Modeling life-cycle inventory for multi-product biorefinery: tracking environmental burdens and evaluation of uncertainty caused by allocation procedure

Svetlana V Obydenkova, Aachen Maastricht Institute for Biobased Materials, Maastricht University, Geleen, The Netherlands; Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands
Panos D Kouris, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands
David M J Smeulders, Michael D Boot, Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands
Yvonne van der Meer, Aachen Maastricht Institute for Biobased Materials, Maastricht University, Geleen, The Netherlands

Received July 10 2020; Revised January 29 2021; Accepted March 03 2021;
View online at Wiley Online Library (wileyonlinelibrary.com);
DOI: 10.1002/bbb.2214; Biofuels. Bioprod. Bioref. (2021)

Abstract: Life-cycle inventory (LCI) is a fundamental phase in the quantification of the environmental performance of products. However, when it comes to the LCI of a multi-product system, discussions about the choice of the appropriate methodology to allocate environmental impacts still continue. A further system subdivision and the implementation of a mechanism allowing environmental burdens to be tracked would help to improve model accuracy. This study focuses on the LCI modeling of a lignocellulosic biorefinery producing ethanol, lignin oligomers, and electricity, and demonstrates the application of the matrix-based approach for detailed system subdivision and environmental burden tracking. Forty scenarios utilizing process-specific allocation methods were tested to account for the global warming potential of outputs. The main findings of the paper are: (i) the importance of specific allocation methods applied to combined heat and power plants that stress the key role of internal energy supply in carrying environmental burdens; (ii) a negligible effect of allocation methods applied to wastewater treatment facilities; (iii) the inconsistency of results obtained via two allocation methods, one based on the total mass and the second based on the dry mass allocation, which raises questions about the validity of water accounting in the allocation procedure of related products; (iv) the role of upstream greenhouse gas (GHG) emissions in lignin-derived outputs, which emphasizes the importance of a proper allocation methodology.
to be applied to this residue; and (v) an important role of the biomass pretreatment and lignin solvolysis processes in the accumulation of emissions, which highlights the importance of decreasing the amount of solids and methanol content in the processes discussed here. © 2021 The Authors. Biofuels, Bioproducts and Biorefining published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

Supporting information may be found in the online version of this article.

Key words: life cycle assessment; inventory modeling; multi-product system; biorefinery; tracking environmental burdens; allocation

Introduction

The environmental problems that mankind faces today require an understanding of the way in which environmental burdens are distributed within the production cycle and how they are mirrored in finished industrial products. The assignment of environmental burdens to outputs refers to the life-cycle inventory (LCI) phase of life-cycle assessment (LCA), and this step is important in many respects, including the quantification of the environmental performance of product alternatives, as well as the definition of critical stages in their value chain. Both issues are reflected in LCA objectives. However, methodological issues remain unresolved regarding the LCI of multi-product or multi-functional systems. The choice of an allocation method that is a part of the LCA analysis of such systems was recognized as one of the main sources of uncertainty in attributional LCA. As long as the goal of LCA consists in analyzing the environmental performance of particular outputs of a multi-functional system, some of the environmental burdens should be assigned to each of the produced commodities, thus converting a multi-functional product system into ‘mono-functional single operation unit processes.’ Following a stepwise allocation procedure, this conversion can be performed either by system subdivision, or by system expansion, or via partitioning environmental burdens using a certain allocation key.

While the system subdivision approach involves further specification of unit processes (UPs), the partitioning option is used where either the subdivision approach is not applicable, which is the case of flows not being separated physically (e.g. (hemi)cellulose and lignin in lignocellulosic biomass), or where this is not feasible. The ISO procedure declares that allocation via partitioning should be avoided, first of all, by the means of specifying individual flows to obtain a comprehensive product-based inventory.

However, the partitioning approach at the system level has been widely applied by LCA practitioners, including in the analysis of refinery and biorefinery products. A few recent studies advanced further towards the specification of separate UPs. In these papers, the main processes were divided and accounted for separately, while upstream burdens from service processes, such as, for example, a combined heat and power (CHP) and a waste-water treatment (WWT) plant, were distributed between products using the system-level allocation key. In the current paper, this approach is referred to as the macro-process LCI modeling procedure. However, such a technique can also potentially distort the results, as UPs can contribute to system co-functions in different ways.

The system-level partitioning approach has been claimed to be less arbitrary, more transparent, and promising in terms of data availability. However, the reliability of this approach is more disputable. While Moretti et al. advocated the consistency of this method, Cai et al. claimed that it might inappropriately reflect greenhouse gas (GHG) emissions associated with the life cycle of products. Overall, it can be concluded, however, that modeling at the system aggregate level is prevailing.

Several problems accompany the system or macro-process level partitioning approaches. Quite often, industries such as biorefineries comprise processes for which LCI procedures have been already standardized, as in the case of CHP plants. Moreover, legislation may impose further limitations on the system-level allocation. For instance, the European Renewable Energy Directive recommends considering process residues, such as bagasse, as having zero upstream GHG emissions. It would be difficult to comply with this if the production system is not subdivided. A similar issue can affect the side-stream of cellulosic biorefineries, lignin residue (LR), which has a low economic value.

Another problem is that material and energy exchanges between processes may entail some environmental burdens inherited from previous processes (upstream burdens), or
via feedback loops; the latter can be illustrated, for instance, by a CHP plant that requires some electricity input to produce the required steam and electric power. The system subdivision would help to improve model accuracy by tracking such burdens through the entire conversion chain. Nonetheless, the practical implementation of tracking mechanisms is not common in scientific papers related to the LCA of engineering systems, partly due to data scarcity, as well as to the amount of time required for its mathematical representation. As an example, models that allow tracking environmental burdens within the product system boundary were developed for petroleum refineries based on both energy and mass balances using a linear programming technique.\textsuperscript{2,18-20} The two approaches involve a series of linear equations designed to define the allocation of environmental burdens to final products. However, an increase in system complexity, especially in the number of material and energy streams, would boost the number of equations dramatically and, thus, impose a heavy burden on the model handling time.

Another approach to track material and energy flows can be found in the economic input–output (IO) analysis and, subsequently, in IO LCA, where the latter utilizes economic IO tables and environmental information to quantify environmental impacts of a product.\textsuperscript{21} One of the core matrixes in the IO analysis is the Leontief inverse matrix, which sets a relation between the cumulative output of an economic sector and the final demand vector. The matrix approach to deal with inventory problems was thoroughly discussed by several authors.\textsuperscript{22} It was also used to address allocation problems of different biomass conversion pathways, where a biorefinery was considered at an aggregate level.\textsuperscript{23}

Given this, the matrix approach seems to be promising for modeling the LCI framework, especially for such complex industrial systems as biorefineries. The LCA of a biorefinery could benefit from using this approach, as it would provide the same level of accuracy as models involving linear programming techniques while reducing handling time and offering a better model transparency. In addition, the matrix approach can be useful in identifying biorefinery hotspots, thus addressing another LCA goal – that of environmental performance improvement. To the best of our knowledge, scarcely any research exists that employs the matrix approach for the modeling of LCI of a multi-product biorefinery, and uses this approach for the analysis of different allocation options and biorefinery hotspots.

This paper demonstrates the use of the matrix-based approach for a detailed subdivision of a lignocellulosic multi-product biorefinery and shows how this approach can be used to track environmental burdens throughout the entire biorefinery conversion chain. To keep in line with ISO 14044, the paper employs statistical tools to evaluate the impact of allocation procedures on final LCA results. The paper also evaluates differences stemming from distinct LCI modeling procedures by comparing GHG emission values obtained from the detailed, macro-process, and system-level LCI models. It also shows how the matrix approach, when used as a tool to track environmental burdens, can be applied to identify hotspots associated with different stages of the product value chain within a biorefinery.

**Methodology**

**The biorefinery model**

A lignocellulosic biorefinery that simultaneously produces ethanol, soluble lignin oligomers (SLO), and electricity is a good representation of an industrial cluster, co-locating the main biorefining processes with power generation, WWT facilities, and other services (Fig. 1).

Data for a benchmark biorefinery producing denatured ethanol and electricity as a by-product was derived from National Renewable Energy Laboratory (NREL) reports,\textsuperscript{24,25} while principal characteristics of the proprietary lignin-to-SLO conversion technology were provided by Vertoro, a Dutch company.\textsuperscript{26} The reference biorefinery model was designed by NREL in the Aspen Plus\textsuperscript* software,\textsuperscript{24} and the lignin-to SLO technology was integrated into this design.

With its hourly processing capacity of 104 167 kg of herbaceous lignocellulosic biomass (corn stover),\textsuperscript{24} the biorefinery aims to produce 22 276 kg h\textsuperscript{–1} of denatured ethanol, 3499 kg h\textsuperscript{–1} of SLO, and 25.1 GJ/h of electricity (net). Corn stover, in the first stage, is treated at high temperature with dilute sulfuric acid to liberate hemicellulose carbohydrates and reduce the cellulose chain length and crystallinity.\textsuperscript{24} At the next stage, cellulase enzyme produced on site is used to hydrolyze cellulose into glucose, which, along with other sugars, undergoes fermentation, resulting in the output of ethanol that is further purified to 99.5%. About 62% of the moist solids obtained at the distillation bottom and containing 33 wt% of lignin is sent to the CHP plant. The remaining solids are initially dried to a moisture content of 0.8% (w.b.), and then converted to SLO via mild solvolysis at the temperature of 200 °C and pressure of 38 bar.\textsuperscript{26} Methanol is applied as a solvolytic medium, and, after that, heterogeneous lignin polymer is separated into methanol-soluble lighter molecular weight lignin and insoluble higher molecular weight fraction (char), where the latter is sent to the CHP plant.
Goal of LCA and functional unit

The goal of LCA is to define the global warming potential (GWP) profile of all three biorefinery products, i.e., ethanol, SLO, and electricity, and, therefore, the analysis refers to the attributional LCA modeling. The cradle-to-gate LCA boundary was defined, and the matrix approach was used to convert the multi-product system into mono-functional unit processes. Thus, three functional units can be set out, namely: 1 GJ of ethanol, 1 GJ of SLO, and 1 GJ of electricity.

LCI modeling approaches and allocation procedures

Two levels of subdivision are applied to the considered biorefinery: (i) the detailed subdivision, and (ii) the macro-process subdivision. A scenario where the entire biorefinery is treated as an aggregate is also considered. The latter is referred to as the system-level modeling approach.

Detailed (matrix-based) LCI modeling approach

The biorefinery can be considered as a product system comprising four main processes of converting feedstock into final products and six service-related processes (Fig. 1). Following the ISO 14044 methodology, all those processes are referred to as UPs, as no further subdivision is required or is possible for those processes. Biorefinery inventory for each UP is provided in Table 1 (the detailed inventory can be found in the supporting information (Table S1)). The details of UP-related allocation methods are summarized in Table 2.

Overall, two classes of uncertainty stemming from specific allocation procedures can be identified in the current biorefinery model, namely: (i) UP product identification, and (ii) allocation methods applied for partitioning burdens between UP products.

UP product identification

Two examples of this class of allocation uncertainty can be considered. For instance, while sewage sludge can be regarded as a primary product of aerobic digestion, clean water can be considered as an alternative product of this UP. However, while sludge can be utilized as fertilizer or for energy purposes, there is no market for clean water unless it is required on site. As in the biorefinery design the ratio of recycled water to fresh water intake amounts to ~2.6, environmental burdens transferred with this stream can be...
### Table 1. Biorefinery inventory.

| Input                                                                 | Unit | Value   | Output                                 | Unit | Value   |
|-----------------------------------------------------------------------|------|---------|----------------------------------------|------|---------|
| UP-1: Biomass pretreatment, enzymatic hydrolysis, fermentation, enzyme production, distillation |      |         | Diluted ethanol\(^\text{d}\) to UP-2  | kg h | 58734   |
| Corn stover\(^a\)                                                    | kg h | 104167  |                                        |      |         |
| Sulfuric acid (93\%)                                                 | kg h | 1981    |                                        |      |         |
| Ammonia                                                              | kg h | 1166    |                                        |      |         |
| Corn steep liquor                                                    | kg h | 1322    |                                        |      |         |
| Diammonium phosphate                                                 | kg h | 142     |                                        |      |         |
| Glucose                                                              | kg h | 1213    |                                        |      |         |
| Sorbitol                                                            | kg h | 44      |                                        |      |         |
| Sulfur dioxide                                                       | kg h | 16      |                                        |      |         |
| UP-2: Ethanol purification, storage                                  |      |         | Ethanol\(^d\)                          | kg h | 22276   |
| UP-3: LR drying                                                      |      |         | LR\(^\text{dy}\)                       | kg h | 9237    |
| UP-4: Lignin solvolysis                                              |      |         | Char\(^f\) to UP-7                    | kg h | 6320    |
| Methanol                                                            | kg h | 580     |                                        |      |         |
| SLO\(^g\)                                                            | kg h | 3499    |                                        |      |         |
| UP-5: SLO storage                                                    |      |         |                                        |      |         |
| Caustic                                                             | kg h | 2252    |                                        |      |         |
| UP-6: WWT plant                                                      |      |         |                                        |      |         |
| Lime                                                                | kg h | 878.4   |                                        |      |         |
| UP-7: CHP plant                                                      |      |         |                                        |      |         |
| Lime                                                                 | kg h | 878.4   |                                        |      |         |
| Process water supply                                                 | kg h | 162403  | Process water consumed in biorefinery: |      |         |
| Well water                                                           | kg h | 162403  |                                        |      |         |
| Emissions: CH\(_4\)                                                 | kg h | 3.14    |                                        |      |         |
| Biogas and sludge to UP-7                                            | %    | 100     |                                        |      |         |
| Clean water to UP-8                                                 | %    | 100     |                                        |      |         |
| Electricity export                                                  | GJ h | 312     |                                        | %    | 25.1    |
| Electricity consumed in biorefinery:                                 |      |         |                                        | %    | 20.3    |
| • UP-1                                                               | %    | 40.6    |                                        |      |         |
| • UP-2                                                               | %    | 0.5     |                                        |      |         |
| • UP-4                                                               | %    | 0.2     |                                        |      |         |
| • UP-6                                                               | %    | 20.2    |                                        |      |         |
| • UP-7                                                               | %    | 3.7     |                                        |      |         |
| • UP-8                                                               | %    | 0.3     |                                        |      |         |
| • UP-9                                                               | %    | 7.1     |                                        |      |         |
| • UP-10                                                              | %    | 7.1     |                                        |      |         |
| HPS1 to UP-1                                                         | %    | 100     |                                        |      |         |
| HPS2 to UP-4                                                         | %    | 100     |                                        |      |         |
| LPS consumed in biorefinery:                                          |      |         |                                        |      |         |
| • UP-1                                                               | %    | 72.4    |                                        |      |         |
| • UP-2                                                               | %    | 12.1    |                                        |      |         |
| • UP-3                                                               | %    | 6.5     |                                        |      |         |
| • UP-4                                                               | %    | 9.0     |                                        |      |         |
significant and, therefore, should not be ignored. Thus, in the current LCI model, two extreme scenarios are to be tested: when all burdens are allocated to either sludge or to clean water exclusively.

The other example of the first uncertainty class concerns LR that can be treated either as the product or as a waste stream of UP-1. The so-called ‘zero-burden’ approach regarding lignin feedstock was used in several papers. Following this approach, LR is treated as a waste stream with no upstream emissions allocated to it before the collection point. Concerning this method, Hermansson et al. concluded that the results are highly sensitive to the choice of the relevant product. However, while ISO 14044 defines waste as ‘substances or objects which the holder intends or is required to dispose of,’ treating LR as a waste can be considered somewhat arbitrary. In fact, LR can be still used in the biorefinery either for energy production or for material recovery. Thus, two extreme scenarios are to be evaluated in this respect: one where the LR environmental profile does not include upstream GHG emissions and one where it does.

Allocation methods applied for partitioning burdens between UP products

The second class of uncertainty refers to allocation methods applied for partitioning burdens between UP products. When it comes to UP-1 and UP-4, said methods can involve either physical or economic criteria.

Following ISO 14044, the distribution of environmental burdens between UP products should follow a physical relationship first. Overall, there is a range of allocation options with underlying physical relationships, including allocation based on energy content and the mass of the respective products. In the case of biofuels, the energy content allocation method is more appropriate; it is also applicable to situations where flows are supplied to the CHP plant. This method uses the lower heating value to define the energy content of streams.

For the chemical sector, allocation based on the total mass of flows could be more appropriate. However, limitations to solid loading and, as a result, the high water content in the biomass-related flows can distort this causality and may give misleading results. From this perspective, such allocation methods as the dry mass of flows or the mass of valuable components might represent the allocation base more correctly.

The group of allocation methods utilizing an economic relationship can either use market values (or production cost) or involve market prices. Generally, it is applied where partitioning based on a physical relationship is not reasonable.

Table 1. (Continued)

| Input             | Unit | Value | Output          | Unit | Value |
|-------------------|------|-------|-----------------|------|-------|
| UP-9: Cooling service |      |       | Cooling service consumed in biorefinery: |      |       |
|                   |      |       | • UP-1          | %    | 30.5  |
|                   |      |       | • UP-2          | %    | 9.3   |
|                   |      |       | • UP-4          | %    | 5.9   |
|                   |      |       | • UP-5          | %    | 0.1   |
|                   |      |       | • UP-7          | %    | 38.4  |
|                   |      |       | • UP-10         | %    | 15.8  |
| UP-10: Chilling service |      |       | Chilling service to: |      |       |
|                   |      |       | • UP-1          | %    | 100   |

| Input       | Unit | Value  |
|-------------|------|--------|
| Biomass (corn stover) LHV: 4.97 MJ kg. |
| Diluted ethanol: ethanol 36.9 wt%; water 62.9 wt%; LHV = 9.97 MJ kg. |
| LR: lignin 32.9 wt%; water: 34.8 wt%; LHV = 8.19 MJ kg. |
| Ethanol: ethanol 97.3 wt%; water 0.5 wt%; LHV = 27.01 MJ kg. |
| LR\textsubscript{dry}: lignin 50.1 wt%; water: 0.8 wt%; LHV = 12.5 MJ kg. |
| Char: lignin 29.2 wt%; water 0.1 wt%; LHV = 8.60 MJ kg. |
| SLO: lignin oligomers: 77.5 wt%; water: 1.6 wt%; methanol: 10.0 wt%; LHV = 24.2 MJ kg. |
use the ‘value on processing’ concept to obtain allocation factors for such intermediates.\textsuperscript{33,34} This factor is calculated based on market prices of final products minus costs of downstream processing of the intermediates, including capital and operational expenses.\textsuperscript{33,34} The effect of market price volatility on such calculations, however, may be undesirable and in such cases, the use of economic allocation based on production cost might be more appropriate.

The current study evaluates such allocation methods applied to UP-1 and UP-4 as the total mass of flows (M), the mass of valuable components (MVC), dry mass (DM), energy content (EC), and economic value of flows. Allocation factors (AF) for these methods are found using Eqn (1):

$$AF_{M, MVC, DM, EC, Economic} = \frac{F_i}{\sum F_i}$$  \hspace{1cm} (1)

where $F_i$ refers to either total mass of $i^{th}$ flow ($M_i$), or to its energy content ($EC_i$), or to dry mass ($DM_i$), or to production cost (where a market price is not applicable), or to mass of valuable component ($MVC_i$) of the flow. The energy content of a flow is defined based on its lower heating value ($LHV_i$). The $LHV$ values are summarized in Table 1.

In the economic allocation, the production costs of ethanol and moist LR are taken equal to 2.15 $ gal^{-1}$ and 249 $ t^{-1}$, respectively,\textsuperscript{17,24} and diluted ethanol is priced based on ethanol content. As char is used for the energy supply to biorefinery processes, it is benchmarked against entraining biomass that was initially considered as a backup fuel for the CHP plant. For this purpose, the price of wet corn stover is taken equal to 51.59 $ t^{-1}$\textsuperscript{24}. The price of fossil methanol, which SLO is benchmarked to, in 2007–2017,\textsuperscript{36} varied between 100 and 500 € t\textsuperscript{-1}, which, after adjusting energy content, allowed us to value SLO at 247 $ t^{-1}$.
The other example of the second uncertainty group refers to the choice of allocation method applied to the CHP plant (UP-7), where environmental burdens are to be partitioned between steam and electricity, as no further subdivision is possible. Following the recommendations of the Environmental Product Declaration and Greenhouse Gas Protocol, the efficiency and work potential methods can be applied to the CHP plant.\textsuperscript{15,37}

The efficiency method assumes the 'best efficiency' allocating principle applied to separate steam and electricity outputs,\textsuperscript{15} and uses Eqns (2) and (3):

\begin{equation}
AF_{\text{steam}} = \frac{H_i}{\varepsilon_H} \left( \sum_{i=1}^{n} \frac{H_i}{\varepsilon_H} + \frac{P}{\varepsilon_P} \right)
\end{equation}

\begin{equation}
AF_{\text{electricity}} = \frac{P}{\sum_{i=1}^{n} \frac{H_i}{\varepsilon_H} + \frac{P}{\varepsilon_P}} = 1 - \sum_{i=1}^{n} AF_{\text{steam}},
\end{equation}

where $H_i$ and $P$ are the energy content of the $i^{th}$ steam extraction and electricity output, respectively; $\varepsilon_H$ and $\varepsilon_P$ are efficiencies of steam and electricity generation, respectively, and $n$ is the total number of steam extractions. The efficiencies of the conversion to steam and electricity are taken as equal to 80% and 35%, respectively.\textsuperscript{24,37}

The working potential method assumes that environmental burdens can be partitioned between the products of a CHP plant based on the maximum theoretical useful work of those products, and utilizes Eqn (4).\textsuperscript{37}

\begin{equation}
AF_i = M_i \left\{ \left( h_i - T_{\text{ref}} \cdot s_i \right) - \left( h_{\text{ref}} - T_{\text{ref}} \cdot s_{\text{ref}} \right) \right\} / \sum M_i \left\{ \left( h_i - T_{\text{ref}} \cdot s_i \right) - \left( h_{\text{ref}} - T_{\text{ref}} \cdot s_{\text{ref}} \right) \right\}
\end{equation}

where: $M_i$ is the mass of $i^{th}$ steam product; $h_i$, $h_{\text{ref}}$ and $s_i$, $s_{\text{ref}}$ are the specific enthalpy and entropy of $i^{th}$ steam product as it is extracted and at the reference conditions, respectively; $T_{\text{ref}}$ is the reference temperature that is taken, equal to the temperature of the return condensate or equal to the ambient temperature, when steam is not returned. For electricity, work potential is taken to be equal to the power produced.\textsuperscript{37} Both methods are considered in more detail in the supporting information. Input data for the calculation of allocation factors for the CHP plant are summarized in Table 3.

On applying UP specific allocation methods, 40 scenarios were generated under the detailed LCI modeling approach (Fig. 2). For consistency, it was assumed that only the same allocation method can be simultaneously used in UP-1 and UP-4.

### System-level LCI modeling approach

For system-level LCI modeling, it is assumed that all environmental burdens are distributed between three main products – ethanol, SLO, and electricity. In this case, only allocation based on energy content can be applied (Table 2).

### Macro-process LCI modeling approach

At the macro-process level of LCI modeling, it is assumed that the main conversion processes are separate UPs, while service-related processes are consolidated in a single UP with a system-level allocation procedure (Table 2). In this case, only allocation based on energy content is possible.

### Substitution (system expansion) LCI modeling approach

Following the stepwise allocation procedure, system expansion or substitution is the next method used after subdivision to deal with the system’s multi-functionality.\textsuperscript{1} This method allows substituting one or more functions for alternative ones that makes it applicable for situations where the goal of the attributional LCA is to analyze system performance with relations to other systems,\textsuperscript{7} including cases where waste streams are being diverted to production purposes.\textsuperscript{38} Overall, the use of the substitution method in the attributional LCA is more disputable,\textsuperscript{39} and, while some authors avoid using this approach,\textsuperscript{32} others indicate that it is the only method enabling them to account for the emission effects of fuel and non-fuel co-products.\textsuperscript{12}

As this study refers to attributional LCA, and it focuses on the development of environmental profiles of commodities produced, the substitution method is here used for

| Table 3. Input data for calculation of allocation factors for products of CHP plant. |
|-----------------|----------------|---------|----------|---------|---------|---------|---------|---------|--------|
| **Product**     | **Mass, kg h\(^{-1}\)** | **T, °C** | **P, bar** | **T\(_{\text{ref}}\), °C** | **h, kJ kg\(^{-1}\)** | **h\(_{\text{ref}}\), kJ kg\(^{-1}\)** | **s, kJ (kg·K)** | **s\(_{\text{ref}}\), kJ (kg·K)** | **Energy, MJ h\(^{-1}\)** |
| HPS1            | 27927          | 273.2   | 13.17    | 25     | 2985.06 | 104.838 | 6.883          | 0.367          | 80 436.0 |
| HPS2            | 1522           | 454.4   | 60.65    | 276.3  | 3312.64 | 1217.08 | 6.731          | 3.034          | 3189.44 |
| LPS             | 87 042         | 240.9   | 9.63     | 178.3  | 2924.48 | 755.685 | 6.907          | 2.122          | 188 776 |
| Electricity     | —              | —       | —        | —      | —       | —       | —              | —              | 124 704  |

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comparative purposes only. Given this, it was assumed that the produced ethanol, SLO and electricity can substitute the US fossil-based gasoline, low sulfur diesel, and the US electricity mix. It should be noted that it is relevant to include well-to-wheel emissions in the inventory of fossil-based counterparts, as the substitution of these fuels will allow GHG emissions associated with both fuel production and combustion phases to be avoided. The GHG emission factors for gasoline, diesel, and electricity are taken to equal 89.66, 91.19, and 134.3 kgCO$_2$-eq/GJ, respectively.\(^\text{40}\)

**Matrix approach for tracking environmental burdens within a biorefinery**

Our methodology utilizes a matrix approach capable of showing the transfer of environmental attributes between interconnected flows within a specified system’s boundary. This approach allows (i) the transformation of a multi-product system into product-specific mono-functional single-operation unit processes, and (ii) the tracking of environmental burdens within biorefinery boundaries.

Analogously to the tracking of flows along the product value chain\(^\text{21}\), the mechanism of tracking environmental burdens in a biorefinery featuring multiple interconnected flows can be described by the equation:

$$e_c = e + Ae + A^2e + A^3e + \ldots$$  \hspace{1cm} (5)\hfill

where:

- $e_c$ is the $n \times 1$ vector of cumulative environmental burdens, i.e. burdens directly or indirectly transferred to products;
- $e$ is the $n \times 1$ vector of input environmental burdens;
A is the non-negative coefficient allocation matrix, i.e. matrix A shows how the flow i accumulates burdens coming directly from the flow j. The effect of the transfer of environmental burdens from one flow to another is defined via the multiplication of transfer coefficients, such as the \(A^2\) matrix shows burdens allocated due to secondary transfer effect and so on.

Equation (5) can be re-written more compactly:

\[
e_c = (I - A)^{-1} e
\]

Where \(I\) is the \(n \times n\) identity matrix.

Matrix \((I - A)^{-1}\) is frequently referred to as the Leontief inverse coefficient matrix, or the matrix of total expenditures. In Eqn (6), matrix \((I - A)^{-1}\) reflects the share of cumulative burdens to be assigned to each flow within the product system boundary, and in the current paper is referred to as the coefficient matrix of cumulative allocation effects.

Figure 3 represents the development of matrixes A and \((I - A)^{-1}\) for the considered biorefinery, where the energy content allocation method is applied to UP-1 and UP-4, the working potential method is used in UP-7 (CHP plant), and clean water is regarded a product of UP-6 (WWT facility). For demonstration purposes, UP-1 is considered an indivisible process; however, for a more detailed analysis, it can be further subdivided into, for example, biomass pretreatment, enzymatic hydrolysis, fermentation, and distillation processes.

Allocation factors for UPs (as taken from Table 2) and split-off factors for intermediates (as taken from Table 1) in matrix A are highlighted in a yellow and gray color, respectively. The share of cumulative burdens for intermediates and final products in the Leontief inverse matrix are highlighted in green and orange color, respectively. As it can be noticed from Fig. 3, the sum of each column related to intermediates in matrix A is equal to 1, while in the matrix \((I - A)^{-1}\) only the unique allocation coefficients of the final products sum up to one. It can be also observed from the Leontief inverse matrix that some of the coefficients related to intermediate products are greater than 1 (e.g., the cumulative coefficient of moist lignin residue, LR(m), related to LR(m) is equal to 1.26). This reflects the physical sense of the cumulative effect matrix: it shows that the production of an intermediate product might require some amount of that product to be consumed downstream and, hence, transfers part of the environmental burden back to the production cycle. The development of the coefficient allocation matrix is demonstrated in the supporting information (Excel file).

**Tools and methods**

Matrix calculations and statistical testing were performed using R software (R Core Team).

The SimaPro® (v.8.0.2) software was used to access LCI databases. The process named 'Corn stover, at conversion plant, 2022/ton/RNA' belonging to the US LCI database (USLCI) was utilized for the modeling of biomass harvest, collection, and transportation operations. This UP incorporates the US average corn stover production process, including the use of fertilizers, and other processes required for harvesting, grinding, conveying, and the transportation of stover to the biorefinery gate. USLCI was also used for quicklime, diammonium phosphate, sodium hydroxide, corn steep liquor, ammonia, sulfuric acid, and methanol processes, whereas glucose and sulfur dioxide processes were derived from Ecoinvent 3 and Agri-footprint, respectively. The well-to-wheel data for fossil-based gasoline and low sulfur diesel, as well as for the US electricity mix were derived from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model (version 1.3.0.13520).

The IPCC 2013 v.1.03 impact assessment method with a 100-year time horizon was used for the quantification of GWP.

**Results and discussion**

**Impact of LCI modeling approach**

Figure 4 demonstrates GHG emission profiles for all three biorefinery products obtained via detailed, macro-process, and system-level LCI modeling approaches when only the energy content allocation method was applied either to main processes or the product system.

When LR comes with upstream environmental burdens, the deviation of results obtained via detailed modeling approach for ethanol (min 26.4, max 28.0 kg CO\(_2\)-eq/GJ) and electricity (min 34.6, max 91.6 kg CO\(_2\)-eq/GJ) can be significant compared to the macro-process model (ethanol 29.2, electricity 11.9 kg CO\(_2\)-eq/GJ) and the system-level model (ethanol and electricity 28.9 kg CO\(_2\)-eq/GJ). This inconsistency may highlight the crucial role of the specific allocation methods used for assigning GHG emissions to the products of the WWT and CHP plants. At the same time, the range of GWP results for SLO obtained from the detailed model (min 28.3, max 34.6 kg CO\(_2\)-eq/GJ) does not allow for distinguishing between modeling procedures (28.9 and 32.1 kg CO\(_2\)-eq/GJ for system and macro-process modeling).

The remarkable difference in the results related to all three outputs can be noticed when burdens are allocated or...
not allocated to LR (Fig. 4). For ethanol, the mean results were 27.3 kgCO$_2$-eq/GJ burdens allocated to LR, and 32.4 kgCO$_2$-eq/GJ burdens not allocated to LR. A higher CO$_2$ rate is assigned to ethanol in the scenario where LR features zero upstream emission, because the entire emission from UP-1 (i.e., from biomass pretreatment, enzymatic hydrolysis, ...
enzyme production, and fermentation processes) is allocated to the ethanol co-product. For the SLO co-product, the mean results were equal to 31.6 and 6.8 kgCO$_2$-eq/GJ, and for electricity 59.1 and 20.8 kgCO$_2$-eq/GJ in scenarios where LR shares and where it does not share upstream GHG emissions. This notable difference between the results dictates the necessity to clarify the status of LR, namely, whether to define the LR stream as a waste, or not. It should be noted that the related classification issue, i.e., whether to refer to a stream as a co-product, or a residue, or a waste, was determined as one of the key issues for the LCA of a biorefinery.42

Concerning the sources of emission, the inconsistency between the detailed and macro-process level modeling on the one side, and system-level allocation on another side, can be observed in the case of SLO output (Fig. 4), for which the system-level allocation would overestimate the contribution of biomass. However, at the same time, it would greatly underrate the contribution of the lignin solvolysis process (20% for detailed, 18% for macro-process, and 4% for system-level allocation).

For the electricity output, the system-level allocation considerably underestimates the contribution of biomass, UP-6 and UP-7 related burdens. For the ethanol co-product, the system-level model results in a contribution of emissions associated with methanol that is two times higher than under the other models. Generally, the macro-process modeling approach is more consistent with the detailed one, and, hence, it can be alternatively used for the analysis of the unit process contribution to the environmental profile of final outputs.

The substitution (system expansion) modeling approach resulted in arbitrarily low values for all three biorefinery products, namely 15.8, −433.9, and −1634.7 kgCO$_2$-eq/GJ for ethanol, SLO, and electricity, respectively (all data given for the US location). It should be noted that obtaining negative environmental impacts is a common issue for the substitution procedure.7 However, as these impacts are interconnected via relative outputs, they should not be treated as independent environmental profiles of products. Moreover, as the carbon intensity of some products may vary significantly with the location of a production system (e.g., carbon intensity of electricity), the latter should always be reported when using this method.

**Impact of UP specific allocation methods in detailed-level LCI modeling**

Since the detailed LCI modeling assumes some uncertainty arising due to different allocation methods applied in UP-1, UP-4, UP-6, and UP-7, the variation of the respective results should be statistically assessed and properly reported. Statistical tests and corresponding P-values are provided in the supporting information (Tables S4–S6).
Allocation methods in UP-1 and UP-4

Although allocation methods applied to UP-1 and UP-4 play a certain role in GWP results, they only have a prominent impact on SLO output resulting in two distinguishable groups of scenarios (Fig. 5).

Where LR shares upstream environmental burdens, the group of scenarios utilizing the mass and economic allocation methods was found statistically different from the group using MVC, dry mass, and energy content allocation methods (P-values 0.048), while no significant difference was identified inside said groups. The consistency between the total mass and economic allocation methods may imply a link between production cost and total material flows in a biorefinery.

The ethanol output revealed variability only under the scenario where LR shares upstream environmental burdens (Fig. 5). Although none of the scenario groups can be utterly isolated for ethanol, there are three extreme allocation methods referring to total mass, economic, and dry mass, which can be considered in more detail. While no statistically significant difference was found between total mass and economic allocation results, the figures obtained via mass allocation were similar to those received via MVC and energy content methods. However, both economic and mass allocation results were statistically different vis-à-vis the results obtained via the dry mass allocation method (P-values 0.003 and 1.3·10^-5, respectively). The inconsistency of the results observed under total mass and dry mass allocation methods is caused by the fact that a considerable amount of water is needed for running the majority of biorefinery processes, which may finally raise questions about the applicability of allocation based on total mass to a biorefinery.

As Fig. 5 shows, the least effect of UP-1 and UP-4 allocation methods refers to electricity, which implies the necessity to analyze other allocation procedures responsible for a high variability of the results obtained (from 30.4 to 155.3 kgCO2-eq/GJ).

Allocation methods in UP-6 and UP-7

Under the scenario where LR shares environmental burdens, the UP-6 (WWT plant) allocation method does not play...
any pivotal role for the final results, implying that burdens transferred with any of the WWT products have a similar effect on the final output (Figs 6 and 7). On the other hand, the UP-7 (CHP plant) allocation method was found to be essential for SLO and electricity ($P$-values <0.01), highlighting the role of the internal energy supply in carrying environmental burdens.

The difference between the results obtained via the efficiency and working potential methods can be crucial for the electricity output assessment. For instance, following the European Renewable Energy Directive, \(^{16}\) installations starting from 2021 must ensure a 70% GHG emission saving, implying life-cycle GHG emissions from bio-electricity that are equal or less than 54.9 kgCO$_2$-eq/GJ. Hence, while the efficiency allocation method with the mean of 46.8 kgCO$_2$-eq/GJ, would fit into this threshold, the use of the working potential method will fail to meet this criterion.

In the scenario where LR is assumed to be a waste stream, the UP-6 allocation method has a more prominent effect, resulting in a significant deviation of the results for ethanol and electricity ($P$-values <0.01), and the UP-7 allocation method has an impact on SLO and electricity outputs with $P$-values <0.01.

### Reporting uncertainty due to allocation procedures

The results indicate that allocation procedures can bring uncertainty to the LCA outcome, and for a biorefinery under modeling such uncertainties cannot be avoided, although their origins vary.

One of the greatest sources of uncertainty arises from the interpretation of residual streams, namely LR. The scenario where LR is treated as a waste stream, differs greatly from those where LR shares environmental burdens and, hence, these results are reported separately (Table 4). The next essential source of uncertainty is the allocation method applied to CHP products that also involve the need to report related ranges of variability. On the other hand, as there is generally no distinction brought about by UP-1 and UP-4 for ethanol and electricity outputs, as well as by UP-6 allocation procedures, the results are mainly reported

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**Figure 6.** Effect of allocation methods in UP-6 and UP-7 on GWP results for ethanol and electricity.

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Biofuels, Bioprod. Bioref. (2021); DOI: 10.1002/bbb.2214
as for the group of statistically similar allocation methods. However, due to the sensitivity of the results to allocation methods applied to the main conversion processes, the results for SLO are reported with regard to distinguished groups of scenarios, where results are identified as statistically different.

Figure 7. Effect of allocation methods in UP-6 and UP-7 on GWP results for SLO.

Table 4. Uncertainty of GWP results due to allocation procedure (kg CO$_2$-eq/GJ).

| Allocation of environmental burdens to LR | UP-1 and UP-4 allocation methods$^a$ | UP-6 allocation method | UP-7 allocation method |
|------------------------------------------|-------------------------------------|------------------------|------------------------|
| Ethanol                                  |                                     |                        |                        |
| LR shares burdens                        | All methods: 27.4 ± 1.7              | —                      | —                      |
|                                          | All methods: 32.5 ± 0.4              | 32.2 ± 0.3             | 32.8 ± 0.2             |
|                                          |                                      |                        |                        |
| SLO                                      |                                      |                        |                        |
| LR shares burdens                        | MVC, DM, EC: 32.2 ± 3.1              | —                      | 35.0 ± 0.6             |
|                                          | Mass, economic: 21.5 ± 2.4           | —                      | 23.5 ± 1.1             |
|                                          |                                      |                        | 19.5 ± 0.9             |
| LR is a waste stream                     | Mass, DM: 4.0 ± 0.7                  | —                      | 4.6 ± 0.4              |
|                                          | MVC, EC, economic: 7.0 ± 1.2         | —                      | 8.0 ± 0.8              |
|                                          |                                      |                        | 6.1 ± 0.5              |
|                                          |                                      |                        |                        |
| Electricity                              |                                      |                        |                        |
| LR shares burdens                        | All methods: 68.2 ± 34.5             | —                      | 46.8 ± 18.0            |
|                                          | All methods: 21.3 ± 10.9             | 28.9 ± 10.1            | 13.6 ± 4.3             |
| LR is a waste stream                     |                                      | 14.4 ± 5.2             | 28.1 ± 11.0            |

$^a$MVC, mass of valuable components; DM, dry mass; EC, energy content.
Tracking environmental burdens

The matrix approach allows environmental burdens to be tracked through biorefinery value chains, and, hence, it can be used for the evaluation of hotspots associated with different stages of the latter. Figure 8 demonstrates the contribution of biorefinery processes to three value chains, namely: ethanol, SLO, and electricity.

All three value chains start with corn stover, and each processing step within a biorefinery adds a certain amount of burden to the environmental profile of the final output. It should be noted that those burdens can either be directly transferred to the process output (e.g., sulfuric acid used in the biomass pretreatment stage), or indirectly, through a network of energy and material exchanges, such as steam, electricity, process water, cooling, and chilling services. As all those exchanges are supplied from on-site facilities, including energy carriers, which are produced from carbon-containing residual streams (moist LR, char, biogas, and WWT sludge), the exchanges may indirectly convey back to the main conversion processes some share of the burden as well. As a result, the amount of burden is expanding irreversibly through the value chain. Figure 9 shows the role of energy and material exchanges in the transfer of GHG emissions to the main biorefinery processes.

Figure 8. Contribution of processes featuring direct environmental burdens into value chains of ethanol, SLO, and electricity.
Concerning the upstream lifecycle GHG emissions of corn stover and UP-1 chemicals, it is worth noting that its amount rises by 27%, 29%, and 39% in the ethanol, SLO, and electricity value chains, respectively, where more than a half of that growth (16%) is owed to the pretreatment technology (Fig. 8). Among the exchanges primarily responsible for this accumulation are high-pressure steam and electricity, with the contribution of 40% and 36%, respectively (Fig. 9).

The contribution of GHG emissions from the WWT facility (UP-6) to the biomass pretreatment process amounts to 10% of the total GHG emissions for the pretreatment slurry, which is followed by a material accumulation of 32% in the hydrolysis, enzyme production, and fermentation processes (Fig. 8). Said burden is primarily conveyed to the pretreatment stage by the processed water (74%), while its accumulation in the hydrolysis, enzyme production, and fermentation processes (Fig. 8). Said burden is primarily conveyed to the pretreatment stage by the processed water (74%), while its accumulation in the hydrolysis, enzyme production, and fermentation processes is due to chilling (34%) and cooling (29%) services, and electricity (28%) (Fig. 9). A significant amount of processed water consumed for biomass pretreatment is caused by the solid loading limit that should not exceed 30% in the pretreatment reactor. Consequently, this also has an impact on the required amount of high-pressure steam and electricity to run the processes. Thus, a decrease in the amount of solids (e.g., via the separation of lignin before the hydrolysis step) could significantly improve the environmental profiles of all produced outputs.

Being a result of transfers via internal exchanges, the GHG emissions associated with the lignin solvolysis process (UP-4), i.e., emission stemming from the methanol lifecycle can already be detected in the pretreatment slurry. Nonetheless, its tangible impact is observed only in the solvolysis process, with an overall contribution to the SLO emission profile of 20% (Fig. 8). Thus, testing technological conditions allowing a smaller amount of methanol in SLO is becoming an important driver for obtaining more sustainable lignin oil.

In addition to hotspots related to the pretreatment and hydrolysis steps, a notable accumulation of burden in the electricity value chain refers to the CHP plant, revealing the accretion of the burden from the plant itself of 415% compared to the previous processing step (Fig. 8). This burden is primarily conveyed to the CHP plant via cooling service (50%) and electricity (36%) (Fig. 9).

At the same time, such processes as ethanol distillation and solids recovery, ethanol purification, and LR drying do not feature any noteworthy accumulation of GHG emission. However, it should be noted that the analysis can be sensitive to allocation methods; hence, testing at least two allocation methods for each unit process could enhance the reliability of the obtained results.

Further discussion

The need for a detailed LCI biorefinery modeling based on the subdivision approach stems from the biorefining
concept itself: structurally different carbohydrates are being separated and valorized within the biorefinery boundary that might require additional material and energy inputs. As a result, the development of product-related environmental profiles should take into account a unique exchange network that is responsible for transferring environmental burdens from initial resources to final products through a set of intermediates, such as LR, char, steam, electricity, etc.

Moreover, when allocation reflects a physical relationship, for a given biorefinery design, the system and macro-process LCI modeling procedures could only use allocation based on energy content, while detailed LCI modeling, because of a deeper system subdivision, was able to work with different allocation methods. However, unlike system-level allocation, the detailed subdivision approach would most likely face difficulties when applying economic allocation based on market prices, as there are no such prices for intermediates (e.g., for diluted ethanol and moist LR). However, as an alternative to market prices, production costs can be used to partition upstream burdens.

Furthermore, concerning allocation, the consistency of LCA results obtained via different allocation methods would significantly enhance their reliability. Generally, the consistency of the results has been demonstrated for allocation methods applied to the main conversion processes (excluding total mass and economic allocation in the SLO case), as well as to the WWT plant. On the other hand, allocation methods applied to the CHP plant have demonstrated a significant variability in GWP results related to SLO and electricity outputs. The latter observation stresses the key role of internal energy supply in carrying environmental burdens within a biorefinery.

Although the detailed modeling can be limited by data availability and time required for inventory compilation, when the matrix approach is used, it can help to track the cumulative capacity of biorefinery exchanges and to identify system hotspots. Moreover, since the coefficient matrix of cumulative allocation effects is a uniform representation of the cumulative capacity of system exchanges, it can be equally applied to a variety of attributes, like, for instance, economic ones and, hence, can be simultaneously used for LCA and life-cycle cost analysis.

**Conclusion**

This paper demonstrated the use of a matrix approach for the detailed subdivision of a second-generation biorefinery, with the final goal of defining the global warming potential profiles of all three co-produced commodities and hotspots associated with their production cycles. Forty scenarios utilizing different allocation approaches for the main conversion processes and services were used in the detailed LCI modeling approach that allowed the use of statistical procedures capable of identifying the uncertainty of the obtained results and related allocation methods responsible for their variability.

Unless allocation cannot be avoided, LCA results might always be disputable, and this paper stresses the issue of using specific allocation methods for assigning burdens to the products of a combined heat and power plant, as these methods have contributed greatly to the variability of the results. The paper also touches on the issue of whether lignin cake should be treated as a zero upstream GHG emission residue, as this can significantly alter the environmental profile of the resulting product.

Furthermore, the ability of the detailed LCI modeling approach to track the cumulative effect of environmental burdens determined unique allocation factors for final products and resulted in a significant difference between results obtained via the detailed subdivision approach and more aggregated LCI modeling procedures, at least for two of three products, ethanol, and electricity. This, in particular, stresses the importance of moving towards the subdivision procedure in LCI modeling.

The tracking of GHG emissions highlights a crucial role of the biomass pretreatment and lignin solvolysis processes in the accumulation of GHG emissions within biorefinery value chains, and indicates the importance of decreasing the amount of solids in the pretreatment slurry (e.g., via the separation of lignin before the hydrolysis step) and methanol content in soluble lignin oligomers for the improvement of the environmental profiles of related biorefinery co-products.

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Svetlana V. Obydenkova

Svetlana Obydenkova is PhD researcher at Maastricht University and Eindhoven University of Technology and Chief sustainability officer at Vertoro. She has an MS degree in mechanical engineering and sustainable fuels economy from Kungliga Tekniska Högskolan (KTH Royal Institute of Technology), Sweden and Akademia Górniczo-Hutnicza (AGH University of Science and Technology), Poland. She focuses on Life Cycle Assessment (LCA) and techno-economic analysis of biorefineries.

Panos D. Kouris

Panos Kouris holds a MSc in chemical engineering and is finalizing his PhD research at Eindhoven University of Technology in the field of thermocatalytic biomass conversion technologies. Since 2017 he has been the co-founder and chief technology officer of the company Vertoro, the commercialization vehicle of a biomass-to-lignin oil technology.

David M.J. Smeulders

Professor David Smeulders holds an MSc in aerospace engineering from Delft University of Technology and a PhD in applied physics from the Eindhoven University of Technology (TU/e). He is a full professor in the energy technology section at TU/e and chairs the energy technology group. He is (co)-author of more than 160 scientific publications, member of the Dutch national ‘topsector’ board TKI Gas, member of the Dutch Advisory and Evaluation Team for the Dutch national ‘topsector’ TKI Urban Energy and member of the Scientific Board of the Netherlands Energy Research Alliance (NERA). He is Scientific Director of the 4TU Energy Centre.

Michael D. Boot

Dr Michael Boot has specialized in combustion technology, with a specific interest in the design of renewable and cleaner transport fuels.

Yvonne van der Meer

Prof Yvonne van der Meer is scientific co-director of the Aachen Maastricht Institute for Biobased Materials and chair of Sustainability of Chemicals and Materials at Maastricht University with 24 years of experience in sustainable chemistry. Her research team develops and applies quantitative sustainability assessment methods for biobased and circular materials.