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Applying Environmental Release Inventories and Indicators to the Evaluation of Chemical Manufacturing Processes in Early Stage Development

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Abstract

As manufacturing processes are developed through the early stages of technology readiness, various assessments can be used to evaluate their performance. Performance indicators describe processes by transforming attributes into scores that represent desirable objectives. One type of assessment is obtained by determining the life cycle inventories of inputs and outputs for processes. For a functional unit of product, the user finds the resources used and the releases to the environment, which can be compared to results for similar processes and/or combined with other processes in the life cycle. In this work, an expanded range of process inputs and releases is modeled, including forklift/loader, fugitive, storage, boiler, and cooling tower emissions. A generic scenario approach for the cooling tower releases provides a first approximation of emission and wastewater flows. These inventory values are used in performance indicators that can be placed on a scale between fixed best- and worst-case limits with the GREENSCOPE methodology, thus allowing comparisons across various technologies. The processes of interest are two conversion pathways for producing cellulosic ethanol from biomass via thermochemical and biochemical routes. The results can be used in risk assessments, decision making, evaluation of research, and in spurring future technology development.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.9b01961](https://doi.org/10.1021/acssuschemeng.9b01961). Thermochemical and biochemical conversion pathway stream summaries, production rates and properties of fuels, process inputs for thermochemical and biochemical processes, and emissions. Spreadsheets for boiler emissions and resource use; cooling tower emissions and resource use; forklift, fugitive, and storage emissions; and indicators summary.

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The authors declare no competing financial interest.

TOC graphic shows how models and emissions are combined with biofuel process data in the GREENSCOPE tool to generate sustainability indicators and interpreted results.

Keywords

Releases; Indicators; Sustainability; Life cycle inventory; Life cycle assessment; GREENSCOPE; Biofuels

Introduction and Background

The aspiration to sustain the planet, quality of life, and ecological goods and services is a rational approach to the myriad stressors and desires that challenge the best intentions. As humans want better economic conditions, an environment that both serves and flourishes, and appropriate social conditions, these aspects of sustainability resonate with the values of many cultures.¹ These same goals, agreed upon in abstract terms, may lose coherent support as detailed plans are drawn for their achievement.²

This same paradox of abstract sustainability goals meeting real-world specific desires and conflicts comes to the forefront in various decision-making contexts,³ including chemical and energy production systems.⁴ Chemical and energy production processes need to be economical, be environmentally sound, and have a social license to operate (i.e., building a sense of community to establish legitimacy, credibility, and trust).⁵

In both the broader context and for chemical and energy production processes, the systems can be designed with economic, environmental, and social targets that are synergistic (i.e., aligned with each other) or with targets that lead to tradeoffs. Aligned targets are easy to manage, as these win-win situations are obviously positive. Tradeoffs create a necessity to consider value choices and balance needs. The question arises as to how one knows whether design choices are aligned with multiple desires or create tradeoffs, and the answer lies in the development of system information that can lead to these answers. Two useful system information analysis techniques at different scales are life cycle assessment,⁶ which looks across the supply chain and product network, and GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective

Process Evaluator),⁷ which focuses on gate-to-gate evaluations of a process. A third system analysis technique, which could be called life-cycle risk assessment, focuses on a chemical of interest and incorporates gate-to-gate analyses for manufacturing, processing, use, and disposal of the chemical.⁸

Life-cycle assessment (LCA) is a methodology for comparing multimedia environmental impacts across multiple categories on the basis of a functional unit of product or activity. An example might compare air emissions, solid waste, and water discharges from paper grocery bags vs plastic grocery bags, with many environmental and human health impact categories.⁹ For chemical and energy production processes, an example might consider a specific amount of product, whether a chemical, a fuel, or other functional unit. On the basis of a functional unit comparison, the amounts of inputs and releases are determined, with resulting impacts determined in categories for human health and environmental hazards (effects) of smog, acidification, toxicity, etc.

To compare the systems for chemical and energy production processes over the life cycle requires consideration of inputs and outputs of materials and energy through upstream and downstream stages. These extended stages include raw material acquisition, precursor manufacturing, product manufacturing, transport, use, and end of life. For a product described as a chemical or fuel, the product manufacturing stage is often the central focus, which in LCA terminology is known as a foreground process. The decision maker can directly influence foreground processes; background processes, which are processes for the production of generic materials, energy, transport, and waste management, are indirectly influenced. Thus, the foreground process is the place where decision makers can change the design and operating attributes to affect the manufacturing process and indirectly other parts of the life cycle (i.e., minimizing resource consumption and environmental releases)

When the design and operating attributes of a process are changed, aspects such as environmental and human exposures and hazards from releases, energy demand, material consumption, and economic feasibility are influenced. To capture the multidimensional impacts of process design and operation, researchers at the U.S. Environmental Protection Agency developed the GREENSCOPE methodology and tool.¹⁰ GREENSCOPE considers indicators in four E's: environment, economics, energy, and (material) efficiency. Previously, GREENSCOPE indicators have been applied to biodiesel fuel production,¹¹ process optimization,¹² decision making,¹³ retrofitting,¹⁴ and process control.¹⁵

Others have developed sustainability indicators for processes. An early review by Cano-Ruiz and McRae¹⁶ presented design alternative generation methods and indicators/techniques for incorporating environmental effects. Hilaly and Sikdar¹⁷ introduced the WASTE Reduction (WAR) algorithm as a pollution index, which was further developed for eight impact categories.¹⁸ In addition, exposure and risk were incorporated into the Environmental Fate and Risk Assessment Tool (EFRAT) for nine relative risk indices.¹⁹

Sustainability indicators were categorized by Sikdar²⁰ into three types: (1) individual indicators in one of the pillars of sustainability (environmental, economic, or social areas), (2) interactive indicators that combine two of the three pillars, and (3) overall indicators that

combine all three pillars. Energy use and material use are two examples of overall indicators that are common in many methodologies. Some have focused on material intensity for pharmaceuticals²¹ and for multiprocess networks,²² while others have focused on energy intensity through exergy²³ and ecosystem goods and services.²⁴ Sugiyama et al.²⁵ evaluated chemistries starting with energy and material use (loss) indicators. Ruiz-Mercado et al.⁷ developed a scaling methodology to use energy and material indicators as a basis for broad environmental, economic, energy, and efficiency indicators.

Other researchers have used broader ranges of indicators. Two chemical engineering societies, AIChE's Center for Waste Reduction Technologies (CWRT)²⁶ and the IChemE's Sustainable Development Working Group,²⁷ developed sets of indicators in the early 2000s. Curzons et al.²⁸ applied 22 indicators to evaluate chemistries for corporate practice, while an early tool on eco-efficiency, now with social indicators, was described by Uhlman and Saling.²⁹ Additional work has simulated processes for computer-aided calculation of various indicators,³⁰ added potential environmental impacts and chemical risk to the indicators,³¹ developed a suite of computer-aided tools for design and evaluation,³² and considered biodegradation of pollutants in the analysis of indicators.³³

The GREENSCOPE methodology and tool are particularly useful for presenting the indicators on sustainability measurement scales³⁴ as defined for all indicators.³⁵ These indicators address process attributes that must be accounted for during comprehensive assessments.³⁶ The resulting framework for decision making is reality based and practical. Comparisons made using GREENSCOPE are accomplished on a standardized basis for about 140 indicators in four areas: efficiency (26 indicators), energy (14 indicators), economics (33 indicators), and environment (66 indicators). These sets of indicators, which are mathematically defined, represent the quantifiable sustainability measurement of process performance, feedstock, utility, equipment, and output information.

The GREENSCOPE methodology can be applied flexibly to a gate-to-gate process or a specific piece of equipment or process unit. The user can apply GREENSCOPE at any point from conceptual design and pilot scale to full-plant scale and on partial or complete processes. This flexibility makes it possible for a direct comparison between several processes manufacturing the same product but employing different raw materials, reaction processes, separation technologies, or generation of different releases and wastes. In addition, one can implement this methodology to evaluate the sustainability performance either before or after making process modifications. The resulting sustainability assessment identifies the "hot spots" (areas that have room for further improvement) of the process under consideration.

The identification of hot spots³⁷ throughout the life cycle is a core aspect of LCA and life-cycle management (LCM).³⁸ This management of life cycle results is intended to use them to improve businesses, especially with respect to products and their supply chains. Improvements are made to economics, environmental, and social aspects, where accurate analysis of the life cycle is the first step in LCM.

To achieve an accurate analysis of a product life-cycle stage requires accurate life-cycle inventories (LCI). The LCI is the basis for life-cycle impact assessment, hot spot assessments, and potential policy decisions. Researchers have studied LCI on various bases: national^{39,40} / regional,⁴¹ industry sector,^{42,43} process,^{44,45} and unit operation.⁴⁶ Process databases including the USLCI Commons⁴⁷ and econinvent⁴⁸ are available to provide easy access to LCIs for covered processes (as long as quality and relevance match users' desires). To gauge the quality of process inventories, Edelen and Ingwersen⁴⁹ described the value and limitations of data quality characteristics, emphasizing the need for a comprehensive methodology.

Accurate and high-quality LCI has been the focus of research at the U.S. EPA using data mining and simulation methods. The data mining of EPA databases provides a top-down LCI for a chemical manufacturing process.⁵⁰ The EPA databases include the National Emissions Inventory, Toxics Release Inventory, RCRAInfo, etc., which provide release data directly from facilities where chemicals of interest are manufactured. Difficulties such as facility allocation of releases to products and only reporting chemicals appropriate for the product of interest are active areas of research. While the simulation, or bottom-up, method⁵¹ does not face these difficulties, it currently needs the hands-on application of engineering knowledge and more extensive calculations as users build processes up from sets of unit operations. Both methods are striving toward automation, and reconciliation of the top-down and bottom-up approaches with the addition of statistical methods (e.g., classification and regression trees) is a focus of current efforts.⁵²

Another place where the reconciliation of top-down and bottom-up LCI data methods will be useful is in the application of life-cycle risk assessment. Unlike LCA, where inventory is collected for a functional unit for comparison purposes, life-cycle risk assessment needs to consider the whole process (not a fraction or multiple of a process) that exists to manufacture, apply, or use a chemical. Since releases from a process do not (often) scale linearly with the amount of chemical production, a need exists to report inventory on a whole-process basis. This inventory can then be used to perform risk assessments: for example, for risk screening of aggregated exposures.⁵³

In the research and development of a new process technology, a techno-economic assessment is generally performed to assess its economic viability, followed by comprehensively assessing its sustainability (including potential exposures and hazards) or its role in a life cycle. At early stages of technology development, simulation models may exist for describing the mass and energy flows of the manufacturing process, but additional information useful for evaluating the process is lacking. In particular, the evaluation of sustainability process indicators and the development of life-cycle inventories for risk assessment are missing. Often this is so for a good reason, as these calculations can be costly in money, effort, and time. The objective of this work is to provide methods to easily evaluate processes in the early stages of technology development as shown through the GREENSCOPE methodology and emission inventories for a gate-to-gate unit process. The latter application is made comprehensive and practical through the development and implementation of realistic LCI models for on-site utility generation such as boilers and cooling water systems and forklift/loader, fugitive, and storage emission models that are

ready for use. Thus, this contribution offers a unified methodology that presents these on-site utility generation and uncontrolled air emission modules, describes the inventory data for environmental emissions and risk assessments, shows how to calculate sustainability indicators for a process, and suggests how to guide process designs or improvements that incorporate knowledge from the indicators.

Methodology

The procedure for developing emission inventory and sustainability indicator data is based on simulated processes that provide primary input-output material and energy flows. Simulation software provides accurate calculations on the basis of various accepted models as well as thermodynamic information that would be difficult to develop for each process of interest.⁵⁴ The converged simulator results describe chemicals and their flow rates for internal and input-output streams. On the basis of a particular production rate and reaction information for a process, the simulator transforms user entries for unit operation specifications and equipment connections into mass and energy flows. Sometimes a simulation may be accomplished with simpler models using tools such as spreadsheets.⁵⁵

The process simulation mass and energy flows are useful as emission inventories and sustainability indicator data. However, they can often be incomplete if uncontrolled and controlled emissions and resource use (e.g., utilities, land, and material footprint) are not considered: for example, when process streams are assumed to be released directly to the environment. Where necessary, end-of-pipe treatment needs to be applied to such streams.⁵⁶ Smith et al.⁵¹ showed how simulations can be improved with vent, storage, and fugitive emission models. This work provides spreadsheet tools for storage and fugitive emission calculations and on-site utility generation. Thus, a method for developing process inventory data is presented in Table 1, where many of the proposed steps are part of the hierarchical steps involved in the conceptual design of chemical processes.^{57,58}

The steps of Table 1 represent a guide to process design that allows inputs and releases to be determined and indicators to be calculated. The summary of flows determined in steps 11–13 represent the inventory, which can be used for chemical management purposes, e.g., for prioritization/screening or risk assessments,⁵⁹ or for calculation of process indicators. This work leaves chemical management determinations and associated calculations to others.

The summary of flows from Table 1 can be used directly in environmental, efficiency, and energy indicator calculations, as described in the following for the GREENSCOPE methodology. Additional information has to be provided on items such as hazardousness, impact characterization factors, elemental content, standard chemical exergy, etc. For economic indicators, the flows of Table 1 are developed with the addition of chemical prices, capital and operating cost information, waste treatment costs, etc. The evaluation of sustainability is assessed by employing a set of indicators capable of transmitting and translating process performance, feedstocks, utilities, equipment, and output information into a sustainability measurement scale. This scale is demonstrated through percent GREENSCOPE scores as⁶⁰

$$\%G_i = \frac{(\text{Actual} - \text{Worst})}{(\text{Best} - \text{Worst})} \times 100\% \quad (1)$$

Users of the GREENSCOPE methodology should select indicators for their study on the basis of experience, education, and stakeholder needs. The selection of indicators from the full list of available ones was suggested in previous work⁷ and shown in another case study.¹² This procedure was accomplished by considering the technology readiness level of the processes, indicators pertinent to biomass to alcohol production, and indicators that would provide a strong representation of the four indicator areas (efficiency, environmental, energy, and economic). After the original list of GREENSCOPE indicators was reviewed,³⁵ which were created in an extensive fashion with the intention of accommodating diverse chemical manufacturing processes, a total of 61 indicators (as described in Table 2) were selected as the most relevant sustainability criteria for the proposed evaluation (i.e., fitting the user's needs and sustainability goals). Then the potential design alternatives were evaluated and the indicator scores were obtained. When considering the indicator scores, one should be aware of the technological readiness level(s) of the processes studied, as data from processes at earlier readiness levels may have more gaps requiring approximated data and larger uncertainties. While the case studies examined here were at the same level, an analysis of widely different case studies in terms of technological readiness should include notes to focus the user or reader on potentially important differences.

As shown in Table 2, the best-case and worst-case scenarios have been identified and selected to establish the sustainability scale for each indicator. In general, GREENSCOPE provides clear guidelines and default values for these two scenarios for each indicator. The percent GREENSCOPE score for each indicator, $\%G_i$, provides a relative assessment for all evaluated processes on the same scale (i.e., with the same limits), thus allowing an “apples-to-oranges” comparison of processes that might not have the same product or feedstock. A process with a higher $\%G_i$ score is better (or more sustainable) for that indicator. Note that this is not necessarily so for other indicator systems that change the limits for the indicators. An additional benefit of GREENSCOPE is the user can always return to the actual attribute knowing the $\%G_i$ and limits. Finally, the $\%G_i$ score lets the user know how close an actual value is to a known target (i.e., the best-case scenario). A high value shows that performance is aligned with the target, while a low value indicates that improvements could be made to improve the sustainability of a process and that perhaps more resources should be invested in the areas with lower percent scores.

Case Studies

Two case studies for producing alcohols from biomass are described, with results presented as inventories and indicator scores. The processes studied are thermochemical and biochemical routes for manufacturing alcohols from biomass, specifically ethanol and mixed alcohols by the thermochemical route and ethanol via the biochemical pathway. These processes are described, and the results are presented for the inventory and the

GREENSCOPE indicators. A subset of the GREENSCOPE indicators has been selected, with modification if necessary, that are pertinent to processes using renewable feedstocks and biomaterials. Considering that some of the indicators would not be expected to be of interest for the studied processes, specific indicators to evaluate were chosen.

Thermochemical Process.

The thermochemical conversion process for making ethanol from woody biomass via gasification is based on the design by the National Renewable Energy Laboratory (NREL).⁶¹ The process steps include: (i) feedstock handling and drying, (ii) indirect gasification of woody biomass to produce raw syngas, (iii) raw syngas conditioning and cleaning through tar and hydrocarbon reforming and scrubbing, followed by syngas compression, (iv) the production of ethanol and higher alcohols via the catalytic conversion of syngas, and (v) product separation, as shown in Figure 1. Additionally, the process design includes an integrated steam system and power generation cycle, cooling water, and other utilities. Flow rates for the streams depicted in Figure 1 are presented in Table S1.

Biochemical Process.

The biochemical conversion process for making ethanol from corn stover is based on a design by the NREL.⁶² The block flow diagram is shown in Figure 2, and the flow rates for the streams shown in Figure 2 are presented in Table S2. The biomass is first treated with dilute sulfuric acid at a high temperature to release the hemicellulose sugars including xylose; the pretreated slurry is then mixed with ammonia. After the biomass pretreatment process, the next step is the enzymatic hydrolysis (also known as saccharification) of the remaining cellulose, which is converted to glucose using cellulase enzymes. This is followed by fermentation of the xylose and glucose (resulting from the pretreatment and enzymatic hydrolysis steps, respectively) to ethanol. The process design also includes (i) biomass feedstock handling, (ii) feedstock, chemical, and product storage, (iii) product separation and purification, (iv) required utilities, (v) on-site wastewater treatment, and (vi) combustion of lignin, unconverted cellulose, and hemicellulose from the feedstock, biogas generation via anaerobic digestion, and biomass sludge from wastewater treatment.

Inputs.

A collection of inventory inputs and releases is presented in Tables 3 and 4 for the thermochemical and biochemical processes. The inputs shown in Table 3 show remarkable differences between the processes on a per gasoline gallon equivalent (GGE) basis (i.e., lower heating values per gallon were used to put ethanol and mixed alcohols on an equal basis, as shown in Table S3). While both use the same yearly amount of biomass (see Tables S4 and S5 for total annual process values and per kilogram values, respectively), the thermochemical process has higher overall fuel yield than the biochemical process does, and therefore the former exhibits a lower biomass per GGE input. Along the same lines, Table 3 shows that, while diesel use for forklift/loader operations has a similar total amount, the biochemical process uses 20% more on a per GGE basis. Other process inputs show greater differences in the magnitude of inputs. For instance, the catalysts and other inputs of the thermochemical process have orders of magnitude mostly in the -3 to -4 range for exponents. The biochemical process inputs such as sulfuric acid, glucose, etc. have orders of

magnitude in the -1 to -3 range for exponents. For two other components that are similar between the two processes, sodium hydroxide and ammonia, the biochemical process uses 2–3 orders of magnitude more per GGE of product. On the basis of the total mass of inputs (shown in Table 3), the biochemical process requires more than twice the mass of inputs on a GGE basis.

The use of fresh water and chemicals for boilers and cooling towers presents mixed trends between the two processes. The amounts of the boiler and cooling tower chemicals used in the processes are relatively small, i.e., the order of magnitude of these chemicals are all 10^{-5} kg per GGE of the product or smaller. Freshwater use for the makeup to boilers and cooling towers does show a much larger value for the biochemical process. The biochemical process is more water intensive than the thermochemical process. In addition to water cooling, many processing steps of the biochemical conversion process are operated in the aqueous phase, such as the biomass pretreatment and fermentation steps, which use steam (i.e., counted through boiler makeup water). Additionally, water is used to control the flowability of the biomass solids, either washed-solid or whole-slurry enzymatic hydrolysis.

No energy inputs such as natural gas or electricity from the grid are required for the two processes. For the biochemical process, the fuels for the boiler are lignin, biogas from anaerobic digestion, and solids from distillation and wastewater treatment, which are combusted to produce high-pressure steam for electricity production and process heat. The boiler produces excess steam that is converted to both electricity for use in the plant and for sale to the grid (2.72 kWh/GGE). For the thermochemical process, combustion of biochar, raw syngas, and fuel gas provides heat for steam and power generation. Some syngas is diverted from liquid fuel production for heat and power production needed by the process (i.e., no net input or export of electricity). This option makes the design energy self-sufficient at the expense of the overall product yield.

Emissions.

The emissions of chemicals on a per GGE basis are displayed in part in Table 4, with direct, fugitive, storage, loading, and total values shown for each case. This table shows the first 30 compounds, which encompass all the direct process emissions (direct emissions include process, boiler, and cooling tower emissions), fugitive emissions, and storage emissions, and a sampling of the boiler, cooling tower, and loading emissions. The listings in the Supporting Information are extensive (Tables S6–S8 with units /GGE, /year, and /kg product, respectively), including a total of 154 compound entries. A vast majority of these are EPA Toxics Release Inventory (TRI) chemicals, and 38 of the compound entries are persistent bioaccumulative toxic TRI chemicals.

Table 4 shows all the process, fugitive, and storage emissions and spreadsheets to calculate these emissions are given in the Supporting Information. Tables S6–S8 in the Supporting Information show additional boiler, cooling tower, and loading emissions. Considering the total emissions for each case, there is not one alternative that is better for all emissions; however, Table 4 shows that the biochemical case has higher emissions for most compounds on a kg per GGE basis. One counterexample is CO_2 , for which the thermochemical case has higher process emissions (i.e., reaction offgas and byproduct char combustion) that lead to

higher total emissions. Other counterexamples that have higher thermochemical emissions are process chemicals that are found only in that case: methanol (which is also a cooling tower emission), propanol, n-butanol, ethylene, acetylene, and hydrogen sulfide.

Forklift/loader and boiler models are available in spreadsheets in the Supporting Information. For the forklift/loader emission calculations the only values needed are entries for the amount of diesel fuel and the hours of operation. Boiler models are provided for natural gas boilers and wood residue boilers, the latter being used as an approximation for burning various forms of biomass. While many boiler parameters can be entered, the user needs to enter the amount of heat needed. Emissions are calculated using AP-42 emission factors.⁴⁶

Cooling tower emissions and a first-level approximation of wastewater flows can be accomplished using the cooling tower model (see spreadsheet in the Supporting Information). The model relies on a generic scenario model for cooling towers,^{65–68} which provides the basic relationships among the flows for evaporative, blowdown, windage, and recycle streams. This work adds to the model by first using the fugitive emission model⁵¹ from heat exchangers and cooling jackets to estimate the flow rate of a pollutant chemical of interest in process cooling water, P_{in} . The now hot cooling water, with pollutant contamination, is returned to the cooling tower. As the generic scenario cooling tower model is used to represent this process, the new model includes the (relative) volatility of the pollutant chemical of interest, and the cooling tower emissions and wastewater flows can be determined. The equation to determine these flows is based on a balance on the pollutant chemical of interest, P ,

$$P_{in} = P_W + P_D + P_E \quad (2)$$

where the amount flowing in from the process (kg/h) is equal to the amount leaving the cooling tower in windage (W), blowdown (D), and evaporation (E). Each right-hand side term is expanded: $P_W = F_W C_P$ ($\text{m}^3/\text{h} \cdot \text{kg}/\text{m}^3$), $P_D = F_D C_P$, $P_E = F_E C_P \alpha_{P, H_2O}$ where α_{P, H_2O} is the relative volatility of the pollutant to water, acting as a modifier on the evaporation rate of water, F_E . P_{in} and the flows, F_i , are known; thus, the concentration, C_P , can be solved for. With C_P known, each of the right-hand side terms can be determined. The quantity P_D can be a first approximation for the amount of a pollutant chemical of interest in wastewater flow for the process.

The Supporting Information Tables S6–S8 list all of the emissions. These include long lists from the boilers and forklifts/loaders. For each case, there are 38 chemicals listed that are persistent bioaccumulative toxic TRI chemicals. Many of the emissions listed in Table S6 are relatively small and are orders of magnitude lower than the emissions reported in Table 4. Note that one cannot conclude on the importance (or lack thereof) of these emissions to specific effects (like toxicity) because small amounts of persistent bioaccumulative chemicals may have serious effects. It is beyond the scope of this work to delineate the importance of these effects.

GREENSCOPE Indicator Limits.

The data required for the calculation of the GREENSCOPE indicators are collected from the outputs of the process models: namely, mass and energy balances across each unit operation and the entire biomass-to-alcohol processes and the outputs of the economic models. The economic models estimate capital and operating costs, given the mass and energy balances from the process models and given assumptions regarding capital and operating costs. Upon collection of all the required data and introduction into the GREENSCOPE evaluation tool, the indicator scores are calculated.

From Table 2 one can notice that some indicator limits for the case studies are not absolute values or hard numbers, since these depend on the amount and composition from the process input and output streams. Values used in the case studies are reported in the indicators summary spreadsheet in the Supporting Information. The thermochemical and biochemical case studies present different chemical compounds and amounts in their inputs and emissions to generate similar fuel products as shown in Tables 3 and 4. For example, the environmental indicators Env1 and Env 2 describe the total number and mass of hazardous material inputs, for which their worst limits are estimated by assuming that all substances (and total mass) fed to the process are hazardous. In addition, other worst-case values are standard measurements and equivalencies given by government agencies to represent and aggregate the effect of several pollutants (e.g., potency factor contributions of different chemicals as equivalent amounts of a reference substance with known effect). The worst-case limits used in the calculations of Eqn. 1 for each indicator are always the worst determined for all the cases studied. Therefore, the indicator limits allow a fair comparison normalized to the same range (the denominator in Eqn. 1). More details regarding best and worst limits can be found elsewhere.³⁵

Results

A comparison of the inputs, emissions, and indicator scores for the thermochemical and biochemical case studies must first acknowledge differences between the two processes. In particular, while the inputs for each case study include 2000 dry metric tons (DMT) of biomass/day, the qualities of the biomass are different. The thermochemical conversion process assumes a woody biomass, as the thermal processing can handle essentially any type of biomass input. However, the biochemical conversion process uses corn stover with preprocessing steps to prepare the biomass for chemical reactions. Another obvious difference between the processes is the product generated. Thermochemical processing creates a mix of alcohols, including ethanol and a 10% mix of methanol, propanol, and butanol (as detailed in Table S1), whereas the biochemical product is 99.5% pure ethanol.

The process differences in alcohol yields are due to the processing reactions, carbon content in the feedstocks, conversion efficiency (C efficiency), etc., as reflected in the indicator scores. The indicators are depicted in Figures 3–6 for the efficiency, energy, economic, and environmental scores, respectively. These figures have been constructed using the conch-shell configuration as suggested by Tan and Biddy,⁶⁹ where the indicators are placed clockwise around the graph in order from largest to smallest score, thus creating a spiral conch shell appearance. The benefit of viewing the indicators in this configuration is the

ease of seeing where a process is performing well (from 12 o'clock clockwise), and where indicators suggest improvements could be made (as they approach 12 o'clock). Of course, the ordering of indicators from largest to smallest score can only be done for one process (e.g., thermochemical in Figure 5), while the other case study (i.e., biochemical) must follow the set order. Details on the calculations are available in the indicators summary spreadsheet in the Supporting Information.

These process indicators are categorized in the areas of environment, efficiency (material), energy, and economics. Therefore, this sustainability assessment describes how well the two biomass conversion processes make use of mass and energy inputs to manufacture renewable bioethanol and their relative overall sustainability. In addition, some indicators provide insights about the environmental release impacts and exposure, material usage environmental characteristics, and economic performance (cost and feasibility) of the processes under evaluation.

As Figure 3 shows for efficiency, many of the indicators are similar, but the values for Eff23, the total water consumption, show that while neither process is near the best-case limit, the biochemical process uses significantly more water. Both the carbon efficiency and reaction mass efficiency, Eff14 and Eff5, respectively, exhibit low indicator scores, thus illustrating these processes as inefficient in their use of mass feeds. However, it is noteworthy that lignin (*ca.* 16 dry wt % of corn stover) in the current baseline biochemical process design is combusted for heat and power generation and is not converted to additional fuel. Similarly, for the thermochemical process, as mentioned in the section above, some raw syngas is diverted from liquid fuel production for heat and power production needed by the process (i.e., no net input or export of electricity). This design option makes the design energy self-sufficient but at the expense of the overall product yield. Results such as this can also be discovered by investigating the data. The value here is in being able to easily visualize the result without investigating (i.e., simply by looking at Figure 3).

The energy indicators presented in Figure 4 show both an obvious result and more nuanced ones. A clear difference between the processes is En8, breeding energy factor, which shows a much smaller indicator score for the biochemical process. The breeding energy factor depends on the renewability of energy inputs, and in this example the biochemical process has much larger nonrenewable feeds. Two other indicators, En3 and En4, energy intensity and waste treatment energy, respectively, show gaps between the scores for the processes. The energy intensity score is higher for the biochemical process because it requires less energy (i.e., steam demand for process heating and electricity), as most biochemical conversion steps take place at relatively low temperature (< 100 °C) and at atmospheric pressure (except the steam plant). Additionally, the biochemical process also makes its own steam and electricity. On the other hand, the waste treatment energy score is higher for the thermochemical process. The biochemical process exhibits a lower waste treatment energy score since it requires more waste treatment, specifically wastewater treatment, whereas the thermochemical process generates significantly less wastewater. The waste treatment energy consumption for thermochemical and biochemical processes are 9.02E-04 and 1.22 MJ/kg, respectively. Both processes show similar intermediate scores (*ca.* 40%) for resource energy efficiency, En6, which is defined as the fraction of energy (i.e., lower heating values or

LHV) in the product per LHV input in feeds (biomass feedstocks). By this information from the GREENSCOPE sustainability evaluation, En6 was identified as one of the opportunities for achieving improved sustainability for the processes. Approaches that can improve En6 indicator score include further conversion technology advancement and process optimization. For example, the current thermochemical process is energy neutral and does not import any external fossil feedstock. One future design option for the thermochemical process could be purchasing electricity from the grid instead of diverting raw syngas from liquid fuel production for onsite power production, thus increasing the fuel yield which in turn would lead to a higher En6 indicator score.

The third area, economics, appears in Figure 5 to have some tradeoffs. The scores for Econ3, discounted payback period, are better for the biochemical process. This represents the significant capital cost associated with thermochemical processes, and while the biochemical process uses additional inputs with associated costs (i.e., has a higher operating expense), the effects are relatively small in relation to capital expenditures. The high capital expenditure of the thermochemical process requires much more time to pay back the initial investment. For specific energy cost, Econ23, both processes use biomass for energy (biochar and offgas for the thermochemical process, and lignin combustion for the biochemical process), with the biochemical process requiring more makeup water, water chemicals, and steam in comparison to the thermochemical process. However, the biochemical process also generates excess electricity which is exported to the grid for credits, and as a result Econ 23 exhibits a high sustainability score of 100%.

The environmental indicators describe a one-sided story that was not clear from looking at the inputs and emissions of Tables 3 and 4. As was discussed above, the biochemical process used more inputs and had more substantial emissions; however, neither of these is definitive in determining the environmental indicator scores. It is possible for characterization factors, which multiply impacts by the amount of process flow, to vary by orders of magnitude depending on the chemicals and to have a strong influence on the final indicator scores. In this study, the size of process flows was not outweighed by the characterization factors. The graph of environmental indicators in Figure 6 shows that the biochemical indicator scores were either similar to or less than those for the thermochemical process, suggesting that the thermochemical process exhibits a relatively higher level of overall environmental sustainability. This appears as the biochemical scores being inside the thermochemical scores in Figure 6. An exploration inside the indicator calculations for Env1 (number of hazardous materials input), Env7 (health hazard, chronic toxicity factor), and Env12 (safety hazard, acute toxicity factor) reveals details about the indicators. The use of large amounts of sulfuric acid causes health hazard, chronic toxicity factor to have a lower score for the biochemical process. In addition, the sulfuric acid, and the high sodium hydroxide and ash flows lead to a lower score for the biochemical process for safety hazard, acute toxicity factor. Confirming these indicators, the biochemical process had twice as many hazardous inputs. The scores for Env60 (specific hazardous solid waste), Env53 (specific solid waste mass), and Env64 (specific liquid waste volume) indicators are lower for the biochemical process due to larger solid and liquid waste flows.

Discussion

The environmental release inventories for the compared processes have been determined according to the methodology set in Table 1. Without this methodology, the inventories would lack loader/forklift, fugitive, storage, boiler, and cooling tower emissions. The cooling tower model provides a first approximation to estimate wastewater flows from a process. If cooling tower and boiler models were not used, the inventory of inputs would be incomplete.

Decisions based on the inventories of inputs and outputs and the indicators can focus on particular attributes or holistically evaluate the processes. A first question is whether the products of ethanol and mixed alcohols are considered equivalent. Since both products are energy products and have similar applications, when they are normalized to a gallon of gasoline equivalent, ethanol and mixed alcohols can be compared on the same (energy) basis. However, in reality, not every circumstance for using fuels is the same; it could be that pure ethanol can be blended with gasoline blendstock as a fuel but perhaps that is not the case for the mixed alcohols.

Without setting values to various indicators, one cannot make decisions because there is too much information available. For instance, someone focused on water use could consider Eff23, total water consumption, which is worse for the biochemical process, and determine that the thermochemical process is favorable. The same is true for someone focused on environmental indicators, which favor the thermochemical process. Someone else might focus on Econ3, discounted payback period, and conclude that the biochemical process is better. A holistic approach could weigh all of the indicators (or a chosen set) and derive a gate-to-gate comprehensive result. Before the inclusion of indicator calculations, the results were a list of data, from which it is extremely difficult to base decisions. The indicators, with best- and worst-case limits, provide context for decision making, such as nondominated solutions of Pareto fronts for determining reasonable tradeoffs or multicriteria optimizations that weight attributes. The analyses and decision-making methods can be useful tools in forcing explicit definitions of the assumptions that are required to make a decision. A life-cycle approach would add supply chain inventories to examine the whole system. The process inventory results point to more and larger inputs for the biochemical process, and so a life-cycle approach would see different components included in any decision.

Future work could use the inventories developed for these processes and implement them in life cycle assessments. Research might consider the indicators as guideposts to consider “what if” analyses, directing the development of technologies to improve process sustainability. Other work might expand upon the indicators to make them customized for biofuel or other processes. Weighting schemes for the indicators could be developed to allow for holistic decisions that incorporate multidimensional aspects and optimize attributes of processes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- (1). Beddoe R, Costanza R, Farley J, Garza E, Kent J, Kubiszewski I, Martinez L, McCowen T, Murphy K, Myers N, Ogden Z, Stapleton K, Woodward J (2009). "Overcoming Systemic Roadblocks to Sustainability: The Evolutionary Redesign of Worldviews, Institutions, and Technologies," *Proc. Natl. Acad. Sci. USA*, 106(8), 2483–2489. DOI: 10.1073/pnas.0812570106. [PubMed: 19240221]
- (2). UN (2012). *Back to Our Common Future: Sustainable Development in the 21st century (SD21) project: Summary for policymakers* United Nations Department of Economic and Social Affairs, Division for Sustainable Development, New York.
- (3). Mardani A, Jusoh A, Nor KMD, Khalifah Z, Zakwan N, Valipour A (2015). "Multiple criteria decision-making techniques and their applications – a review of the literature from 2000 to 2014," *Economic Research-Ekonomska Istraživanja*, 28(1), 516–571, DOI: 10.1080/1331677X.2015.1075139.
- (4). Rangaiah GP (2017). *Multi-Objective Optimization: Techniques and Applications in Chemical Engineering*. *Advances in Process Systems Engineering*, Vol. 5 Second edition. World Scientific Publishing, Singapore.
- (5). Sociallicense.com (2018). <https://sociallicense.com/definition.html>, accessed on 3/30/18.
- (6). U.S. EPA (2006). *Life Cycle Assessment: Principles and Practice* EPA/600/R-06/060, National Risk Management Research Laboratory, Office of Research and Development, Cincinnati, OH.
- (7). Ruiz-Mercado GJ, Smith RL, Gonzalez MA (2014). "Expanding GREENSCOPE beyond the Gate: A Green Chemistry and Life Cycle Perspective," *Clean Technol. Environ. Policy*, 16, 703–717.
- (8). Udo de Haes HA, Sleeswijk AW, Heijungs R (2006). "Similarities, Differences and Synergisms Between HERA and LCA – An Analysis at Three Levels," *Hum. Ecol. Risk Assess*, 12(3), 431–449. DOI: 10.1080/10807030600561659
- (9). Bare J (2011). "TRACI 2.0: The Tool for the Reduction and Assessment of Chemical and other Environmental Impacts 2.0," *Clean Technol. Environ. Policy*, 13, 687–696.
- (10). Gonzalez MA, Smith RL (2003). "A Methodology to Evaluate Process Sustainability," *Environmental Progress*, 22(4), 269–276.
- (11). Ruiz-Mercado GJ, Gonzalez MA, Smith RL (2013). "Sustainability Indicators for Chemical Processes: III. Biodiesel Case Study," *Ind. & Eng. Chem. Res*, 52, 6747–6760.
- (12). Smith RL, Ruiz-Mercado GJ, Gonzalez MA (2015). "Using GREENSCOPE Indicators for Sustainable Computer-Aided Process Evaluation and Design," *Comput. Chem. Eng*, 81, 272–277.
- (13). Smith RL, Ruiz-Mercado GJ (2014). "A Method for Decision Making using Sustainability Indicators," *Clean Technol. Environ. Policy*, 16, 749–755.
- (14). Ruiz-Mercado GJ, Carvalho A, Cabezas H (2016) "Using Green Chemistry and Engineering Principles to Design, Assess, and Retrofit Chemical Processes for Sustainability," *ACS Sust. Chem. Eng*, 4(11), 6208–6221. DOI: 10.1021/acssuschemeng.6b02200.
- (15). Li S, Mirlekar GV, Ruiz-Mercado GJ, Lima FV (2016). "Development of Chemical Process Design and Control for Sustainability", *Processes*, 4(3), 23 DOI: 10.3390/pr4030023.
- (16). Cano-Ruiz JA, McRae GJ (1998). "Environmentally Conscious Chemical Process Design," *Annu. Rev. Energy Environ*, 23, 499–536.
- (17). Hilaly AK, Sikdar SK (1994). "Pollution Balance: A New Methodology for Minimizing Waste Production in Manufacturing Processes," *J. Air & Waste Manage. Assoc*, 44(11), 1303–1308.

- (18). Young DM, Cabezas H (1999). "Designing Sustainable Processes with Simulation: The Waste Reduction (WAR) Algorithm," *Comput. Chem. Eng.*, 23, 1477–1491.
- (19). Shonnard DR, Hiew DS (2000). "Comparative Environmental Assessments of VOC Recovery and Recycle Design Alternatives for a Gaseous Waste Stream," *Environ. Sci. Technol.*, 34, 5222–5228.
- (20). Sikdar SK (2003). "Sustainable Development and Sustainability Metrics," *AIChE J.*, 49(8), 1928–1932.
- (21). Jimenez-Gonzalez C, Ponder CS, Broxterman QB, Manley JB (2011). "Using the Right Green Yardstick: Why Process Mass Intensity is Used in the Pharmaceutical Industry to Drive More Sustainable Processes," *Org. Process Res. Dev.*, 15 (4), 912–917. DOI: 10.1021/op200097d.
- (22). Piluso C, Huang Y, Lou HH (2008). "Ecological Input-Output Analysis-Based Sustainability Analysis of Industrial Systems," *Ind. Eng. Chem. Res.*, 47, 1955–1966. DOI: 10.1021/ie061283s.
- (23). Dewulf J, Van Langenhove H, Muys B, Bruers S, Bakshi BR, Grubb GF, Paulus DM, Sciubba E (2008). "Exergy: Its Potential and Limitations in Environmental Science and Technology," *Environ. Sci. Technol.*, 42(7), 2221–2232. DOI: 10.1021/es071719a. [PubMed: 18504947]
- (24). Hau JL, Bakshi BR (2004). "Expanding Exergy Analysis to Account for Ecosystem Products and Services," *Environ. Sci. Technol.*, 38(13), 3768–3777. DOI: 10.1021/es034513s. [PubMed: 15296331]
- (25). Sugiyama H, Fischer U, Hungerbuhler K, Hirao M (2008). "Decision Framework for Chemical Process Design Including Different Stages of Environmental, Health, And Safety Assessment," *AIChE J.*, 54(4), 1037–1053.
- (26). Schwarz J, Beloff B, Beaver E (2002). "Use Sustainability Metrics to Guide Decision-Making," *Chem. Eng. Prog.*, 7 58–63.
- (27). IChemE (2002). Sustainable Development Progress Metrics: Recommended for use in the Process Industries, Institution of Chemical Engineers, Sustainable Development Working Group, Rugby, Warwickshire, UK.
- (28). Curzons AD, Constable DJC, Mortimer DN, Cunningham VL (2001). "So You Think Your Process is Green, How Do You Know? – Using Principles of Sustainability to Determine what is Green – A Corporate Perspective," *Green Chem.*, 3, 1–6. DOI: 10.1039/B007871I.
- (29). Uhlman BW, Saling PR (2017). "The BASF Eco-Efficiency Toolbox: Holistic Evaluation of Sustainable Solutions," in Abraham MA, ed., *Encyclopedia of Sustainable Technologies*, Elsevier, pp. 131–144. DOI: 10.1016/B978-0-12-409548-9.10042-9.
- (30). Jensen N, Coll N, Gani R (2003). "An Integrated Computer-Aided System for Generation and Evaluation of Sustainable Process Alternatives," *Clean Technol. Environ. Policy*, 5, 209–225.
- (31). Martins AA, Mata TM, Costa CAV, Sikdar SK (2007). "Framework for Sustainability Metrics," *Ind. Eng. Chem. Res.*, 46, 2962–2973.
- (32). Carvalho A, Matos HA, Gani R (2012). "SustainPro – A Tool for Systematic Process Analysis, Generation and Evaluation of Sustainable Design Alternatives," *Comput. Chem. Eng.*, 50, 8–27. DOI: 10.1016/j.compchemeng.2012.11.007.
- (33). Smith RL (2016) "Conceptual Chemical Process Design for Sustainability," in *Sustainability in the Design, Synthesis and Analysis of Chemical Engineering Processes*, Ruiz-Mercado G and Cabezas H, eds., Elsevier: Cambridge, MA; pp.67–85.
- (34). Smith RL, Gonzalez MA (2004). "Methods for Evaluating the Sustainability of Green Processes," *Computer-Aided Chemical Engineering* 18, Barbosa-Povoa A and Matos H, eds., ESCAPE-14, 16–19 May 2004, Lisbon, Portugal.
- (35). Ruiz-Mercado GJ, Smith RL, Gonzalez MA (2012a). "Sustainability Indicators for Chemical Processes: I. Taxonomy," *Ind. & Eng. Chem. Res.*, 51, 2309–2328. DOI: 10.1021/ie102116e.
- (36). Ruiz-Mercado GJ, Smith RL, Gonzalez MA (2012b). "Sustainability Indicators for Chemical Processes: II. Data Needs," *Ind. & Eng. Chem. Res.*, 51, 2329–2353. DOI: 10.1021/ie200755k.
- (37). Barthel M, Fava JA, Harnanan CA, Strothmann P, Khan S, Miller S (2015). "Hotspots Analysis: Providing the Focus for Action," Chapter 12 in *Life Cycle Management*, Sonnemann G, Margni M, eds., Springer, New York.
- (38). Hunkeler D, Saur K, Stranddorf H, Rebitzer G, Finkbeiner M, Schmidt W-P, Jensen AA, Christiansen K (2003). *Life Cycle Management* SETAC Press, Pensacola, FL.

- (39). Matthews E, Amann C, Bringezu S, Fischer-Kowalski M, Huttler W, Kleijn R, Moriguchi Y, Ottke C, Rodenburg E, Rogich D, Schandl H, Schutz H, Voet E. van der, Weisz H (2000). The Weight of Nations: Material Outflows from Industrial Economies, World Resources Institute, Washington, DC.
- (40). Ryberg M, Vieira MDM, Zgola M, Bare J, Rosenbaum RK (2014). "Updated US and Canadian Normalization Factors for TRACI 2.1," *Clean Technol. Environ. Policy*, 16, 329–339. DOI: 10.1007/s10098-013-0629-z.
- (41). World Resources Institute (2014). Global Protocol for Community-Scale Greenhouse Gas Emission Inventories: Executive Summary, accessed on 2/1/18 at <https://wri.org/publication/global-protocol-community-scale-greenhouse-gas-emission-inventories>.
- (42). Suh S (2005). "Developing a Sectoral Environmental Database for Input-Output Analysis: The Comprehensive Environmental Data Archive of the US.," *Economic Systems Research*, 17(4), 449–469. DOI: 10.1080=09535310500284326.
- (43). Sengupta D, Hawkins TR, Smith RL (2015) "Using National Inventories for Estimating Environmental Impacts of Products from Industrial Sectors: A Case Study of Ethanol and Gasoline," *Int. J. LCA*, 20, 597–607. DOI 10.1007/s11367-015-0859-x
- (44). Jimenez-Gonzalez C, Kim S, Overcash MR (2000). "Methodology for Developing Gate-to-Gate Life Cycle Inventory Information," *Int. J. Life Cycle Assess*, 5(3), 153–159.
- (45). Wernet G, Hellweg S, Hungerbuhler K (2012). "A Tiered Approach to Estimate Inventory Data and Impacts of Chemical Products and Mixtures," *Int. J. Life Cycle Assess*, 17, 720–728. DOI: 10.1007/s11367-012-0404-0.
- (46). U.S. EPA (2015). Compilation of Air Pollution Emission Factors, Volume I: Stationary Point and Area Sources, AP 42, Fifth Edition, Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- (47). NREL and USDA (2018). US Life Cycle Inventory Database National Renewable Energy Laboratory and the United States Department of Agriculture (USDA) National Agricultural Library, accessed on 2/2/18 at <https://uslci.lcacommons.gov/uslci/search>.
- (48). Wernet G, Bauer C, Steubing B, Reinhard J, Moreno-Ruiz E, Weidema B (2016). "The ecoinvent database version 3 (part I): overview and methodology," *Int. J. Life Cycle Assess*, 21(9), 1218–1230. DOI: 10.1007/s11367-016-1087-8.
- (49). Edelen A, Ingwersen WW (2017). "The creation, management, and use of data quality information for life cycle assessment," *Int. J. Life Cycle Assess* DOI: 10.1007/s11367-017-1348-1.
- (50). Cashman SA, Meyer DE, Edelen A, Ingwersen WW, Abraham JP, Barrett WM, Gonzalez MA, Randall P, Ruiz-Mercado GJ, Smith RL (2016). "Mining Available Data from the United States Environmental Protection Agency to Support Rapid Life Cycle Inventory Modeling of Chemical Manufacturing," *Environ. Sci. Technol*, 50, 9013–9025. DOI: 10.1021/acs.est.6b02160 [PubMed: 27517866]
- (51). Smith RL, Ruiz-Mercado GJ, Meyer DE, Michael A Gonzalez MA, Abraham JP, Barrett WM, Randall PM (2017). "Coupling Computer-Aided Process Simulation and Estimations of Emissions and Land Use for Rapid Life Cycle Inventory Modeling," *ACS Sust. Chem. Eng*, 5, 3786–3794. DOI: 10.1021/acssuschemeng.6b02724.
- (52). Meyer DE, Mittal VK, Ingwersen WW, Ruiz-Mercado GJ, Barrett WM, Gonzalez MA, Abraham JP, Smith RL (2018). "Purpose-Driven Reconciliation of Approaches to Estimate Chemical Releases," *ACS Sust. Chem. Eng*, 7, 1260–1270. DOI: 10.1021/acssuschemeng.8b04923.
- (53). Csiszar SA, Meyer DE, Dionisio KL, Egeghy P, Isaacs KK, Price PS, Scanlon KA, Tan Y-M, Thomas K, Vallero D, Bare JC (2016). "Conceptual Framework to Extend Life Cycle Assessment Using Near-Field Human Exposure Modeling and High-Throughput Tools for Chemicals," *Environ. Sci. Technol*, 50, 11922–11934. DOI: 10.1021/acs.est.6b02277. [PubMed: 27668689]
- (54). Hill D (2009). "Process Simulation from the Ground Up," *Chem. Eng. Prog*, 4, 50–53.
- (55). Burk C (2018). "Techno-Economic Modeling for New Technology Development," *Chem. Eng. Prog*, 1 43–52.
- (56). Li S, Feliachi Y, Agbleze S, Ruiz-Mercado GJ, Smith RL, Meyer DE, Gonzalez MA, Lima FV (2018). "A Process Systems Framework for Rapid Generation of Life Cycle Inventories for

- Pollution Control and Sustainability Evaluation,” *Clean Technol. Environ. Policy*, 20, 1543–1561, DOI: 10.1007/s10098-018-1530-6. [PubMed: 30245612]
- (57). Douglas JM (1988). *Conceptual Design of Chemical Processes* McGraw-Hill: New York.
- (58). Turton R, Bailie RC, Whiting WB, Shaeiwitz JA (2009). *Analysis, Synthesis, and Design of Chemical Processes*, 3rd ed.; Prentice Hall: Upper Saddle River, New Jersey.
- (59). U.S. EPA (2018). *A Working Approach for Identifying Potential Candidate Chemicals for Prioritization*, Office of Chemical Safety and Pollution Prevention, Washington, DC.
- (60). Gonzalez MA, Smith RL (2003) “A Methodology to Evaluate Process Sustainability,” *Environmental Progress*, 22(4), 269–276.
- (61). Dutta A, Talmadge M, Hensley J, Worley M, Dudgeon D, Barton D, Groenendijk P, Ferrari D, Stears B (2011) *Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol: Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis* Golden, CO: National Renewable Energy Laboratory; 2011 Report No.: NREL/TP-5100–51400.
- (62). Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, Schoen P, Lukas J, Olthof B, Worley M, Sexton D, Dudgeon D (2011) *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover* Golden, CO: National Renewable Energy Laboratory; 2011 Report No.: NREL/TP-5100–47764.
- (63). Accepta 2972 (2019). Accessed on 2/1/19 at <https://accepta.com/water-treatment-chemicals-wastewater-effluent-treatment-products/boiler-water-treatment-chemicals/oxygen-scavengers-boiler-water-treatment-chemicals/196-oxygen-scavenger-for-boiler-water-systems-2972>.
- (64). CoolingTowerChemicals (2019). Accessed on 2/1/19 at <https://www.coolingtowerchemicals.com/Cooling-Tower-Chemicals-Literature-s/140.htm>.
- (65). Beychok MR (1952). “How to Calculate Cooling Tower Control Variables,” *Petroleum Processing*, 1452–1456.
- (66). Cheremisinoff NP, Cheremisinoff PN (1981). *Cooling Towers: Selection, Design and Practice*, Ann Arbor Science Publishers, Ann Arbor, MI; pp.114–122, 257.
- (67). Perry RH, Green DW (1984). *Perry’s Chemical Engineers’ Handbook* New York: McGraw-Hill; p.12–15.
- (68). U.S. EPA (2013). *ChemSTEER User Guide, Chemical Screening Tool for Exposures and Environmental Releases*, Office of Pollution Prevention and Toxics, Washington, DC.
- (69). Tan ECD, Bidy M, (2018) “An Integrated Sustainability Evaluation of Indirect Liquefaction of Biomass to Liquid Fuels,” 7th International Congress on Sustainability Science & Engineering (ICOSSE ‘18: Industry, Innovation and Sustainability), Cincinnati, OH, August 12–15 Available at: <https://www.osti.gov/biblio/1471294>.

Figure 1. Thermochemical process flow diagram and stream numbers associated with Dutta et al.⁶¹

Figure 2.
Biochemical process flow diagram and stream numbers associated with Humbird et al.⁶²

Figure 3.
Efficiency (Eff) indicators for the thermochemical (TC) and biochemical (BC) processes.

Figure 4.
Energy (En) indicators for the thermochemical and biochemical processes.

Figure 5.
Economic (Econ) indicators for the thermochemical and biochemical processes.

Figure 6.
Environmental (Env) indicators for the thermochemical and biochemical processes.

Table 1.

Steps for Developing Process Inventory Data

Number	Description
1	Draw a flowsheet of the process of interest.
2	Model the flowsheet material and energy flows, accounting for electricity, cooling, and heating needs and material input, product, wastewater, and purge streams.
3	Model all end-of-pipe treatments (for example, for purge streams) as appropriate.
4	Identify process equipment that will be modeled for fugitive emissions.
5	Use the fugitive emission spreadsheet (in the Supporting Information) to calculate emissions.
6	Note any fugitive emissions that end up in process water (i.e., cooling water).
7	Use the process boiler and cooling tower spreadsheets (in the SI) to define associated electricity, fuel, and material resource use and emission and wastewater amounts.
8	For every reactant, intermediate, and product determine how it is stored.
9	Use the storage spreadsheet (in the SI) to determine emissions.
10	Use the forklift/loader emission spreadsheet (in the SI) to identify fuel use and emissions.
11	Sum the process inputs from Steps 2, 3, 7, and 10 for each component, electricity, and fuel.
12	Sum the wastewater amounts from Steps 2 and 7 for each component.
13	Sum the emissions from Steps 2, 3, 5, 7, 9, and 10 for each component.

Table 2.

Selected Key Indicators for Sustainability Performance Assessment in Terms of Efficiency, Environmental, Energy, and Economic Areas^a

		Indicator	Symbol	Best case	Worst case
Efficiency	Eff 5	Reaction mass efficiency	RME	1	0
	Eff 7	Mass intensity	MI	1	40
	Eff 10	Environmental factor	E	0	39
	Eff 13	Effective mass yield	EMY	0	40
	Eff 14	Carbon efficiency	CE	1	0
	Eff 18	Renewability-material index	RI _M	1	0
	Eff 23	Total water consumption	V _{water, tot}	0	All water requirement is supplied by fresh water
	Eff 24	Fractional water consumption	FWC	0	2.95 m ³ /kg
Environmental	Env 1	Number of hazardous materials input	N _{haz. mat.}	0	All substances fed to the process are hazardous
	Env 2	Mass of hazardous materials input	m _{haz. mat.}	0	All total mass fed to the process is hazardous
	Env 3	Specific hazardous raw materials input	m _{haz. mat. spec.}	0	All total mass fed to the process is hazardous per unit of valuable product
	Env 4	Total mass of persistent, bio-accumulative and toxic (PBT) chemicals used	m _{PBT mat.}	0	All substances fed to the process are PBT
	Env 7	Health hazard, chronic toxicity factor	HH _{chronic toxicity}	0	1.00E+07 m ³ /kg
	Env 12	Safety hazard, acute toxicity	SH _{acute tox.}	0	1.00E+05 m ³ /kg
	Env 14	Specific toxic release	TR _s	0	All waste is TRI
	Env 15	Toxic release intensity	TR	0	All waste is TRI per unit of annual sales
	Env 17	Human health burden, cancer effects	EB _{cancer eff.}	0	All waste is at least 1 Benzene-equivalent per unit of annual sales
	Env 20	Environmental hazard, water hazard	EH _{water}	0	1.00E+05 m ³ /kg
	Env 23	Global warming potential	GWP	0	All waste is at least 1 CO ₂ e-equivalent per unit of valuable product
	Env 24	Global warming intensity	GW	0	All waste is at least 1 CO ₂ -equivalent per unit of annual sales
	Env 25	Stratospheric ozone-depletion potential	ODP	0	All waste is at least 1 CFC-11-equivalent per unit of valuable product
	Env 26	Stratospheric ozone-depletion intensity	ODI	0	All waste is at least 1 CFC-11-equivalent per unit of annual sales

	Indicator		Symbol	Best case	Worst case
	Env 27	Photochemical oxidation (smog) potential	PCOP	0	All waste is at least 1 ethylene - equivalent per unit of valuable product
	Env 28	Photochemical oxidation (smog) intensity	PCOI	0	All waste is at least 1 ethylene - equivalent per unit of annual sales
	Env 29	Atmospheric acidification potential	AP	0	All waste is at least 1 SO ₂ - equivalent per unit of valuable product
	Env 30	Atmospheric acidification intensity	API	0	All waste is at least 1 SO ₂ - equivalent per unit of annual sales
	Env 31	Aquatic acidification potential	WP _{acid. water}	0	All waste has the potential to offer at least 1 H ⁺ per unit of valuable product
	Env 32	Aquatic acidification intensity	WPI _{acid. water}	0	All waste has the potential to offer at least 1 H ⁺ per unit of annual sales
	Env 33	Aquatic basification potential	WP _{basif. water}	0	All waste has the potential to offer at least 1 OH ⁺ per unit of valuable product
	Env 34	Aquatic basification intensity	WPI _{basif. water}	0	All waste has the potential to offer at least 1 OH ⁺ per unit of annual sales
	Env 39	Ecotoxicity to aquatic life potential	WP _{tox. other}	0	All waste is at least 1 formaldehyde -equivalent per unit of valuable product
	Env 40	Ecotoxicity to aquatic life intensity	WPI _{tox. other}	0	All waste is at least 1 formaldehyde -equivalent per unit of annual sales
	Env 43	Eutrophication potential	EP	0	All waste is at least 1 phosphate - equivalent per unit of valuable product
	Env 44	Eutrophication potential intensity	EPI	0	All waste is at least 1 phosphate - equivalent per unit of annual sales
	Env 53	Specific solid waste mass	$m_{s, spec.}$	0	All types of solid waste are released
	Env 60	Specific hazardous solid waste	$m_{s, haz. spec.}$	0	All hazardous solid waste generated is released per unit of valuable product
	Env 64	Specific liquid waste volume	$V_{l, spec.}$	0	All liquid releases are rated as waste per unit of valuable product
	Env 66	Polluted liquid waste volume	$V_{l, poll.}$	0	All liquid releases are rated as pollutant
Energy	En 2	Specific energy intensity	R_{SEI}	0	1949 MJ/kg
	En 3	Energy intensity	R_{EI}	The total product energy value per sales revenue	10 times the total product energy value per sales revenue
	En 4	Waste treatment energy	WTE	0	10% of the total energy consumed per mass of product
	En 6	Resource-energy efficiency	η_E	1	0
	En 7	Renewability-energy index	RI_E	1	0
	En 8	Breeding-energy factor	BF_E	1	0

	Indicator		Symbol	Best case	Worst case
Economic	Econ 1	Net present value (worth)	NPV	NPV @ discount rate (r_d) = 0%	NPV @ r_d = 40%
	Econ 3	Discounted payback period	DPBP	1	Plant life
	Econ 4	Discounted cash flow rate of return	DCFROR	40	0
	Econ 7	Rate of return on investment	ROI	40	0
	Econ 8	Payback period	PBP	1	Plant life
	Econ 9	Turnover ratio	TR	4	0.2
	Econ 13	Revenue from eco-products	REV	Total revenue	0
	Econ 14	Revenue fraction of eco-products	REV _{eco-prod}	1	0
	Econ 16	Total product cost	TPC	1.4*COM _{best-case}	1.2*COM _{worst-case}
	Econ 19	Manufacturing cost	COM	0.38*TPC + 0.025*0.497*FCI	1.7*TPC + 0.3*FCI
	Econ 20	Specific raw material cost	C _{SRM}	0.1*TPC _{best-case}	0.8*TPC _{worst-case}
	Econ 22	Total energy cost	C _{E, tot.}	Consumed energy from cheapest source (coal) @ \$1.72×10 ⁻⁶ /kJ	Consumed energy from expensive source (electricity) @ \$1.68×10 ⁻⁵ /kJ
	Econ 23	Specific energy cost	C _{E, spec.}	Consumed energy from cheapest source (coal) @ \$1.72×10 ⁻⁶ /kJ/TPC _{best-case}	Consumed energy from expensive source (electricity) @ \$1.68×10 ⁻⁵ /kJ/TPC _{worst-case}
	Econ 28	Total solid waste cost	C _{s tot.}	0	All solid waste is categorized as hazardous at \$2/kg
	Econ 29	Specific total solid waste cost	C _{S, spec.}	0	All solid waste is categorized as hazardous at \$2/kg/TPC _{worst-case}
	Econ 30	Total liquid waste cost	C _{l tot.}	0	All liquid waste is categorized as hazardous at \$2/kg
	Econ 31	Specific liquid waste cost	C _{l, spec.}	0	All liquid waste is categorized as hazardous at \$2/kg/TPC _{worst-case}

^aThe best- and worst-case values determined for comparison will be the most extreme values, which create the largest Best–Worst range in the denominator of Eqn. 1. More details regarding the indicators are available.^{35,36}

Table 3.

Process Inputs for Thermochemical and Biochemical Processes (kg/GGE)

Input	Thermochemical	Biochemical
Biomass (dry basis) ^a	1.45×10^1	1.74×10^1
Catalyst, Tar Reformer	9.50×10^{-4}	-
Catalyst, Alcohol Synthesis	1.53×10^{-3}	-
Catalyst, Chelated Iron (LO-CAT)	2.51×10^{-4}	-
Olivine	4.25×10^{-2}	-
Magnesium Oxide	5.52×10^{-4}	-
Dimethyl Ether of Polyethylene Glycol	1.42×10^{-4}	-
Methyldiethanolamine	1.58×10^{-5}	-
Sodium Hydroxide	1.58×10^{-3}	4.69×10^{-1}
Ammonia	3.34×10^{-4}	2.43×10^{-1}
Diesel	5.62×10^{-3}	6.72×10^{-3}
Sulfuric Acid, 93%	-	4.14×10^{-1}
Glucose	-	5.03×10^{-1}
Sorbitol	-	9.18×10^{-3}
Sulfur Dioxide	-	3.35×10^{-3}
Enzyme Nutrients	-	1.40×10^{-2}
Corn Steep Liquor	-	2.75×10^{-1}
Diammonium Phosphate	-	2.95×10^{-2}
Lime	-	1.87×10^{-1}
Gasoline Denaturant	-	9.70×10^{-2}
Boiler Feed Water Makeup	5.70×10^0	7.37×10^0
Potassium Hydroxide ^b	7.84×10^{-6}	1.55×10^{-6}
Sodium Bisulfite ^b	1.96×10^{-5}	3.87×10^{-6}
Sodium Hexametaphosphate ^b	7.84×10^{-6}	1.55×10^{-6}
Cooling Tower Water Makeup	7.20×10^0	3.22×10^1
Phosphonocarboxylic Acid, Potassium Salt ^c	2.82×10^{-6}	1.49×10^{-5}
Hydroxyphosphonoacetic Acid, Potassium Salt ^c	2.82×10^{-6}	1.49×10^{-5}
Potassium Phosphate ^c	2.82×10^{-6}	1.49×10^{-5}
Sodium Tolytriazole ^c	9.41×10^{-7}	4.98×10^{-6}
Potassium Hydroxide ^c	4.71×10^{-7}	2.48×10^{-6}
Sodium Hypochlorite ^c	1.33×10^{-6}	1.74×10^{-5}
Input Total	2.75×10^1	5.92×10^1

^a – For TC, the feedstock is woody biomass; for BC, the feedstock is corn stover.

^b – Boiler feedwater circulation chemicals.⁶³

^c – Cooling tower circulation chemicals.⁶⁴

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Table 4.

Emissions for Thermochemical and Biochemical Processes (kg/GGE)

kg/GGE	Biochemical					Thermochemical				
Chemical	Direct	Fugitive	Storage	Loading	Total	Direct	Fugitive	Storage	Loading	Total
Ammonia *	6.35×10^{-3}	9.33×10^{-5}	5.16×10^{-4}	1.74×10^{-7}	6.96×10^{-3}		1.94×10^{-4}	2.04×10^{-6}	1.45×10^{-7}	1.96×10^{-4}
Sulfuric Acid *	6.55×10^{-9}	8.90×10^{-5}	2.38×10^{-10}		8.90×10^{-5}					
Diammonium Phosphate *	1.49×10^{-3}				1.49×10^{-3}					
Sodium Nitrate *	1.52×10^{-2}				1.52×10^{-2}					
NO ₂	1.29×10^{-2}			8.75×10^{-5}	1.30×10^{-2}	5.43×10^{-3}	6.22×10^{-9}		7.32×10^{-5}	5.51×10^{-3}
CO	1.29×10^{-2}			6.72×10^{-5}	1.30×10^{-2}	6.49×10^{-3}	7.78×10^{-4}		5.62×10^{-5}	7.32×10^{-3}
CO ₂	1.53×10^1	7.27×10^{-8}		2.14×10^{-2}	1.53×10^1	1.83×10^1	7.94×10^{-4}		1.79×10^{-2}	1.83×10^1
SO ₂	1.12×10^{-2}	9.95×10^{-6}	8.18×10^{-9}	1.19×10^{-7}	1.12×10^{-2}	2.32×10^{-3}	2.28×10^{-9}	1.04×10^{-9}	9.91×10^{-8}	2.32×10^{-3}
N ₂ O	2.53×10^{-4}				2.53×10^{-4}	1.46×10^{-4}				1.46×10^{-4}
PM	1.33×10^{-3}			2.98×10^{-7}	1.33×10^{-3}	7.38×10^{-4}			2.49×10^{-7}	7.38×10^{-4}
PM, Cooling Tower	5.65×10^{-6}				5.65×10^{-6}	4.33×10^{-7}				4.33×10^{-7}
Methanol *	1.76×10^{-7}				1.76×10^{-7}	1.35×10^{-8}	6.32×10^{-4}	1.91×10^{-7}		6.33×10^{-4}
Ethanol		5.33×10^{-4}	2.93×10^{-5}		5.62×10^{-4}		1.49×10^{-4}	2.34×10^{-5}		1.73×10^{-4}
Propanol							3.88×10^{-5}	1.01×10^{-6}		3.98×10^{-5}
n-Butanol *							4.96×10^{-8}	4.15×10^{-10}		5.00×10^{-8}
Acetic Acid		2.83×10^{-6}			2.83×10^{-6}					
Furfurals		7.99×10^{-6}			7.99×10^{-6}					
Gasoline *		7.61×10^{-5}	1.95×10^{-5}		9.56×10^{-5}					
Diesel *		4.59×10^{-5}	9.92×10^{-9}		4.59×10^{-5}		3.84×10^{-5}	8.29×10^{-9}		3.84×10^{-5}
Methane	3.94×10^{-4}	4.54×10^{-6}		7.49×10^{-7}	4.00×10^{-4}	2.20×10^{-4}	7.09×10^{-5}		6.26×10^{-7}	2.91×10^{-4}
Ethane	3.55×10^{-5}				3.55×10^{-5}	4.13×10^{-5}	2.11×10^{-6}			4.34×10^{-5}
Ethylene *							6.51×10^{-6}			6.51×10^{-6}
Acetylene							5.47×10^{-7}			5.47×10^{-7}
Propane	1.79×10^{-5}				1.79×10^{-5}	2.14×10^{-5}	2.36×10^{-6}			2.37×10^{-5}
n-Butane	2.34×10^{-5}				2.34×10^{-5}	2.80×10^{-5}	5.39×10^{-9}			2.80×10^{-5}
Benzene *	7.39×10^{-5}			4.49×10^{-7}	7.44×10^{-5}	3.77×10^{-5}	2.16×10^{-7}	1.02×10^{-8}	3.75×10^{-7}	3.83×10^{-5}
Hydrogen Sulfide *							4.60×10^{-6}			4.60×10^{-6}
Hydrogen Chloride *	3.35×10^{-4}				3.35×10^{-4}	1.70×10^{-4}				1.70×10^{-4}

kg/GGE	Biochemical					Thermochemical				
Chemical	Direct	Fugitive	Storage	Loading	Total	Direct	Fugitive	Storage	Loading	Total
VOC otherwise unspecified	[†] 3.62×10 ⁻⁴			9.67×10 ⁻⁶	3.72×10 ⁻⁴	[†] 2.26×10 ⁻⁴			8.09×10 ⁻⁶	2.34×10 ⁻⁴
Ethylene Thiourea *	[‡] 8.46×10 ⁻⁷				8.46×10 ⁻⁷	[‡] 6.47×10 ⁻⁸				6.47×10 ⁻⁸

[†] - indicates values from boiler model spreadsheet.

[‡] - indicates values from cooling tower spreadsheet

* - indicates an EPA TRI chemical, where gasoline and diesel have TRI chemicals as components.