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Environmental Performance of Oxidized Kraft Lignin-Based Products

Neethi Rajagopalan [1,2], Iris Winberg [3], Olesya Fearon [3], Giuseppe Cardellini [1,2,*], Tiina Liitia [3,4] and Anna Kalliola [3,*]

[1] Vlaamse Instelling voor Technologisch Onderzoek (VITO), Boeretang 200, 2400 Mol, Belgium
[2] EnergyVille, Thor Park 831, 3600 Genk, Belgium
[3] VTT Technical Research Centre of Finland Ltd., P.O. Box 1000, FI-02044 Espoo, Finland
[4] Kemira Oy, Research and Development Center, Luoteisrinne 2, FI-02270 Espoo, Finland
* Correspondence: giuseppe.cardellini@vito.be (G.C.); anna.kalliola@vtt.fi (A.K.);
Tel.: +32-14335687 (G.C.); +358-405885748 (A.K.)

Abstract: Bio-based products can help us to reach sustainability goals and reduce our dependency on fossil-based raw materials. Lignin is an abundantly available bio-based material. Recently, a concept of an alkali–O_2 oxidation (LigniOx) process for feasibly producing lignin dispersants at a kraft pulp mill has been introduced. The oxidation process uses O_2 gas to increase the anionic charge of lignin and the final oxidized lignin can serve as a concrete plasticizer or versatile dispersant. Life cycle assessment (LCA) is a tool widely used to holistically evaluate the environmental benefits of various products. The goal of this study was to evaluate the versatility of the novel lignin dispersants produced from kraft lignin and to compare the environmental performance with the synthetic products using an attributional cradle-to-gate LCA. Results showed that LigniOx impacts were lower than synthetic equivalents for both the end uses—superplasticizer and dispersants—in most of the impact categories. The only negative impact was on eutrophication that arises from fly ash purging at the kraft pulping process even without the integrated LigniOx production. In addition, the production of LigniOx lignin appeared to be more attractive than conventionally recovered kraft-lignin. LigniOx contributed minimally to the total impacts with the majority of impacts arising from the kraft pulping process.

Keywords: kraft pulping; oxidation; plasticizer; dispersant; life cycle assessment; bio-based products; product environmental footprint; bioeconomy

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Citation: Rajagopalan, N.; Winberg, I.; Fearon, O.; Cardellini, G.; Liitia, T.; Kalliola, A. Environmental Performance of Oxidized Kraft Lignin-Based Products. *Sustainability* **2022**, *14*, 10897. https://doi.org/10.3390/su141710897

Academic Editors: Lisandra Rocha Meneses, Boboescu Iulian Zoltan, Nemailla Bonturi and Clelton A Santos

Received: 17 July 2022
Accepted: 25 August 2022
Published: 31 August 2022

1. Introduction

The use of bio-based products can help in reducing our dependency on fossil-based raw materials and reach sustainability goals [1]. After cellulose, lignin is the most abundant biopolymer found on earth [2] and has potential as a raw material for several bio-based products. With 100 Mt/y extracted mostly as a by-product of the pulping industry and used for energy production at the mills [3], lignin is a crucial renewable resource for bio-based industries. Driven by the increased biofuel production, this volume is expected to further increase by 2030 to 225 Mt/y [4]. In addition to energy production, it is thus vital to develop technologies that can valorize the lignin by-products into high-value products [5]. Despite this urgent need, less than 2% of the lignin produced worldwide is used to produce bio-based value-added chemicals, such as adhesives and dispersants [4]. To fully exploit these raw material streams, there is an urgent need to commercialize economically and sustainably viable lignin upgrading process technologies that are adaptable to lignin side-streams originating from different processes and raw materials.

Kraft pulping, applied to softwoods and hardwoods, is the most commonly used pulping technology [6]. In the kraft pulp mill, lignin is usually used as fuel on site but it can also be recovered from black liquor using carbon dioxide (CO_2) precipitation followed by sulfuric acid (H_2SO_4) washing, and thereafter marketed [7]. Lignin could be used as a replacement raw material for a variety of chemicals and fossil-based products, such as carbon fiber, bitumen used in asphalt, syngas, bio jet fuel, marine fuel, building material and various oxidized products [8]. However, the market of large volume lignin products is still under development. Currently, kraft lignin is used to replace phenols in phenol formaldehyde (PF) resins for plywood and laminate production. Furthermore, sulfonated kraft lignin is used as a dispersant, similar to lignosulfonates [7,9]. The technical performance of sulfonated lignin is low compared to the current state-of-art synthetic products and only partial phenol substitution is possible in PF resins. The ultimate goal is to create sustainable lignin products that can compete in cost-performance with the current synthetic products, and with a market volume high enough considering the potential lignin capacity.

Recently, a concept of an alkali–O_2 oxidation (LigniOx) process for feasibly producing lignin dispersants at a kraft pulp mill has been introduced. The oxidation process uses O_2 gas to increase the anionic charge of lignin and the final oxidized lignin is water soluble and can serve as a concrete plasticizer or versatile dispersant [10].

Anionic dispersants cover most of the dispersant market. Concrete superplasticizers, such as the fossil-based polycarboxylate ethers (PCE) or sulfonated naphthalene condensate (SNF) are anionic dispersants that disperse cement particles to allow good workability of fresh concrete and ensure good strength properties of the matured concrete. Similarly, anionic dispersants, such as fossil-based polyacrylic acids (PAA) are used in preparing paints and coatings containing a high portion of different inorganic pigments. LigniOx dispersants have been demonstrated to work in these applications. Their performance has been measured to be superior to commercial lignosulfonate products and even to compete with some of the synthetic superplasticizers [11,12].

Lignin and lignin-based products have the potential to contribute to reducing the impact of global warming by substituting a number of fossil-based products [13–15]. Life cycle assessment (LCA) is a tool widely used to holistically evaluate the environmental benefits of various products [16–18]. Several LCAs have been conducted for lignin extraction and lignin-based products in the past e.g., [19–26].

More specially, Moretti et al. [20] found that lignin-based asphalts could reduce the impact on climate change by 30% to 75% compared to conventional asphalts and that using lignin from local biorefineries can reduce the climate change impact of producing bio-based asphalt up until 45% and the environmental cost by 60% compared to that obtained using kraft lignin [21]. Asphalt with 25% lignin instead of bitumen binder was found to reduce by 6% the impact on climate change by Tokede et al. [22]. Yuan et al. [23] showed the environmental superiority of medium-density fiber board (MDF) made using hybrid-modified ammonium lignosulfonate as a binder compared to conventional MDF. Hermansson et al. [24] found indications that shifting to lignin as a source for carbon fibers in the case of carbon fiber reinforced polymer products can result in lower environmental impact than current ones. Bernier et al. [25] showed the environmental soundness of untransformed kraft lignin over synthetic organic compounds of similar molecular complexity. Culbertson et al. [26] showed the environmental potential of using lignin extracted from a kraft pulp mill as a biopolymer.

Previous LCA studies have demonstrated that lignin-based products may be environmentally preferable to synthetic organic compounds of similar molecular structures [25]. In a review by Moretti et al. [27], the cradle-to-gate impact of producing kraft lignin ranges between 0.1 and 2.7 kg CO_2 eq/kg of dry lignin, and lignin-based products are found to reduce the global warming impact compared to the fossil-based references between 2% (lignin-based catechols) and 78% (adipic acid). The authors found important trade-offs between the impact on climate change and that of other areas of protection, which makes it difficult to generalize the results for lignin-based products.

Assessing bio-based products using LCA is challenging due to a variety of value-based choices made in the modeling of products by individual researchers [28,29]. In the literature, the LCAs of lignin have high variability either due to methodological choices, such as system boundaries, functional units, or allocation methods. Furthermore, data uncertainties due to the lack of maturity of some of the processes related to the large-scale manufacturing of lignin-based products and the use of laboratory measurements, such as proxies cause uncertainty [27,30–32].

The goal of this study was to compare the environmental performance of the novel lignin dispersant produced from kraft lignin with the synthetic references using an attributional cradle-to-gate LCA.

2. Materials and Methods

2.1. Lignin Recovery and Oxidation at a Kraft Pulp Mill

The data used for the life cycle assessment were based on a simulation conducted using a model of a softwood kraft pulp mill located in Finland. The model comprises a single-line mill with wood handling, continuous cooking, two-stage oxygen delignification, elemental chlorine-free bleaching (D0-Eop-D1-P), pulp drying, seven-stage evaporation with tall oil recovery, a recovery boiler, recausticizing, a bark-fired lime kiln and a condensing turbine. Some outside boundary limit areas, such as chemical preparation, air separation unit and wastewater treatment plant are excluded from this model. The reference pulp mill was modeled using Wingems 5.3 modeling tool [33] as described in detail by Kangas et al. [34].

For the simulation of the integrated LigniOx process in an existing kraft pulping process, the reference pulp mill was modified by placing lignin recovery, oxidation and membrane filtration steps between evaporators at the pulp mill, as described by Kalliola et al. [10]. In the simulation, lignin is recovered by acidifying the black liquor stream with CO_2, resulting in the precipitation of the lignin. As only 20% of the lignin is recovered, the remaining 80% of lignin in the black liquor still covers the energy need of the mill. The filtrate from the separation stage is directed back to the evaporation plant of the pulp mill, while the recovered lignin continues to the oxidation stage, without needing an acid wash step. After oxidation, the oxidized lignin solution is concentrated by membrane filtration. A schematic representation of the kraft pulp mill including the LigniOx process concept is presented in Figure 1. Parameters relating to lignin recovery and oxidation, as well as to membrane filtration of the oxidized lignin solution are listed in Table 1.

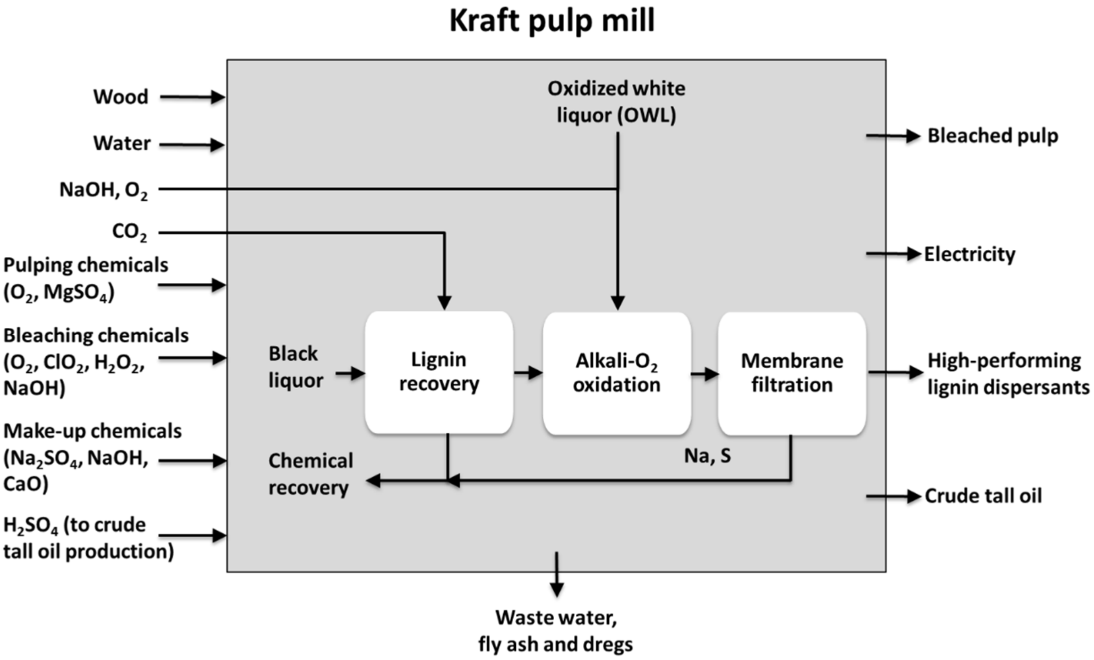


Figure 1. A kraft pulp mill with high-performing lignin dispersants (oxidized kraft lignin) as one of the products along with pulp, crude tall oil (CTO), and electricity.

Table 1. Parameters used in production of oxidized kraft lignin (LigniOx lignin).

Parameter	Unit	Value
Lignin recovery		
Amount of lignin	[%]	20
Black liquor dry content	[%]	37
CO_2 charge	[kg/t lignin]	275
Lignin oxidation		
OWL charge	[kg/t lignin]	205
NaOH charge	[kg/t lignin]	220
Lignin content	[%]	15
Lignin yield	[%]	90
Membrane filtration		
Yield, ox. lignin	[%]	89
Na to retentate	[%]	32
S to retentate	[%]	35

Lignin oxidation was conducted by first dissolving the precipitated lignin in an alkaline solution. Both fresh sodium hydroxide and oxidized white liquor (OWL) produced at the pulp mill were used as a source of alkali. Next, the lignin was oxidized by introducing pressurized O_2 gas into the system. After oxidation, the solution was concentrated using membrane filtration in two stages, of which the first includes a washing step (a diafiltration). In order to recycle sodium (Na) and sulfur (S) back to the pulp mill, the permeate from the membrane filtration process was merged with the black liquor stream. After membrane concentration, the oxidized lignin solution is further concentrated by evaporation to reach a dry content of 40%.

As concluded by Kalliola et al. [10], the integrated lignin oxidation technology using membrane filtration does not increase fly ash purging (composed of Na_2SO_4 and Na_2CO_3) in a kraft pulp mill, as opposed to conventional lignin recovery with H_2SO_4 washing. Increased fly ash purging is unwanted due to increased environmental load and increased costs by make-up NaOH needed in the mill to stabilize the Na/S balance. The conventional lignin recovery process introduces excess sulfur to the mill, which increases the need for both fly ash purging and makeup NaOH. Since unwashed lignin is used for oxidation, such complications are avoided in the studied concept. Although NaOH is added in the oxidation stage, its effect on the chemical balance and total sodium consumption can be minimized by partly using oxidized white liquor as an alkali source.

2.2. *Life Cycle Assessment*

Life cycle assessment (LCA) is a cradle-to-grave or cradle-to-cradle analysis technique to assess the environmental impacts associated with all stages of a product's life. The assessment includes the extraction of raw material through to materials processing, manufacture, distribution, and use and disposal of the final product [35]. In this study, we conducted a cradle-to-gate study for LigniOx lignin. The LigniOx product was expected to replace some fossil-based chemicals, in this sense, the process was compared to the impacts of the conventional materials in order to define the benefits and disadvantages of using a bio-based product. Hence, the production of LigniOx lignin through the kraft pulp mill route was compared with the production of a conventional concrete admixture and a dispersant.

This study aimed to evaluate the potential environmental impacts of the LigniOx lignin used in concrete as a plasticizer or as a versatile dispersant, e.g., in paints, inks, and coatings. The LCA of the production of LigniOx through the oxidation process described in Section 2.1 was compared with the production of plasticizers from fossil raw materials, such as polycarboxylate ethers (PCE) or sulfonated naphthalene. The performance of LigniOx lignins has been experimentally tested in comparison to PCE and sulfonated naphthalene based superplasticizers as well as with polyacrylic acid (PAA) based dispersants. The results have been very promising and in some cases, LigniOx lignin has even outperformed fossil-based products. [11,12]. Thus, the functional unit selected for this study is 1 kg of product (LigniOx or fossil-based superplasticizers and dispersants).

This study was focused only on the production process of LigniOx lignin (Figure 2). It was not relevant to consider all the other life cycle steps since the concrete admixture manufacturing (assembly), as well as the commercialization step, was similar for the LigniOx lignin and the conventional chemicals. In addition, no environmental impacts from the LigniOx were identified during the use phase and this step was omitted. The disposal of the product was omitted as separation of the plasticizer from concrete after use is not seen as a viable option after the end of life. Finally, the infrastructures' impacts were not considered in this study either. Thus, a cradle-to-gate approach is used for this LCA. To summarize, the steps included in this approach are:

1. The raw material supplies (softwood).
2. The transportation of raw materials to the production plant.
3. The manufacturing of the product (including the provision of energy, production of auxiliaries and consumables and waste treatment).

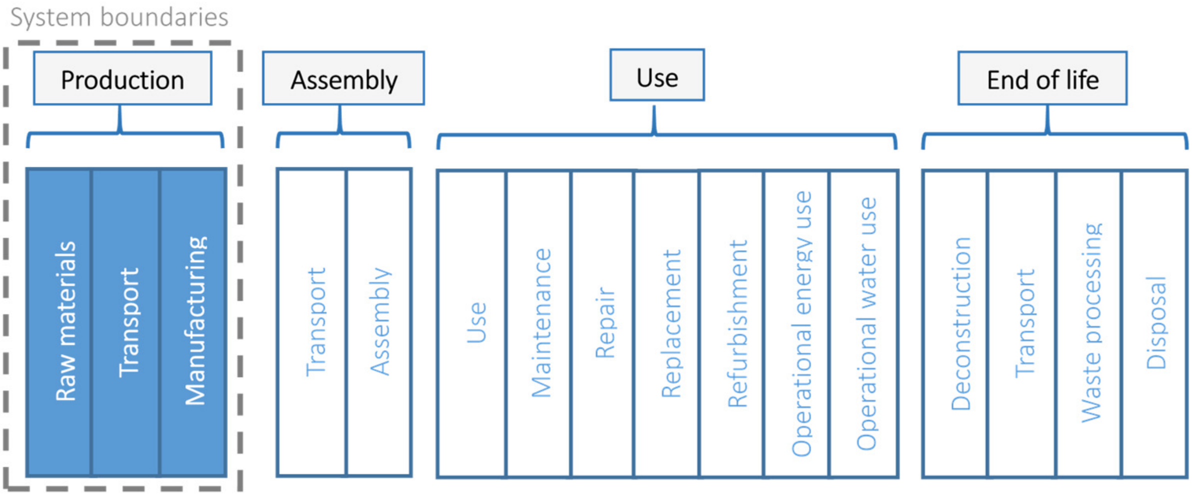


Figure 2. A cradle-to-gate system boundary adopted for conducting LCA of oxidized kraft lignin (LigniOx lignin).

As the kraft pulping process is multifunctional, several approaches can be envisaged. Any system that produces multiple by-products needs to solve the multifunctionality problem either by applying system expansion or allocation, as referred to in ISO 14040-44 [36]. The simulated kraft pulp mill provides three coproducts: bleached pulp, crude tall oil and LigniOx lignin amongst which environmental impacts must be allocated. The ISO standard recommends avoiding allocation by expanding the system to include all by-products in the functional unit or partitioning the system under investigation to mono-function processes. If this kind of partitioning is not possible, then the allocation is conducted based on physical properties, such as mass, energy, or revenue [37]. This study adopted a mass-based allocation between the LigniOx lignin and other by-products, as the price of the novel LigniOx product was not fixed.

All the modeling for this study was conducted using the SimaPro software tool (version 9.2) [38] and Ecoinvent version 3.7.1 [39] and the complete life cycle inventory is shown in Table 2.

Table 2. Life Cycle Inventory for the production of 1000 kg of bleached pulp, 84.2 kg of LigniOx lignin and 38.5 kg of crude tall oil. In parenthesis the geographical representativeness of the datasets (RER: Rest of the World; GLO: Global; FI: Finland).

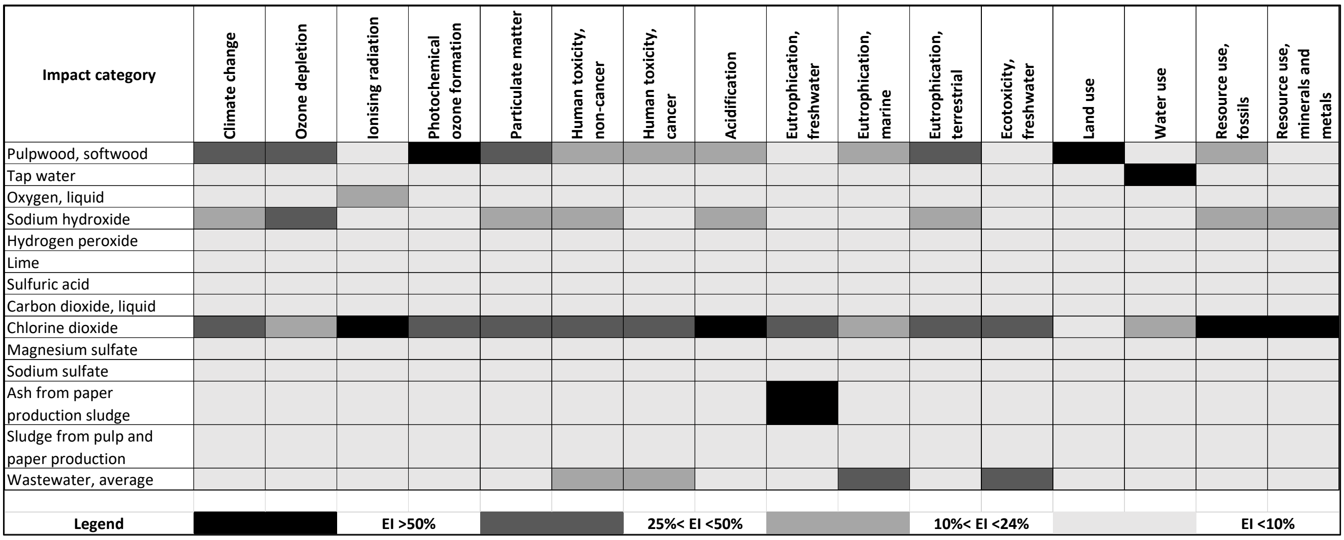
Inputs	Unit	Kraft Mill Integrated Case	Related Dataset of Ecoinvent (v3.7.1)
Wood	m^3	5.7	Pulpwood, softwood, measured as solid wood under bark (Europe without Switzerland)
Water	m^3	46.8	Tap water (RER)
Oxygen	kg	62.6	Oxygen, liquid (RER)
Magnesium sulfate	kg	3.77	Magnesium oxide (RER)
Chlorine dioxide	kg	39	Chlorine dioxide (RER)
Sodium hydroxide	kg	49.2	Sodium hydroxide, without water, in 50% solution state (GLO)
Hydrogen peroxide	kg	7.4	Hydrogen peroxide, without water, in 50% solution state (GLO)
Lime	kg	5.56	Lime (GLO)
Sulfuric acid	kg	4.9	Sulfuric acid (RER)
Carbon dioxide	kg	28.8	Carbon dioxide, liquid (RER)
Sodium sulfate	kg	12.4	Sodium sulfate, anhydrite (RER)
Membrane	m^3	0.06	Polystyrene, general purpose (GLO); Thickness of membrane: 250 micron; density of PS: 50 kg/m^3
Electricity	kWh	416	Electricity, medium voltage (FI)
Fly ash	kg	12	Ash from paper production sludge (Europe without Switzerland)
Brine	kg	1.6	Sludge from pulp and paper production (Europe without Switzerland)
Wastewater	m^3	19.1	Wastewater, average (Europe without Switzerland)
Wastewater	m^3	19.1	Wastewater, average (Europe without Switzerland)

The benchmark used for this study was a fossil-based superplasticizer consisting of sulfonated naphthalene formaldehyde, sulfonated melamine formaldehyde, vinyl copolymers and polycarboxylic ethers and a fossil-based poly sodium acrylate. The data for the fossil-based superplasticizer were obtained from an environmental product declaration from the European Federation of Concrete Admixture Associations [40]. The active content noted in the eco-profile of the superplasticizer was 30–45%. Hence, an average value of 37.5% was used and all inputs and outputs were divided by 37.5% to provide the LCIA for the superplasticizer since LigniOx lignin was evaluated at 100% active content. The poly sodium acrylate was derived from Gontia and Janssen [41] and was used as a proxy for fossil-based poly acrylic acid (PAA) since no detailed life cycle inventory was available for the PAA.

3. Results

A life cycle impact assessment (LCIA) was conducted on the LigniOx lignin case and compared with a fossil-based dispersant and a fossil-based superplasticizer. The life cycle impact assessment for LigniOx lignin and the fossil-based products was conducted using the Environmental Footprint method 3.0 (EF 3.0). The European Commission developed the Product Environmental Footprint (PEF) method as a way to "Establish a common methodological approach to enable member states and the private sector to assess, display and benchmark the environmental performance of products, services and companies based on a comprehensive assessment of environmental impacts over the life-cycle ('environmental footprint')" [42]. The environmental footprint method provides a detailed approach to full life cycle accounting for a product along with relevant environmental impact indicators to measure performance. All products were evaluated for all the 16 midpoint impact categories available in the EF 3.0 method. Of these sixteen impact categories, the impact categories of climate change, acidification, eutrophication of freshwater and use of fossil resources were chosen for comparison across the LigniOx lignin and fossil-based benchmark superplasticizer and dispersant. A complete LCIA of all sixteen impact categories is shown in Appendix A.

Detailed hotspot analysis of the LigniOx product was conducted to identify impacts emanating from each impact category. The results are shown in Figure 3 and include the impacts for LigniOx lignin in all impact categories. The hotspot analysis for LigniOx showed that chlorine dioxide used for bleaching pulp had the highest contribution in most impact categories. Chlorine dioxide had a greater than 50% impact on the categories of photochemical ozone formation, acidification, use of fossil resources and the use of minerals and metals (Figure 3). The chlorine dioxide input was used in the bleaching of pulp and contributed the most to the environmental impact. Additional impacts arose from the use of softwood pulpwood as the biomass for producing kraft pulp. The pulpwood had a greater than 50% contribution to the impact categories of land use, photochemical ozone formation and the use of water. The output of ash from the pulp mill contributed more than 50% to the impact category of eutrophication of freshwater. The contribution analysis showed that the LigniOx process itself had minimal impacts in this integration to the pulp mill and the majority of impacts arose from the kraft pulp mill used to produce the lignin.



Impact category	**Climate change**	**Ozone depletion**	**Ionising radiation**	**Photochemical ozone formation**	**Particulate matter**	**Human toxicity, non-cancer**	**Human toxicity, cancer**	**Acidification**	**Eutrophication, freshwater**	**Eutrophication, marine**	**Eutrophication, terrestrial**	**Ecotoxicity, freshwater**	**Land use**	**Water use**	**Resource use, fossils**	**Resource use, minerals and metals**
Pulpwood, softwood	▓	▓	░	■	▓	▒	▒	▒	░	▒	▓	░	■	░	▒	░
Tap water	░	░	░	░	░	░	░	░	░	░	░	░	░	■	░	░
Oxygen, liquid	░	░	▒	░	░	░	░	░	░	░	░	░	░	░	░	░
Sodium hydroxide	▒	▓	░	░	▒	▒	░	▒	░	░	▒	░	░	░	▒	▒
Hydrogen peroxide	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Lime	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Sulfuric acid	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Carbon dioxide, liquid	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Chlorine dioxide	▓	▒	■	▓	▓	▓	▓	■	▓	▒	▓	▓	░	▒	■	■
Magnesium sulfate	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Sodium sulfate	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Ash from paper production sludge	░	░	░	░	░	░	░	░	■	░	░	░	░	░	░	░
Sludge from pulp and paper production	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
Wastewater, average	░	░	░	░	░	▒	▒	░	░	▓	░	▓	░	░	░	░
Legend	■		**EI >50%**		▓		**25%< EI <50%**		▒		**10%< EI <24%**		░		**EI <10%**	

Figure 3. Contribution analysis for the LigniOx process showing the relative contribution to the environmental impact (EI) of each input.

A comparison with fossil-based products was conducted to evaluate all impact categories. The oxidized kraft lignin performed better than the fossil-based dispersant in the impact categories of climate change, acidification and the use of fossil resources (Figure 4) (normalized results are shown here and readers can refer to actual values for each impact category for each product in Appendix A).

The impact category of freshwater eutrophication was higher for the oxidized kraft lignin than for the fossil reference. This was due to the high ash production from the kraft pulping process. The fossil-based dispersant performed better than the LigniOx lignin in the eutrophication of freshwater impact category due to this.

The LigniOx lignin performed better than the fossil-based superplasticizer in all the impact categories of climate change, acidification, eutrophication of freshwater and use of fossil resources (Figure 5). Similarly to Figure 4, normalized results are shown in Figure 5 and the reader is referred to Appendix A for more detailed data.

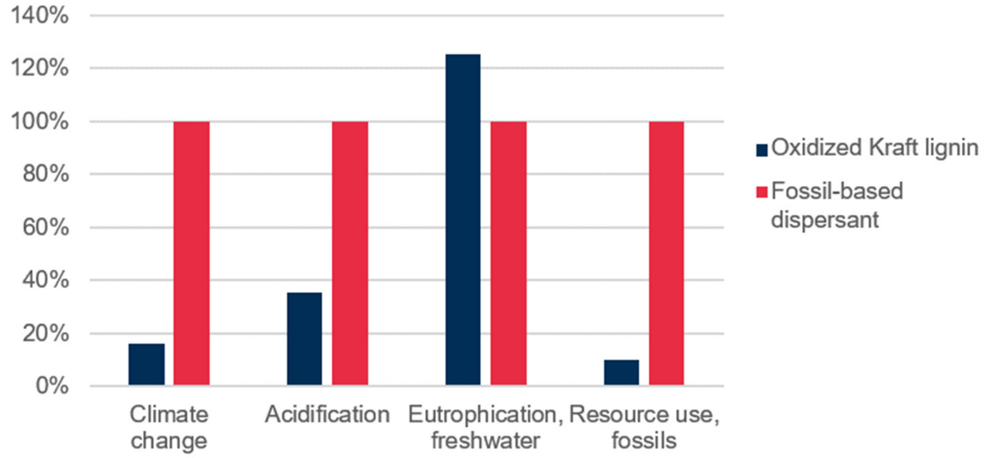


Figure 4. Comparison of the oxidized kraft lignin (LigniOx lignin) and a fossil-based dispersant (poly (sodium acrylate) acid).

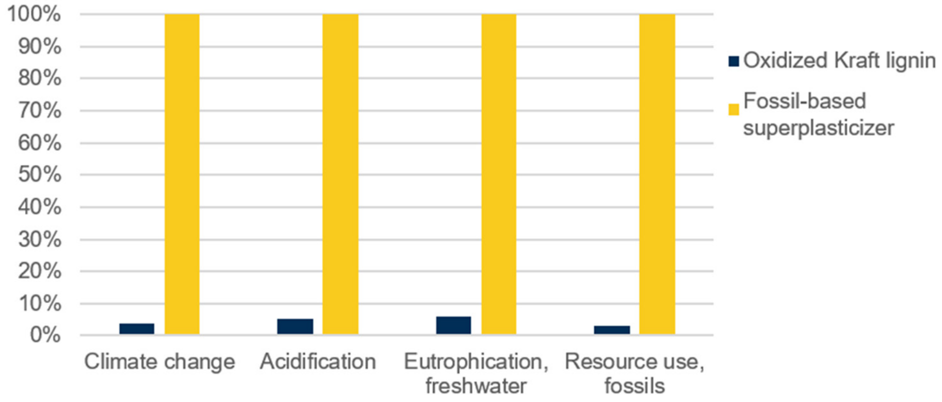


Figure 5. Comparison of oxidized kraft lignin (LigniOx lignin) with fossil-based superplasticizer admixture.

For the current research, it is beneficial to understand how oxidized kraft lignin performs from an environmental point of view, in comparison with other bio-based alternative products available on the market. The impact of LigniOx lignin was thus compared to the impact of other lignin and carbohydrate-based products, in addition to the widely utilized fossil-based dispersants—lignosulfonates, carboxymethyl cellulose and hemicellulose originated poly sodium acrylate acid are used as bio-based dispersants or rheology modifiers. The reference products used were a conventionally recovered kraft lignin from a kraft pulp mill [26,31], hybrid modified ammonium lignosulfonate (a binder) [23], carboxymethylated cellulose (a rheology modifier) obtained from the Ecoinvent database 3.7.1 [39] and a bio-based poly sodium acrylate which is a proxy for bio-based PAA [43]. Yuan et al. [23] conducted the LCA on the basis of 1 m^3 of a lignosulfonate-based binder. To compare results with our work, the results provided in 1 m^3 were harmonized to 1 kg of the product by using the provided density for the product (0.86 g/cm^3). LigniOx lignin performed clearly better in the impact category of global warming than carboxymethyl cellulose and a bio-based PAA (Figure 6). Furthermore, only the lignosulfonate-based binder outperformed the oxidized lignin in the global warming potential.

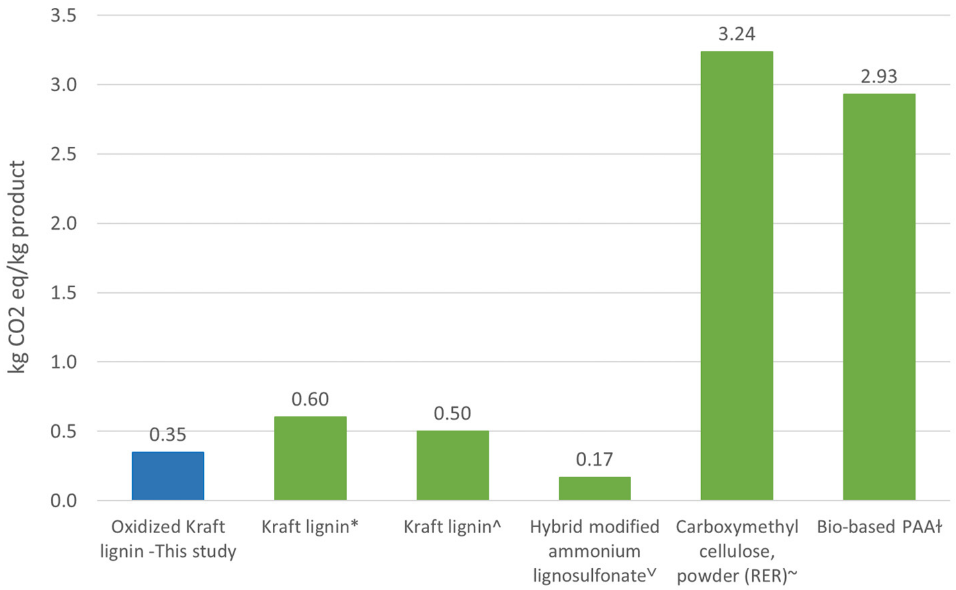


Figure 6. Global warming potential—Comparison of oxidized kraft lignin (LigniOx) with kraft lignin, modified lignosulfonate, and other bio-based products, such as carboxymethylated cellulose and a bio-based poly sodium acrylate acid which is a proxy for bio-based poly acrylic acid (PAA). The legend for the symbols on the figure indicates the source from where data is obtained: * Culbertson et al. [26], ∧ Hermansson et al. [31], ∨ Yuan et al. [23], ~ Ecoinvent 3.7.1 dataset [39], ⱡ Nuss et al. [43].

The results indicate that LigniOx lignin is competitive when compared with other lignin-based products when global warming impacts are analyzed. Taking into account that the compared studies are all cradle-to-grave and follow a mass-based allocation makes them relatively comparable from a methodological perspective. The fact that they differ in the production location obviously influences the results, e.g., the carbon intensity of the energy mix is different from country to country. Due to differences in impact assessment methods used in various studies, a complete comparison with all impact categories affecting human health or ecosystems was not evaluated. Harmonization of all the data would be required to conduct this study which is considered beyond the scope of this paper.

4. Discussion

Our results indicate that LigniOx performs better than the fossil-based equivalents in most impact categories. The impact on water eutrophication was higher for LigniOx when compared with fossil-based dispersants (PAA). This was due to the generation of fly ash in/by the kraft pulping process already without a lignin recovery or valorization process. The LigniOx process itself caused minimal impacts when integrated with the kraft pulping process. However, when compared to a fossil-based superplasticizer, LigniOx lignins had better performance in all impact categories. Furthermore, as demonstrated by the recent study [10], the conventional production of kraft lignin (including H_2SO_4 washing) at a pulp mill strongly increases the purging of fly ash when compared to the pulping process without lignin recovery or to the integrated production of LigniOx lignin. Additionally, when considering the data on global warming potential presented in recent studies [26,31], the production of LigniOx lignin appeared to be more attractive than the production of conventionally recovered kraft lignin.

Although the use of bio-based products is perceived as ecological when compared to the fossil sourced counterparts, the increased use of bio-based products can cause negative effects. The main negative effects include rising demand for land, owing to the increased consumption of the biomass feedstock requiring the additional land area to be grown and the increased risk of eutrophication of aquatic environments, which is mainly caused by the release of fly ash [1]. Currently, there are several methods proposed for an ecological and economic valorization of fly ash [44]. Although the proposed technologies have yet to be successfully commercialized, this is expectable to happen in the future. The utilization of fly ash for sustainable applications will contribute to drastically mitigating the eutrophication impact of lignin-based products.

It should be highlighted that care needs to be applied when interpreting these results. The system boundary is relatively narrow since it only included the extraction of raw materials extraction and the manufacturing phases. The LigniOx lignins do not have any significant impacts in the use phase and the end-of-life phase and will be similar to fossil-based products. The LigniOx lignin cannot be easily extracted from the application it is used in and hence recycling is not an option. These barriers prevent a complete life cycle assessment for LigniOx and hence only the raw materials extraction and manufacturing were evaluated to maintain consistency with the comparative product. It is relevant to mention that when bio-based products are included in building LCAs (such as concrete superplasticizers used in building materials), limiting the system boundary to only the manufacturing phase can lead to incomplete results [45,46]. Given the multiple possible end uses of LigniOx lignin, a cradle-to-gate system boundary provides an opportunity to compare across multiple products. The study also does not include the biomass growth phase apart from not including the end of life of LigniOx even though these are critical aspects in a life cycle study of bio-based products [47]. Nor does it tackle the issue of multiple systems of bio-based products and claims on carbon capture in each system. The multiple end uses of LigniOx prevent such calculations that might be possible for a product, such as a timber beam that can either be incorporated back into forestry or can be used as a source of heat or electricity [48,49].

The mass allocation method favors the LigniOx product over the co-products (pulp and crude tall oil) due to the physical nature of the allocation. A sensitivity analysis with economic allocation would be highly uncertain as LigniOx lignin is not commercially produced and costs are variable and confidential across manufacturers. In the future, given that LigniOx lignin is in larger scale production, accurate economic values can be obtained for a thorough sensitivity analysis using economic allocation.

It should be noted that a majority of the impacts for LigniOx arose from the kraft pulping process. LigniOx did not interfere with the main process and contributed minimally to the total environmental impacts. This bodes well for future commercialization of the product as the lignin oxidation process described in this study can be adapted for various other cases.

The biodegradation of a dispersant plays an important role in LCA and the waste management of the end-products. PAA is considered non-harmful to the environment and human health. However, recent studies demonstrated that PAA could accumulate in the environment and during biodegradation some toxic compounds could be released. Some discussions on regulations for controlling the use and waste management of acrylic polymers (AP) have been raised [50]. Sodium naphthalene-1-sulfonate which is utilized for dispersant formulations was reported not to be readily degradable in nature. Based on the ECHA information, sodium naphthalene-1-sulfonate is not persistent in the soil environment nor in sediment in the water, and therefore, the risk to soil-dwelling animals and the exposure risk to aquatic animals are moderate to low, respectively [51]. Additionally, microplastic regulations will be adopted relatively soon. In some versions of the regulation, lignin recovered from biorefineries could be considered a microplastic, due to its particle size, insolubility and low biodegradation. Recently, the biodegradability of LigniOx lignins in soil and the aquatic environment was followed by measuring CO_2 evolution. Kraft lignin and a lignosulfonate product were tested for comparison. The study indicated that oxidation of lignin increases its biodegradation [52]. Moreover, LigniOx lignins are fully soluble in water at room temperature, and therefore, they are expected to be excluded from the coming microplastic regulations.

5. Conclusions

An attributional cradle-to-gate life cycle assessment shows that the impacts of alkali-O_2 oxidized (LigniOx) kraft lignin, a versatile biodispersant, are lower than the synthetic equivalents of a concrete superplasticizer admixture or a polyacrylic acid-based dispersant. In this study, the production of LigniOx lignin was integrated into an existing kraft pulp mill. The majority of environmental impacts of LigniOx lignin were from the main kraft pulping process, e.g., eutrophication that originates from the fly ash purging as well as chlorine dioxide and acidification that originate from chlorine dioxide bleaching of kraft pulp fibers. This study indicates that the production of LigniOx lignin is more attractive than the production of conventionally recovered kraft lignin. In addition, the results of LigniOx lignin were better when compared with other bio-based products, such as polyacrylic acids and carboxymethylated cellulose. The novelty and sustainability of this unique LigniOx lignin are established through this study. Future research on various other end-uses and their sustainability should be evaluated at a later stage when LigniOx is commercialized at a larger scale.

Author Contributions: Conceptualization, N.R., I.W., O.F. and A.K.; methodology, N.R., I.W., O.F. and A.K.; formal analysis, N.R. and I.W.; writing—original draft preparation, N.R. and I.W.; writing—review and editing, N.R., O.F., G.C. and A.K.; funding acquisition, T.L. and A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement n° 745246. Programme: H2020 BBI-2016-D03: Valorization of lignin and other side-streams to increase the efficiency of biorefineries and increase the sustainability of the whole value chain.

Acknowledgments: Katariina Kemppainen from Metsä Spring is acknowledged for the discussion and consultancy. Miriam Kellock is acknowledged for helping to edit this manuscript.

Conflicts of Interest: The authors declare no conflict of interests.

Appendix A

Table A1. Life cycle impact assessment of LigniOx lignin, fossil-based superplasticizer and the fossil-based dispersant. The impact assessment method used is Environmental Footprint (EF) method 3.0.

Impact Category	Unit	Ligniox Lignin	Fossil-Based Superplasticizer	Fossil-Based Dispersant
Climate change	kg CO_2 eq	3.47×10^{-1}	9.32×10^{0}	2.16×10^{0}
Ozone depletion	kg CFC11 eq	6.92×10^{-8}	7.24×10^{-7}	3.77×10^{-7}
Ionizing radiation	kBq U-235 eq	2.08×10^{-2}	1.28×10^{0}	1.66×10^{-1}
Photochemical ozone formation	kg NMVOC eq	1.75×10^{-3}	2.40×10^{-2}	4.78×10^{-3}
Particulate matter	disease inc.	1.95×10^{-8}	2.15×10^{-7}	6.53×10^{-8}
Human toxicity, non-cancer	CTUh	8.89×10^{-9}	5.76×10^{-8}	2.09×10^{-8}
Human toxicity, cancer	CTUh	5.48×10^{-10}	1.61×10^{-9}	7.13×10^{-10}
Acidification	mol H+ eq	2.56×10^{-3}	4.79×10^{-2}	7.25×10^{-3}
Eutrophication, freshwater	kg P eq	5.99×10^{-4}	1.03×10^{-2}	4.78×10^{-4}
Eutrophication, marine	kg N eq	9.17×10^{-4}	9.13×10^{-3}	1.39×10^{-3}
Eutrophication, terrestrial	mol N eq	4.75×10^{-3}	8.07×10^{-2}	1.37×10^{-2}
Ecotoxicity, freshwater	CTUe	1.67×10^{1}	7.59×10^{1}	2.35×10^{1}
Land use	Pt	2.76×10^{2}	1.59×10^{1}	3.34×10^{0}
Water use	m^3 depriv.	1.41×10^{0}	2.60×10^{-1}	9.70×10^{-1}
Resource use, fossils	MJ	4.32×10^{0}	1.41×10^{2}	4.31×10^{1}
Resource use, minerals and metals	kg Sb eq	4.67×10^{-6}	1.41×10^{-5}	1.91×10^{-5}

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