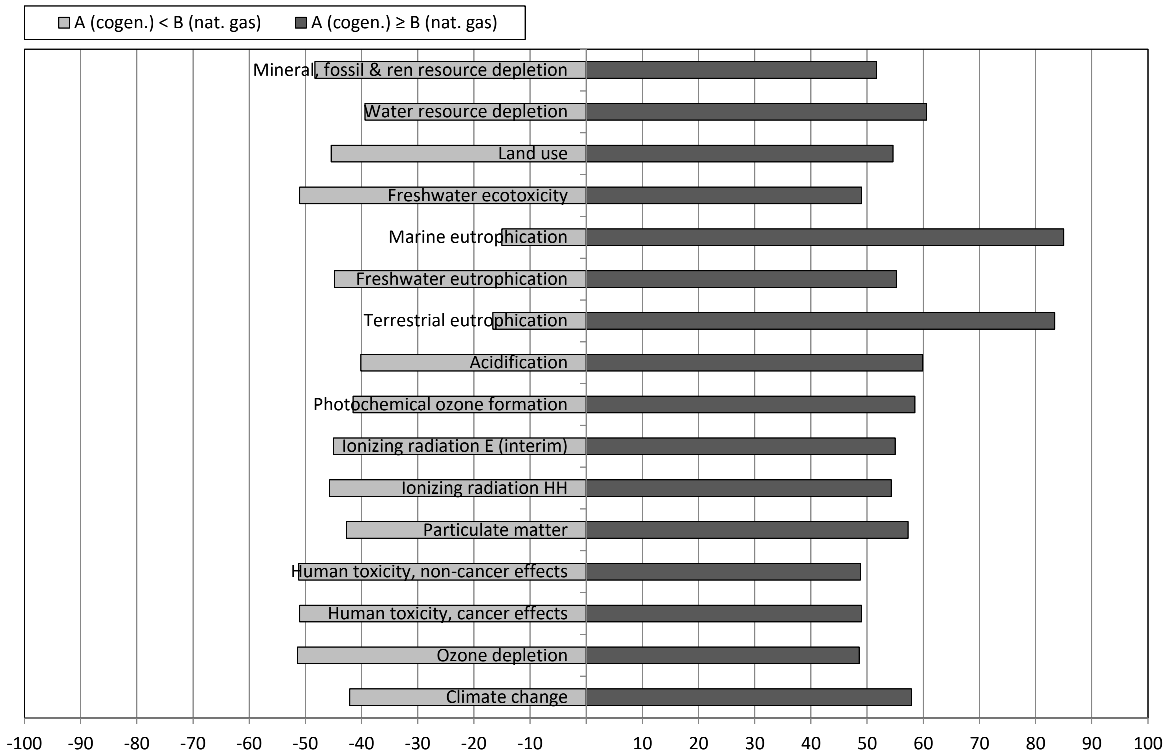

Fig. S7: Cogeneration vs natural gas substitution. Bioethanol production Monte Carlo analysis

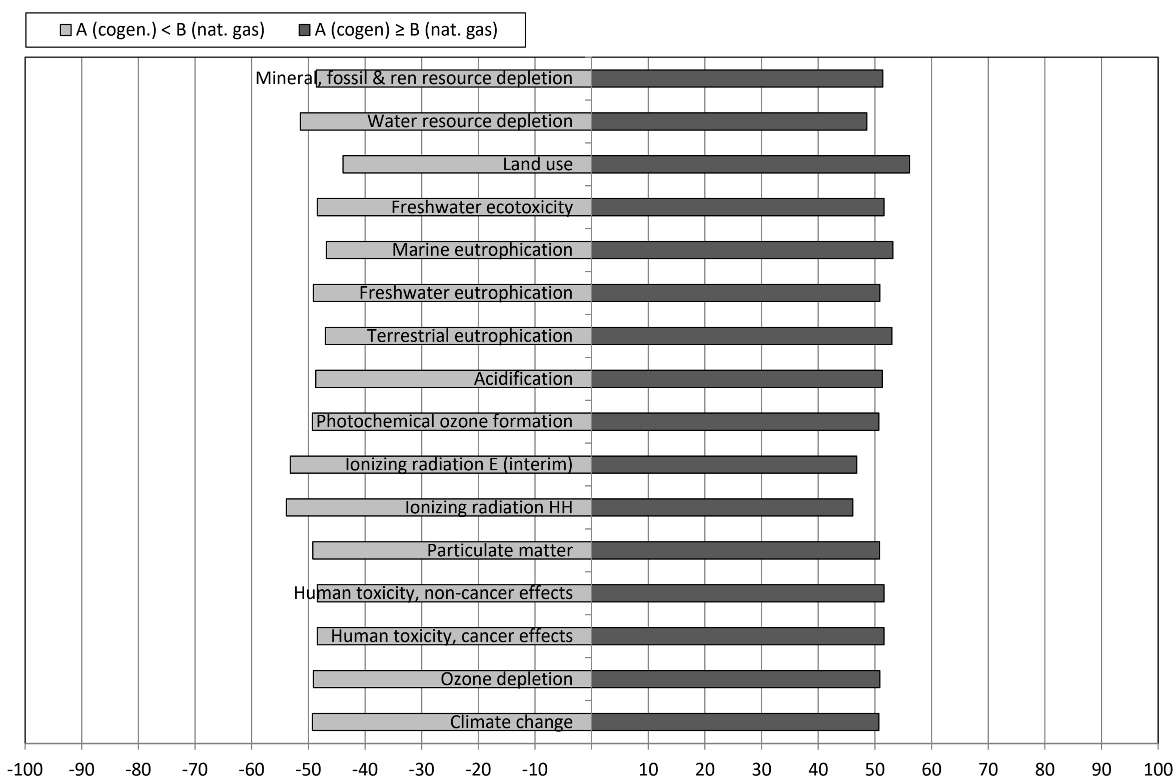

Fig. S8: Cogeneration vs natural gas substitution. SW pulp production Monte Carlo analysis

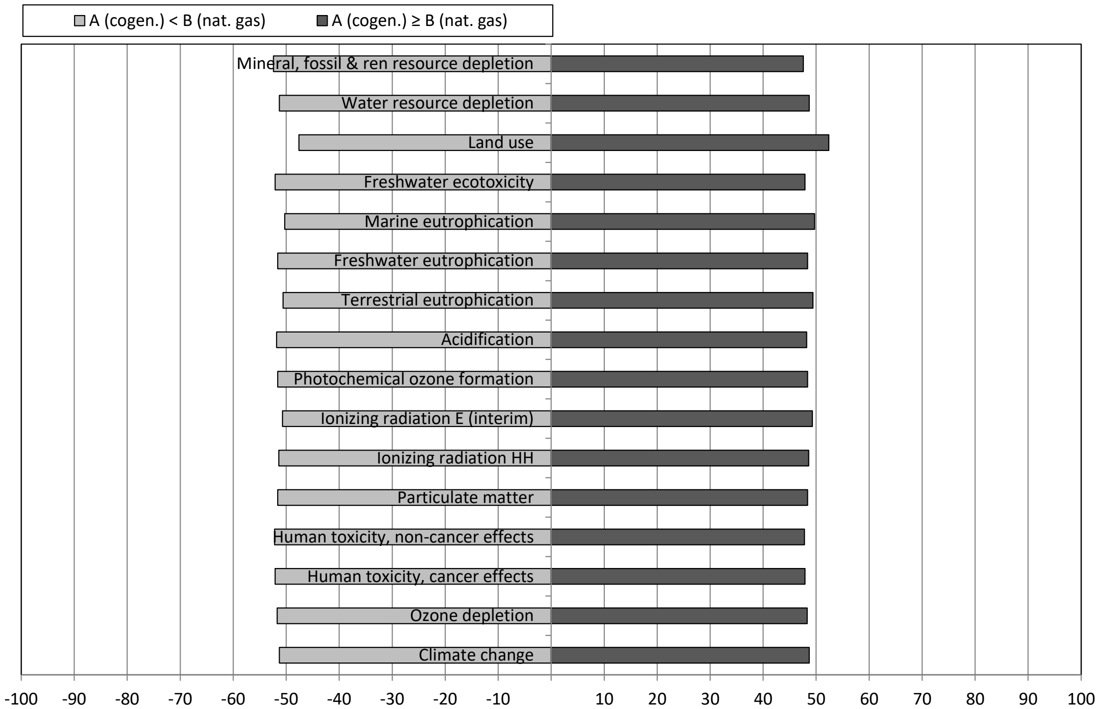

Fig. S9: Cogeneration vs natural gas substitution. HW pulp production Monte Carlo analysis

Sensitivity Analyses

Removed lignin amount

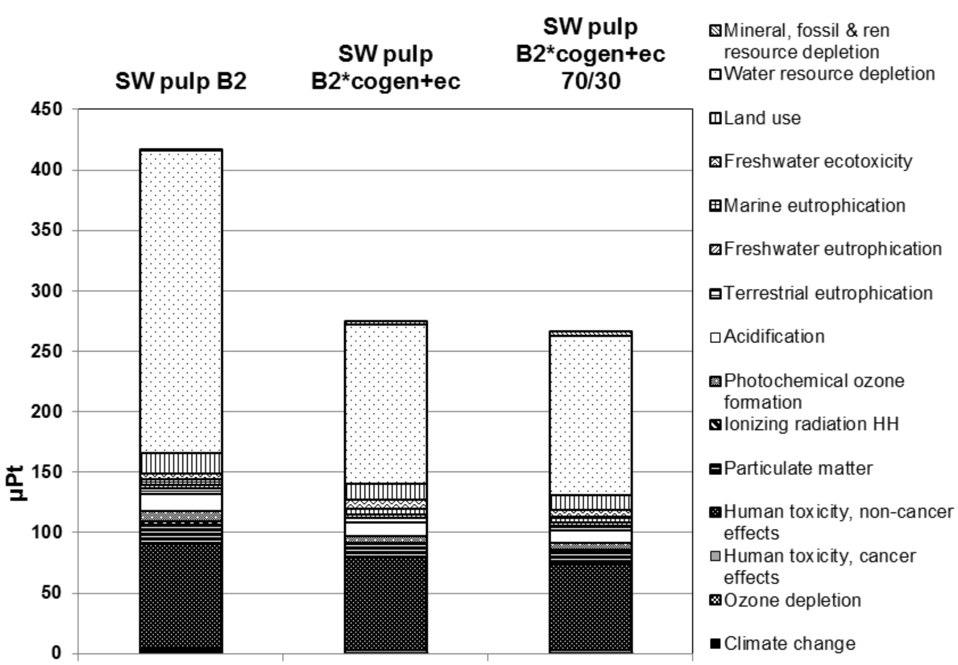

Fig. S10. Comparison of different SW pulp production scenarios: grid electricity and 100% black liquor [baseline = no removal, B2]; black liquor and cogeneration (50% of heat and 100% of electricity) [B2*cogen+ec]; black liquor and cogeneration (30% of heat and 100% of electricity) [B2*cogen+ec 70/30].

Lignin market price

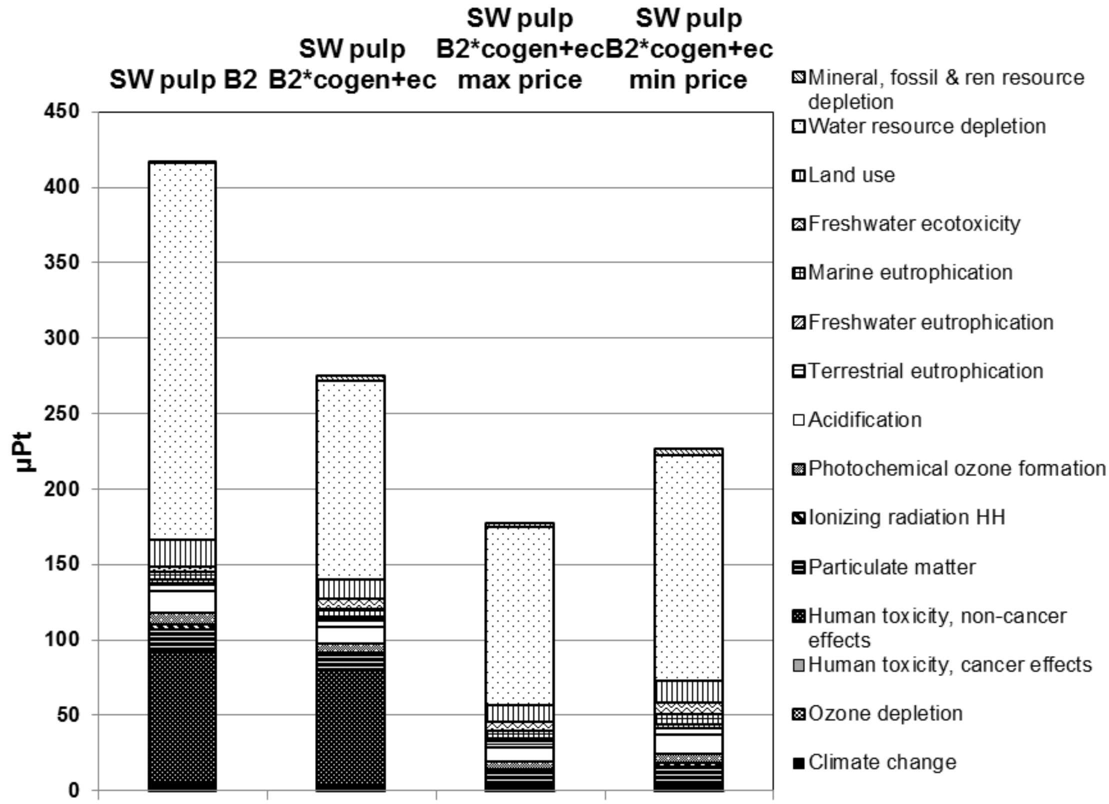

Fig. S11. SW pulp: influence of lignin market value in economic allocation tested cogeneration substitution. Baseline = no removal [B2]; Lignin removal average price (1500€/t) [B2*cogen+ec]; Lignin removal max price (2000€/t) [B2*cogen+ec max price]; Lignin removal min price (1000€/t) [B2*cogen+ec min price].

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