

Life Cycle Environmental Impact Considerations in the Design of Novel Biobased Polyurethane Coatings

Heather E. Wray,[‡] Stefania Luzzi,^{*,‡} Paola D'Arrigo, and Gianmarco GriffiniCite This: *ACS Sustainable Chem. Eng.* 2023, 11, 8065–8074

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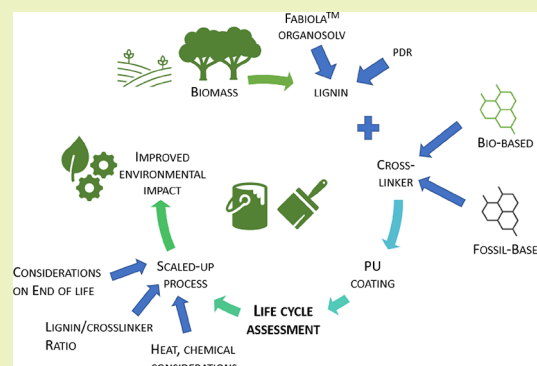
Article Recommendations



Supporting Information

ABSTRACT: Substituting fossil-based with biobased chemical building blocks can potentially decrease the environmental impact of polyurethane (PU) coating production. This study applies life cycle assessment methods in the early development of three processes that incorporate biobased elements into PU coating production: a fully biobased coating made with organosolv lignin (OSL) and a biobased cross-linker from vanillic acid (VA) and two hybrid coatings made with a fossil-based cross-linker and either OSL or depolymerized OSL. Coatings with biobased elements had impacts of 1.5, 2.6, and 19.9 kg CO_{2eq}/kg_{coating} for coatings made with OSL, depolymerized OSL, and the fully biobased coating, respectively. Emissions are mostly associated with the fossil-based cross-linker in hybrid coatings and with solvents and heat needed for the production of the biomass-derived cross-linker. While this study demonstrates that the use of biobased compounds in hybrid coatings can reduce the environmental impacts of PU coatings in comparison to fossil-based versions, additional development of biobased cross-linkers and research into end-of-life scenarios are needed to further reduce the environmental impacts of biobased PU coating production.

KEYWORDS: life cycle assessment, biobased, polyurethane coatings, organosolv lignin, environmental impact



INTRODUCTION

The ongoing energy and materials transitions prescribe a shift from fossil-based to biobased resources. To “de-fossilize” materials and chemicals, some biomass feedstocks are becoming increasingly popular as alternatives to fossil-based feedstocks as they may have a lower environmental impact, for example, greenhouse gas (GHG) emissions.¹ The chemical structure of biomass-derived molecules allow for the production of novel biobased materials, such as polymers.²

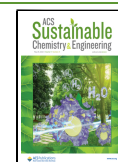
Polyurethanes (PUs) are a class of polymeric materials widely used for various applications including coatings, foams, adhesives, sealants, and elastomers.³ Coatings represent a particular use-case for PUs with a large market (5.9 million tons of global sales valued at EUR 28 billion in 2020)⁴ and numerous applications, in particular for automotive, transportation, construction, electronics, wood, and furniture industries. Today, PUs, including coatings, are principally made from fossil-derived resources such as crude oil and natural gas⁵ and their production has negative impacts with respect to the environment and human health.⁶ As a result, water-borne PU (WB-PU) production from petroleum sources⁷ has gained significance over traditional solvent-borne PU processes to comply with increasingly strict environmental and occupational health regulations. However, efforts are still needed to develop biobased pathways for PU coating production (both water-borne and solvent-borne),

substituting all or part of the petroleum-based building blocks, i.e., polyols and isocyanates, with those from biomass sources. Recent LCA studies on biobased PU production methods have shown greenhouse gas emissions reductions when compared to the production of fossil-based PU. For example, vegetable oil-based polyols were shown to have up to 3.0 kg CO_{2eq} reduction per kg polyol when compared to fossil-based polyols.⁸ In addition, a novel biobased polyester polyol has also been cross-linked with a fossil-based polyisocyanate to create a PU coating with up to a 79% reduction in GHG emissions when compared to a fossil-based coating.⁹ Lignin is also of increasing interest as a biobased feedstock for the production of aromatic-based materials and chemicals,¹⁰ including PUs,¹¹ specifically as a polyol replacement.¹² Organosolv processes are frequently used to fractionate lignocellulosic biomass into different streams, including lignin. One such method is the Fabiola process, which is an acetone organosolv process that has been successfully used on hardwood and herbaceous biomass feedstocks.^{13,14} Recent

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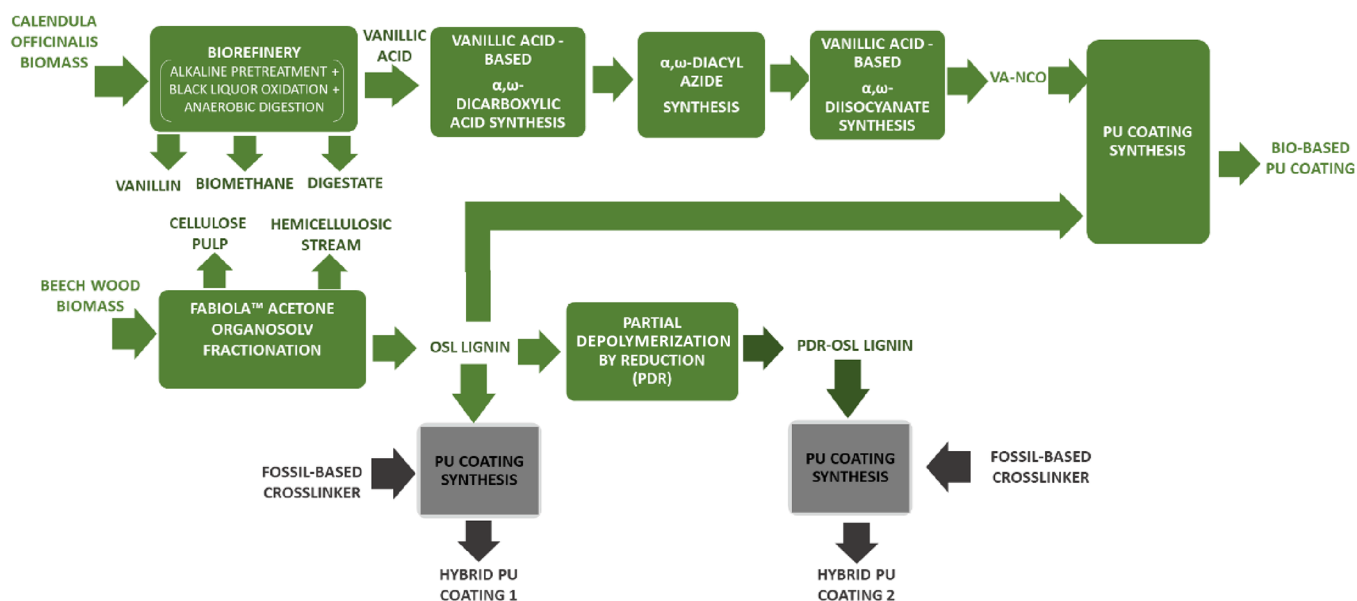


Figure 1. Schematic of the processes to produce a fully biobased PU coating¹⁷ and hybrid PU coatings; VA = vanillic acid, OSL = organosolv lignin. Impacts are allocated using economic allocation among the products of the biorefinery process and the organosolv fractionation.

research has also demonstrated that Fabiola organosolv lignin (OSL) can be further tailored via partial depolymerization by reduction (PDR), allowing tunability of the lignin characteristics to specific applications, including coatings.¹⁵

Biobased isocyanates represent a particular challenge for PU coating production, and research and development has been mainly limited to isocyanate-free PUs as a means of de-fossilizing the process.¹⁶ Recent research has led to the development of a fully biobased PU coating, including biobased isocyanates, at laboratory scale.¹⁷

Although promising for de-fossilizing PU coating production, the use of biobased building blocks will still have environmental impacts, in particular associated with the use of energy, solvents, and chemicals. With respect to environmental and human health impacts of different biobased PU coatings, a better understanding of “hotspots” of environmental impact and comparisons between different production pathways is needed, especially for fully biobased coatings. Life cycle assessment (LCA) is a tool that is widely used to quantify environmental impacts of a product or process over its life cycle. This evaluation is particularly important at early stages of development of new biobased production pathways as this information can be used to improve the environmental performance of the process before scale-up.

The main objectives of this study are to (1) evaluate the environmental impact of the production of PU coatings from biobased materials, both 100% biobased (lignin as polyol and biobased cross-linker) and partially (hybrid) biobased (lignin as polyol and fossil-based isocyanate as cross-linker), and (2) compare the environmental impacts of the biobased and hybrid PU coatings with those of fossil-based PU coatings. The LCA is used to evaluate the environmental impact of the biobased PU coatings and provide recommendations for improvement of the processes for prospective scaled-up production.

DESCRIPTION OF CASE STUDIES

This study examined the environmental impacts of three novel processes for the production of biobased PU coatings: two

partially biobased processes (hybrid approach) and one fully biobased process. These processes were then compared to production of PU coatings with fossil-based building blocks.⁷ The hybrid processes for PU coatings used lignin obtained *via* pilot-scale acetone organosolv (OSL) or partially depolymerized (PDR) OSL^{18,19} as polyols and a commercially available hexamethylene diisocyanate-based poly-isocyanate cross-linker (pHMDI) with the trade name Desmodur N 3900 (Covestro AG, Germany). The fully biobased coating was modeled based on the process described by de Haro et al.¹⁷ This study used unmodified technical lignin as macropolyols and a diisocyanate (1,4-bis(4-isocyanato-2-methoxyphenoxy)butane, referred to as VA-NCO) based on vanillic acid (VA) for the production of PU coatings. Lignin derived from different pulping processes was utilized, namely, beech wood Fabiola OSL, softwood kraft lignin, and wheat straw soda lignin. The current study focused on the use of OSL only for LCA of biobased PU coatings. A schematic of the different PU coating production pathways with biobased elements is presented in Figure 1. For comparison with fossil-based PU coatings, four different methods of water-borne PU coating production with fossil-based building blocks were used as reference cases. In all cases, target PU materials of comparable performance were considered, with tunable glass transition temperatures (T_g) ranging between 110 and 180 °C, high adhesion on different substrates (e.g., glass, metal, wood), and tunable surface energy as a function of composition and lignin type.¹⁵

MODELING SECTION: BUILDING THE LCA MODEL

The LCA methods were used as a tool to assess the environmental impacts and identify areas for improvement of different processes to synthesize PU coatings. The LCA models were built according to the international standards ISO 14040²⁰ and ISO 14044.²¹ SimaPro v.9.4 software in combination with Ecoinvent v.3.8 and Industry 2.0 databases was used to develop the models and for inventory data that was not available from the literature or experiments.

Goal and Scope of the LCA Study. The goal of the current study was to determine the environmental impacts of

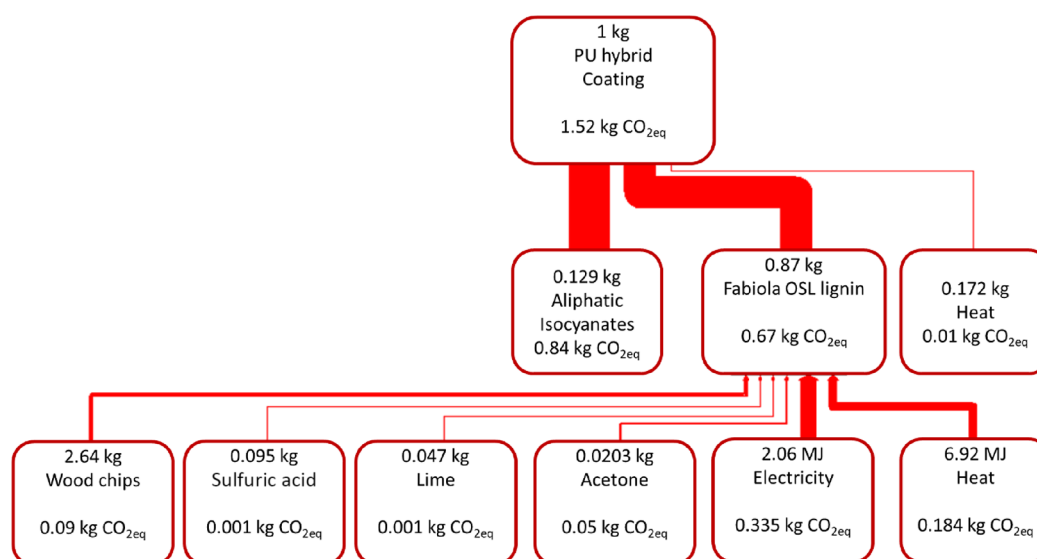


Figure 2. Most significant contributors to global warming potential (GWP) impacts, i.e., CO_{2eq} emissions, for the production of 1 kg of hybrid PU coating (organosolv lignin and fossil-based cross-linker).

PU coatings synthesized fully and partially from biobased building blocks and compare these impacts with those of conventional PU coatings synthesized entirely from fossil-based components. This study measured impacts for lab-scale production of PU coatings via the different processes and aims to provide insight into the potential for improved environmental impacts for further process development and scale-up.

Environmental impacts were measured as CO₂ equivalent (CO_{2eq}) emissions according to the IPCC2021 method.²² Results of the LCA models are presented both with and without CO₂ uptake considered; where CO₂ uptake is included, it accounts for biogenic CO₂ uptake during the biomass growth. The actual amount of carbon (as CO₂ equivalents) stored in the final product/coating is also reported. Impact is expressed as Global Warming Potential over a 100-year horizon (GWP100), in units of kg CO_{2eq}. Additional impacts were evaluated via the ReCiPe method,²³ which derives weighted values for damages to 18 different midpoint level categories that can be aggregated into three end-point impact categories: ecosystems, human health, and resource scarcity. Economic allocation was applied to allocate environmental impact among the main products and by-products of the Fabiola process (i.e., lignin, cellulose pulp, and hemicellulose C5 sugars) and among the main products of the biorefinery process (vanillic acid, vanillin, and biomethane). Economic allocation was used because it best represents the connection with the overall biorefinery process, i.e., the biorefinery operates to produce multiple marketable and high-value products. Further results and descriptions of the models, including with mass allocation, are presented in the [Supporting Information](#).

System Boundaries. This study uses a “cradle-to-gate” LCA model, meaning that the final product considered is the prepared PU coating. The LCA therefore considered the impacts of the feedstock(s) and the synthesis of the PU coatings. End-of-life (waste treatment) of the PU coatings was not considered as part of the LCA model in this work, but implications of end-of-life scenarios are discussed in detail in the [Results and Discussion](#) section.

Functional Unit. The functional unit for the study is the production of 1 kg of PU coatings via the different processes.

Life Cycle Inventory Data. The LCA model was developed with data from the literature, in particular for lab-scale experiments for the production of biobased and hybrid coatings. Data for the extraction of lignin *via* the Fabiola process was obtained from Smit et al.¹⁹ for a commercial-scale process. Data for subsequent depolymerization of OSL was also taken from the literature.¹⁸ Literature data was also used to generate the inventory of specific chemicals used in the synthesis of VA.²⁴ Life cycle inventory data for the production of water-borne PU coatings from fossil-based processes was taken from Klug et al.⁷

Additional data was sourced from databases (Ecoinvent 3.8 and Industry 2.0), namely, data for the impacts associated with biomass feedstocks (including cultivation, fertilizer, pesticides, harvesting, and transportation as appropriate) commonly used solvents, catalysts, and chemicals. For inventory materials not present in any database, the best available proxy was used. For example, biomass for VA production was *Calendula officinalis* (marigold), which is not available in Ecoinvent. Therefore, a proxy (alfalfa) was used. The energy input required for the synthesis of the biobased and hybrid coatings and for the PDR process was estimated using ASPEN Plus (Aspen Technology, Inc., Bedford, MA). A complete overview of the life cycle inventory data and methodology used to perform mass and economic allocations for the different PU coating production processes are available in the [Supporting Information](#). The Data Quality Requirement (DQR) for the PU coating production processes and biomass is reported in [Table S12](#). The DQR for each process step/biomass was assessed following the International Reference Life Cycle Data System (ILCD) handbook,²⁵ where 1 is “very good” and 5 is “poor”. Most of the data quality ranges from 1.0 to 3.0, with the exception of the biorefinery process and biomass to produce vanillic acid, which have a DQR of 3.4 and 3.6, respectively.

RESULTS AND DISCUSSION

Organosolv Lignin Production. The impact of producing 1 kg of Fabiola OSL is 0.77 kg CO_{2eq} per kg of lignin produced

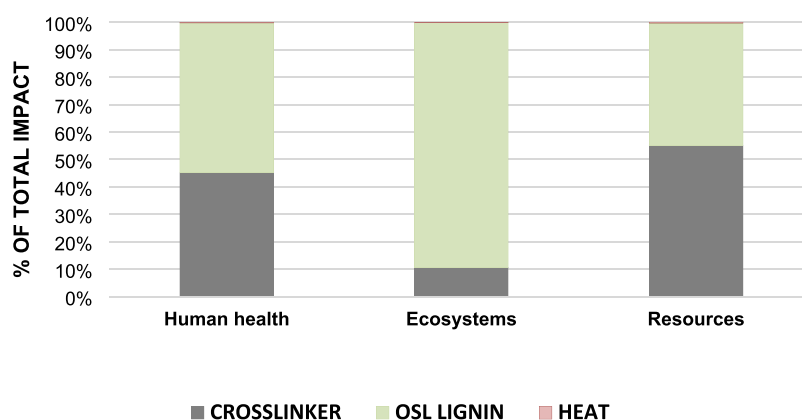


Figure 3. Relative impacts associated with *Fabiola* organosolv lignin (OSL) and fossil-based cross-linker in the production of 1 kg of hybrid PU coating (87% lignin, 13% cross-linker by mass) for various endpoint environmental impact categories (hierarchist perspective).

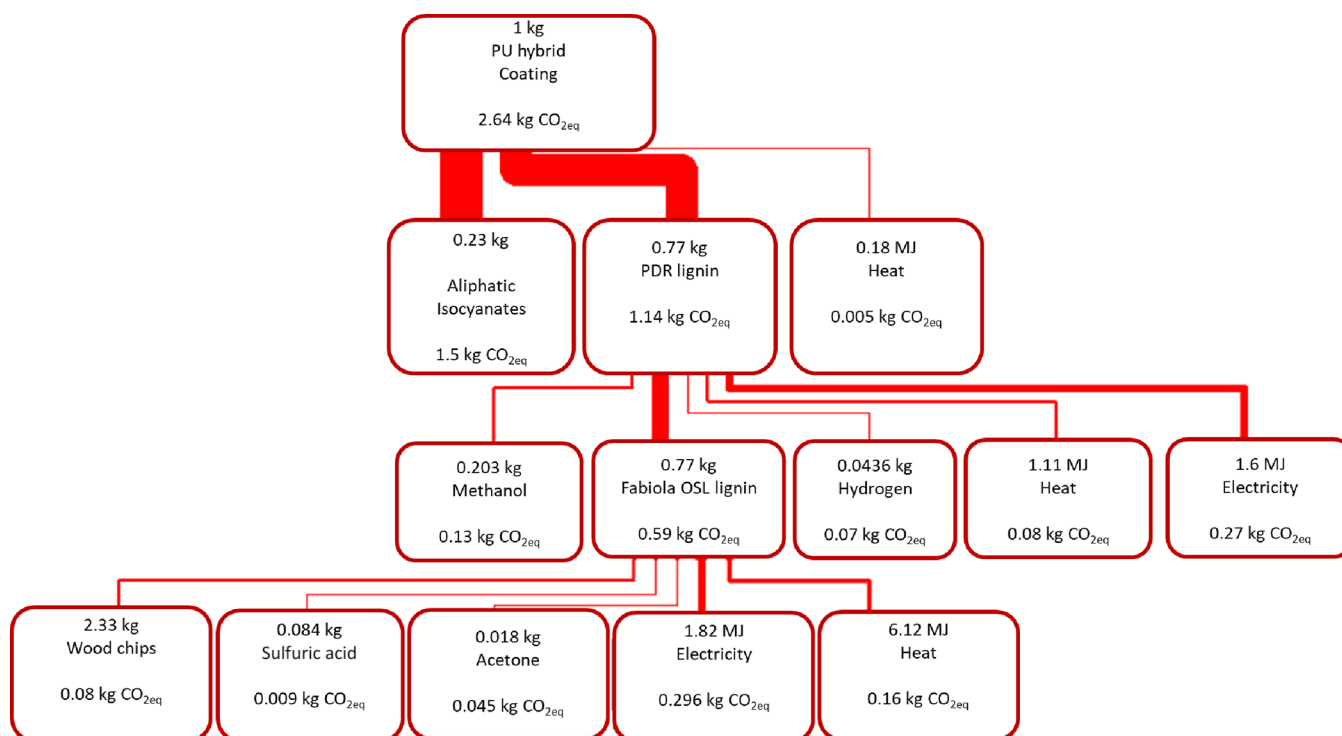


Figure 4. Most significant contributors to global warming potential (GWP) impacts, i.e., CO_{2eq} emissions, for the production of 1 kg of hybrid PU coating (PDR organosolv lignin and fossil-based cross-linker).

according to the LCA model. This takes into account the emissions associated with the beech wood feedstock production and the *Fabiola* process. The impacts for lignin extraction are somewhat lower when compared to other studies, which report between 1.42 and 1.85 kg CO_{2eq}/kg lignin, for different biomasses and extraction processes,^{26,27} likely resulting from the relatively mild *Fabiola* fractionation conditions and use of acetone as the solvent. If CO₂ uptake is considered, negative emissions (−4.71 kg CO_{2eq}/kg lignin) are calculated via the life cycle model (with 2.26 kg CO_{2eq}/kg lignin actually stored in the final OSL). In addition, because the models are highly dependent on the impacts of lignin, given that it is a main component of the coatings, allocation is important. If mass allocation is used instead of economic allocation, the positive environmental impacts of the lignin are less pronounced (i.e., 0.6 kg CO_{2eq}/kg lignin for mass allocation), given lignin's relatively high value vs mass in the

Fabiola process. Results with different modeling approaches (allocation, CO₂ uptake) are presented in the [Supporting Information](#).

Hybrid Biobased PU Coating: Organosolv Lignin and Commercial Binder. Production of the hybrid coating comprising OSL and a fossil-based cross-linker as building blocks has an impact of 1.52 kg CO_{2eq} emissions per 1 kg of coating produced (Figure 2). Most (55%) of the emissions in the process are related to the use of the fossil-based cross-linker (0.84 kg CO_{2eq}/kg_{coating}) and the lignin contributes 44% of the emissions (0.67 kg CO_{2eq}/kg_{coating}), with the remaining 1% of impacts from heat. The main impacts from the *Fabiola* process are related to the use of electricity (50%), heat (27%), beech wood biomass (13%), and acetone make-up (7%). If CO₂ uptake by the biomass is taken into account, the overall production of the coating is associated with −3.25 kg CO_{2eq}/

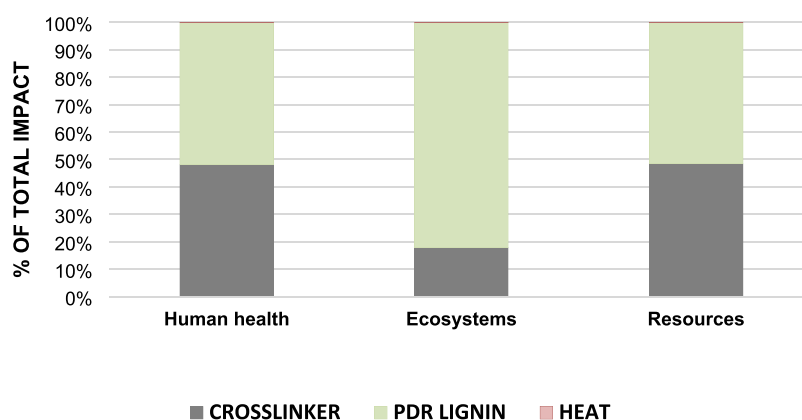


Figure 5. Relative impacts associated with depolymerized OSL and fossil-based cross-linker in the production of 1 kg of hybrid PU coating for various environmental impact categories, for a coating that is 77% depolymerized OSL and 23% cross-linker (hierarchist perspective).

kg coating (Figure S4), whereas actual CO₂ equivalents stored in this coating is 1.97 kg CO_{2eq}/kg coating.

Impacts on ecosystems, human health, and resource scarcity from the production of the hybrid coating with OSL are presented in Figure 3. For this coating, the ratio of OSL to cross-linker is 6.7 (i.e., 87% lignin), and the results show the disproportionately high negative impacts of the fossil-based cross-linker for almost all categories. The main impact category where the lignin has a disproportionately high impact is the ecosystem category; these impacts are associated with land use (Figure S3) for the growth of the beech wood feedstock for the Fabiola process. This is important because the land use impacts (including indirect land use change (ILUC)) could be significant if large-scale biomass production would be required for biobased PU products. The Fabiola biorefinery approach has shown enhanced compatibility with sustainable feedstock supply chains, enabling isolation of high purity lignin from complex residues.¹⁴ It would also be beneficial for future research to examine the use of such lignin as feedstocks for biobased PUs.

Given the high environmental impact of the fossil-based cross-linker relative to the OSL for the hybrid coating production, development of biobased cross-linkers with improved sustainability has potential to further reduce the overall impact of the PU coating. Increasing the ratio of lignin to cross-linker could also be a strategy to further reduce the negative environmental impacts, with the exception of land use impacts (Figure S3), which are solely tied to the use of lignin in the process. However, increasing the lignin ratio may not be possible depending on the impacts on the final coating quality and characteristics. Different types of lignin may also have different environmental impacts,¹⁴ which should be considered in future research; for example, a recent study highlighted the environmental impact of Kraft lignin (up to 2.4 kg CO_{2eq}/kg lignin),²⁸ which is 68% higher than the impacts of Fabiola lignin.

Hybrid Biobased Polyurethane Coating: Depolymerized Organosolv Lignin and Commercial Binder. As detailed in a separate contribution, partial depolymerization of OSL reduced its molar mass and polydispersity and significantly improved lignin reactivity toward the cross-linker.¹⁵ As a result, coatings were produced showing low glass transition temperature (T_g) values and high coating flexibility. The addition of the lignin depolymerization step results in a PU coating production impact of 2.64 kg CO_{2eq}/

kg_{coating} (Figure 4). This represents a 42% emission increase for the PDR coating when compared with the hybrid OSL coating. In total, the production of PDR lignin has an impact of 1.48 kg CO_{2eq}/kg lignin, a 48% increase when compared to non-depolymerized lignin.

This is not surprising as the depolymerization process uses additional heat, electricity, and solvent (methanol), which contribute 0.08, 0.27, and 0.13 kg CO_{2eq}, respectively, to the production of 1 kg of coating. However, partial depolymerization of organosolv lignin proved to be a versatile strategy for the production of coatings with tailored properties. Future studies are needed to compare the impacts of PDR lignin and fossil-based polyols for coatings with specific applications for which the PDR lignin is beneficial.

Overall, the PDR lignin contributes 1.14 kg CO_{2eq} and the fossil-based cross-linker contributes 1.5 kg CO_{2eq} to this coating, representing 43% and 57% of the total impacts, respectively. Furthermore, if CO₂ uptake is taken into account over the life cycle, negative emissions of −1.57 kg CO_{2eq}/kg_{coating} are calculated for this coating (1.79 kg CO_{2eq}/kg_{coating} stored in the final coating) (Figure S5). Impacts on ecosystems, human health, and resource scarcity are also influenced by the PDR process for the OSL (Figure 5). The cross-linker has higher relative impacts than the PDR lignin. Given that the cross-linker makes up 23% of the coating by mass, the negative impacts on ecosystems, human health, and resources are disproportionately high for the cross-linker (Figure 4). The depolymerized OSL has similar relative impacts to the OSL in the other hybrid coating due to the higher proportion of cross-linker in the coating with PDR OSL. For this specific coating, the PDR reaction used 30 g of OSL in 1 L of methanol. One strategy to decrease the impacts of the PDR process is to increase the ratio of OSL to methanol; up to 100 g OSL in 1 L of methanol is currently feasible at the lab scale (data not shown). This adjustment alone improves the impact of the PDR lignin by 24% to 1.11 kg CO_{2eq}/kg_{coating} and the impact of the overall coating production by 11% to 2.36 kg CO_{2eq}/kg_{coating}.

Fully Biobased Polyurethane Coating. Production of the fully biobased PU coating is associated with 19.9 kg CO_{2eq}/kg coating. This is 92% and 87% higher than the OSL and PDR-OSL hybrid coatings, respectively. The increase in impact for the fully biobased coating is attributed to the production of the biobased VA-NCO cross-linker from VA, which involves many steps using a variety of chemicals,

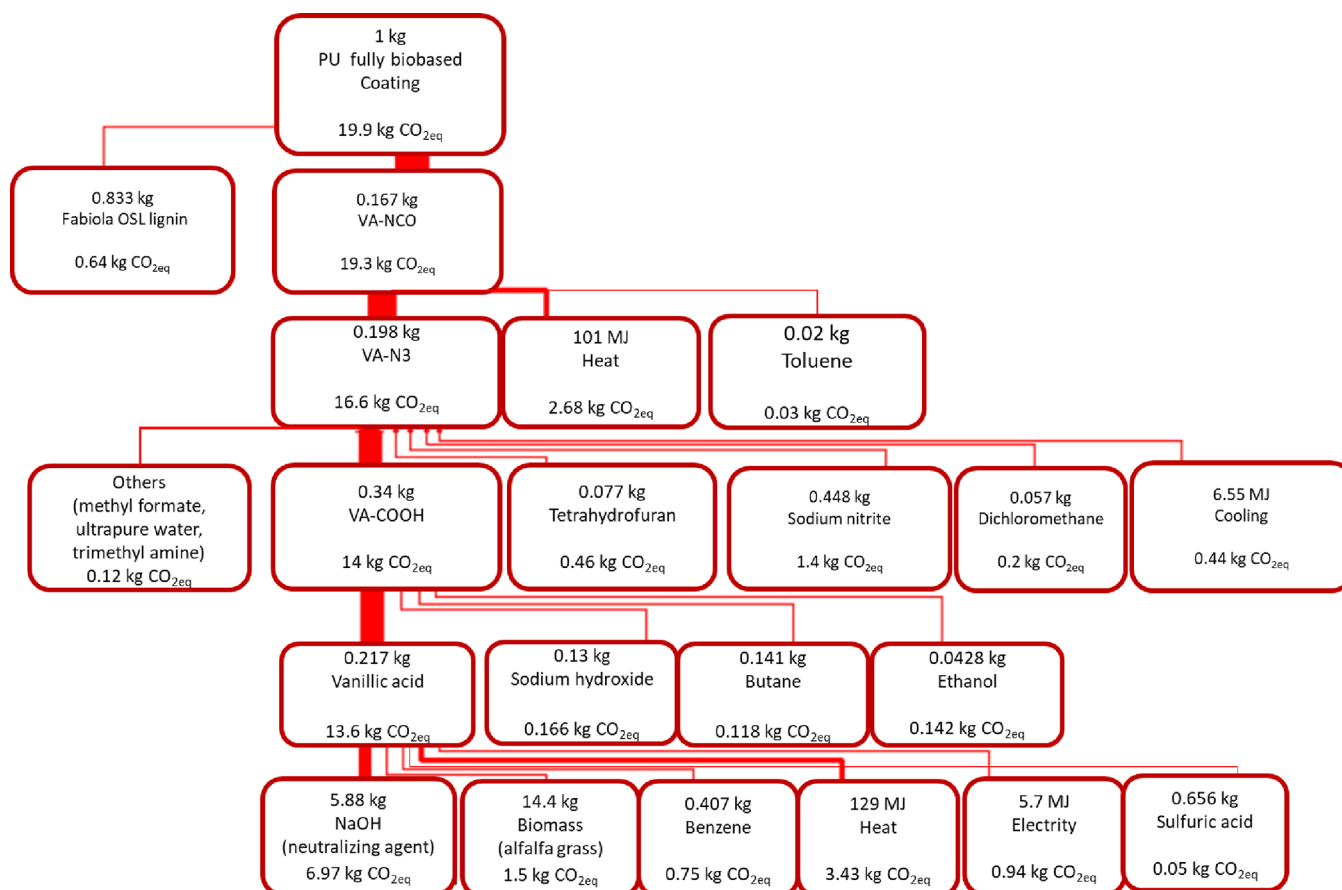


Figure 6. Most significant contributors to global warming potential (GWP) impacts, i.e., CO_{2eq} emissions, for the production of 1 kg of fully biobased PU coating made from organosolv lignin and VA-NCO cross-linker based on vanillic acid (VA). Economic allocation was applied to the products of the biorefinery process for the production of VA.

including the biorefinery steps to produce VA (Figure 6). Details of the biorefinery process and the allocation used is detailed in the Supporting Information (Table S3). For the final biobased coating, 97% of the impacts are associated with the production of the biobased cross-linker.

The main contributors to CO_{2eq} emissions from the production of the VA-NCO cross-linker include the use of heat (total 6.11 kg CO_{2eq}) and the use of NaOH (6.97 kg CO_{2eq}). Interestingly, because of the large amount of biomass used in the biorefinery process to make the VA, if CO₂ uptake is considered for the coating production life cycle, the fully biobased coating is associated with −8.15 kg CO_{2eq}/kg coating. The actual amount of biogenic CO₂ stored in the coating via the lignin and VA is 2.34 kg CO_{2eq}/kg coating.

Furthermore, if mass allocation is applied to the products of biorefinery to produce VA, the impact of CO₂ uptake is reduced due to the small amounts of VA produced relative to the other products (see the Supporting Information). This highlights the importance of allocation and CO₂ uptake when considering life cycle impacts of biobased products.

Impacts related to damage to ecosystems, human health, and resource scarcity from the production of fully biobased coatings show that most (average 96%) of the impacts are attributed to the production of VA-NCO cross-linker. Given that the biobased coating is 80% lignin by mass,¹⁷ this highlights the disproportionately high impacts of the biobased VA-NCO cross-linker across all impact categories (Figure 7).

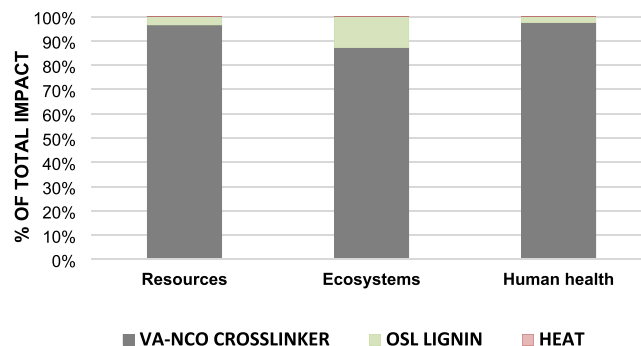


Figure 7. Relative impacts associated with Fabiola organosolv lignin (OSL) and VA-NCO cross-linker in the production of 1 kg of biobased PU coating (87% lignin, 13% cross-linker by mass) for various endpoint environmental impact categories (hierarchist perspective).

Based on these results, the impact of further development of biobased cross-linkers will have to carefully consider the use of neutralizing agent (NaOH) and heat, as these have considerable impacts on the process. Further, it should be noted that the VA-NCO molecule is not the only biobased cross-linker that can be considered for PU coating production. Depending on availability and economics of extraction, vanillic acid may also be better utilized for applications that make use of its therapeutic effects rather than for the development of PU coatings. Although not extensively studied, biobased cross-

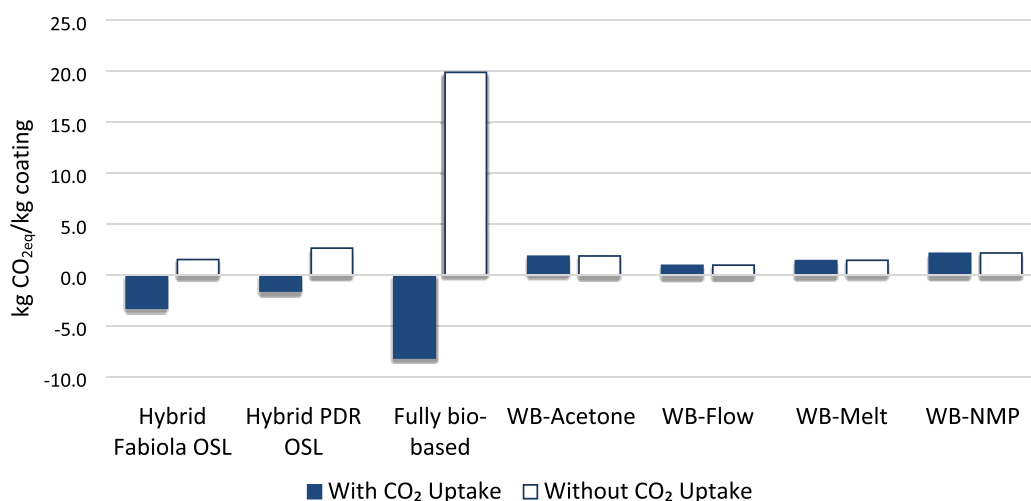


Figure 8. Global warming potential (GWP) impacts of the production of 1 kg PU coating via different methods, including and excluding CO₂ uptake, by different methods, including four different processes to make water-borne, fossil-based PU coatings (as described in Klug et al.⁷). WB = water-borne, NMP = *N*-methyl-2-pyrrolidone (NMP). WB-PUs are made with fossil-based building blocks. Hybrid and biobased PUs are made partly and fully with biobased building blocks, respectively.

linkers can also be made from palm oil²⁹ and dimer fatty acids.^{30,31} Since biobased cross-linkers are required to produce fully biobased coatings, different routes of production, including alternative biobased cross-linkers, require investigation and development in future research.

Comparison of Biobased and Hybrid PU Coatings with Commercially Available Fossil-Based PU Coatings.

Environmental impacts were compared for the biobased and hybrid coatings production and water-borne PU coatings (WB-PU) made with fossil-based building blocks according to four different methods.⁷ With respect to GWP, hybrid coatings made with OSL have similar or lower emission footprints than the water-borne PU coatings (Figure 8). For the WB-PU, the Flow Process has the lowest GWP impacts, with 0.95 kg CO₂eq per kg of coating produced; this is lower than the impacts of any of the biobased coatings investigated in this study (not factoring in CO₂ uptake). However, if CO₂ uptake is considered over the entire production process, replacing the fossil-based building blocks in part or in whole with biobased components decreases the GWP of the fossil-based PU coatings by >100%, into negative emissions.

This demonstrates the potential positive effects of incorporating biobased building blocks into PU coating production with respect to CO₂ emissions. The different production methods follow similar patterns for ecosystem, human health, and resource scarcity impacts. In general, the hybrid coatings have similar impacts to the fossil-based coatings (all production methods), when CO₂ uptake is not considered (Figure 8). It should also be noted that among fossil-based coatings, solvent-based PU coatings have a higher impact (>50% greater GHG emissions associated with the raw materials for the coating when compared to water-based coatings),³² given the fossil-based building blocks and the use of solvents.

Considerations for End-of-Life for Biobased and Hybrid PU Coatings. This section discusses end-of-life scenarios for the different PU coatings assessed in this study. PUs are, in general, not commonly recycled. PU coatings in particular are very difficult to recycle given that they are typically mixed (and disposed of) with a variety of other materials, such as wood or metals, making their separation and

recovery challenging. As a result, the coatings are typically landfilled or incinerated with the associated materials (e.g., wood) at their end-of-life.⁵

When considering end-of-life for PU coatings in an LCA framework, limited scenarios are available for inclusion in the models. Disposal via landfilling and incineration of waste PU can be modeled, but no distinction can be made between biobased, hybrid, and fossil-based PU coatings. It is reasonable to assume that impacts of landfilling or incineration of biobased or hybrid coatings would be different than that of fossil-based coatings. For example, research has demonstrated that including lignin in PU coatings can improve biodegradability, and increase strength,³³ which may affect how these materials behave in a waste scenario and their subsequent environmental impacts. The lack of data on this topic and in LCA databases represents a gap to be studied in future research. In addition, use of the Circular Footprint Formula³⁴ may be useful in future studies to account for benefits and impacts of recycling, energy recovery, and landfilling of biobased PU coatings at the end-of-life. As part of the current study, end-of-life pathways of incineration and landfilling were modeled for 1 kg of waste PU (fossil-based). The results indicate that the end-of-life scenario is potentially very significant with respect to overall life cycle impacts of PU coatings: incineration results in approximately 3.51 kg CO₂eq per kg of coating incinerated and landfilling results in approximately 0.004 kg CO₂eq per kg of coating landfilled. Incorporating energy recovery into the incineration can reduce this impact by up to 55%. Combining these impacts with the impacts measured in the production of the coatings via the different processes, the end-of-life scenario can contribute anywhere from 1% to 79% of GWP impacts for fossil-based PU coatings. Therefore, for biobased or hybrid coatings, the end-of-life scenarios could potentially also be very impactful, especially if the materials are incinerated.

The use of biobased components in PU coatings opens up discussion and possibilities for end-of-life scenarios, which include recycling, biodegradation, and chemical degradation. However, there are many potential challenges associated with these scenarios that require additional investigation. Recycling may be difficult and potentially inefficient given that the

amount of coating per product is typically low and the coatings may be composed of different layers, possibly with different properties, making separation challenging. Biodegradation of coatings may not be a desirable property with respect to long-term durability. Chemical degradation or dissolution may be feasible but would be associated with environmental impacts from the use of chemicals. As new products and PU coatings are being developed, the intent for the end-of-life should be considered, e.g., designing for recycling/biodegradation, or recovery of building block molecules, to facilitate the move toward circular economy principles. In addition, more research is needed on methods for end-of-life scenarios for biobased PU coatings and associated impacts.

CONCLUSIONS

This LCA study was designed to evaluate the environmental impacts of the production of biobased and hybrid PU coatings. The main contributors to the environmental impacts were identified, and subsequent adjustments or alternatives were further evaluated to determine potential pathways for minimizing impacts. In particular, this study demonstrates that the inclusion of lignin as biobased building block (polyol) in the production of hybrid PU coatings results in similar environmental impacts (emissions) when compared to fossil-based coating production (water-borne coatings). If CO₂ uptake is factored in for all biomass in the production processes, hybrid and fully biobased coatings are associated with net negative CO₂ emissions from the production process. There is a need for the development of biobased cross-linkers (non-isocyanate based) for PU coating production. Production of fully biobased coatings still requires additional research, with particular attention to the use of solvents and heat in the processes to make fully the coatings more sustainable. Other hotspots of environmental impact that should be addressed in future research and prior to scale-up include improving solvent recycling, increasing the ratio of lignin to solvent in depolymerization processes, and considering end-of-life scenarios early, including designing coatings for biodegradability, chemical degradability, molecule recovery or recycling from the early stages of process development. This study further demonstrates the value of LCA at early stages of process development for the production of biobased and hybrid PU coatings to identify hotspots of environmental impacts that should be addressed prior to process scale-up.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00619>.

Table S1: life cycle inventory data from online databases; Table S2: process inventory data used to model the production of 1 kg of Fabiola organosolv lignin; Table S3: biorefinery process inventory data used to model the production of 1 kg of vanillic acid; Table S4: process inventory data used to model the production of 1 kg of hybrid coating using Fabiola organosolv lignin and a fossil-based commercial binder; Table S5: process inventory data used to model the production of 1 kg of hybrid coating using Fabiola partially depolymerized by reduction (PDR) organosolv lignin; Table S6: process inventory data used to model the production of 1 kg biobased linker (VA-NCO); Table S7: process inventory

data used to model the production of 1 kg of fully biobased coating using Fabiola organosolv lignin and biobased cross-linker VA-NCO; Table S8: prices used for products (vanillin, vanillic acid, biomethane, and digestate) of the biorefinery process utilized for the production of vanillic acid; Table S9: different allocations for products (vanillin, vanillic acid, biomethane, and digestate) of the biorefinery process utilized for the production of vanillic acid; Table S10: prices of the products (lignin, pulp, hemicellulose) of the Fabiola process; Table S11: characteristics and different allocations for products (lignin, pulp, hemicellulose) of the Fabiola process; Table S12: data quality rating (DQR) for each process step modelled and biomass used; Figure S1: global warming potential (GWP) impacts of the production of 1 kg organosolv lignin when CO₂ uptake is included and excluded; Figure S2: global warming potential impacts associated with the production of 1 kg of vanillic acid (pre-cursor to VA-NCO cross-linker) using different allocation methods and including and excluding CO₂ uptake; Figure S3: relative impacts associated with Fabiola organosolv lignin and fossil-based cross-linker; Figures S4, S5, and S7: most significant contributors to global warming potential (GWP) impacts; Figures S6 and S8: relative impacts associated with depolymerized OSL and fossil-based cross-linker (PDF)

AUTHOR INFORMATION

Corresponding Author

Stefania Luzzi – Biobased & Circular Technologies group, The Netherlands Organisation for Applied Scientific Research (TNO), unit Energy & Materials Transition, 1755 ZG Petten, The Netherlands; orcid.org/0000-0001-9801-7756; Email: stefania.luzzi@tno.nl

Authors

Heather E. Wray – Biobased & Circular Technologies group, The Netherlands Organisation for Applied Scientific Research (TNO), unit Energy & Materials Transition, 1755 ZG Petten, The Netherlands; orcid.org/0000-0002-3435-9375

Paola D'Arrigo – Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, 20133 Milano, Italy; orcid.org/0000-0001-8435-7215

Gianmarco Griffini – Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, 20133 Milano, Italy; orcid.org/0000-0002-9924-1722

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00619>

Author Contributions

[†]H.E.W. and S.L. contributed equally to this work and should be considered co-first authors.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

CO_{2eq}, CO₂-equivalent; GWP100, Global Warming Potential over a 100-year horizon; OSL, Fabiola mild acetone organosolv lignin; GHG, greenhouse gas; LCA, life cycle assessment; NMP, N-methyl-2-pyrrolidone; PU, polyurethane; PUs, polyurethanes; VA, vanillic acid; VA-COOH, α,ω -dicarboxylic acid (4,4'-(butane-1,4-diylbis(oxy))bis(3-methoxybenzoic acid)); VA-N₃, α,ω -diacyl azide (4,4'-(butane-1,4-diylbis(oxy))bis(3-methoxybenzoyl azide)); WB-PU, water-borne polyurethane

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