Science of the Total Environment 882 (2023) 163660

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Consequential life cycle assessment of kraft lignin recovery with chemical recycling

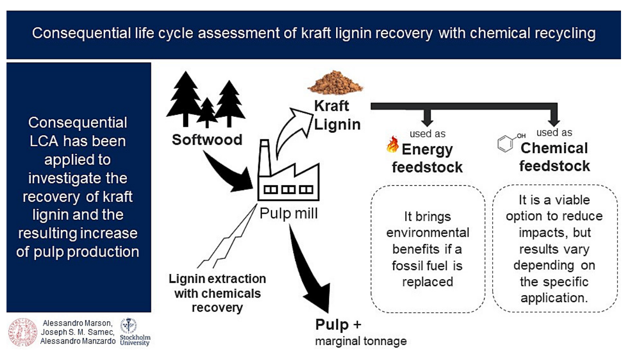
Alessandro Marson [a,b], Joseph S.M. Samec [c], Alessandro Manzardo [a,*]

[a] CESQA (Quality and Environmental Research Center), University of Padova, Department of Civil, Environmental and Architectural Engineering, Via Marzolo 9, 35131 Padova, Italy
[b] University of Padova, Department of Industrial Engineering, Via Marzolo 9, 35131 Padova, Italy
[c] Stockholm University, Department of Organic Chemistry, Svante Arrhenius väg 16C, SE 106 91 Stochholm, Sweden

HIGHLIGHTS

- Consequential life cycle assessment of kraft lignin (KL) recovery was presented.
- Benefits related to a newly developed chemical recovery strategy was assessed.
- The use of KL as an energy feedstock is not advantageous.
- Use of KL as chemical feedstock showed the highest potential for impacts reduction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Deyi Hou

Keywords:
Kraft lignin
Life cycle assessment
Pulp
Sulfur recycling
Phenol

ABSTRACT

The recovery of kraft lignin from black liquor allows an increasing of the pulp production of a kraft mill (marginal tonnage) and at the same time provide a valuable material that can be used as energy or chemical feedstock. However, because lignin precipitation is an energy- and material-consuming process, the environmental consequences from a life cycle perspective are under discourse. The aim of this study is to investigate, through the application of consequential life cycle assessment, the potential environmental benefits of kraft lignin recovery and its subsequent use as an energy or chemical feedstock. A newly developed chemical recovery strategy was assessed. The results revealed how the use of lignin as energy feedstock is not environmentally advantageous compared to producing energy directly from the pulp mill's recovery boiler. However, the best results were observed when lignin was used as a chemical feedstock in four applications to replace bitumen, carbon black, phenol, and bisphenol-A.

1. Introduction

Global production of wood pulp has more than quadrupled in the last 60 years, and the market is projected to continue to grow until 2027 (Statista, 2022). Despite this, production of total pulp (market + integrated pulp) in Europe over the last 20 years has been fairly stable; over the same period the number of pulp mills in Europe constantly decreased mainly due to closure of mechanical pulp mills, but maintaining a constant total pulp production capacity (higher than the domestic consumption) (CEPI, 2022). If only the market pulp is considered (90 % of which is sulphate pulp), the scenario is quite different. In fact, European production is lower than annual consumption (slightly increased in recent years) (CEPI, 2022). In most pulp mills the recovery boiler operates at maximum capacity and becomes the bottleneck (Moretti et al., 2021). Therefore there are two options to increase the pulp production for wood pulp: building new pulp mills/new recovery boilers or de-bottlenecking the pulping process by

* Corresponding author at: Via Marzolo 9, 35131 Padova, Italy.
E-mail addresses: alessandro.marson@unipd.it (A. Marson), joseph.samec@su.se (J.S.M. Samec), alessandro.manzardo@unipd.it (A. Manzardo).

http://dx.doi.org/10.1016/j.scitotenv.2023.163660
Received 23 January 2023; Received in revised form 17 April 2023; Accepted 18 April 2023
Available online 23 April 2023

lignin precipitation and recovery. This second option allows to increase the pulp mill's production (the increase in pulp production capacity by this practice is called marginal tonnage) and to recover a material with a potential value (lignin). On the other hand, the lignin precipitation process consumes energy and chemicals, and energy surpluses that would normally be sent to the grid and available for other purposes are lost.

With the development of lignin recovery technologies and their implementation on a commercial scale, LignoBoost, a quantitative tool to assess the environmental consequences of their implementation has become essential. There has been great interest in studying lignin from a life cycle assessment (LCA) perspective over the last decade. This interest concerned both the evaluation of the environmental performance of the system and the LCA methodological challenges due to multifunctional aspects. Several authors have focused on the allocation management for the co-products of the pulping process (Cherubini et al., 2011; Hermansson et al., 2020; Moretti et al., 2021; Sandin et al., 2015). Hermansson et al. (2020) tested twelve different allocation approaches for lignin produced using LignoBoost process in Kraft pulp mills, obtaining results with high variability. Sandin et al. (2015) pointed out that this phenomenon is accentuated because lignin is not the dominant co-product of the process (which is pulp). Another approach is to evaluate the effects of lignin recovery from the pulp perspective. Culbertson et al. (2016) applied attributional LCA using 1 ton of bleached pulp as functional unit (FU) with system expansion, mass and economic allocation to deal with the multifunctionality. This comprehensive study shows the benefits from a macro perspective of a pulp mill, especially including benefits coming from the phenol substitution by lignin. Bernier et al. (2013) performed an attributional LCA study using kraft lignin (KL) as the FU and attributing the difference in emissions of a pulp mill with and without lignin recovery to the lignin (note that the introduction of the lignin recovery system allows for an increase in pulp production, the so-called marginal tonnage). According to Hermansson et al. (2020), this approach could be suitable in a consequential LCA study. Bernier et al. (2013) concluded that lignin is favorably comparable to similar synthetic organic compounds (e.g. phenol) and identified that the reduction of chemicals consumption for the precipitation (liquid carbon dioxide, sulfuric acid and sodium hydroxide) would be a driver to reduce the negative impacts of lignin recovery. The significance of chemicals consumption was also highlighted by Secchi et al. (2019) and Tokede et al. (2020).

All these previous contributions applied attributional LCA, and to our knowledge there are no studies using consequential LCA to assess lignin recovery from kraft pulp mill. An application of consequential LCA for adipic acid from lignin is presented by Corona et al. (2018), however, the lignin was derived from a waste stream of ethanol production.

Herein, the aim is to investigate the environmental consequences associated with the recovery of KL and the resulting increase in the production of USP termed marginal tonnage. To do this we have applied consequential LCA. To target raised questions concerning chemicals consumption during KL extraction (Bernier et al., 2013; Secchi et al., 2019; Tokede et al., 2020), a newly developed chemical recovery strategy was evaluated and benchmarked to conventional KL outtake. Different options for the conversion of KL into different end-products, both energy and chemicals, were investigated.

2. Materials and methods

In Section 2.1 a description of the USP production technologies is provided. Section 2.2 describes the LCA methodological approaches adopted to deal with the research objectives. Section 2.3, supported by Appendix A, provides a description of the Life Cycle Inventory (LCI) of all USP and KL production processes, as well as a discussion of the possible uses of the latter as energy and chemical feedstock. Finally, Sections 2.4 and 2.5 present the choices for life cycle impact assessment (LCIA) and sensitivity analyses.

2.1. Description of the USP production technologies

During pulping, the carbohydrate matrix is liberated from the lignin that is solubilized (Sixta et al., 2006). In kraft pulping, which is the dominating technology (90 % of chemical pulping), nucleophilic sulfide and hydroxide are responsible for lignin depolymerization and solubilization (Gierer, 1980). Both the hydroxide and the sulfide target the lignin and the resulting pulp comprise both cellulose and hemicellulose. The presence of hemicellulose in the pulp gives additional strength where kraft is the Swedish name for strength and force. In the less common sulfite pulping, the reactive sulfite targets the hemicellulose which gives a purer cellulose pulp, however the fibers are weaker.

During kraft pulping, the reactive sulfide is oxidized to sulfates (Ragnar et al., 2014). Modern pulping regenerates the sulfite from sulfates in the recovery process. The reduction of sulfates takes place in the recovery boiler where lignin is used as a reducing agent to regenerate the sulfide. The recovery process generates substantial energy that is used as process heat. However, all pulp mills generate excess energy and this energy can be used to produce heat and power (Jönsson et al., 2013). It is important to note that the recovery boiler is the most CapEx intensive unit in a pulp mill, and thus most pulp mills run with the recovery boiler as the bottleneck of the pulp production. To increase pulp production, investment in a new recovery boiler is an expensive option that many mills cannot afford. An alternative is to remove parts of lignin from the black liquor by a simple precipitation (Ragnar et al., 2014). By this method, the mill can increase the production of pulp. This additional pulp produced, is termed marginal tonnage. A byproduct from this operation is precipitated lignin. There are a few technologies for lignin precipitation where LignoBoost has been implemented in Domtar, USA and Sunila, Finland (Tomani et al., 2011). This technology comprises lowering the pH of the black liquor by carbon dioxide to around 10, where the phenolic lignin is protonated and precipitated from the aqueous phase. The precipitated lignin is then washed with sulfuric acid to lower the ash content of the lignin and to recover the inorganics. However, this also leads to disruption of the sulfur:sodium balance. Thus, additional sodium hydroxide is added to recuperate the balance. Very recently, a sulfur regeneration technology has been developed that circumvents usage of virgin sulfuric acid and make-up sodium hydroxide (Valmet, 2023).

Therefore, three technology options for the production of marginal tonnage of USP were considered in this research: building new plants for traditional (without KL recovery) pulp production (S1), debottlenecking the recovery boiler of an existing pulp mill by KL recovery with sulfur regeneration (S2), debottlenecking the recovery boiler of an existing pulp mill by KL recovery without sulfur regeneration (S3).

2.2. Goal and scope definition

This study aims to assess the effects in terms of potential environmental impacts of different decisions on how to produce USP and use KL, which is why the consequential LCA is more appropriate (Schaubroeck et al., 2021; UNEP-SETAC, 2011).

Two sub-objectives can be identified: (1) to test whether the KL recovery system with sulfur regeneration (S2) provides a reduction in impacts compared to the recovery system without sulfur regeneration (S3); (2) to compare the environmental performance of USP marginal tonnage production through building new pulp mills with the traditional system (S1) and with the KL recovery system with sulfur regeneration (S2) considering different lignin utilization scenarios (either as energy or chemical feedstock). More details on the methodological approach used to address the two sub-objectives are given in Sections 2.2.1 and 2.2.2, respectively.

The intended geographical scope is the European one. The pulping process was assumed to take place in Sweden and Finland, as they are by far the largest European producers of wood pulp (together they account for the 60 % of the total wood pulp production (Statista, 2022)). This assumption has been tested through a sensitivity analysis. Where possible, the background data were selected in such a way as to be representative of the specific countries (in particular for the choice of energy mixes). For the characterization of the subsequent transformation of the recovered KL, as well as the production processes of the substituted materials, an average European scenario was considered. According to the recommendation from the Moretti et al. (2021) review, the substitution scenarios were defined taking into account the effects in final application. The analysis was carried out using SimaPro v9.3 (PRé Sustainability, 2022) and background data from Ecoinvent 3.8 consequential (Wernet et al., 2016). To characterize the consumption and surplus of electricity, an average of the marginal electricity mix of Sweden and Finland was calculated according to the procedure proposed by Weidema and Muñoz (2022), while the substitution of biomass (95 % for Sweden and 80 % for Finland) and coal (5 % and 20 %) was assumed for heat (see SI-1). The calculated marginal Sweden market mix is composed by wind (89.3 %), solar (5.6 %), coal (3.7 %), hydro (0.8 %) and oil (0.6 %). For Finland the considered mix is composed by wind (63.5 %), nuclear (20.3 %), wood (13.0 %), solar (2.5 %) and oil (0.7 %).

2.2.1. Functional unit and system boundary for sub-objective 1

To evaluate the benefits of introducing sulfuric acid regeneration in the pulping process with KL recovery the two technologies S2 and S3 were compared. The considered processes generate the same quantity of valuable outputs, i.e., USP, KL, bark chips, sawdust, tall oil, turpentine. The FU chosen is the production of 1.00 kg of USP, 0.77 kg of KL, and other co-products. This FU avoids allocation, which is preferred choice according to ISO 14044 (ISO, 2020). More details on quantities can be found in the LCI section. A simplified scheme of the two systems is reported in Fig. 1.

2.2.2. Functional unit and system boundary for sub-objective 2

The considered system boundaries include all processes until the pulp mill gate and the consequences of KL management. According to the sub-objective 2, only KL recovery with sulfur regeneration (S2 technology) has been considered. The FU chosen in this case is the production of 1 kg of USP. This FU focuses on determining product and is consistent with previous studies (Culbertson et al., 2016). All the co-products are treated by substitution (more details in 2.3).

Fig. 2 shows the alternative scenarios S1, S2-E, and S2-Chem-*i* (where *i* stands for Bit, CB, Phen, and BPA). In S1 the FU is satisfied by increasing production building new pulp mills. From the pulping process different co-products are obtained, both materials and energy. All of them were managed using the substitution method, according to the hierarchy proposed by ISO 14044. In particular, for the electricity and heat recovered from the black liquor combustion, the substitution of marginal country mixes has been considered. In S2, as described above, the typical kraft pulping process is modified by partial extraction of KL from the black liquor, which can be destined to become energy or chemical feedstock rather than being burnt in the recovery boiler. In this case, the inventory was constructed considering the flows directly attributable to the marginal production of USP. The choice of materials potentially substitutable by KL has been reported to be pivotal for analysis. For instance, Moretti et al. (2021) found 8 applications of KL (polymers, carbon fibers, adhesive, cement additives, activated carbon, aromatics, bitumen, fertilizers). A review of the KL applications as biofuels and thermosets is provided by Lawoko and Samec (2023). In the present study, we have studied five different substitution alternatives: energy (S2-E), bitumen (S2-Chem-BIT), carbon black for tires production (S2-Chem-CB), phenol for phenolic resin production (S2-Chem-Phen), and bisphenol-A (S2-Chem-BPA). Specific market trend forecasts of KL uses were not considered in selecting these scenarios, but these were chosen

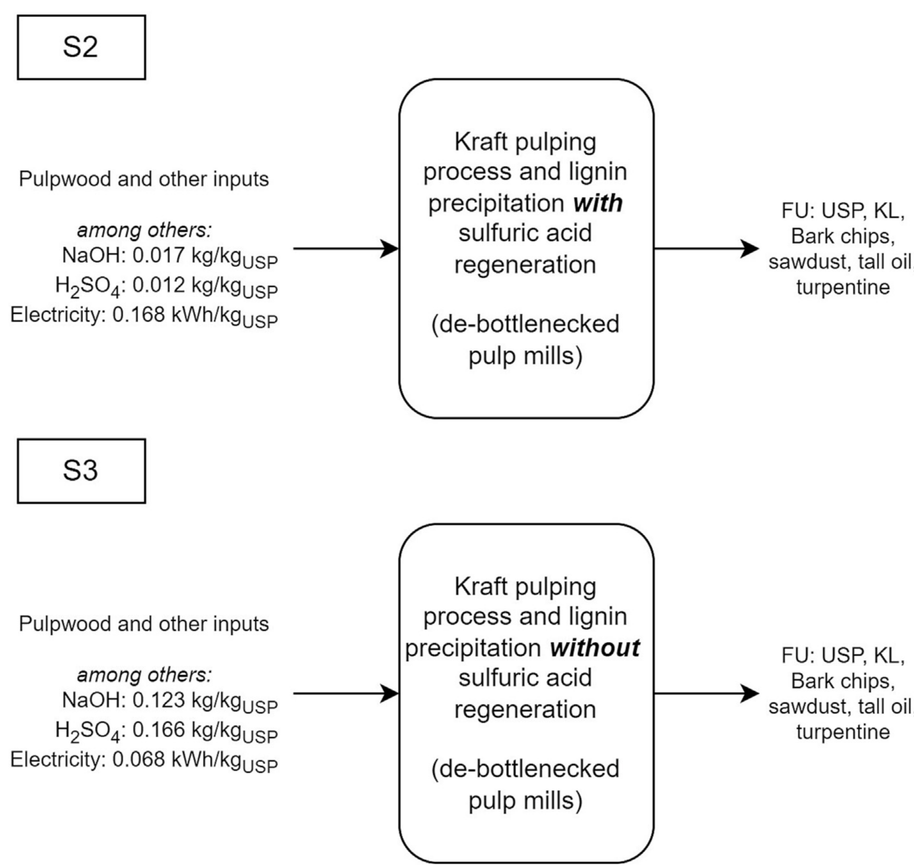


Fig. 1. Scheme of S2 and S3 (for sub-objective 1).

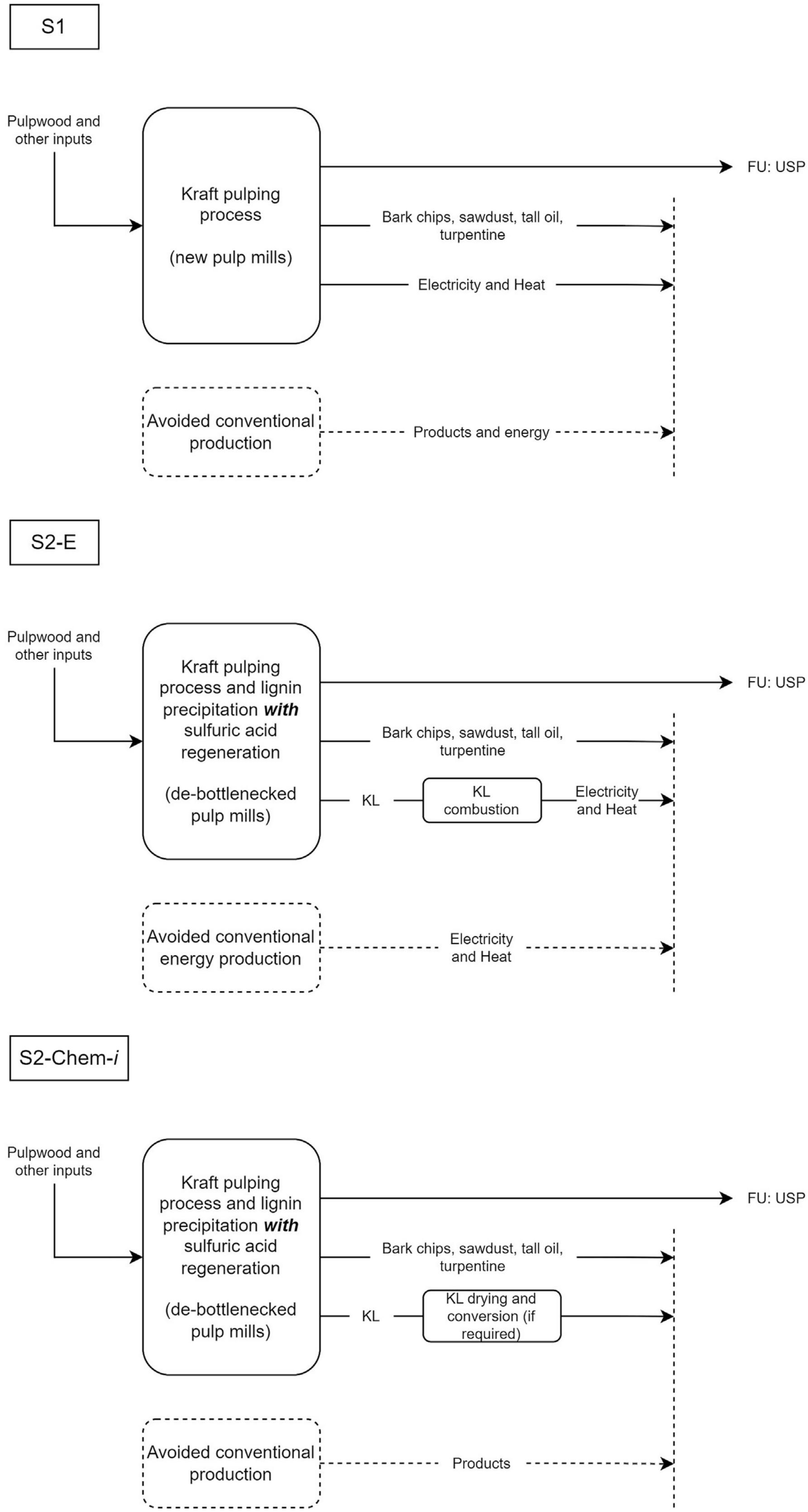


Fig. 2. Scheme of the investigated product systems (S1, S2-E, and S2-Chem-*i*) (for sub-objective 2).

based on available data and attempting to represent different levels of KL valorization. The use of lignin in asphalts and phenolic resins has already been studied in the literature with an attributional LCA perspective (Culbertson et al., 2016; Moretti et al., 2022a). Consistency between the results obtained in this research and previous studies is presented in Section 3.

2.3. Life cycle inventory

2.3.1. LCI for traditional pulping process (S1)

The kraft pulping process for S1 has been characterized starting from the inventory proposed by Ecoinvent v3.8 for USP. The dataset is based on data generated by 'The European pulp Industry Sector Association - AISBL' and is representative of unbleached kraft pulp production in Northern Europe in 2017 (AISBL, 2021). The geographic scope of the dataset is therefore consistent with the scope of this research. In addition, the data are recent enough to provide an acceptable representation of the processes. These background data have been modified to implement the energy mixes of Sweden and Finland. The proposed value of co-produced tall oil (0.2 kg/kg USP) is in contrast to the primary data collected in a Swedish pulp mill and literature. For this reason, this amount has been modified according to Kuparinen et al. (2019) (0.025 kg/kg input dry ton). In this way, the net biogenic C balance is guaranteed (originally unbalanced). An explanation of the changes is provided in Table S-2.1. To characterize the products substituted by co-products other than energy the choices in the background dataset were maintained (also in other scenarios).

2.3.2. LCI for pulping with KL recovery systems (S2 and S3)

To characterize the pulping processes in S2 and S3, the inventory of S1 was integrated with primary data to describe the KL recovery. The life cycle inventories for S2 and S3, as well as their biogenic carbon balance, are reported in Table S-3.1. The main differences between the inputs of S1 and S2/3 are an increase in the consumption of wood chips and electricity and the introduction of the consumption of liquid carbon dioxide, sulfuric acid and sodium hydroxide. According to Culbertson et al. (2016) a fraction of lignin can be extracted without requiring an increase of natural gas consumption (Moretti et al., 2021). At the same time, energy surpluses are lost in favor of KL co-production. The absence of the combustion process avoids the generation of certain wastes such as wood ash, green liquor dregs, and other hazardous wastes (less than a few grams per kg of USP). The fossil carbon dioxide emissions (attributable to the use of fuel oil and liquid carbon dioxide) and biogenic carbon dioxide emissions have been adjusted according to the mass balance. Cautiously, the amounts of other waste, air, and water emissions have been increased according to the higher input of wood chips (+1.7 % with respect to the sum of pulpwood and wood chips in S1). As mentioned above, S3 compared to S2 does not implement sulfuric acid regeneration. This allows for a reduction in electricity consumption, against a higher consumption of sulfuric acid and sodium hydroxide. In both S2 and S3, 0.77 kg of lignin (dry weight) per kg USP is obtained. The recovered lignin is in 65 % dry substance condition. According to Bengtsson et al. (2019), a carbon content of 0,60 kg C_{bio}/kg lignin has been considered.

2.3.3. LCI for KL as energy feedstock

To characterize the KL combustion for energy co-generation in the S2-E scenario, the Ecoinvent dataset '*Heat, district or industrial, other than natural gas {SE}| heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | Conseq, U*' was taken as reference. According to the dataset the heat recovery efficiency is equal to 45 %, while 0.144 kWh of electricity for MJ of heat are produced. The assumed low heating value (LHV) for KL (35 % moisture content) was 23.6 MJ/kg (dry mass) (see SI-4). According to these values, from the combustion of 1 kg of lignin (dry mass), 10.62 MJ of heat and 1.53 kWh of electricity can be produced. The substitution of the marginal energy mixes (as described in 2.2.1) was considered.

2.3.4. LCI for KL as chemical feedstock

Bitumen substitution (S2-Chem-Bit) was analyzed with an LCA perspective by Tokede et al. (2020) and Moretti et al. (2022b). In both cases, the analysis was conducted with an attributional approach. Tokede et al. (2020) considered a lignin derived from kraft process via LignoBoost extraction, while Moretti et al. (2022b) referred to a biorefinery lignin production. In this study, the substitution scenario was constructed using the asphalt formulations (base layer) reported in Moretti et al. (2022b), in which bitumen is partially replaced by dried lignin, with corrections to the sand and gravel content and the addition of linseed oil (Table S-5.1). In accordance with Moretti et al. (2022b), the carbon contained in both bitumen (0.762 kgC/kg) and lignin was assumed not to be released over a 100-year time horizon. For this reason, the release of CO_2 from bitumen into the air was not considered (2.690 kgCO_2/FU), and instead the storage of biogenic carbon in lignin was considered (1.694 kgCO_2/FU - the uptake during the growth phase of the plant is not taken into account by the Life Cycle Impact Assessment (LCIA) method used to avoid double counting).

The use of lignin as a (partial) substitute for carbon black in the production of tires has been investigated for more than 60 years (c&en archives, 1957). The use of spray-dried lignin as a substitute for carbon black up to 50 % wt. is described by Veas and Hotaling (2011). For the S2-Chem-CB scenario, direct substitution of carbon black by dried lignin is therefore considered (Table S-5.2). The difference in fossil carbon dioxide emissions at tire end of life (assuming complete release) was quantified. The carbon content of carbon black (0.85 kgC/kg) was taken from Ecoinvent documentation.

The potential of lignin as a phenol substitute is well documented in the literature. In particular, Siddiqui et al. (2017) demonstrated how depolymerized KL can partially replace petroleum-based phenol (up to 75 %) in the production of phenol-formaldehyde resoles (PFR) for application in plywood. Several studies have shown that the introduction of lignin can lead to lower formaldehyde-to-phenol (F/P) ratios and higher shear strength, but on the other hand, higher curing time and/or temperature (i.e., higher energy consumption once in plywood production) (Danielson and Simonson, 1998a; Li et al., 2017; Siddiqui et al., 2017; Solt et al., 2018). Although the use of pre-treated lignin (e.g., through organosolv or fractionation) as a substitute for phenol has also been analyzed using LCA (Hildebrandt et al., 2019; Lettner et al., 2018; Perederic et al., 2020), this is not the case for unmodified lignin. To describe the inventory of scenario S2-Chem-Phen inventory data from Danielson and Simonson (1998a) have been used, taking into account the 50%wt replacement ratio (unmodified KL to phenol) for which industrial application in plywood production has been demonstrated (Danielson and Simonson, 1998b) (see Table S-5.3). To estimate the increase in thermal energy consumption for curing stage, the energy demand suggested by Ecoinvent for curing a urea formaldehyde resin (at an average temperature of 100 °C) in plywood was considered. According to Danielson and Simonson (1998a, 1998b), KL containing resin require an increase of 30 % of the curing time at 135 °C in plywood application. Cautiously, the heat consumption from light fuel oil suggested by Ecoinvent (0.61 MJ/kg of resin) was doubled. Like the previous scenario, the difference in fossil carbon dioxide emissions at resin end of life (assuming complete release) was quantified. The carbon content (0.77 kgC/kg for phenol and 0.4 kgC/kg for formaldehyde) was taken from Ecoinvent documentation. The LCI is described in Table S-5.5.

The use of unmodified lignin as a substitute for bisphenol-A in the production of epoxy resin has been investigated successfully by several researcher, e.g., Nikafshar et al. (2021). For the S2-Chem-BPA scenario, direct substitution of bisphenol-A by dried lignin is therefore considered. The difference in fossil carbon dioxide emissions at end of life (assuming complete release) was quantified. The carbon content (0.79 kgC/kg) was taken from Ecoinvent documentation. The LCI is described in Table S-5.6.

For the characterization of the spry-drying of lignin the inventory of spry-dried milk provided by Ecoinvent has been considered as proxy (0.085 kWh of electricity and 5.25 MJ of heat for 1 kg of evaporated water).

2.4. Life cycle impact assessment

The results of the impact assessment are presented using the set of 16 midpoint impact categories EF method 3.0 (Zampori and Pant, 2019). EF method 3.0 has been chosen due to its comprehensiveness and focus to the European scenario. The list of impact categories, indicators, abbreviations, and units can be found in Table S-6.1. For the sake of clarity, only the results of the six categories with the highest weighting factors according to the PEF methodology (Zampori and Pant, 2019) will be presented and discussed in the article, while the complete results are given within the additional information. The impact categories discussed in the main text are therefore climate change (GWP-total), particulate matter (PM), land use (SQP), water use (WDP), resource use, fossil (ADP-fossil) and resource use, mineral and metals (ADP-min&met). In this study, the optional steps of impact assessment according to ISO 14044, that are normalization and weighting, are not addressed. According to this method, biogenic carbon dioxide uptake and emissions are not associated with a characterization factor for the impact category GWP-total. Only in the scenario of the substitution of bitumen in asphalt production was the storage of biogenic carbon considered, as it is assumed to be longer than one hundred years. The influence of this approach on conclusions are discussed in Section 3.

2.5. Sensitivity analysis

To cover potential uncertainties related to different assumptions and scenarios, two sensitivity analyses were conducted. The first aspect investigated was the geographical scope. For the pulping process in the base case, a combined scenario of Sweden and Finland was considered as a proxy for the European one. A sensitivity analysis evaluated the effects on the results of considering the energy mixes of Sweden, Finland, and an average European scenario separately. The second aspect investigated by sensitivity analysis concerns the source of the liquid CO_2 used in the lignin precipitation process from black liquor. In the base case, it was assumed CO_2 from a fossil source, while through this sensitivity analysis, the effects of using biogenic CO_2 have been assessed. This sensitivity analysis seeks to assess the effects of reducing fossil carbon dioxide consumption, indicated by Bernier et al. (2013) as a driver for impacts reduction.

3. Results and discussion

3.1. LCIA for sub-objective 1

The results of the comparison between lignin recovery with and without sulfur regeneration (S2 and S3) are shown in Table 1. The analysis shows how the sulfuric acid regeneration system brings benefits in the six main impact categories. Even extending the analysis to all indicators (Table S-7.1) S3 outperforms S2 only in ODP (−8 %) and IRP (−74 %). This means that increasing the consumption of electricity by 0.1 kWh/ kg_{USP} to reduce the consumption of sulfuric acid (−0.15 kg/kg_{USP}) and sodium hydroxide (−0.11 kg/kg_{USP}) is beneficial from an environmental point of view. These results remain almost unchanged even when considering an average European energy mix, although the differences become slightly smaller (Table S-7.1). These variations are modest because the main impact contributions at this stage are the production and supply of the raw materials (e.g., pulpwood and wood chips) and not the electricity consumptions (about 0.23 kWh/kg_{USP} for S2 considering both the pulping and liquid CO_2 production).

It can therefore be concluded that S2 shows more promising results than S3 with good stability with respect to changes in plant location (although trade-offs were observed in some impact categories such as ODP and IRP). These results are consistent with what was hypothesized by Bernier et al. (2013).

Table 1
Results of the comparison between S2 and S3 for sub-objective 1.

Input	Unit	S2	S3	var%
GWP-total	kg CO2 eq	8.07E-01	9.17E-01	14 %
PM	disease inc.	-8.18E-09	8.24E-09	201 %
SQP	Pt	3.13E+02	3.19E+02	2 %
WDP	m3 depriv.	1.56E+00	2.03E+00	30 %
ADP-fossil	MJ	5.17E+00	5.39E+00	4 %
ADP-min&met	kg Sb eq	9.84E-06	2.40E-05	143 %

3.2. LCIA for sub-objective 2

This section presents the LCA results of USP production with five different KL applications compared to the reference system S1. The LCIA results and the graphic summary of the main impact categories are shown, respectively, in Table 2 and Fig. 3, while the full results are reported in Table S-7.2. The results in the main impact categories do not uniquely identify a best-performing application from an environmental perspective. For this reason, each main impact category will be presented and discussed considering also the contribution analysis results provided in Fig. 4.

In GWP-total all the assessed scenarios using KL as chemical feedstock perform better than S1 (−0.12 $kgCO_2eq/kg_{USP}$), ranging from −1.04 $kgCO_2eq/kg_{USP}$ of S2-Chem-Bit to −6.19 $kgCO_2eq/kg_{USP}$ of S2-Chem-Phen. For this impact category, the contribution of avoided end-of-life emissions compared to the fossil-based alternative is a key element, ranging from about −3.36 $kgCO_2eq/kg_{USP}$ for S2-Chem-Phen to −1.69 $kgCO_2eq/kg_{USP}$ for S2-Chem-Bit. However, even not considering this contribution, all the scenarios still have lower impacts than S1, except for S2-Chem-Bit (due to the release of the biogenic carbon stored in lignin). Analyzing in more detail the best performing scenario in respect to GWP-total, the greatest benefits come from phenol substitution (i.e., S2-Chem-Phen gave −3.00 $kgCO_2eq/kg_{USP}$), while the lower consumption of formaldehyde brings a more limited contribution (−0.41 $kgCO_2eq/kg_{USP}$). Impact due to increased heat consumption in resin curing use is negligible (0.07 $kgCO_2eq/kg_{USP}$). The positive effects of phenol substitution are consistent with what has been observed in previous studies with attributional approach (Culbertson et al., 2016). In contrast, the results obtained for bitumen replacement are not completely in line with previous studies. Moretti et al. (2022b) identified significant benefits on climate change, while in the present study it was found that the impact was dependent on the carbon storage accounting approach. It should be noted, however, that the authors did not consider KL, but lignin obtained from biorefineries, and a great variability is observed in literature (Moretti et al., 2022b). In another case, Tokede et al. (2020) studied the implementation of KL by LignoBoost process in asphalt, obtaining similar results to the present study. The authors obtained with a 25 % substitution of the bitumen a reduction of 5.7 % of the asphalt GWP impacts on a cradle to gate base. However, variations in asphalt composition, that bring relevant contributions of impact, were not considered by Tokede et al. (2020).

The use of KL as a chemical feedstock presents notable advantages, but the same cannot be said for its application as an energy feedstock. In fact, the S2-E scenario shows the highest GWP-total. This result is highly dependent on the substituted energy mix, as discussed in the sensitivity analyses in Section 3.3.

Also for PM indicator the considered scenarios have lower impacts than S1, but in this case the highest performing alternative is S2-Chem-CB. In particular, benefits arise from the replacement of carbon black, avoiding direct emissions in its production process. For the SQP category the trend is reversed. The heat recovered in S1 from the combustion of black liquor avoids the production of heat from biomass (accounting for a significant share of the marginal energy mixes considered). This results in the avoided consumption of wood chips and related land use impacts for harvesting. Similar conclusions can be drawn for the out-of-mill energy recovery (S2-E). Scenarios with lignin extraction thus lose the benefits of energy recovery, leading to impacts up to 30 % higher than S1. Impacts related to water scarcity (WDP indicator) come from direct consumption during the pulping process. In the S2-Chem-CB scenario, the impact attributable to the cultivation of linseed used in asphalt formulation is relevant (27 %), leading to a value 45 % higher than S1. S2-Chem-Phen results as the least impactful alternative in this impact category (again, the most significant contribution is by far the avoided production of phenol). A similar result can be observed for S2-Chem-BPA, in which phenol is found as a raw material in the production of bisphenol A. The results obtained for the ADP-fossil indicator are very similar to those observed for GWP-total. In this case, the fossil-based substitution scenarios are always favorable compared to S1. The values obtained range from −38 MJ/kg_{USP} for S2-

Table 2
Results of the comparison between S1, S2-E, S2-Chem-Bit, S2-Chem-CB, S2-Chem-Phen, and S2-Chem-BPA for sub-objective 2.

Input	Unit	S1	S2-E	S2-Chem-Bit	S2-Chem-CB	S2-Chem-Phen	S2-Chem-BPA
GWP-total	kg CO2 eq	1,19E-01	5,30E-01	-1,04E+00	−2,85E+00	−6,19E+00	−4,04E+00
PM	disease inc.	3,33E-08	−2,80E-08	2,05E-08	−2,28E-07	−7,91E-08	−7,63E-08
SQP	Pt	2,11E+02	2,19E+02	3,53E+02	3,04E+02	2,99E+02	3,15E+02
WDP	m3 depriv.	1,44E+00	1,44E+00	2,09E+00	1,47E+00	−1,26E+00	−1,20E-01
ADP-fossil	MJ	2,81E+00	3,12E+00	−3,81E+01	−5,12E+01	−8,58E+01	−5,82E+01
ADP-min&met	kg Sb eq	−3,68E-06	−3,73E-06	1,10E-05	−1,93E-05	−8,37E-05	−6,88E-05

Chem-Bit to −86 MJ/kg_{USP} for S2-Chem-Phen. Finally, in the ADP-min&met category, the importance of infrastructure construction and materials used becomes apparent. In fact, in S1 the main impacts are related to pulp mill production, while the benefits come mainly from recovered electricity. Again, the benefits of replacing fossil-based substances and the infrastructure for their transformation are emphasized.

The contribution analysis shown in Fig. 4 allows us to observe the net contribution associated with the processing of the extracted KL and the impacts and benefits associated with the substitution scenarios. For the S2-Chem-CB, S2-Chem-Phen, and S2-Chem-BPA scenarios, this net contribution is negative in almost all impact categories (i.e. leads to environmental benefits). In contrast, for the S2-Chem-Bit scenario, the net benefits are limited to two impact categories (GWP-total and ADP-fossil). In fact, as explained above, for the other indicators, the changes in the asphalt formulation are critical and lead to an increase in the overall impact.

Comparison with the literature becomes more complex for impact categories other than GWP-Total, as they have rarely been investigated in previous studies. In addition, LCIA methods may have significant differences. However, Culbertson et al. (2016), applying system expansion considering phenol substitution and using TRACI LCIA method (Bare, 2002), obtained an overall improvement in all impact categories except Non-Carcinogenics toxicity. Among the categories of the TRACI method, there are no indicators attributable to SQP and IRP with which to compare the identified trade-offs. Bernier et al. (2013) also confirm that the results obtained for KL are lower than those for phenol (based on 1 kg of substance) for all indicators in the IMPACT2002+ LCIA method (Jolliet et al., 2003). For the substitution of bitumen in asphalts, in the study by Moretti et al. (2022b) the characterized results are not available (except for GWP), but a reduction in the weighted indicator can be observed for formulations containing lignin.

In conclusion, the use of KL as chemical feedstock can lead to overall environmental benefits. However, as already pointed out, the choice of application plays a key role. In general, S2-Chem-Phen proved to be the best alternative in four of the six main impact categories, while S2-Chem-Bit always emerged as the least performing scenario with lignin recovery. The categories not shown in the main text also confirm similar trends compared to those of the six main indicators. In fact, S2-Chem-Phen turns out to be the best alternative in 8 of the 10 additional categories (Table S-7.2). Finally, the use of lignin for energy production shows inferior or equivalent results to traditional production where energy is produced directly in the recovery boiler (without the chemical and energy consumption of the KL recovery process). However, these conclusions should be limited to the geographical scope and associated energy mixes of Northern Europe. The variability of these conclusions with changing energy mixes is discussed in the following section.

3.3. Sensitivity analysis

The performed sensitivity analyses allowed the assessment of the model stability with respect to the assumptions on the geographical location of the pulp mill. The most significant variations were observed for S1 and S2-E, with the average European scenario being more favorable. This effect can be attributed to the higher emission factor of the average European energy

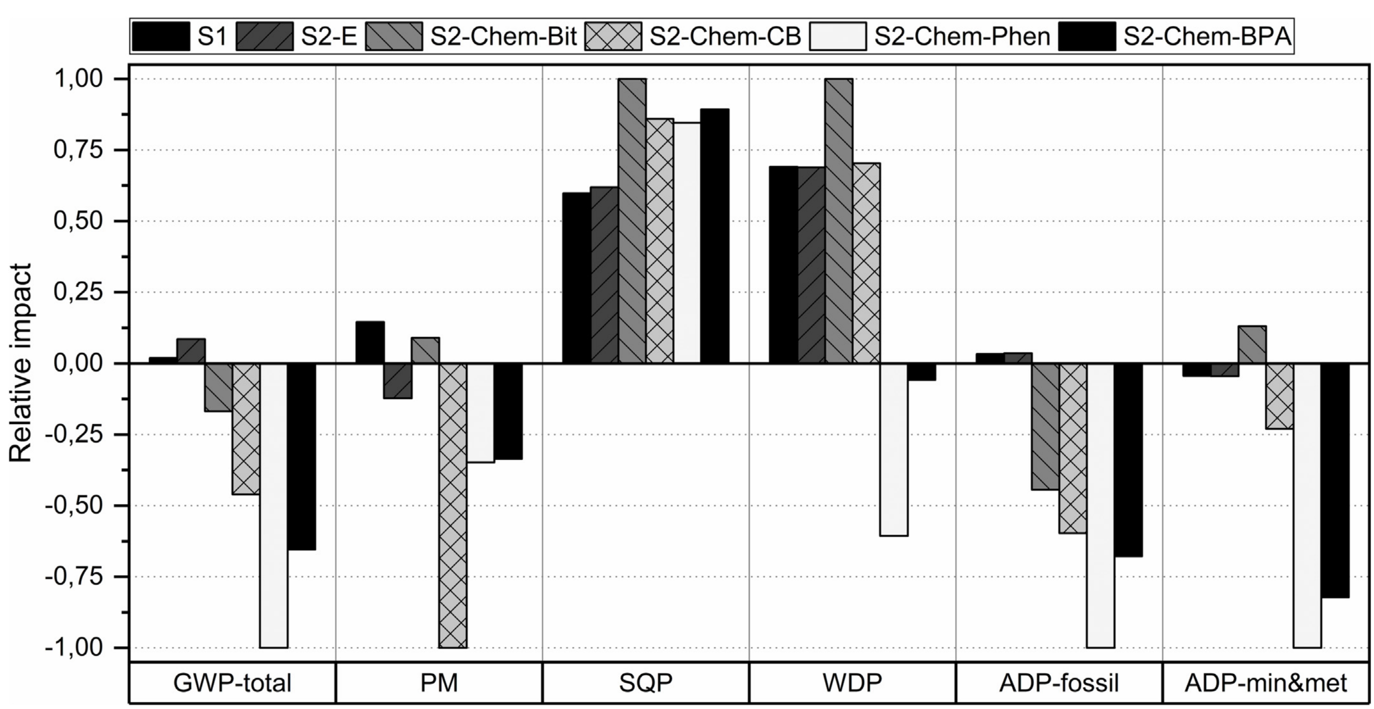


Fig. 3. Life Cycle Impact Assessment relative results for S1, S2-E, S2-Chem-Bit, S2-Chem-CB, S2-Chem-Phen, and S2-Chem-BPA scenarios. Results are normalized respect the maximum absolute value in the impact category.

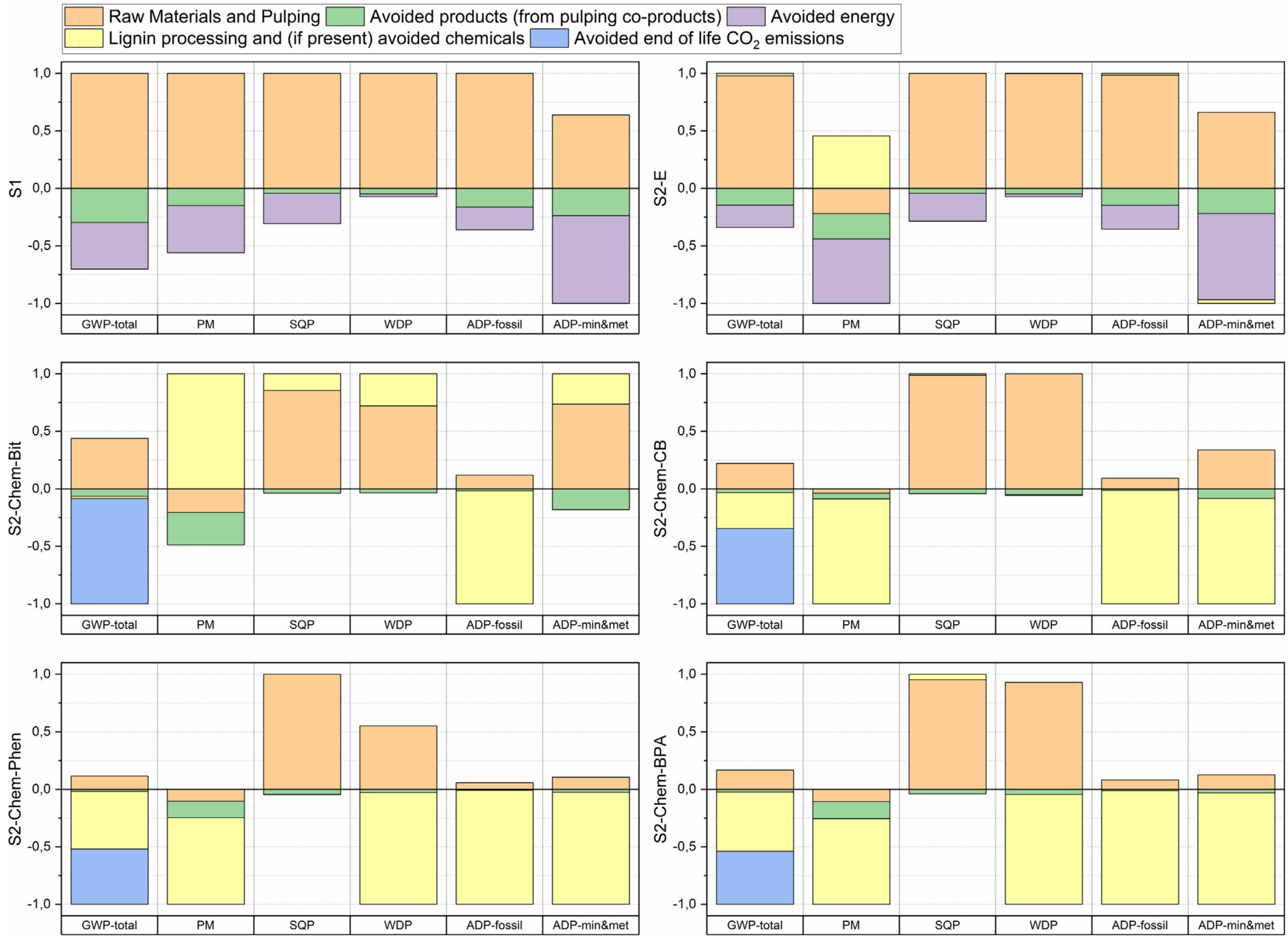


Fig. 4. Contribution analysis for for S1, S2-E, S2-Chem-Bit, S2-Chem-CB, S2-Chem-Phen, and S2-Chem-BPA scenarios. Results are normalized respect the maximum absolute value in the impact category.

mix (0.218 $kgCO_2eq/kWh$ of electricity for the European scenario versus 0.070 $kgCO_2eq/kWh$ for the baseline scenario), resulting in higher benefits from recovered energy. This trend is confirmed in the scenario using KL as energy feedstock (S2-E). It can be inferred that the extraction of lignin for energy purposes can only lead to an overall reduction in GHG emissions if energy mixes with a high fossil shares are replaced. On the other hand, its use as a substitute for biomass, such as wood chips, is deleterious. Culbertson et al. (2016) had previously observed that in general KL had greater impacts than wood pellets and therefore substitution would not be beneficial. It follows that the use of lignin as an energy feedstock may be a viable solution in this transition period, but with the increasing decarbonization of the energy system, other areas of applications with a more highly added valued are predicted to become advantageous.

A different trend was observed when KL is used as a chemical feedstock. In these cases, the European scenario is characterized by slightly higher impacts. This is due to the higher consumption (and lower recovery) of electricity resulting from KL recovery, which in the average European scenario is characterized by a higher emission factor compared to Sweden and Finland. However, in S2-Chem-*i* scenarios, the results are quite stable with respect to geographical location, as the contribution of energy consumption of the pulping process is limited, as shown in Fig. 5. For these scenarios, the variations due to different location assumptions are less than 5 % for S2-Chem-CB, -Phen, -BPA and 11 % for S2-Chem-Bit. Furthermore, the ranking between alternatives in different locations is not affected. Thus, the assumption of considering the two largest European pulp producers as a proxy for the average European scenario does not undermine the conclusions of the study.

The use of biogenic liquid CO_2 brings a benefit of 0.154 kgCO2eq/kg_{USP}, which lowers the impacts of all scenarios with lignin recovery, but does not affect the conclusions of the study, as the ranking remains unchanged. The use of a biogenic source (or even an internal recirculation within the pulp mill) is thus a potential driver for further reduction in the impacts of substances used for precipitation, as advocated by Bernier et al. (2013). For instance, recuperating off gases from either the recovery boiler or lime kiln are possible.

The absolute values for all the performed sensitivity analysis and all impact categories are given from Tables S-7.3 to S-7.6.

4. Conclusions

Consequential LCA was successfully applied to determine impacts and benefits related to the recovery of KL in a kraft mill. The scope of the consequential LCA proved to be suitable for achieving its objectives. The marginal tonnage perspective is representative of the main incentive for KL recovery, which is to increase USP production. The main highlights are: (i) the recovery of chemicals used in lignin precipitation was beneficial for all but two impact categories and the use of biogenic or off-gases instead

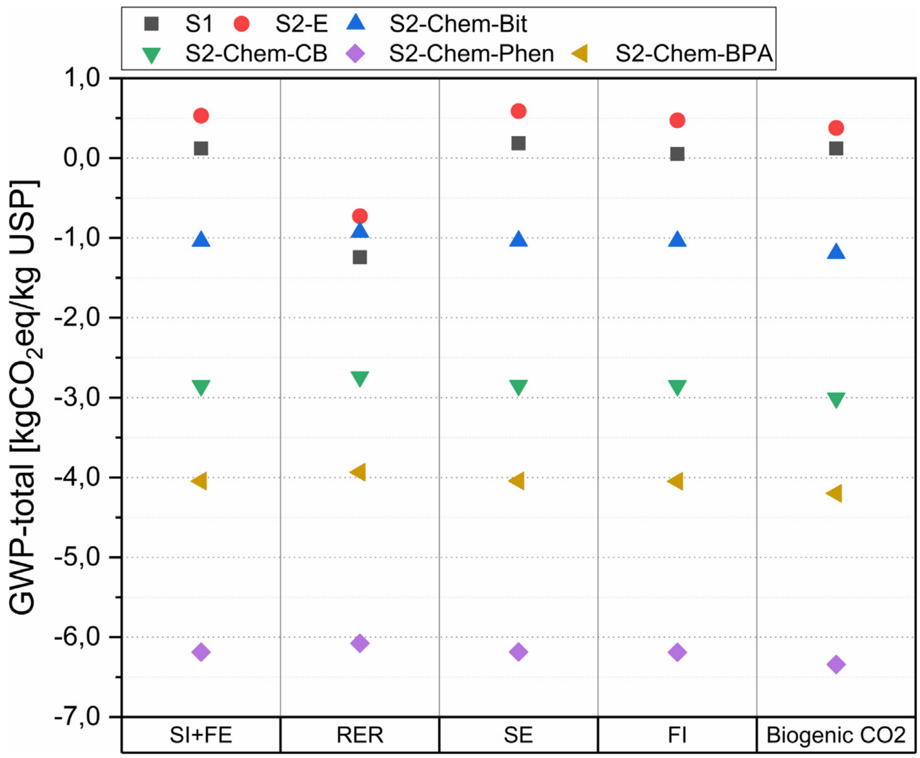


Fig. 5. Variability of GWP-total results depending on the location (i.e. energy mixes) considered for the USP production process and on the use of biogenic liquid CO_2 in the kraft liginin precipitation process.

of fossil-derived carbon dioxide could further reduce the GWP-total impacts; (ii) the use of KL as an energy feedstock is not advantageous compared to producing energy directly from the recovery boiler of the pulp mill (for the same substituted energy mix); (iii) the use of KL as a chemical feedstock proved to have better environmental performance and reduced impacts than its use as energy source, particularly with respect to GHG emissions, however the results are highly variable depending on the specific application. Generally, the applied consequential approach confirmed the main conclusions obtained from previous studies with attributional LCA.

The main limitation concerns the quality of the inventory data used to characterize the substitution scenarios, which are all secondary and have been extrapolated from various sources. Although the processes were subsequently modeled homogeneously (e.g., based on the same database), this could lead to discrepancies in the results. Furthermore, this study only analyzes the environmental performance and does not address the economic feasibility of the different applications.

Finally, the study contributes to the ongoing debate on the pulp production system and lignin exploitation. Further research should investigate in several directions: improving data quality through primary data on KL applications; investigating new alternatives for KL use; integrating social and economic perspectives into the assessment; and prioritizing different alternatives through multi-criteria analysis tools.

CRediT authorship contribution statement

Alessandro Marson: Conceptualization, Data curation, Methodology, Formal analysis, Visualization, Writing – original draft. **Joseph S.M. Samec:** Conceptualization, Data curation, Methodology, Investigation, Writing – original draft, Writing – review & editing, Supervision. **Alessandro Manzardo:** Conceptualization, Validation, Writing – review & editing, Supervision.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Joseph S.M. Samec reports financial support was provided by Swedish Foundation for Strategic Environmental Research. Joseph S.M. Samec reports a relationship with RenFuel that includes: board membership. JS is professor at SU and co-founder of RenFuel, a company valorizing lignin.

Acknowledgements

JS thanks the Swedish Foundation for Strategic Environmental Research (Mistra:project Mistra SafeChem, project no. 2018/11). We thank Martin Wimby at Valmet for providing primary data for precipitation of lignin and sulfur recycling.

Appendix A. Supplementary data

Supplementary data to this article can be found in online version of the paper.

References

AISBL, 2021. Sulfate Pulp Production, From Softwood, Unbleached.

Bare, J.C., 2002. Traci. The tool for the reduction and assessment of chemical and other environmental impacts. J. Ind. Ecol. 6, 49–78. https://doi.org/10.1162/108819802766269539.

Bengtsson, A., Bengtsson, J., Sedin, M., Sjöholm, E., 2019. Carbon fibers from lignin-cellulose precursors: effect of stabilization conditions. ACS Sustain. Chem. Eng. 7, 8440–8448. https://doi.org/10.1021/acssuschemeng.9b00108.

Bernier, E., Lavigne, C., Robidoux, P.Y., 2013. Life cycle assessment of kraft lignin for polymer applications. Int. J. Life Cycle Assess. 18, 520–528. https://doi.org/10.1007/s11367-012-0503-y.

c&amp, en archives, 1957. Lignin filler for tires: new process permits waste ligniïn to replace carbon black in tread stock. Chem. Eng. News Arch. 35, 28–32. https://doi.org/10.1021/cen-v035n022.p028a.

CEPI, 2022. KEY STATISTICS 2021 European Pulp & Paper Industry. Confederation of European Paper Industries.

Cherubini, F., Strømman, A.H., Ulgiati, S., 2011. Influence of allocation methods on the environmental performance of biorefinery products—a case study. Resour. Conserv. Recycl. 55, 1070–1077. https://doi.org/10.1016/j.resconrec.2011.06.001.
Corona, A., Biddy, M.J., Vardon, D.R., Birkved, M., Hauschild, M.Z., Beckham, G.T., 2018. Life cycle assessment of adipic acid production from lignin. Green Chem. 20, 3857–3866. https://doi.org/10.1039/C8GC00868J.
Culbertson, C., Treasure, T., Venditti, R., Jameel, H., Gonzalez, R., 2016. Life cycle assessment of lignin extraction in a softwood kraft pulp mill. Nord. Pulp Pap. Res. J. 31, 30–40. https://doi.org/10.3183/npprj-2016-31-01-p030-040.
Danielson, B., Simonson, R., 1998a. Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood. J. Adhes. Sci. Technol. 12, 923–939. https://doi.org/10.1163/156856198X00542.
Danielson, B., Simonson, R., 1998b. Kraft lignin in phenol formaldehyde resin. Part 2. Evaluation of an industrial trial. J. Adhes. Sci. Technol. 12, 941–946. https://doi.org/10.1163/156856198X00551.
Gierer, J., 1980. Chemical aspects of kraft pulping. Wood Sci. Technol. 14, 241–266. https://doi.org/10.1007/BF00383453.
Hermansson, F., Janssen, M., Svanström, M., 2020. Allocation in life cycle assessment of lignin. Int. J. Life Cycle Assess. 25, 1620–1632. https://doi.org/10.1007/s11367-020-01770-4.
Hildebrandt, J., Budzinski, M., Nitzsche, R., Weber, A., Krombholz, A., Thrän, D., Bezama, A., 2019. Assessing the technical and environmental performance of wood-based fiber laminates with lignin based phenolic resin systems. Resour. Conserv. Recycl. 141, 455–464. https://doi.org/10.1016/j.resconrec.2018.10.029.
ISO, 2020. ISO 14044:2006 + A2:2020 Environmental Management. Life Cycle Assessment. Requirements and Guidelines.
Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., Rosenbaum, R., 2003. IMPACT 2002 +: a new life cycle impact assessment methodology. Int. J. LCA 8, 324. https://doi.org/10.1007/BF02978505.
Jönsson, J., Pettersson, K., Berntsson, T., Harvey, S., 2013. Comparison of options for utilization of a potential steam surplus at kraft pulp mills-economic performance and CO 2 emissions: comparison of options for utilizing excess steam at kraft pulp mills. Int. J. Energy Res. 37, 1017–1035. https://doi.org/10.1002/er.2905.
Kuparinen, K., Vakkilainen, E., Tynjälä, T., 2019. Biomass-based carbon capture and utilization in kraft pulpmills. Mitig. Adapt. Strateg. Glob. Chang. 24, 1213–1230. https://doi.org/10.1007/s11027-018-9833-9.
Lawoko, M., Samec, J.S.M., 2023. Kraft lignin valorization: biofuels and thermoset materials in focus. Curr. Opin. Green Sustain. Chem. 40, 100738. https://doi.org/10.1016/j.cogsc.2022.100738.
Lettner, M., Solt, P., Rößiger, B., Pufky-Heinrich, D., Jääskeläinen, A.-S., Schwarzbauer, P., Hesser, F., 2018. From wood to resin—identifying sustainability levers through hotspotting lignin valorisation pathways. Sustainability 10, 2745. https://doi.org/10.3390/su10082745.
Li, Jiongjiong, Zhang, J., Zhang, S., Gao, Q., Li, Jianzhang, Zhang, W., 2017. Fast curing bio-based phenolic resins via lignin demethylated under mild reaction condition. Polymers 9, 428. https://doi.org/10.3390/polym9090428.
Moretti, C., Corona, B., Hoefnagels, R., Vural-Gürsel, I., Gosselink, R., Junginger, M., 2021. Review of life cycle assessments of lignin and derived products: lessons learned. Sci. Total Environ. 770, 144656. https://doi.org/10.1016/j.scitotenv.2020.144656.
Moretti, C., Corona, B., Hoefnagels, R., van Veen, M., Vural-Gürsel, I., Strating, T., Gosselink, R., Junginger, M., 2022a. Kraft lignin as a bio-based ingredient for dutch asphalts: an attributional LCA. Sci. Total Environ. 806, 150316. https://doi.org/10.1016/j.scitotenv.2021.150316.
Moretti, C., Hoefnagels, R., van Veen, M., Corona, B., Obydenkova, S., Russell, S., Jongerius, A., Vural-Gürsel, I., Junginger, M., 2022b. Using lignin from local biorefineries for asphalts: LCA case study for the Netherlands. J. Clean. Prod. 343, 131063. https://doi.org/10.1016/j.jclepro.2022.131063.
Nikafshar, S., Wang, J., Dunne, K., Sangthonganotai, P., Nejad, M., 2021. Choosing the right lignin to fully replace bisphenol A in epoxy resin formulation. ChemSusChem 14, 1184–1195. https://doi.org/10.1002/cssc.202002729.
Perederic, O.A., Mountraki, A., Papadopoulou, E., Woodley, J.M., Kontogeorgis, G.M., 2020. Life cycle analysis of phenol - formaldehyde resins substituted with lignin. Computer Aided Chemical Engineering. Elsevier, pp. 607–612 https://doi.org/10.1016/B978-0-12-823377-1.50102-6.
PRé Sustainability, 2022. SimaPro.
Ragnar, M., Henriksson, G., Lindström, M.E., Wimby, M., Blechschmidt, J., Heinemann, S., 2014. Pulp. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 1–92 https://doi.org/10.1002/14356007.a18_545.pub4.
Sandin, G., Røyne, F., Berlin, J., Peters, G.M., Svanström, M., 2015. Allocation in LCAs of biorefinery products: implications for results and decision-making. J. Clean. Prod. 93, 213–221. https://doi.org/10.1016/j.jclepro.2015.01.013.
Schaubroeck, T., Schaubroeck, S., Heijungs, R., Zamagni, A., Brandão, M., Benetto, E., 2021. Attributional & consequential life cycle assessment: definitions,conceptual characteristics and modelling restrictions. Sustainability 13, 7386. https://doi.org/10.3390/su13137386.
Secchi, M., Castellani, V., Orlandi, M., Collina, E., 2019. Use of lignin side-streams from biorefineries as fuel or co-product? Life cycle analysis of bio-ethanol and pulp production processes. Bioresources 14, 4832–4865.
Siddiqui, H., Mahmood, N., Yuan, Z., Crapulli, F., Dessbesell, L., Rizkalla, A., Ray, A., Xu, C. (Charles), 2017. Sustainable bio-based phenol-formaldehyde resoles using hydrolytically depolymerized kraft lignin. Molecules 22, 1850. https://doi.org/10.3390/molecules22111850.
Sixta, H., Sss, H.-U., Potthast, A., Schwanninger, M., Krotscheck, A.W., 2006. Pulp bleaching: Sections 7.1–7.3.5. In: Sixta, H. (Ed.), Handbook of Pulp. Wiley-VCH Verlag GmbH, Weinheim, Germany, pp. 609–708 https://doi.org/10.1002/9783527619887.ch7a.
Solt, P., Rößiger, B., Konnerth, J., van Herwijnen, H., 2018. Lignin phenol formaldehyde resoles using base-catalysed depolymerized kraft lignin. Polymers 10, 1162. https://doi.org/10.3390/polym10101162.
Statista, 2022. Pulp Industry Worldwide. Statista Dossier on the Global Pulp Industry (No. did-81577-1).
Tokede, O.O., Whittaker, A., Mankaa, R., Traverso, M., 2020. Life cycle assessment of asphalt variants in infrastructures: the case of lignin in australian road pavements. Structures 25, 190–199. https://doi.org/10.1016/j.istruc.2020.02.026.
Tomani, P., Axegard, P., Berglin, N., Lovell, A., Nordgren, D., 2011. Integration of lignin removal into a kraft pulp mill and use of lignin as a biofuel. Cellul. Chem. Technol. 45, 533–540.
UNEP-SETAC, 2011. Global Guidance Principles for Life Cycle Assessment Databases—A Basis for Greener Processes and Products, Shonan Guidance Principles. UNEP-SETAC, Paris, France.
Valmet, 2023. Sulfuric Acid Plant [WWW Document]. URL https://valmet.my.salesforce-sites.com/solutionfinderweb/FilePreview?id = 06958000006k9D0AAI&_ga = 2.20762747.2136867898.1640775242-1307220896.1609846772.
Veas, C., Hotaling, E., 2011. LIGNIN IN TIRE COMPONENTS.
Weidema, B.P., Muñoz, I., 2022. Example – Marginal Electricity in Denmark [WWW Document]. URLconsequential-lca.org. www.consequential-lca.org.
Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., Weidema, B., 2016. The ecoinvent database version 3 (part I): overview and methodology. Int. J. Life Cycle Assess. 21, 1218–1230. https://doi.org/10.1007/s11367-016-1087-8.
Zampori, L., Pant, R., 2019. Suggestions for Updating the Product Environmental Footprint (PEF) Method.