

Comparison between Different Hybrid Life Cycle Assessment Methodologies: A Review and Case Study of Biomass-based *p*-Xylene Production

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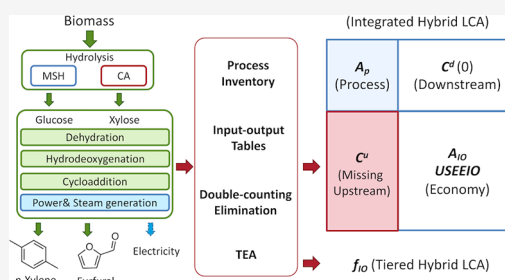


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ABSTRACT: Two common life cycle assessment (LCA) methods are process LCA and economic input–output LCA, which suffer from truncation error and aggregation error, respectively. Many hybridization techniques are developed to improve the accuracy of analysis by combining both methods. This work aims to review different hybrid LCA methodologies under various data availabilities through a case study of two biomass-based *p*-xylene production technologies using concentrated acid (CA) and molten salt hydrate (MSH) hydrolysis. The MSH process without selling electricity to the grid has a lower global warming potential than the CA process when evaluated by process LCA, tiered hybrid LCA, and integrated hybrid LCA after binary correction for double counting. With prior knowledge on LCA databases or assumptions on economic activities that are irrelevant to the production, double counting could be further eliminated, and the MSH process would behave similarly or even worse than the CA process.



1. INTRODUCTION

As a method to evaluate environmental impacts of products/processes, life cycle assessment has been widely used in process design,^{1–3} supply chain optimization,^{4–8} emerging technologies development,^{9–11} and decision and policy making.^{12–14} Apart from reduced costs, one main driving force for producing biomass-based chemicals is the common belief that they are more likely to be environmentally friendly than their oil-based counterparts.^{15–17} However, such an assertion based solely on the feedstock will not be convincing without the justification from the life cycle assessment.

Tremendous effort has been paid to the production of biomass-based chemicals in recent years for its promising potential to replace fossil-based production that causes increasing concern over global warming.^{3,18–21} One notable example is the life cycle assessment (LCA) study on bioethanol production.^{17,22,23} With the rapid development of technology, there is plenty of room for improving each unit process, emphasizing the importance of identifying main contributors to emissions. NREL reports provide detailed fermentation unit process information²⁴ used in many LCA studies.^{1,25} Other stages of bioethanol production can also greatly influence the assessment. For instance, in the harvest stage, the decrease in soil organic carbon (SOC) increases carbon dioxide emissions.²⁶ Also, as farmers clear land in undisturbed ecosystems for biomass production, direct and indirect effects of land-use change may be significant.^{27,28}

Four phases of conducting LCA research proposed by the International Organization for Standardization (ISO) are goal and scope definition, inventory analysis, impact assessment,

and result interpretation.^{29,30} There are no limitations, however, on the specific inventory analysis methods. Both process LCA and economic input–output LCA (EIO-LCA) are common tools in the inventory analysis.

Process LCA is a bottom-up approach with relatively low uncertainty but requires a lot of detailed data. The data collection in LCA could be time-consuming and challenging. Thus, most LCA studies of biochemicals focus on collecting detailed “gate-to-gate” foreground process data from experiments, simulations, or other literature.³¹ The raw materials and energy usage in the inventory are supplemented by generic background data from the databases. Commercialized databases, including Ecoinvent and GaBi,³² contain a large amount of unit processes and emission data.^{33–35} Using process LCA, Akanuma and colleagues³⁶ studied different pathways of synthesizing purified terephthalic acid. Chaudry et al.¹⁵ analyzed the CO₂ and total greenhouse gas (GHG) emission during the milking process in hydrocarbon production from microalgae. Yang et al.³⁷ illustrated the advantage of producing ethylene from biomass over shale gas through comparative process LCA. The conventional process LCA is also widely used to evaluate the environmental impacts of the biorefinery where multiple products are produced.^{38–40}

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Despite its extensive usage, process LCA also suffers from two major drawbacks. First, even though process LCA data are considered to be detailed and reliable, significant truncation errors are observed in many cases.⁴¹ The error differs from case to case and is mainly due to difficulties in tracking infinite supply chains and collecting data.⁴² Second, not all chemicals are covered in the database; only a fraction of more than 80 000 chemicals sold in the United States are in the commercial database.⁴³ Among the data captured, only a few necessary chemicals use the primary data directly obtained from chemical plants. Most chemical production processes are kept confidential. Thus, aggregated report data and estimations have to be utilized, which increases the chance for aggregation errors in chemical production.⁴⁴

EIO-LCA, on the other hand, is a top-down method that considers the interactions between different industries. Introduced by Nobel Laureate Wassily Leontief⁴⁵ to study the U.S.'s economic structure, this method was later developed to include environmental impacts associated with economic activities.⁴⁶ By tracking monetary transactions and environmental impacts of monetary flows, a comprehensive analysis that includes all the economic activities could be performed. This method underlines the supply chain relationship in production. In theory, since every economic activity is captured throughout the supply chains, the input–output analysis is thought to have a more complete system boundary than process LCA.^{47,48} Franchetti⁴⁹ studied the food waste's anaerobic digestion process that produced methane for energy conversion using EIO-LCA. Lee et al.⁵⁰ applied the EIO-LCA model to biohydrogen development in the United States. Urban and Bakshi²⁵ used EIO-LCA as one assessment tool to compare biobased and fossil-based 1,3-propanediol production. The EIO-LCA method is also utilized to analyze the global impacts of biofuels transport policies.⁵¹

Since monetary flows rather than physical flows are used as inputs, EIO-LCA is inevitably subject to price fluctuation.^{35,52,53} More importantly, the whole industry is divided into less than a few hundred sectors. This means that all products in the same sector are considered to have the same emission profile, leading to the so-called aggregation error.^{53–55}

It is natural to consider a hybrid model that could take advantage of both the precision of process LCA and the comprehensiveness of EIO-LCA.⁵⁶ The similarity in the computational structures of both process LCA and EIO-LCA makes this hybridization possible.⁵⁷ When process LCA is chosen as the starting point of hybridization, the aim of the research is to expand its system boundary.^{58,59}

Since tiered hybrid LCA and integrated hybrid LCA are the most common choices in linking the process and input–output data,⁶⁰ this paper will illustrate these two methods through a case study. Nevertheless, apart from the tiered and integrated hybrid LCA, other input–output based hybrid LCA methods are also used by many researchers.⁴⁸ Those input–output based hybrid LCA methods include the path exchange (PXC) hybrid⁶¹ and the matrix augmentation.^{62,63} Interested readers are encouraged to refer to the review by Crawford et al.⁶⁰ for more information.

During chemical process design, encountering the data gap of chemicals not included in the background database is common in traditional process LCA.⁶⁴ There are many “streamlined” LCA methods to simplify the analysis by cutting-off, replacing with similar molecules, and estimating

by the stoichiometric ratio of raw material chemicals.^{64,65} These simplified LCA methods inevitably leave out some inputs and introduce considerable truncation errors. Processes using more chemicals that are not in the database will have more missing flows from upstream chemical production than those that are well captured by the process LCA database. Different magnitudes of truncation errors pose challenges to accurately evaluating a specific process and make it difficult to compare two technology alternatives with unknown but potentially different boundary completeness.⁵⁸ Hybrid LCA could be used under these circumstances to improve the LCA results and guide decision making.

In this paper, the above-mentioned process LCA, EIO-LCA, tiered hybrid LCA, and integrated hybrid LCA methods are reviewed and demonstrated in two biomass-based *p*-xylene productions. Simulations and technoeconomic analysis (TEA) results for *p*-xylene production using the concentrated acid (CA) and the molten salt hydrates (MSH) technology are taken from Athaley et al.'s work.² Assumptions and information about the process plays an important role in hybridizing process LCA with EIO-LCA. Double-counting elimination techniques are then applied to the tiered and integrated hybrid LCA. The case study highlights the significance of utilizing hybrid LCA in chemical process design. Truncation errors from chemicals not captured by the database would go unnoticed and result in misleading conclusions when using process LCA. The integrated hybrid LCA with double-counting elimination based on prior background database knowledge is recommended since it could reveal the missing flows and provide more robust insights into environmental impacts. This work also provides suggestions on the LCA method selection under various data availability.

2. METHODS

2.1. Matrix Representation of Process LCA. As suggested by the name, process LCA's inventory is based on the processes of significant environmental impacts within the system boundary. Formalized by Heijungs and Suh, the matrix method is a good representation of intermediary flow exchanges within different unit processes, especially in large systems with loops.⁵⁷ First, the processes of interest are set as the columns and each product involved in the production as the rows of technological matrix A_p .⁶⁶ The element a_{ij} (row i , column j) of the technological matrix, for example, represents the raw material i used in the process j .⁶⁶ The rows could be further generalized to represent the amount of process and services used instead of physical material flows. Next, functional units are selected to represent the final demand for production (e.g., 1 kg of *p*-xylene). Then, the scaling factor vector s that corresponds to this production activity is calculated by performing a simple matrix inversion.

$$s = (I - A_p)^{-1} \cdot f_p \quad (1)$$

where square matrix I is the identity matrix with the same size as A_p and f_p is the vector that contains the functional units. The matrix inversion is equivalent to solving the system of linear equations so that the demand for each process matches the output of final products in the functional units. This step serves the same function as compiling the inventory of all raw material and utilities in the conventional LCA based on the process flow diagram.⁶⁷

Some authors^{55,57} prefer to use the notation A_p^{-1} instead of $(I - A_p)^{-1}$ in the calculation. This is merely a difference in the representation of the technological matrix that does not change the final results. The $(I - A_p)^{-1}$ notation is used in this work to show the similarity in the computation structure between process LCA and EIO-LCA.

The matrix inversion could only be performed when A_p is a square matrix, which requires all processes to be monofunctional without byproducts in each production stage. When multiple byproducts are produced in the multifunctional process, different techniques, including system disaggregation, substitution, allocation, and system expansion, are recommended to convert the rectangular matrix into a square one.⁵⁷ Another special case is when multiple technologies are available to produce the same product. The optimization tools under different constraints are recommended to deal with this type of rectangularity.^{66,68}

The final step is to connect each production stage with environmental impacts by the environmental intervention matrix B_p . The element b_{mj} in the matrix B_p represents the environmental impact m (e.g., global warming potential) of the process j . In this paper, only one environmental impact, global warming potential (GWP), is considered, so that B_p is a vector. And the total environmental impact of the system is

$$g = B_p \cdot (I - A_p)^{-1} \cdot f_p \quad (2)$$

The contribution of each process could be represented in a vector as

$$\text{Contributions} = B_p \cdot \text{diag}((I - A_p)^{-1} \cdot f_p) \quad (3)$$

where $\text{diag}((I - A_p)^{-1} \cdot f_p)$ is a diagonal matrix with the elements of $(I - A_p)^{-1} \cdot f_p$ on its main diagonal.

2.2. EIO-LCA. Economic input–output LCA tracks the monetary flow through a similar matrix to the process LCA, which is compiled from input–output tables published by the government in different regions of the world.⁶⁹ The detailed procedure of constructing this input–output direct requirement matrix A_{IO} is well documented in many textbooks.^{30,69,70} In particular, the USEEIO model developed by Yang et al.⁷¹ is used in this paper. Its direct requirement coefficients matrix A_{IO} is a commodity-by-commodity table⁶⁹ that is based on the 2007 make-and-use tables published by the Bureau of Economic Analysis (BEA) of the U.S.⁷² Carnegie Mellon University also provides the web-based EIO-LCA computational tool, which enables practitioners to use the input–output method without building the model from scratch.⁷³

Similar to the technological matrix A_p in process LCA, each column of A_{IO} describes a production process requirement on the intermediate inputs from itself and other processes in order to produce one unit of output.³⁵ For instance, a_{ij} represents the average cost spent on the raw material in sector i to produce \$1 worth of product in sector j . The environmental intervention matrix (or satellite table) B_{IO} of the USEEIO model serves the same function as B_p from process LCA. It links economic activities (in monetary units) to environmental impacts. With the vector f_{IO} representing the final monetary demands from each economic sector, the total environmental impact is calculated from eq 4:

$$g = B_{IO} \cdot (I - A_{IO})^{-1} \cdot f_{IO} \quad (4)$$

The term $(I - A_{IO})^{-1}$ is known as the Leontief inverse and could be decomposed by the Taylor series, representing the

sum of environmental impacts from different layers of the supply chain.⁷⁴

$$g = B_{IO} \cdot (I + A_{IO} + A_{IO}^2 + A_{IO}^3 + \dots) \cdot f_{IO} \quad (5)$$

The first term of eq 5, $B_{IO} \cdot I \cdot f_{IO}$, is the direct impact of the process, while the second term, $B_{IO} \cdot A_{IO} \cdot f_{IO}$, represents the environmental impacts of raw materials from the first tier of suppliers.³⁰ This decomposition is useful in calculating the coverage of each sector at different depths of supply chain layers and analyzing the contributions.

The prices of raw materials should be consistent with the input–output table. When a price in a different year is used, necessary conversions based on price index are needed.⁴⁹ Another price conversion for f_{IO} is that from the purchaser's prices (prices paid by the customers) to the producer's prices (prices at the plant site). The producer's price is converted from the purchaser's price by deducting the retail margin, wholesale margin, and transportation costs.⁷⁰ These costs for each economic sector could be found from the IO tables published by U.S. BEA. In reality, however, the difference between them is not very significant unless transportation or taxes are the main contributors.⁷⁰

The most significant feature of EIO-LCA is its use of economic values instead of physical material flows. There are generally two ways of selecting the final monetary demand f_{IO} : choosing the final product sector with the producer's price as the input or selecting the monetary inputs for each component used in the production.²⁵ The first method is a quick but very rough estimation based solely on the final product's selling price, which is the producer's price paid to the chemical producer without transportation and retail cost. The ignorance of production details makes the result highly aggregated. Nevertheless, it demonstrates EIO-LCA's versatility to make estimations based on even the least amount of information.

When more information is available, the inputs to different processes could be used to refine the estimation, as done in the second method of EIO-LCA. Here, the final selling price is only for the estimation of zero-order direct emission, and the material flows and energy usage are converted to expenditures on each economic sector. The EIO-LCA serves as a source of background data, which is the same as the process database in process LCA.

There are two main advantages of EIO-LCA. First, many input–output analysis tools for LCA, including Comprehensive Environmental Data Archive (CEDA)⁷⁵ and the Economic Input–Output Life Cycle Assessment tool (EIO-LCA),⁷⁰ are free of charge for academic usage because less confidential and easily accessible data are used for compilation. Second, every material flow calculated from EIO-LCA is, in theory, complete in the upstream, which avoids the truncation error of process LCA.

Alvarez-Gaitan et al.⁵² extend the use of EIO-LCA by estimating missing flows for the services based on the cost of raw materials and utilities. For the production of chemicals, the ratio of variable cost (raw materials and energy usage) to fixed cost (other services required to run a plant) could be obtained from the technoeconomic analysis (TEA). For instance, this ratio has been taken as 80:20 from the European Integrated Pollution Prevention and Control Bureau's (EIPPCB) technical report about chlor-alkali plants.⁷⁶ The estimated total fixed cost is then assigned to relevant service sectors by the average commodity usage profile in the use table from the input–output analysis.

2.3. Tiered Hybridization. In the hybrid LCA, the system described by the process technological matrix A_p is sometimes referred to as the process system, while that described by the direct requirement matrix A_{IO} is referred to as the IO system.⁴ Tiered hybrid LCA generally refers to the hybridization methods that are based on process LCA but also include the input–output information to expand the system boundary.⁶⁰ Material and energy flows, services, or different life cycle stages missing from the process system are captured by the IO systems.^{66,77}

One way of performing tiered hybrid LCA evaluates the process system and IO system separately without considering their interactions, especially when some services are not covered in the traditional process LCA background database.⁷⁸ The overall environmental impacts could be written as the sum of the process LCA and EIO-LCA results.⁶⁰

$$g = B_p \cdot (I - A_p)^{-1} \cdot f_p + B_{IO} \cdot (I - A_{IO})^{-1} \cdot f_{IO} \quad (6)$$

In eq 6, the main focus is to obtain the direct requirement vector f_{IO} for flows that are neglected in the process system. The technoeconomic analysis contains the operating costs to run the plants, which is well-suited as the direct requirement from the economy. After removing the raw material and utility costs to avoid double counting, the remaining operating cost is the fixed operating cost. This hybridization is straightforward, but depending on the choice of functional units for the process and IO systems, double counting or incomplete boundary might be a potential concern.⁶⁷

Equation 6 can be reformulated to match the integrated hybrid LCA matrix representation, which will be covered in section 2.4.⁶⁰ The block matrices on the off-diagonal are all null, which indicates the lack of coupling or interaction between these two systems.

$$g = (B_p B_{IO}) \cdot \begin{pmatrix} I - A_p & 0 \\ 0 & I - A_{IO} \end{pmatrix}^{-1} \cdot \begin{pmatrix} f_p \\ f_{IO} \end{pmatrix} \quad (7)$$

Many authors also use the term tiered hybrid LCA when considering only the purchase of upstream IO sector's flows from the process system.⁵⁶ This may cause overlapping of concepts in a particular case of the integrated hybrid LCA, where the downstream cutoff matrix is assumed to be zero, which is usually the case in chemical production. To avoid confusion, the tiered hybrid LCA in this paper refers only to the hybridization that does not use the integrated hybrid LCA matrix framework. A tiered hybrid method that considers the interactions between the economy and the processes is illustrated here because it follows a stepwise procedure and is hard to formulate via an integrated matrix notation.⁵² It begins with defining the depth of the interface between the IO and process models for each input by examining the process background data. Then, the coverage of different sectors at the corresponding depth is calculated following the decomposition of the Leontief inverse. Each input is then corrected by the system incompleteness factors (from eq 9) for remaining flows from the economy. These flows make up for the contributions that are not captured by the process system.⁵²

Coverage up to N th layer

$$= \left(\sum_{n=0}^N B_{IO} \cdot A_{IO}^n \right) \cdot (B_{IO} \cdot (I - A_{IO})^{-1}) \quad (8)$$

System incompleteness factor

$$= J - \left(\sum_{n=0}^N B_{IO} \cdot A_{IO}^n \right) \cdot (B_{IO} \cdot (I - A_{IO})^{-1}) \quad (9)$$

where J is a matrix of ones that has the same size as B_{IO} , and \cdot represents “element-wise” matrix division, i.e., if $G = C/D$, then $g_{ij} = c_{ij}/d_{ij}$.

2.4. Integrated Hybridization. When a similar matrix notation to that shown above is used, the integrated hybrid LCA could be written as⁷⁹

$$g = (B_p B_{IO}) \cdot \begin{pmatrix} I - A_p & -C^d \\ -C^u & I - A_{IO} \end{pmatrix}^{-1} \cdot \begin{pmatrix} f_p \\ 0 \end{pmatrix} \quad (10)$$

In eq 10, the functional unit is chosen as only the final demand from the process system, while the requirement of the economy comes from the upstream (C^u) and downstream (C^d) cutoff matrix. The block matrix in the second term that contains the process, economy, upstream, and downstream is referred to as the integrated matrix by Crawford et al.⁶⁰

Ideally, the LCA practitioner that performs the integrated hybrid LCA in a company should ask for the sales record to build the downstream cutoff matrix (information about the products purchased by other industries) and the bills to construct the upstream cutoff matrix (raw material and energy usage).⁸⁰ Most of the time, however, the LCA during the process design stage is based on a plant that is not built yet. Consequently, estimations need to be made from the input–output table.

For the cases with no feedback loop,⁵⁶ and where the economic structure does not change, or the products are for the final demand and not used in another industry,³⁵ the downstream cutoff matrix could be neglected. This is the assumption often made in the cradle-to-gate analysis of chemical production. In this case, the integrated hybrid approach and tiered hybrid approach would yield the same result,^{48,56} which is why the integrated hybrid LCA with a null C^d is also referred to as the tiered hybrid LCA, as mentioned in section 2.3. However, the integrated hybrid matrix formulation is more flexible to include new information and update C^d by following the works of Suh⁸⁰ and Teh et al.⁸¹ Because of this, the hybridization using the integrated matrix is referred to as the integrated hybrid LCA even when its downstream cutoff matrix is zero throughout this paper.

Many terms in eq 10 are known from the process LCA and EIO-LCA, so the only task left is to construct the upstream cutoff matrix (C^u). This matrix has the same number of rows as the direct requirement matrix A_{IO} and the same number of columns as the process technological matrix A_p . For the hybridization of each column (a production process), a concordance matrix that matches the processes to sectors in the economy is first built. For example, in the production of *p*-xylene, electricity generation is the 17th process listed in the CA process's technological matrix. This electricity generation process belongs to the “221100/electricity/us” sector, the 22nd sector in the A_{IO} . Thus, for all the elements in the 17th column of the concordance matrix, $h_{K,17}$ ($K = 1, 2, 3, \dots$), only $h_{22,17}$ is one while the rest are zero. The uncorrected upstream cutoff matrix is calculated from eq 11.^{62,82}

$$c_{M,k}^{\text{uncorrected}} = a_{M,K}^{\text{io}} \cdot h_{K,k} \cdot \pi_k \quad (11)$$

In eq 11, a_{MK}^{io} is the element in the M th row and K th column of the matrix A_{IO} . The element h_{Kk} in the concordance matrix connects the process k and sector K as shown in the example. And π_k stands for the unit price of the product from process k . This hybridization is to choose the column from A_{IO} that corresponds to the process of interest, multiplying it by its unit price, and adding this column to the upstream cutoff matrix.⁸²

The hybridization could be performed column by column, which means that there is flexibility in selecting which process to be hybridized. When background processes from the database are considered detailed and reliable enough, there is no need to hybridize and estimate the missing flows for them. For instance, Perkins and Suh⁵⁶ set the background processes' upstream cutoff matrix to null in the hybrid LCA study of the jacket production. On the other hand, even the detailed background data may still miss certain essential flows, including some services. Thus, all the background unit processes in the Ecoinvent can be hybridized, which sometimes requires a heavy workload.⁶²

The upstream cutoff matrix C^u is the connection between the process and the economy, through which the IO model estimates the missing parts of the process model.⁵⁹ It could be demonstrated from the inversion of the block matrix in eq 10.⁸³ Since both A_p and A_{IO} are square and C^d is 0, the matrix inversion yields a relatively simple result in eq 12.

$$g = (B_p B_{IO}) \cdot \begin{pmatrix} (I - A_p)^{-1} & 0 \\ (I - A_{IO})^{-1} \cdot C^u \cdot (I - A_p)^{-1} & (I - A_{IO})^{-1} \end{pmatrix} \cdot \begin{pmatrix} f_p \\ 0 \end{pmatrix} \quad (12)$$

It could be further expanded as

$$g = B_p \cdot (I - A_p)^{-1} \cdot f_p + B_{IO} \cdot (I - A_{IO})^{-1} \cdot C^u \cdot (I - A_p)^{-1} \cdot f_p \quad (13)$$

When C^u is completely occupied with 0, the integrated matrix of the hybrid system degenerates to that of the tiered hybrid LCA without the interactions in eq 7. The more elements that are nonzero in the C^u , the more that the interactions between the process and economy are considered. The integrated hybridized matrix that contains the process system, the economy, and the upstream is also a mixed unit model which could be interpreted in the same way as the process technological matrix.⁸¹ Similar to eq 3 used to represent the process LCA contribution of each unit process, their upstream contributions can be calculated from

Upstream contributions

$$= B_{IO} \cdot (I - A_{IO})^{-1} \cdot C^u \cdot \text{diag}((I - A_p)^{-1} \cdot f_p) \quad (14)$$

Each column in C^u represents the upstream requirements from the economy for this process. In the *p*-xylene production example, the 17th column of the upstream cutoff matrix estimates the average expenditure on all 388 sectors of the economy (e.g., natural gas, metal, and others) to produce one unit of electricity. In Figure 1, this input estimation comes from the IO system (shown in yellow) and expands the process system's boundary (shown in green). As the input–output analysis includes all activities in the economy, the addition of the C^u will bring in the missing flows like sales and other

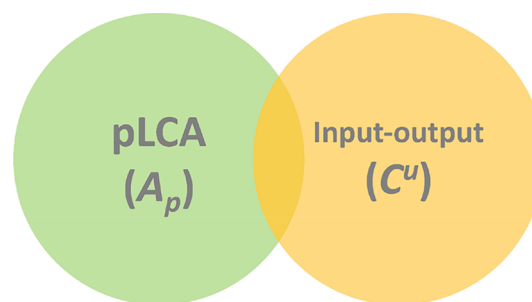


Figure 1. System boundary of process LCA (in green) and flows introduced by the upstream cutoff (in yellow).

services. However, it inevitably accounts for some processes (in the overlapping region) twice, highlighting the importance of double-counting elimination in the next section.

2.5. Double-Counting Correction for Integrated Hybridization. The most widely used double-counting elimination method is termed the binary correction by Agez et al.⁸² because of the binary filter matrix λ introduced. Li et al.⁸⁴ used this method to correct the upstream cutoff matrix in U.S. beef production. Wiedmann and co-workers⁶² applied this correction to wind power in the U.K. It is also utilized by Zhao and You⁴⁷ in the LCA of Li-ion batteries. Equation 11 is modified to be⁸²

$$c_{Mk}^{\text{binary}} = \lambda_{Mk} \cdot a_{MK}^{io} \cdot h_{Kk} \cdot \pi_k \quad (15)$$

The only information needed to construct the binary matrix is the technological matrix A_p in the process LCA and the concordance matrix h described in section 2.4. The logic behind eq 15 is that, when the element on the k th column and i th row of the A_p is nonzero, the contribution of the process i is already considered in the process LCA. Graphically, the process i is in the overlapping region in Figure 1 and counted twice by the process LCA and the input–output analysis. Since the process i corresponds to the economic sector M , and since the process data are generally more reliable, the estimation of this flow in C^u needs to be removed.

The second double-counting elimination technique is an improvement on the binary correction, which introduces a new filter matrix θ to remove all the elements that represent the processes known to be complete.³⁵ It is named Strømman and Solli Method (SSM) by Agez et al.⁸² after the two authors who first reported this method.³⁵

$$c_{Mk}^{\text{SSM}} = \theta_{Mk} \cdot c_{Mk}^{\text{binary}} = \theta_{Mk} \cdot \lambda_{Mk} \cdot a_{MK}^{io} \cdot h_{Kk} \cdot \pi_k \quad (16)$$

The binary element θ_{Mk} is set to zero whenever the process k that corresponds to sector M is known to be complete. For example, if the production of sulfuric acid is known to use no agricultural product, agricultural-related sectors in the cutoff matrix for the sulfuric acid process should be set to zero in order not to include the flow that does not exist. The decision on which processes to be neglected depends on the prior knowledge of the process and may sometimes seem arbitrary. It is reasonable to define a few scenarios that include different economic sectors so that a confidence interval of the impacts is established.⁴²

The SSM correction would have the same result as that of the binary correction when θ_{Mk} consists of entirely ones. Because of the flexibility in choosing sectors that are complete, all the processes, including both the foreground and background ones, are hybridized first in the SSM correction case

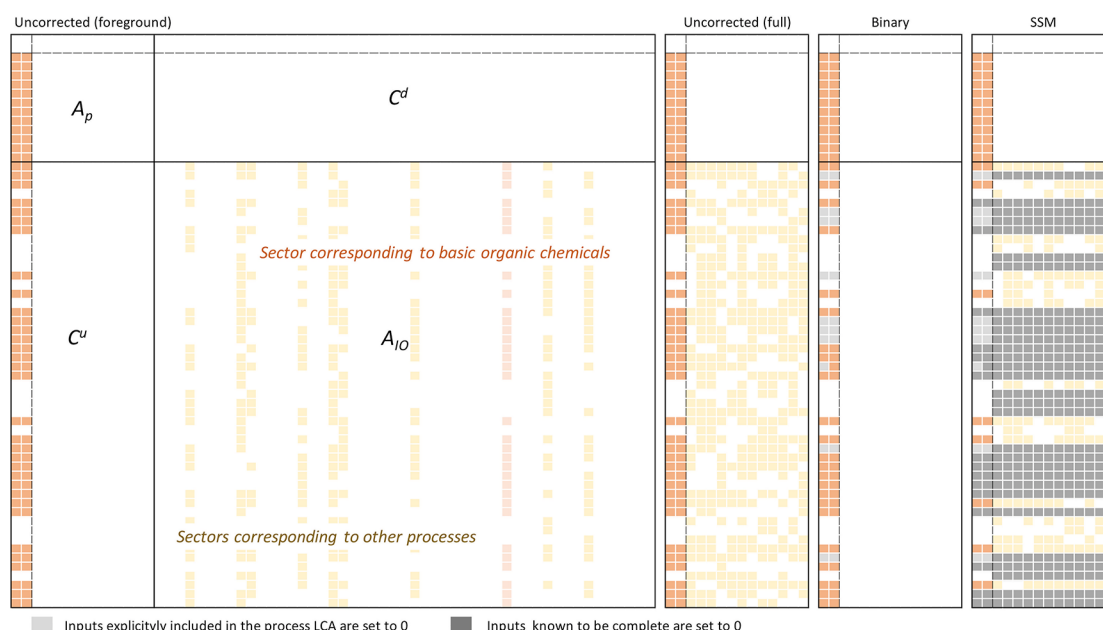


Figure 2. Integrated matrices and double-counting elimination methods applied to the CA process for *p*-xylene production. [The first two columns represent the foreground production processes of furfural and *p*-xylene. The size of matrices is merely for demonstration purposes, thus not reflecting the real situation. A detailed example could be found in the [Supplementary Spreadsheet S1](#).]

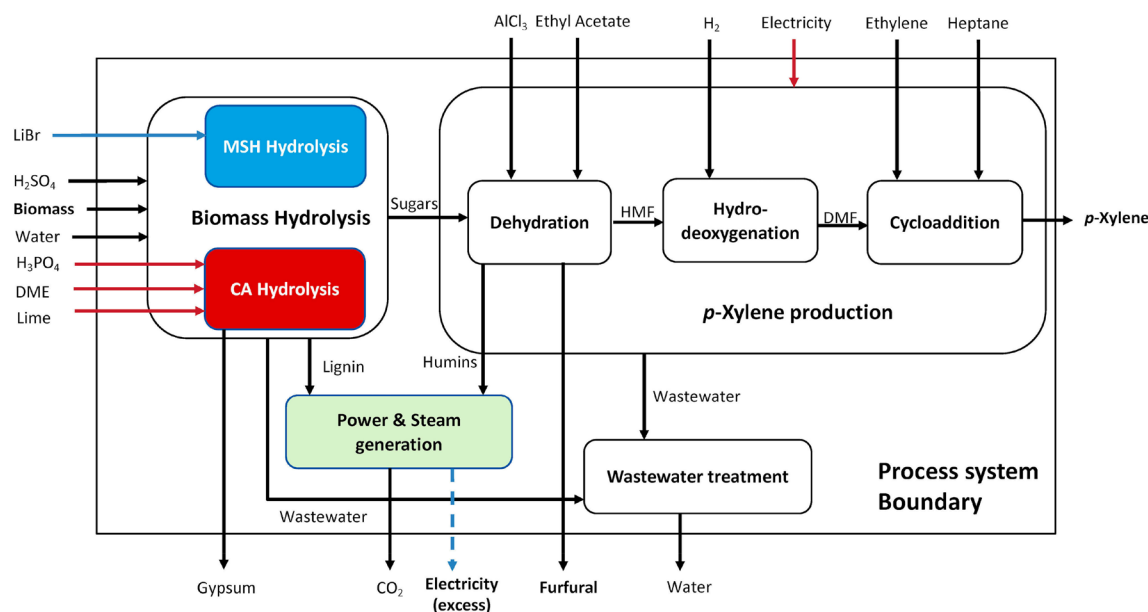


Figure 3. Adapted process flow diagram from Athaley et al.² Reproduced with permission from ref 2. Copyright 2019 Elsevier Ltd. [Red, flows specific to the CA process; blue, flows specific to the MSH process; blue dashed line, the MSH scenario with extra electricity sold to the grid.]

study of this paper. For the binary correction used in this paper, both the foreground process hybridization and full hybridization are discussed.

There are some other methods for correcting double counting, which more or less requires additional information and other models.^{82,85,86} The integrated hybrid LCA and double-counting elimination techniques used in this paper are illustrated in Figure 2.

3. CASE STUDY: P-XYLENE PRODUCTION USING CA AND MSH TECHNOLOGY

3.1. Process Description. The LCA methodologies reviewed above are illustrated through a comparative life

cycle assessment of two biomass-based *p*-xylene productions. Most of the *p*-xylene comes from petroleum fractions and catalytic reforming and is widely used in the polymer industry.⁸⁷ Many biomass-based *p*-xylene productions have been proposed recently. Concentrated acid (CA) hydrolysis is one of the technologies currently used in the pilot plant.⁸⁸ And the University of Delaware's Catalysis Center for Energy Innovation (CCEI) proposed the use of molten salt hydrate (MSH) for biomass hydrolysis.⁸⁹ Athaley et al.² developed the process flow sheets for the simulation of these two processes. The whole process is heat integrated to reduce utility usage at the expense of a higher capital cost. The process design, raw material, and utility flows used in this Review are extracted

Table 1. Input and Output Values for MSH and CA Processes of *p*-Xylene Production

MSH				CA			
input		output		input		output	
biomass (metric ton)	50	furfural (metric ton)	8.23	biomass (metric ton)	50	furfural (metric ton)	7.23
H ₂ SO ₄ (metric ton)	0.004	<i>p</i> -xylene (metric ton)	10.16	DME (metric ton)	0.71	<i>p</i> -xylene (metric ton)	8.92
water (metric ton)	562.41	electricity (GJ)	55.09	H ₃ PO ₄ (metric ton)	0.38	CaSO ₄ (gypsum waste)	2.82
LiBr (metric ton)	1.77	wastewater (metric ton)	11.92	H ₂ SO ₄ (metric ton)	0.75	wastewater (metric ton)	121.88
ethyl acetate (metric ton)	0.02	CO ₂ (metric ton)	47.06	lime (metric ton)	1.00	CO ₂ (metric ton)	46.97
AlCl ₃ (metric ton)	0.17			water (metric ton)	479.63		
H ₂ (metric ton)	0.60			ethyl acetate (metric ton)	0.07		
heptane (metric ton)	0.09			AlCl ₃ (metric ton)	0.95		
ethylene (metric ton)	2.81			H ₂ (metric ton)	0.51		
transport (tkm)	5000			heptane (metric ton)	0.60		
hot oil (GJ)	11.29			ethylene (metric ton)	2.81		
MP steam (GJ)	91.03			transport (tkm)	5000		
				electricity (GJ)	9.49		
				hot oil (GJ)	10.00		
				refrigerant cooling (GJ)	40.00		

from the Aspen Plus (Aspen Technology, Burlington, MA) simulation, with more details documented in the original paper.² Figure 3 shows the process inputs, outputs, and system boundary of both MSH and CA *p*-xylene production technologies.

In the first step of *p*-xylene production, lignocellulosic biomass is hydrolyzed by concentrated acid (CA) or molten salt hydrate (MSH) methods into the glucose and xylose. Both the CA and MSH plants operate at 50 t of biomass per hour for 8000 h a year. The CA process uses concentrated sulfuric acid and phosphoric acid to break down the biomass into sugars and unreacted lignin. The excess acid is neutralized by lime to form gypsum. In the next step, glucose is converted to hydroxymethylfurfural (HMF) and xylose to furfural in a biphasic reactor. Humins are also produced and removed in this step. With furfural separated and sold as a byproduct, HMF undergoes the hydrodeoxygenation (HDO) reaction with hydrogen to generate 2,5-dimethylfuran (DMF). Finally, DMF reacts with ethylene to produce *p*-xylene by the cycloaddition reaction. Lignin and humin byproducts are burnt at the power-and-steam section to generate the electricity and steam used in the plant, reducing utility usage. According to the simulation, 7.227 t of furfural and 8.918 t of *p*-xylene are produced each hour in the CA plant.

LiBr is chosen as the molten salt used in the first MSH hydrolysis step, and the rest of the production is the same as the CA process. In the MSH process, the combustion of lignin and humins generates more electricity than consumed in the plant. If the extra electricity is sold to the grid, which is the assumption made in the technoeconomic analysis of this process, the electricity could be treated as the avoided burden by the substitution method.⁵⁷ In this case study, another MSH scenario is also considered where the power plant is not connected to the grid. Then, the extra electricity generated could not make the process greener and is cut off from the system, which is similar to what Athaley et al.² considered in the LCA of this process. This scenario is referred to as the MSH (no grid) case in the rest of this paper. The MSH plant produces 8.227 t of furfural and 10.164 t of *p*-xylene every hour.

3.2. Goal and Scope Definition. This paper aims to conduct the “cradle-to-gate” assessment comparing two biomass-based *p*-xylene productions (the CA and MSH) by

process LCA, EIO-LCA, tiered hybrid LCA, and integrated hybrid LCA. The goal is to have a comprehensive system boundary by considering the production of *p*-xylene and its upstream raw materials and services. The construction of the plant and downstream application of the *p*-xylene is not included, as was done in Athaley et al.’s process LCA.² As no downstream application of *p*-xylene is considered, the functional unit is chosen to be one metric ton of *p*-xylene produced. This study is an attributional LCA that only focuses on comparing existing and stable technologies, as opposed to the consequential LCA that analyzes future scenarios involving decision-making.^{59,90}

3.3. Inventory Method and Process LCA. The background data are taken from the Ecoinvent 3.3 database that includes comprehensive and regional data.^{33,34} The data associated with the U.S. are preferred, while global data are also used when their U.S. counterparts are not available. Since the USEEIO database for EIO-LCA has its environmental interventions evaluated by the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) 2.1 LCIA method,⁹¹ this method is also chosen for process LCA. The global warming potential (GWP) is one of the matrices shared by both process and input–output LCA, as well as the most discussed indicator in LCA.⁹² It is thus selected as the environmental impact of interest in the case study. On the basis of the accumulative effects of radioactive forcing, the global warming potentials of different greenhouse gases are normalized to that of carbon dioxide and have a unit of kg CO₂ eq.^{91,93}

As mentioned earlier, byproducts are treated with three methods: substitution on excess electricity produced (avoided burden), cutoff on electricity when it could not be sold to the grid, and mass/economic allocation of furfural and *p*-xylene. To perform the substitution, a stand-alone U.S. electricity generation process is chosen from the background database and added to the process system. The cutoff method is used to remove the electricity row from that process’s technological matrix. For the allocation method, the total raw material and utility usage are divided into two parts for furfural and *p*-xylene production based on their production volumes or economic values. Table 1 lists the inventories of the CA and MSH processes, which are based on the simulation details and could be directly used for process LCA.²

When the allocation based on mass is performed on the CA process, for instance, the total material flows in the above inventory are assigned to furfural and *p*-xylene using the ratio of the production volume (8.92 metric ton/[8.92 + 7.23 metric ton]) of the total resources to *p*-xylene production). In the technological matrix, the negative values correspond to the products (or byproducts) generated, while the positive sign represents the raw material and utility requirement. Next, each column is normalized by the production volume of the main product to represent the production of one unit of that commodity (e.g., divided by 8.918 to represent 1 t of *p*-xylene production). The first two columns of A_p are the foreground processes of furfural and *p*-xylene production (shown in Table 2). The rest of the columns not shown in the table are

Table 2. First Two Foreground Processes of the CA Process in the Technological Matrix (Mass Allocation; Columns Normalized to Represent the Production of 1 Metric Ton Chemicals)

	furfural (metric ton)	<i>p</i> -xylene (metric ton)
furfural (metric ton)	0	0
<i>p</i> -xylene (metric ton)	0	0
biomass (metric ton)	3.097	3.097
DME (metric ton)	0.044	0.044
H ₃ PO ₄ (metric ton)	0.023	0.023
H ₂ SO ₄ (metric ton)	0.047	0.047
lime (metric ton)	0.062	0.062
gypsum (metric ton)	0.175	0.175
water (metric ton)	29.71	29.71
wastewater (metric ton)	7.549	7.549
ethyl acetate (metric ton)	0.004	0.004
AlCl ₃ (metric ton)	0.059	0.059
H ₂ (metric ton)	0.031	0.031
heptane (metric ton)	0.037	0.037
ethylene (metric ton)	0.174	0.174
transport (tkm)	309.7	309.7
electricity (GJ)	0.588	0.588
hot oil (GJ)	0.619	0.619
refrigerant cooling (GJ)	2.478	2.478

background processes taken from the Ecoinvent database covering cradle-to-gate environmental impacts. Another allocation method, the economic allocation, will be discussed in section 3.7, and the complete technological matrices for both the CA and MSH processes could be found in Supplementary Spreadsheet S1.

By performing the matrix calculation described in section 2.1, the CA process's global warming potential is 4379 kg CO₂ eq, and that of the MSH process is 3677 kg CO₂ eq. While the power and steam generation in the CA plant could not provide enough electricity for production, the power section in the MSH plant produces more electricity than needed. This extra electricity, when sold to the grid, is considered as the avoided burden, and its contribution is deducted from the total greenhouse gas emission, making the MSH process much greener than the CA process. When the electricity could not be sold in the MSH process, the GWP is 4219 kg CO₂ eq, close to that of the CA process.

3.4. EIO-LCA. The USEEIO model developed by Yang et al.⁷¹ is used here to account for the U.S.'s production in 2013. The raw materials' unit prices come from the TEA assumptions in the original paper of Athaley et al.² A

conversion to the year 2013 is performed based on the Independent Commodity Intelligence Services (ICIS)'s Petrochemical index to match that of the USEEIO's input–output table.⁹⁴ The transportation cost is taken from the EU's report⁹⁵ to be \$0.24/tkm and verified by similar results used in the work of Tanzer et al.²² A summary of unit prices used in this case study could be found in the Supporting Information Table S4 and Table S5.

In the input–output direct requirement matrix A_{IO} , there is no sector specifically covering the heat and steam production. Consequently, the fuel used for generating the heat, e.g., natural gas, is chosen as the input. The CO₂ emission of burning natural gas is estimated explicitly through the stoichiometry of the combustion reaction,⁷⁰ detailed information on which is in the Supporting Information.

The monetary inputs come from the multiplication of requirements for each material flows and their unit prices. Then, these inputs are matched to the economic sectors to form the final demand f_{IO} . The total environmental impact is $B_{IO} \cdot (I - A_{IO})^{-1} \cdot f_{IO}$, with the term $B_{IO} \cdot f_{IO}$ corresponding to the emission happening in the plant during the production stage.

Using only *p*-xylene's final selling prices from the MSH and CA processes, the GWP is 942 kg CO₂ eq and 1506 kg CO₂ eq. The ratio between these results is merely that of the selling prices from TEA (\$724.7 vs \$1158.5/metric ton) since the product is the same. Differences in raw material and utility usage are reflected in the minimum selling prices, which translate linearly into the environmental impacts in EIO-LCA.

For the second EIO-LCA method, the calculation is carried out using the process inventory and the EIO-LCA as background data. In this way, the MSH process has a GWP of 1339 kg CO₂ eq, while that of the CA process is 1706 kg CO₂ eq.

When the detailed breakdown of operating costs is unavailable, the ratio of fixed and variable costs in a similar process could be used to estimate the expenditure on the services. It is noteworthy that even for the production using the same technology, the fixed-to-variable-cost ratio would change according to the capacity and flowsheet design.¹⁹ The relationship between the fixed and variable cost is about 15:85 in both the MSH and CA cases from the TEA.² For instance, the sum of raw material and utility cost to produce one metric ton of *p*-xylene in the CA process is \$746.5. On the basis of the 15:85 ratio of fixed and variable costs, the CA process's fixed cost is \$131.7. It is then assigned to the nonmanufacturing sectors in the A_{IO} according to their coefficients in the use table. Before using the fixed cost in input–output analysis, a transformation from the purchaser's prices to producer's prices should be conducted. The result without price correction is 1393 kg CO₂ eq and 1768 kg CO₂ eq for MSH and CA, respectively. They decrease to 1316 kg CO₂ eq and 1648 kg CO₂ eq after the correction. In this case, the effect of price conversion is not significant, as taxes and transportation are not the dominant factors.⁷⁰

As shown in Figure 4, all EIO-LCA results are significantly lower than those from the process LCA, even though the input–output approach is believed to be more comprehensive. A similar trend is also reported by Zhang et al.⁹⁶ One reason for this discrepancy is the aggregation error. For instance, the productions of sulfuric acid and aluminum chloride use different raw materials and are expected to behave differently. However, they are both classified as the "basic inorganic chemicals" in the USEEIO sectors, so that their emissions

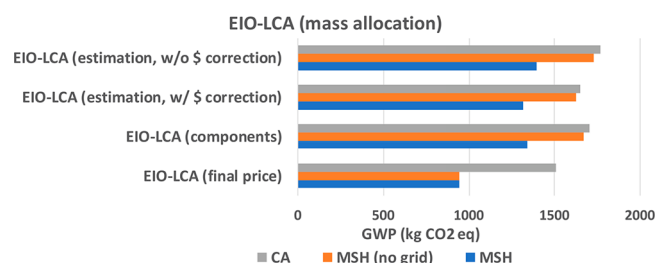


Figure 4. EIO-LCA results for the CA and MSH processes.

depend only on the prices. In both the MSH and CA processes, the on-site combustion of lignin and humins emits a large amount of carbon dioxide, which is unusual in other chemical plants. This heterogeneity further increases the error. Another factor is the price fluctuation—some chemicals have very volatile prices that change significantly even within a year. Moreover, the prices used for furfural and *p*-xylene are minimum selling prices from TEA, which are likely to be lower when compared to other chemicals on the market. Nevertheless, the relative order of the three processes' GWPs is the same as in the process LCA, which justifies the EIO-LCA as a fast screening tool for the qualitative study.

3.5. Tiered Hybrid LCA. When the interactions between the process system and the economy are ignored, their contributions could be calculated separately. The operating cost from the TEA includes the expenditure on raw materials, utilities, and necessary services to run a chemical plant (shown in Table S6 and Table S7). These services are ignored in the conventional process LCA due to the lack of process data. They need to be supplemented by EIO-LCA in the tiered hybrid LCA.

The extra contribution from the input–output analysis is 27.5 kg CO₂ eq for the MSH process and 27.4 kg CO₂ eq for the CA process. These impacts are small compared with the process LCA, but since they are due to the missing flows, they should not be neglected.

When TEA is not performed for the process, neglected upstream services could be estimated by the ratio of variable cost and fixed cost, as done in section 3.4. After the demand for services is estimated, the next step is to define the depth of the interface between the process and IO systems by tracing back the supply chain in the process system. For instance, electricity used in the *p*-xylene plant comes from the transmission of electricity, which is of the first order in the supply chain. This electricity is from the power plant that uses natural gas as fuel, which is the second layer of the supply chain. It would be further traced back to the transportation of natural gas and natural gas production from the environment. The fourth layer of this supply chain, natural gas production, is the direct natural resource extraction. Above this layer, there is no process or supply chain information in the database. Thus, the process LCA database only considers the electricity supply chain with detailed process information up to the fourth layer. Since all four of these processes above are well documented in the Ecoinvent background database, the interface between the process system and the IO system is set to be on the fourth layer of the supply chain for electricity.⁵²

The coverage up to *N*th layer and the system incompleteness factors are calculated from eqs 8 and 9 in section 2.3. For electricity, its coverage up to the fourth layer of the supply chain is 0.9958, which means that only 0.42% (system incompleteness factor) of the electricity's upstream contribution is not included in process LCA and needs to be

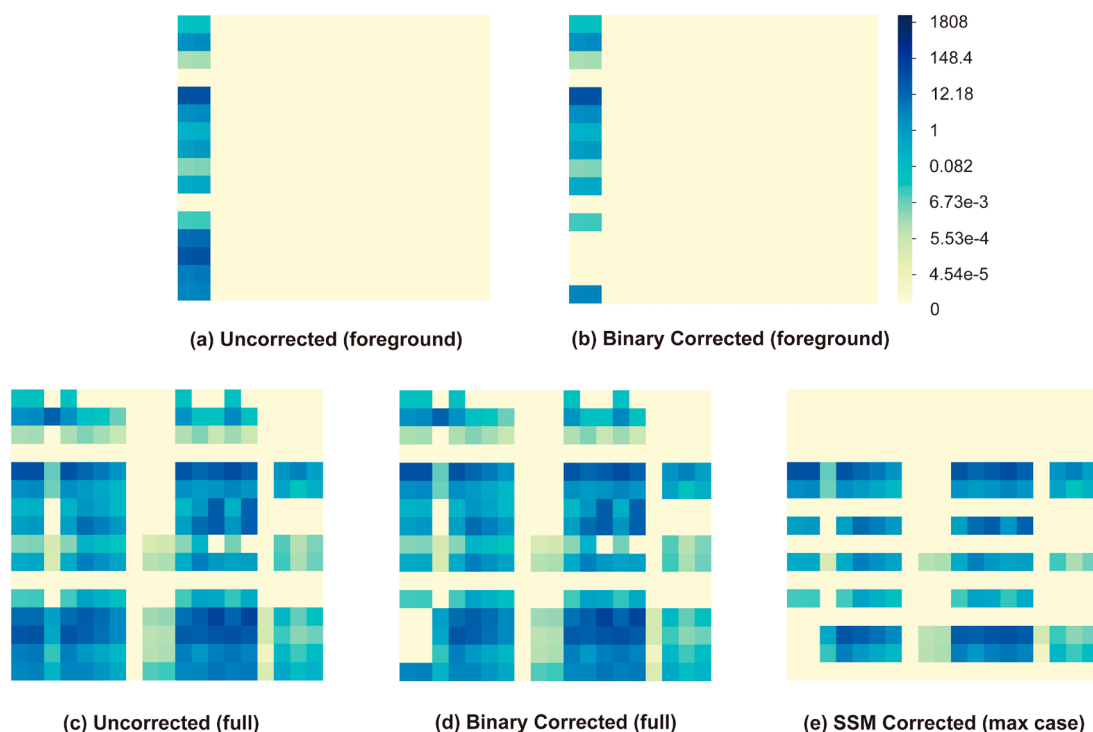


Figure 5. A fraction of C^u (10th to 25th rows) of the CA process by different double-counting elimination methods. [(a and c) Uncorrected C^u constructed from multiplying columns of A_{IO} with products' unit prices; (b and d) binary corrected C^u by removing elements included in A_p (e.g., electricity and water treatment); (e) SSM correction removes manufacturing sectors in d since these sectors are well-captured in the process background database (e.g., rows representing electricity and metal productions).].

supplemented by EIO-LCA. The same analysis is performed on all other material flows of the process LCA and is combined with the fixed cost as the final demand of EIO-LCA.

The total GWP is 3884 kg CO₂ eq (3907 kg when the price is not corrected) for the MSH process and 4552 kg CO₂ eq (4568 kg when the price is not corrected) for the CA process. When electricity could not be sold to the grid in the MSH process, the total GWP increased to 4376 kg CO₂ eq (4397 kg when the price is not corrected).

3.6. Integrated Hybrid LCA. The steps of constructing the upstream cutoff and integrated matrices are introduced in section 2.4, and detailed examples of the CA and the MSH processes are shown in [Supplementary Spreadsheet S1](#). The integrated LCA method is especially suited for the MSH process of *p*-xylene production because one raw material, LiBr, is not in the Ecoinvent database. Since the upstream information is entirely missing, using the input–output direct requirement matrix A_{IO} to estimate the missing flows will significantly reduce the truncation error. In the LiBr production process, only the stoichiometric ratio of raw materials used in the reaction is known (HBr and LiOH).⁹⁷ This, however, is a conservative estimation because more chemicals are needed to achieve the same conversion in reality. This assumption can be improved with more information about the conversion and separation of LiBr in a future study. Apart from that, all other upstream demands need to be estimated from the average commodity requirement profile in A_{IO} .

Following the aforementioned steps, the integrated hybridization of the CA system could be performed on only the foreground processes (less missing upstream)⁵⁶ or all the processes (more missing upstream).^{4,62} After adding the contributions from missing upstream in process LCA, the GWPs are 5399 and 5844 kg CO₂ eq for the foreground-hybridized and fully hybridized CA process, respectively. A binary correction is then conducted to remove the flows explicitly covered in the process LCA. After the binary correction, the GWPs decrease to 5010 kg CO₂ eq and 5455 kg CO₂ eq, respectively.

As illustrated in [Figure 5](#), part a applies the hybridization to only foreground processes (furfural and *p*-xylene production), while c hybridizes both the foreground and background processes. Some elements (e.g., electricity and natural gas) are removed by the binary method in both b and d. The SSM correction in e further removed sectors that are likely to be covered by process LCA, including electricity and wood products.

The same hybridization and binary correction are performed on the MSH system that has four foreground processes. When only these four processes are hybridized, its total GWP decreases from 4565 kg CO₂ eq to 4306 kg CO₂ eq after the binary correction. And the MSH process without electricity sent to the grid has a higher GWP of 4848 kg CO₂ eq (5108 kg CO₂ eq without binary correction). If all processes are hybridized, the GWP is 4964 kg CO₂ eq, and 5523 kg CO₂ eq when excess electricity is not sold to the grid. After binary correction, the GWPs of these two fully hybridized MSH processes are 4705 kg CO₂ eq and 5264 kg CO₂ eq, respectively.

As for the SSM correction, three scenarios of different sectors are chosen based on the work of Acquaye et al.⁴² The minimum case includes financing, services, and office-related activities. The base case consists of the above-mentioned

sectors together with furniture and construction sectors. Finally, the maximum case also includes the mining, wood, and electronics production sectors along with all those in the base case. These sectors are believed to be incomplete and would remain in the final cutoff matrices, while the others are set to zero.

Two examples of the SSM double-counting elimination are demonstrated in the [Supplementary Spreadsheet S1](#). It is noteworthy that for the LiBr and HBr production processes, the binary correction feature is retained because no material flow is known to be complete. The SSM correction thus treats these two processes differently and does not remove even the flows from the manufacturing sectors, including the utilities used.

The SSM correction results for the CA, MSH, and MSH without selling electricity are summarized in [Table 3](#).

Table 3. Summary of Mass Allocated LCA Results by Different Methods

LCA methods	total (kg CO ₂ eq)		
	MSH	MSH (no grid)	CA
process LCA	3677	4219	4379
EIO-LCA (final price)	942	942	1506
EIO-LCA (components)	1339	1671	1706
EIO-LCA (estimation, w/ \$ correction)	1316	1628	1648
EIO-LCA (estimation, w/o \$ correction)	1393	1729	1768
tiered hybrid (TEA)	3705	4247	4406
tiered hybrid (w/ \$ correction)	3884	4376	4552
tiered hybrid (w/o \$ correction)	3907	4397	4568
uncorrected (full)	4964	5523	5844
uncorrected (foreground)	4565	5108	5399
binary (full)	4705	5264	5455
binary (foreground)	4306	4848	5010
SSM (min)	3927	4470	4399
SSM (base)	3939	4483	4418
SSM (max)	4084	4633	4616

In [Figure 6](#), the MSH process without selling electricity to the grid (shown in orange) has less global warming effect than

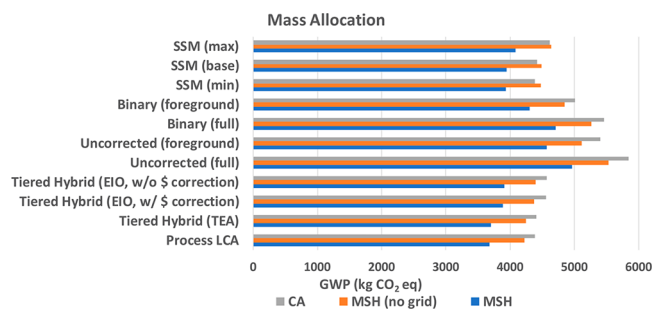


Figure 6. Comparison between process LCA and different hybrid LCA results for three processes.

the CA process (shown in gray) when evaluated by process LCA and tiered hybrid LCA methods. The integrated hybrid LCA without correction and with the binary correction shows the same relationship. However, in all scenarios of the SSM corrected integrated hybrid LCA, the MSH process without electricity sold to the grid performs worse than the CA process. The difference between the GWP is the largest in the

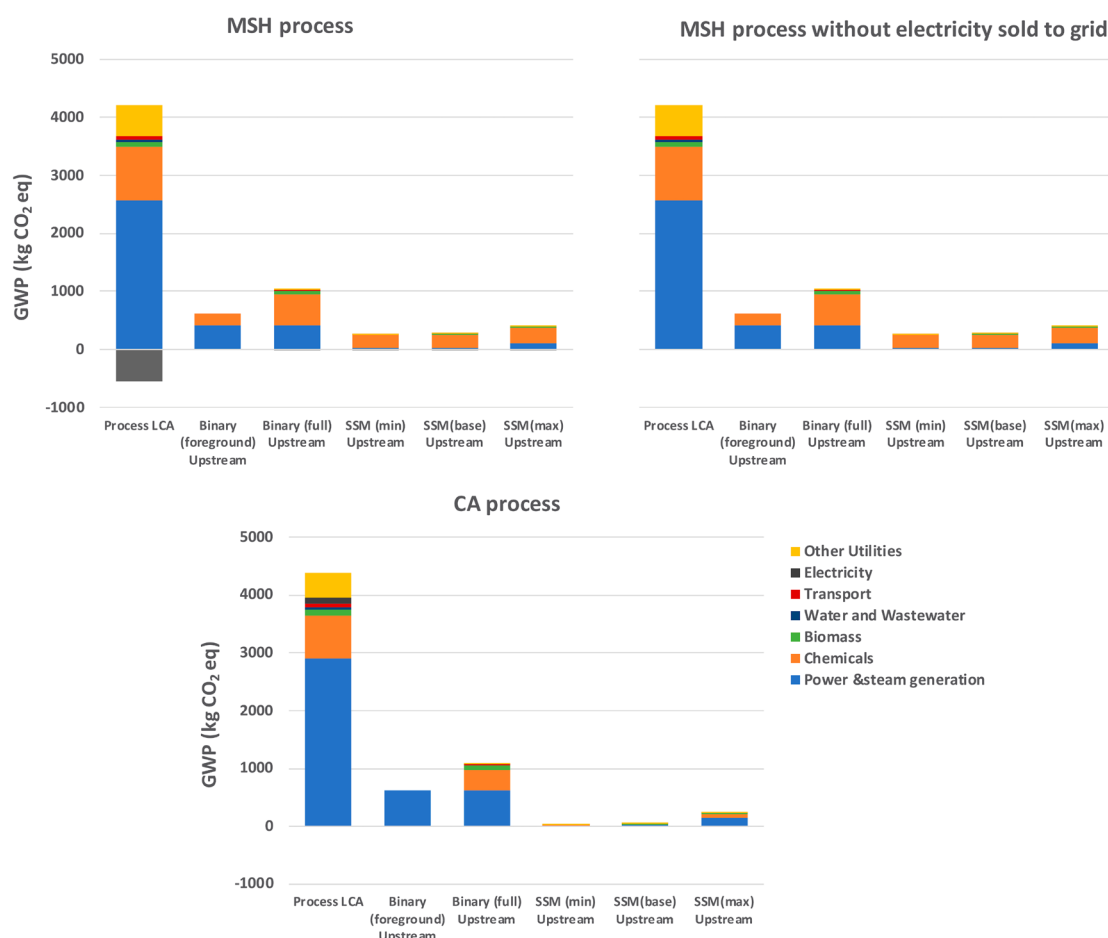


Figure 7. Contributions of different processes and upstream of the *p*-xylene production.

minimum cases where only the service-related sectors are considered, then decreases as more sectors are included in the base and maximum cases. This is most likely due to the fact that the LiBr and HBr productions are not captured well in process LCA. With only the stoichiometric ratio of raw materials as the inputs, all other material flows are missing, introducing considerable truncation errors.

Using the decomposition of process contributions described in section 2.4, the process LCA contribution of each input and upstream is estimated from the hybridization and shown in Figure 7. The upstream emissions for the LiBr and HBr are 76.6 and 144.8 kg CO₂ eq, the sum of which contributes to 35.2% of the upstream GWP in the foreground hybridized and binary corrected case. When the background data are also hybridized, they only account for 21.2% of the upstream GWP. However, in all SSM scenarios, manufacturing-related sectors are largely removed from processes except for LiBr and HBr production. Consequently, the additional material flows in *p*-xylene production become smaller. The LiBr and HBr's upstream contribute to 88.3%, 84.0%, and 53.5% of the total upstream GWP in the minimum, base, and maximum cases.

From Figure 7, it is illustrated that the major contributor to the process LCA GWPs for both MSH and CA processes is "power and steam generation," which accounts for 60.6% and 66.4% in each case. This is in line with Lin et al.'s process LCA⁹⁸ that the utility (steam) takes up nearly 50% of the GWP in starch-based *p*-xylene production. Alvarez-Gaitan et al.⁵² illustrate that when the zero-order on-site emission

dominates the overall emission, the effect of hybridization is not very significant. Generally, in these three cases of *p*-xylene production, the upstream contribution from hybridization ranges from almost negligent, in the SSM minimum case and tiered hybrid LCA using the TEA result, to around 20% in fully hybridized and binary corrected integrated LCA. Zhao and You⁴⁷ reported that nearly 10% of the integrated LCA contribution of GWP in the Li-ion battery comes from the EIO upstream. Acquaye et al.⁹⁹ used the integrated LCA to study the biofuel production in the UK, showing that the upstream emission accounts for 3.6% to 36.7% in the overall emission when various feedstocks are used. In a study of the rape methyl ester (RME) biodiesel supply chain, it is found that the unit process emission is 2.7 kg CO₂ eq, while the IO upstream emission is 1.7 kg CO₂ eq.⁴²

3.7. Allocation by Economic Values. It is recommended to divide the multifunctional process into its constituent monofunctional processes to avoid allocation altogether.^{57,100} In the case study, this method is not adopted since all processes are connected through both the heat integration and process synergies that use waste lignin and humins to generate heat and electricity.¹⁰¹ The allocation methods are applied to divide the multifunction process into monofunctional ones. All raw materials, utilities, and on-site zero-order emissions are assigned to furfural and *p*-xylene by the ratio of their mass or economic values.

In previous discussions, only the mass allocation is used because it is based on physical properties and does not change

under the price fluctuation.¹⁰² However, it is sometimes more reasonable to use the economic allocation when the mass is not the driving force for the demand of products, and the price differences are substantial.^{34,39} For example, hydrogen produced from the electrolysis as a byproduct of sodium hydroxide has a high unit price, but its low density makes its environmental impacts too small by mass allocation.³⁴ The sensitivity of GWP on the mass or economic allocation methods has also been revealed in corn stover bioethanol production.¹⁰³ The difference in the results due to the choice of allocation method is defined as the scenario uncertainty. It is reported to be more important than the data uncertainty in the biofuel system.¹⁰⁴

When the economic allocation is used, the new results for CA and MSH processes are summarized in Table 4.

Table 4. Summary of Economic Allocated LCA Results by Different Methods

LCA methods	total (kg CO ₂ eq)		
	MSH	MSH (no grid)	CA
process LCA	3222	3697	4756
EIO-LCA (final price)	942	942	1506
EIO-LCA (components)	1211	1502	1810
EIO-LCA (estimation, w/ \$ correction)	1191	1464	1748
EIO-LCA (estimation, w/o \$ correction)	1258	1553	1879
tiered hybrid (TEA)	3249	3725	4783
tiered hybrid (w/ \$ correction)	3404	3834	4943
tiered hybrid (w/o \$ correction)	3423	3852	4960
uncorrected (full)	4429	4918	6259
uncorrected (foreground)	4079	4554	5775
binary (full)	4173	4663	5870
binary (foreground)	3823	4299	5387
SSM (min)	3443	3919	4777
SSM (base)	3455	3931	4796
SSM (max)	3592	4073	5000

Process LCA and hybrid LCA results for CA and MSH processes using the economic allocation are shown in Figure 8.

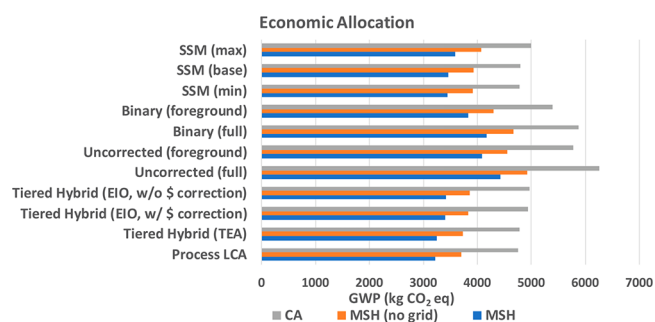


Figure 8. Comparison between different process LCA and hybrid LCA results for three processes.

The economic-allocated results for the MSH process are lower than their mass-allocated counterparts, no matter whether the extra electricity is sold to the grid or not. However, the CA process always has a higher GWP after switching to the allocation based on economic values. As indicated in the technoeconomic analysis, the selling price of *p*-xylene (\$724.7/metric ton) in the MSH process is lower than that of furfural (\$953.5/metric ton). Thus, the economic allocation approach

assigns more emissions to furfural than those in mass allocation. On the other hand, the price of *p*-xylene (\$1158.5/metric ton) is higher than that of furfural in the CA process, so the trend is reversed in this case.

3.8. Discussion. Different processes and hybrid LCA methods generate different but generally similar results for the same process. While the EIO-LCA results are all lower in this case study, it is not necessarily the case for other processes. The price fluctuation and aggregation error that treats every product in the same sector as homogeneous are likely to affect the EIO-LCA results. However, EIO-LCA calculation is fast and free of charge, making it an ideal choice for a fast screening evaluation.⁹⁶

Various hybridization methods expand the system boundary of the process by considering missing flows that lead to the truncation error. As each methodology takes a different set of assumptions and uses different information, the LCA results vary from case to case. The applicability of these methods mainly depends on the practitioner's knowledge and understanding of the system under study. This shows the flexibility of hybrid LCA—even with just operating costs, the estimation of missing flows will help to build a more complete system boundary. With more information about whether some foreground and background processes are complete, or the depth of interface between the process and IO systems, the system boundaries could be further refined.

In many cases, the use of different methods does not change the conclusion about which process is better, as shown in the comparison between the MSH and CA *p*-xylene production. This is partly because these two plants are very similar, with only differences in the first hydrolysis step. Since the zero-order emission primarily comes from the power and steam generation section, the effect of hybridization is not significant. One typical situation in the comparative process LCA is that the two processes of interest have incomplete boundaries with unknown but potentially different truncation errors. Then, the tiny difference between the environmental impacts may be due to merely the data uncertainty. With the help of hybridization, both processes' boundaries will be expanded to nearly complete with much smaller truncation error so that a fair comparison is possible. Moreover, additional contributions from the economy for both cases may behave differently so that one process might have a much more significant advantage.⁵⁹

On the other hand, LCA results may favor different options when different LCA methodologies are used. Yue et al.⁴ demonstrated through a fictitious example of two toasters that the process LCA and hybrid LCA might lead to different conclusions as to which toaster emits less CO₂ in the life cycle. When comparing the MSH process without selling electricity with the CA process, process LCA, tiered hybrid LCA, and binary corrected integrated hybrid LCA all indicate that the CA process has a higher emission. However, the SSM correction of integrated LCA leads to the opposite conclusion that the MSH process has a higher global warming potential when electricity is not sent to the grid in all three scenarios (Figure 6). It is essential to carefully choose the proper methodologies based on the understanding of the system and the data.

4. CONCLUSION AND FUTURE WORK

Different LCA methodologies are reviewed in this paper and applied to the comparative study of two biomass-based *p*-

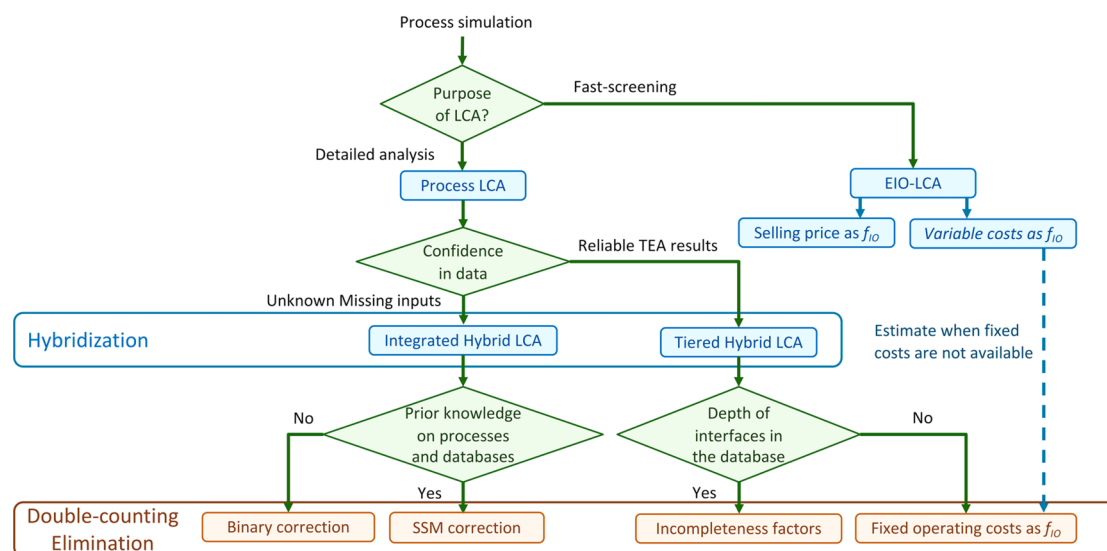


Figure 9. Choice of LCA method under different available information.

xylene production processes. Because of the similar computational structures of process LCA and EIO-LCA, it is natural to introduce various hybridization tools under the same matrix framework. The choice of methodologies relies on the availability of data and knowledge of the system (shown in Figure 9). This review highlights the choice of LCA method, especially hybrid methods, under different data availability. For instance, EIO-LCA is well suited for a screening analysis that requires the least amount of information and provides a basic understanding of the environmental impacts. The hybrid LCA aims to reduce the truncation error intrinsic to the process LCA by estimating the missing flows through EIO-LCA. With more insights into the supply chain and the process, a more complete system boundary is built through hybridization. When the unit prices for raw materials and utilities are known, the fixed cost to run a plant could be estimated from variable cost and used as additional inputs in the tiered hybrid LCA. If the TEA results are also available, the expenditure on different services could then be directly used as the demands to EIO-LCA. Moreover, the background data's depth of interface enables tiered hybrid LCA practitioners to remove the contributions already covered in the process LCA. The integrated hybrid LCA represents missing flows through the construction of the upstream cutoff matrix, C^u . The missing upstream could be estimated from the direct requirement matrix A_{IO} and unit prices. The binary correction method is able to remove the double-counting without any new information.⁸² Furthermore, with the knowledge or assumptions on which process is complete, the SSM correction could further prevent the overestimation of the missing flows.

Although the benefit of hybridization may be small in cases where all inputs of the system are well captured by a comprehensive database, hybrid LCA is particularly beneficial when some process inputs are not in the process LCA database. It is especially the case for chemical production. Even the most comprehensive process background database currently only covers a small fraction of all chemicals sold on the market.⁴³ In the chemical process design, it is not uncommon to face the data gap of chemicals. The most common method in process LCA to fill the data gap is to use the stoichiometric ratio of raw materials.^{44,105} This treatment,

however, increases the truncation error and may lead to misleading conclusions, as illustrated in [section 3.8](#). The SSM corrected hybrid LCA considers missing upstream flows and the background database to provide the same boundary completeness for a fair comparison between technology alternatives. The case study demonstrates that hybrid LCA is well suited for comparative LCA in the chemical process design.

Recently, there has been a continuing debate over hybrid LCA. One focus of the debate is the uncertainty issue. The effectiveness of hybridization largely depends on the trade-off between the existing truncation error in process LCA and the introduced aggregation error associated with input-output analysis. There are carefully constructed cases where the aggregation error is more significant than the truncation error so that it is not beneficial to hybridize.⁵⁵ However, Pomponi and Lenzen¹⁰⁶ proved that the high interconnectivity, supported by large dominant eigenvalues, in most IO and process systems would lead to more accurate results after hybridization. It is also acknowledged that the uncertainty in LCA is more of a data issue than a methodology issue.^{78,107,108}

Another focus of discussion is whether the linear model used by hybrid LCA is useful in decision-making. As both process LCA and EIO-LCA use the linear model to calculate environmental impacts, certain limitations carry over to the hybrid LCA. For decisions on future scenarios with non-marginal changes, linear assumptions need to be relaxed, and the consequential LCA is preferred.¹⁰⁹ Some researchers^{59,90,109,110} argue that more complicated and nonlinear models should be used to capture the complexity of the economy in the consequential LCA. However, this is more of a discussion on attributional LCA versus consequential LCA and is out of the scope of the current linear LCA framework. Also, additional assumptions and more complex models are needed to account for nonlinear effects.¹⁰⁴

Some assumptions made to simplify the analysis could be relaxed in future work. And other models and techniques could be included to improve hybrid LCA.

(1) It has been reported that the utilization of Leontief's price model could help balance the cost structure.^{35,82} This

financial balance would improve the upstream estimation in the input–output part of hybrid LCA.

(2) To be strict, LCA should evaluate the environmental impact throughout the product's entire life cycle.⁴⁸ Thus, cradle-to-gate LCA can be improved by including more life cycle stages in the future as more information is available. Downstream processes may also play an essential role in the life cycle. In the current case study, *p*-xylene is not produced at a significant volume compared to the sector it belongs to—the basic organic chemicals. However, for other chemicals produced in large quantities each year, the assumption that the downstream cutoff matrices are zero may not be realistic.

(3) The structural path analysis (SPA) uses the Taylor expansion to track different supply chains' contributions. It is similar to the depth of the interface concept illustrated in section 3.5. As a powerful tool to evaluate the structure of supply chains and identify “hot spots” in the system, SPA helps decide what to be emphasized in the future process design and data collection.^{42,66,111,112}

(4) One major assumption in EIO-LCA is that imported products have the same economic structure as those produced locally. When one product is manufactured by different technologies in different regions or has different supply chain structures, the assumption may not stand. Thus, multiregional models are needed to account for this difference.^{4,47,62,77}

(5) EIO-LCA uses IO tables that are often published years after the survey on the economy. For instance, USEEIO, as one of the latest input–output models for EIO-LCA, is based on 2007 US IO tables and represents the year 2013.⁷¹ Even though the economic structure is shown to be relatively stable within a short period of time, this time lag could still add to the uncertainty of this LCA study.

(6) The precision and uncertainty of LCA are not systematically addressed in this work. Apart from the scenario analysis,¹¹³ such as the three sets of sectors selected for the SSM correction,⁴² Monte Carlo simulation is another common method to deal with uncertainties in LCA input data.^{114–116} Perkins and Suh⁵⁶ proposed the progressive hybridization and refinement to reduce the uncertainty of hybrid LCA that is characterized by Monte Carlo simulation. Implementing these uncertainty analysis methods will increase the reliability of LCA results and enable better decision making.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c04709>.

Spreadsheet of technological matrices for MSH and CA processes by mass and economic allocation; depth of interface between process and IO system for CA; sectors considered in SSM correction of integrated hybrid LCA; binary and SSM corrected integrated matrices (XLSX)

Inputs and outputs for process LCA (Table S1, Table S2); foreground processes of MSH technology (Table S3); unit prices (Table S4, Table S5); technoeconomic analysis for MSH and CA processes (Table S6) (PDF)

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Notes

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