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Coupling Computer-Aided Process Simulation and Estimations of Emissions and Land Use for Rapid Life Cycle Inventory Modeling

Raymond L. Smith*, Gerardo J. Ruiz-Mercado, David E. Meyer, Michael A. Gonzalez, John P. Abraham, William M. Barrett, and Paul M. Randall

National Risk Management Research Laboratory, United States Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, United States

Abstract

A methodology is described for developing a gate-to-gate life cycle inventory (LCI) of a chemical manufacturing process to support the application of life cycle assessment in the design and regulation of sustainable chemicals. The inventories were derived by first applying process design and simulation to develop a process flow diagram describing the energy and basic material flows of the system. Additional techniques developed by the United States Environmental Protection Agency for estimating uncontrolled emissions from chemical processing equipment were then applied to obtain a detailed emission profile for the process. Finally, land use for the process was estimated using a simple sizing model. The methodology was applied to a case study of acetic acid production based on the Cativa process. The results reveal improvements in the qualitative LCI for acetic acid production compared to commonly used databases and top-down methodologies. The modeling techniques improve the quantitative LCI results for inputs and uncontrolled emissions. With provisions for applying appropriate emission controls, the proposed method can provide an estimate of the LCI that can be used for subsequent life cycle assessments.

Graphical Abstract

* smith.raymond@epa.gov.

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Keywords

Acetic Acid; Fugitive; LCA; LCI; Process; Production; Storage; Vent

Introduction

The chemical inventory list maintained by the United States Environmental Protection Agency (U.S. EPA) under the Toxic Substances Control Act (TSCA) has grown to about 85000 entries when including both new and historically used substances⁽¹⁾ with 7690 active chemicals reported in commerce as of 2012.⁽²⁾ Both chemical manufacturers and regulators are facing the challenge of how best to manage these chemicals given the emerging importance of sustainability. Regulatory chemical decisions have traditionally focused on minimizing a chemical's risk to human health and ecotoxicity while manufacturers make chemical design choices to achieve desired product functionality for minimal cost. The National Research Council (NRC)⁽³⁾ has recommended sustainability as a framework that can accommodate the simultaneous pursuit of both regulatory and industry goals because it ultimately seeks to maximize the benefits of a system while minimizing the perceived risks.

Life cycle assessment (LCA), a tool for environmental sustainability, is an internationally standardized methodological framework^(4, 5) to account for the effects of resource use and environmental releases from a network of processes within the life cycle of a product, process, or system, including extraction of raw materials, production of value-chain precursors, production, use, and disposal/recycling. For this reason, it is useful during chemical design and manufacturing. The NRC included life cycle thinking and LCA as key tools for designing alternative chemicals in their framework for alternatives assessment.⁽⁶⁾ Similarly, the NRC supported the use of LCA to incorporate environmental sustainability into regulatory decision making.⁽⁷⁾

This recognition of the broader utility of LCA should make it highly desirable for chemical decision making. However, key methodological challenges have slowed the adoption of LCA for this context, despite a history dating back to the 1970s.⁽⁸⁾ Perhaps the most significant of these challenges is the large amount of data needed to support the assessment. A foundation of any LCA is the creation of the life cycle inventory (LCI) because the assessment results will only be as good as the underlying data used to generate them. In simple terms, the LCI is a collection of material and energy flows describing each of the processes within a chemical or product life cycle (Figure 1). Ideally, this information is primary measurement data from real-world unit operations. In reality, this information is difficult if not impossible to obtain. For new and emerging chemicals, like those identified during alternatives assessment, the data simply may not exist because the manufacturing process is only theoretical or bench-scale in nature. Manufacturers often treat the data for existing chemicals as confidential business information and decline disclosure. Under either circumstance, it is necessary to estimate the LCI.

Estimating Life Cycle Inventory

There are two general approaches for approximating an LCI. The top-down approach applies data mining to economy- or facility-level data(9–11) while the bottom-up approach relies on process design methods for sets of unit operations.(12, 13) For both approaches, the goal is to create an accurate LCI given limited time and resources. Cashman et al.(9) proposed a data mining method to rapidly generate process LCI for chemical manufacturing using U.S. EPA databases containing emission data collected under various regulatory statutes. The benefit of this approach is the data are often reported by companies and are therefore presumed to be more accurate. The potential issues with the method include large data gaps related to material and energy inputs, variations in reporting requirements affecting data submission, a potential lack of transparency regarding the underlying process technology represented in the databases, challenges with accurately allocating facility-level emissions to a single chemical production process within multiprocess facilities, and chemical coverage currently limited to those with production volumes reported in U.S. EPA's Chemical Data Reporting Tool.(9) Many of these challenges echo similar findings for economy-based inventories developed to support environmentally extended input–output LCA.(10)

The bottom-up approach offers its own set of benefits and challenges. For example, the bottom-up approach estimates material and energy inputs, which allows the resulting LCI to be connected with the upstream life cycle. The process-specific focus avoids the need to apply allocation to the inventory and provides a definitive understanding of the technology coverage. However, the extensive engineering knowledge required to apply a bottom-up approach can be a significant challenge. Inexperience in process design can lead to lengthy modeling times and poor design choices that yield inaccurate inventory approximations. Bottom-up design methods may include short-cut design methods, correlations and look-up tables, or computer-aided process simulation. While all three methods have their value, this work focuses on computer-aided simulation because of its widespread use in chemical process design and manufacturing.

Chemical engineering process design techniques for LCI estimation were employed by Jimenez-Gonzalez et al.(14) to determine mass balances, major impurities, and simple fugitive emissions. In building the ecoinvent(15) database simplified estimation methods are used when data is not available.(16) More recent work still points to the lack of LCI data for the vast majority of chemicals.(17) In considering particular examples, Bojarski et al.(18) developed a framework to apply process simulation to aid with the generation of a chemical LCI while considering its uncertainty. The framework was evaluated using a case study of the production of phosphoric acid. Although the resulting uncertainty for much of the simulated inventory was quite low, modeling assumptions regarding the treatment of waste streams yielded an inventory with only two air emissions and three water discharges, while resource use was limited to chemicals. Morais et al.(19) used process simulation to evaluate three proposed alternative routes for biodiesel production from waste vegetable oils. The resulting inventory for all the alternatives included detailed energy and mass flow data and nonchemical resources but again contained a limited selection of emissions and waste generation with only solid and hazardous waste streams generated for off-site treatment. Petrescu et al.(20) investigated the influence of carbon capture and fuel choices for steam

generation on acrylic acid production using process simulation and LCA. Given the focus on treatment of the flue gas for carbon capture, the resulting inventory included a more detailed emission profile for the flue gas stream in addition to the detailed material and energy flows that can be obtained from simulations. As with the previous examples, resources were limited to those required for synthesis and energy. The fact that two of the three examples present limited emissions data and the third focuses only on a single stream of emissions suggests there is a need to develop better methods for handling emission modeling when simulating LCI given the importance of these flows in environmental impact calculations. Furthermore, Cashman et al.(9) found with their data mining method that the list of emissions reported by facilities is much larger than what is reported in commercial LCI databases, especially when the commercial databases were modeled using reaction kinetics and stoichiometry. While this can be partly attributed to difficulties with modeling multioutput facilities and properly assigning emissions to their associated chemical processes, some of the additional species arise because the top-down databases include additional emission sources like fugitive emissions, equipment leaks, and storage losses that are known to occur in chemical plants and refineries(21, 22) but which are often excluded in most LCIs. The potential issue with these omissions is the additional emissions can lead to impacts that might be otherwise missed during impact assessment.(9) Again, properly handling extra emission sources with top-down methods is challenging when a facility involves multiple production process and chemical products. Therefore, there is a need to develop complementary inventory modeling methods based on computer-aided process simulation methods that can fill the recognized resource use gaps and identify a more precise list of anticipated emission species when considering all possible emission sources associated with a chemical process. In addition, the wide-ranging applicability of computer-aided process simulation can help address the current chemical coverage limitations of the data mining approach.

Although methodologies for estimating or assessing emissions from chemical processes have been proposed for regulatory and other applications,(21–23) they have not yet been translated into practice during LCI modeling to address data gaps in the inventory emissions. In addition, there are reliable methods to estimate uncontrolled process vent, storage, and fugitive emissions that can improve the quality of an LCI. Developing such practices will constitute a worthy contribution to LCI modeling. In addition, it is possible to expand the consideration of resource use for simulated processes by adding consideration of land use, which is a growing concern in environmental decision making because of its impact on issues ranging from biodiversity to food production. Addressing these needs motivates the objectives of this research (1) to develop a methodology based on computer-aided process simulation for generating more accurate chemical process LCIs that account for land resources, uncontrolled process vent and storage emissions, and fugitive emissions and (2) to demonstrate the utility of the methodology using a case study of acetic acid production by the Cativa process.

Methodology

Developing a chemical manufacturing LCI using simulation and emission and land use models involves a general approach that is iterative and adjustable to achieve a desired

accuracy. This includes researching production of a chemical, designing the manufacturing process, simulating the process, and applying emission and land use models. Although the approach is common to process design, careful consideration of key details can greatly enhance process LCI development. Research of a chemical's production must identify the desired process technology, production rate, and product purity because these parameters will determine the broader applicability of the resulting LCI. When performing process design,(24–26) the designer must define the system boundaries to promote consistency in the life cycle model, including which utilities from Figure 1 are generated off-site or at the facility-level (upstream LCIs) and which are generated as part of the process LCI. A less rigorous estimation of LCI may overlook important aspects that can be included with process design, such as storage vessels for inputs and outputs and detailed chemistries that include all inputs in addition to feedstocks (i.e., process essentials of Figure 1). Examples of process essentials are catalysts and reaction promoters, solvents for reactions or separations, regularly replaced packing materials for separation vessels, etc. In addition, integrating pollution control and abatement can make the simulation (and LCI) more realistic. If the simulation does not incorporate emission and land use models, they can be applied manually after the fact to augment the simulated LCI. The detailed discussion of methods that follows focuses on this last concept of manual inventory augmentation given the abundance of available process design literature. The U.S. EPA provides emission estimate methods for a number of processes and activities that, because of their use of simplifying assumptions and calculations, can benefit process LCIs.(27, 28) This work examines such methods for storage vessels, process vents, and fugitive emissions with an original method provided to approximate land use for unit operations.

Storage Emissions

Storage tanks house liquid feedstocks prior to their introduction into the chemical process, intermediates prior to transfer to another process train, and final products and coproducts before transportation to packaging and distribution. These tanks are significant sources of emissions and need to be included in the overall life cycle inventory of a chemical process. (22) There are various types:(28) fixed, floating (external and internal), horizontal, pressurized, variable-space, and liquefied natural gas. Fixed-roof tanks are widely used in industry and will be modeled here.(29)

Two sources of emissions from tanks are breathing (or standing) and working losses. For a fixed-roof tank, the type of tank assumed to be used in this work for all storage operations, breathing losses result from the release of vapors from its headspace arising from fluctuations in temperature and barometric pressure. It is assumed that there is no change in the liquid level associated with breathing losses. Working losses arise from either filling or emptying the tank. As additional liquid is added, headspace volume decreases; pressure increases and eventually exceeds the relief pressure of the tank, and vapors are expelled. As air is drawn into the tank, to facilitate emptying, the air becomes saturated with organic vapor and expands. This resulting pressure is expelled via the relief valve.

To quantify these emissions, the U.S. EPA has developed detailed calculations and software (TANKS).(30) However, while these calculations are more accurate, they require significant

amounts of information and are too detailed to accompany a conceptual design/first-level process flow diagram. As a result, simplified methods adapted from the detailed method have been developed and are within differences of 2–9%;(29) however, the chemicals for comparison may have been chosen because they fit the simplified model well. Using the simplified model facilitates the inclusion of these emissions early into the development/evaluation of a process. The simplified calculations (eqs 1 and 2) for a fixed-roof tank are as follows. For working losses, L_w ,

$$L_w = \frac{\dot{V}}{22.4} \left(\frac{273.15}{T} \right) \left(\frac{P_i^{sat}}{760} \right) (MW) K_N K_P \quad (1)$$

where $\dot{V}$ is the volumetric throughput (m^3/yr), T is the temperature (K), P_i^{sat} is the saturation vapor pressure (mmHg), MW is the molecular weight (kg/kmol), K_N is the annual turnover factor (often set to one), and K_P is the product factor (equal to one for organic liquids). The details of this calculation are described in Section S1 of the Supporting Information.

Breathing losses are determined by a similar calculation, although it depends on the day/night temperature fluctuation, which affects the number of moles of gas in the vapor space of the tank. The breathing losses, L_B , are given by,

$$L_B = 16.3 V_v \left(\frac{273.15}{T} \right) \left(\frac{P_i^{sat}}{760} \right) (MW) \left(\frac{T_R}{T} \right) \quad (2)$$

where V_v is the vapor space of the tank (m^3). The average ambient temperature, if not available, can be assumed to be an average for the U.S. (i.e., 285.68 K). Likewise, the average temperature fluctuation T_R can represent an average for the U.S. (i.e., 13.5 K).(31) The details of these calculations are provided in Section S1 of the Supporting Information.

Process Vent Emissions

Process vessels holding liquid contents can have headspace vapors that are vented. These vessels can include (but are not limited to) decanters, distillation column reflux drums, and reactors. Input gases such as nitrogen and air can sweep the headspace to provide an inert or diluted atmosphere. The generation or unintentional introduction of gases in the vessel can stimulate venting. Finally, if the reactor pressure increases, for instance due to a temperature increase, then the reactor headspace may vent. The vented material may be emitted, piped to a control technology, or captured for its value. The U.S. EPA has presented information and calculations on venting.(32)

When liquids are maintained in a vessel, evaporated contents can fill the headspace. The extent to which this evaporation occurs depends on the liquid component vapor pressures, evaporative mass transfer rates, and time. The evaporation time can be approximated by the rate at which the volume of gases are vented from the headspace, as fast and continuous venting does not allow much time for evaporation.

The composition of the vapors in the headspace can be modeled with Raoult's Law, which at equilibrium relates the partial pressure, P_i , to the mole fraction in the liquid phase, x_i , the liquid-phase activity coefficient, γ_i , and the saturation vapor pressure, P_i^{sat} :

$$P_i = y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (3)$$

The partial pressure can be expressed as the mole fraction in the vapor phase, y_i , multiplied by the system pressure, P .

If a balance is written on one evaporating component, then the rate at which the vapors are vented out of the vessel can be set equal to the rate of evaporation, and the balance is

$$\frac{F P_i^b}{RT} = \frac{k_i A}{RT} (x_i \gamma_i P_i^{\text{sat}} - P_i^b) \quad (4)$$

where F is the volumetric flow rate out, P_i^b is the bulk vapor partial pressure of i , and $k_i A$ is the mass transfer rate (i.e., mass transfer coefficient times the interfacial area). Multiplying both sides by RT and multiplying $k_i A$ through the right-hand side, one can rearrange and solve for P_i^b :

$$P_i^b = \frac{k_i A x_i \gamma_i P_i^{\text{sat}}}{k_i A + F} \quad (5)$$

which follows the method of Hatfield(33) in defining S_i as a dimensionless quantity between 0 and 1, representing the degree of saturation:

$$S_i = \frac{P_i^b}{x_i \gamma_i P_i^{\text{sat}}} = \frac{k_i A}{k_i A + F} \quad (6)$$

S_i approaches one as the bulk partial pressure approaches the equilibrium value (the denominator) defined by Raoult's Law. Another way of understanding S_i is that it approaches one as the mass transfer rate, $k_i A$, becomes large compared to the volumetric flow rate, F .

For purposes of life cycle inventories, when venting occurs, the value of F can be conveniently approximated by one of three ratios between F and $k_i A$. When the flow of gas into the headspace is small (e.g., perhaps a small amount of noncondensable gases are trapped in a feed or a small amount of gas byproduct evolves in a vessel), $F = k_i A/9 = 0.11 k_i A$. When the flow of gas into the headspace is large (e.g., a sweep gas is applied or a large amount of gas byproduct evolves in a vessel), $F = 9 k_i A$. For intermediate conditions, $F = k_i A$. Solving eq 6, the resulting S_i values for these three conditions are $S_i = 0.9$, $S_i = 0.1$,

and $S_i = 0.5$, respectively. While Hatfield(33) solves for the various S_i for mixture components, the assumption here is that individually calculated component values are sufficient for life cycle inventories.

To determine the vented emissions before pollution controls, one must first include any gases input or generated in the vessel (i.e., very volatile gases will enter the headspace and be vented). For evaporating liquids, one can use the left-hand side of eq 4 as a representation for the rate of moles exiting in the vent. Multiplying by the molecular weight, MW_i , gives the mass vented, E_i :

$$E_i = \frac{FP_i^b}{RT}(MW_i) \quad (7)$$

Rearranging eq 6 for P_i^b , one can substitute into eq 7 in terms of S_i to obtain

$$E_i = \frac{Fx_i y_i p_i^{\text{sat}}}{RT} S_i (MW_i) \quad (8)$$

Although uncertain, all of the parameters in eq 8 are known (normally assuming that $\gamma_i = 1$ for ideal behavior), with the possible exception of F . One can use the input amount of gas or the evolved amount of gas to estimate F , which could be a good approximation if the evaporated gas rates are relatively low. When process vents dominate the uncontrolled emissions, the uncertainties in F and S_i as described above are important parameters for sensitivity analysis. Additional details for process vent emission calculations are provided in Section S2 of the Supporting Information.

Fugitive Emissions

Fugitive emissions represent leaks from process equipment that would not normally pass through a stack, vent, or similar opening. U.S. EPA provides guidance for calculating these emissions as part of its leak detection and repair (LDAR) program.(34) The fugitive emissions for a process can be calculated for LCI purposes based on the average emission factor approach.(21) The method requires three steps: (1) determining equipment counts for fugitive sources, (2) applying average emission factors, and (3) calculating total fugitive emissions and speciated emissions.

Definitive information on the number of each type of fugitive source is typically not available for conceptual design and simulated processes and must be approximated. Among the complexities is the design of the process control system, which can be accomplished with various equipment and configurations. The source estimates developed for this study are shown in Table 1 for various pieces of equipment. Equipment pieces generally represent the main vessel and its inputs/outputs with control systems. For more complex equipment like distillation columns, the user needs to add heat exchangers for the reboiler and condenser, a reflux vessel represented by a decanter or flash vessel, and pumps to circulate the process streams. A pump can also be used to represent the fugitive emissions for adding

mixers to vessels. Once the number of each type of fugitive source is established for the process, the emissions can be estimated using average emission factors. Emission factors for the synthetic organic chemical manufacturing industry (SOCMI) are shown in Table 2 with factors for other industrial subsectors (e.g., refinery factors) available elsewhere.(22)

While U.S. EPA presents calculations for VOC emissions,(21) one can consider all fugitive emissions with an equation for each unit operation,

$$E_T = \sum_i (\text{no. of components})_i (\text{emission factor } i) (\text{hours of operation per year}) \quad (9)$$

where E_T is the total mass emission per year for a chemical summed over i types of fugitive sources. If a unit operation has chemicals in it during nonproductive time (e.g., storage during process shutdown), then the time for that unit operation could be a full year (8760 h per year).

Speciated emissions are obtained from

$$E_x = E_T (\text{weight fraction of chemical } x) \quad (10)$$

where E_x is the mass emission per year for chemical x . If desired, one can calculate E_x directly by substituting eq 9 into eq 10.

Land Use

The land area occupied by a vessel and its surroundings can be approximated based on the land area used by the vessel. Turton et al.(35) describe distances between vessels of 5–10 m. Because most process(24) and storage(36) vessels have diameters around 5–10 m, the distances between vessels can be related to their diameters as described by Bausbacher and Hunt(37) (5 m between reactors, pumps, and towers, and one to two tank diameters for storage tanks). Instead of considering the interplay between vessels, an approximation can be made that a vessel uses its land area plus eight equivalent additional areas (pictured as the actual vessel footprint surrounded by eight blocks). The resulting total area, A , for an upright cylindrical vessel is

$$A = 9d^2 \quad (11)$$

and if the vessel is laying on its side so that its length and diameter make up its footprint,

$$A = 9Ld \quad (12)$$

Using this method the total area for a production process is the sum of the areas for the vessels, as calculated in eqs 11 and 12. This method considers only process and storage

vessels, and while the nine-block area may be large for two vessels next to each other, the extra area approximates the space used by other smaller equipment and open space.

Acetic Acid Process Simulation

To fulfill the second objective of this work, simulation and the above methods were applied to an acetic acid case study. Acetic acid was chosen because its preparation is well-described in various forms of literature, and the resulting inventory can be compared with existing LCIs prepared using different techniques. Encyclopedia sections,(38) technical reports,(39) patents,(40) journal articles,(41) and online sources are available to research acetic acid production. The specific process modeled here is the Cativa process, which carbonylates methanol using an iridium catalyst with, for example, ruthenium and methyl iodide promoters.(42) On the basis of various production rates found in the literature,(41) a large but intermediate rate of 300000 t per year was modeled.

The initial list of process constituents was developed from the chemistry of methanol carbonylation:

Unlike common chemical process modeling, which focuses on materials entering and leaving the process flow diagram, the storage of methanol (CH_3OH), carbon monoxide (CO), and acetic acid (CH_3COOH) were also included as unit operations. Although eq 13 suggests a simple emission profile consisting of methanol, carbon monoxide, and acetic acid, the actual chemistry and process are more complex. The catalyst depicted in this reaction is not simple. It is an iridium compound with a ruthenium promoter and requires an additional promoter such as methyl iodide to achieve fast reactions. Adding the additional promoter to the simulation meant additional storage and another possible emission. In addition to acetic acid, the following byproducts are formed: CO_2 and CH_4 at 0.47% of the product reaction rate and propionic acid, methyl acetate, and hydrogen iodide (HI) at 0.005, 0.93, and 0.09% of the product reaction rate, respectively.(39, 41) These compounds were also treated as potential emission species.

Specification of key operating conditions helped fulfill the simulation input needs and identify additional process requirements. A reaction pressure of 30 bar was chosen,(43) while the temperature, methyl iodide reactor concentration, and product reaction rate were set to 189 °C, 11.4% by weight, and 20 gmol/liter-hour, respectively, based on the range of values reported.(41) Under these operating conditions, pressure and temperature swings between ambient conditions and at least 30 bar and 190 °C were assumed to occur, which meant heating, cooling, and compression/pumping were needed.

Additional material inputs included combustion fuels and utilities (steam, cooling water, and electricity). Electricity usage was collected for compressor and pump simulation results. Steam and electricity were the only energy inputs to the process and were treated as upstream unit processes with their own LCIs.

The reactor was modeled as a continuously stirred tank reactor with well-mixed feeds of carbon monoxide and methanol. The sparged carbon monoxide feed was distributed through the liquid reactants. A carbon monoxide conversion of 91.5% was used,(41) and a 98.5% conversion was chosen for methanol.(39) The reactor inputs also include recycled (plus makeup) methyl iodide and impurities for each feed. Specification sheets were found for the methanol, carbon monoxide, and methyl iodide feeds. Water is an impurity for all three feeds, while CO also has CO₂ and methane impurities.

The various design choices were input to the ChemCAD process simulation package(44) and used to generate the corresponding material and energy flows for the Cativa process. The resulting process flow diagram is shown in Figure 2. In addition to the design choices and generalities described above, a detailed description of the process is provided in Section S3 of the Supporting Information.

The results from the simulation were used to apply the offline emission and land use models. For instance, on the basis of the flow rates of the feeds and acetic acid product, storage vessels were designed, and eqs 1 and 2 were applied to determine working and breathing losses for the liquids. Process vents were calculated in two ways. For reflux drum 19 in Figure 2, the vessel was modeled in ChemCAD (i.e., online) as a flash drum with the top exit stream eventually becoming the vent. For the reactor (combination of vessels 10 and 12 in Figure 2), the vent calculations were done offline using the method described in eqs 3–8. The fugitive emissions were determined for storage vessels, process vessels, and other equipment shown in Figure 2 using eqs 9 and 10. Makeup amounts of feeds and a reduced production rate of acetic acid were adjustments applied due to the offline calculations. Note that when makeup amounts of feeds can affect design and operation, one can refine the LCI results by simulating the process again with appropriate adjustments. Example calculations for applying the storage, process vent, and fugitive emission models are provided in Section S4 of the Supporting Information.

Results and Discussion

Inputs to Acetic Acid Production

The results for LCI inputs are shown in Table 3 for the simulation both with and without additional emission and land use modeling. (The catalyst/promoter combination of iridium/ruthenium is a known process essential input, but their amounts were not calculated in this process simulation.) As indicated in Table 3, land use (recurring every year) was quantified only for the full method (simulation plus modeling) with 1.023×10^{-4} m²/kg or a total of 31500 m² (7.8 acres) required for the whole process (compared to 8.9 acres for an actual process approximated in Section S5 of the Supporting Information). Although estimated utility use is reported, the inputs (and emissions) related to fuel use to generate the steam and electricity are assumed to occur in upstream processes.

The required inputs increase when the modeled emissions are added because of the additional production required to offset the 0.08% loss of acetic acid as an emission. The simulation does not account for this loss. Some input materials have an additional increased requirement to account for their own loss as an emission. For example, methanol

experiences a total makeup increase of 0.12%, which is 0.04% above that described for the change due to acetic acid. The change in methyl iodide input due to its losses through emission is over 10%. The reason for this relatively large percentage change is that methyl iodide is not a very large input into the process, while its estimated emissions are large. Thus, using only simulation would lead to a 10% error for the input in this case.

Emissions from Acetic Acid Production

The uncontrolled air emissions from simulation with and without modeling are reported in Table 4. Although depicted in Figure 1, wastewater discharges and solid waste releases were not calculated here. It is acknowledged that they are important LCI categories, and their inclusion is the focus of future refinements of the methodology.

The simulation generates LCI results that are more detailed than what would be expected based on the simplified chemistry of eq 13 because it includes various aspects of the reaction chemistry that create a correspondingly appropriate list of compounds circulating through the process. The flows of compounds in the simulated vent column originate from an absorber vent (vented in Stream 29 of Figure 2; finally emitted in Stream 36). These flows increase when the modeled (reactor vent) emissions are added, with acetic and propionic acids also showing up in the vent streams. The total venting emissions for the entire methodology show that many of the emissions are greater than 1.0×10^{-3} kg species per kg of acetic acid product, or 300 tons per year. This potentially represents both a large loss in value and increased environmental impacts.

Storage breathing and working losses (i.e., storage in Table 4) represent additional emissions through storage vessel vents. For the three chemicals stored as liquids (methanol, acetic acid, and methyl iodide), the storage emissions represent approximately 46 tons per year. This is counterintuitive to the typical approach of many studies to treat storage losses as being negligible. Comparison of these emissions (normalized for storage volume and throughput) with data reported by four acetic acid manufacturers to EPA's 2011 National Emissions Inventory found that the data in Table 4 may overestimate breathing losses for methanol by 12% but underestimate breathing losses for acetic acid by 42%. Working losses for both chemicals may be underestimated by 10–12%, which means the total losses could be even larger. Although the NEI data were themselves estimated by the reporting facilities, they represent the best available data for comparison because they represent what is officially reported under regulatory requirements and accepted by states and federal agencies. Given the need for storage in nearly every chemical process, the additional storage emissions could lead to a large loss of value and increased environmental impacts, much like the process vents.

Fugitive emissions occur for every compound in this process. Acetic acid occurs throughout the process unit operations and has the highest fugitive emissions (Table 4). The nearly 10 tons of acetic acid lost through fugitive emissions increase the overall material and energy requirements of the process by forcing more material to be processed to achieve the same desired annual production rate. Because fugitive leaks are relatively small, it takes effort to reduce them.⁽³⁴⁾

Comparison and Limitations

A qualitative comparison of the uncontrolled air emissions for the simulated inventories with the inventories reported by Cashman et al.(9) for data mining and commercially available inventories from the U.S. LCI database and the ecoinvent database is shown in the Supporting Information, Table S2. Emissions related to fuel use were removed from the commercially available inventories to facilitate an equal basis for comparison. The simulated inventory includes eight species, which increases to 10 with the inclusion of modeled emissions (Table 4). This is more than the five emissions reported in the U.S. LCI and the six species included in the ecoinvent LCI (10 for the market-average LCI) but less than the 18 species reported for the data mining inventory. Although the data mining inventory has a much greater number of species, its technology coverage is unknown, and some of the emissions could be improperly allocated to acetic acid production based on the underlying modeling methodology.(9) In contrast, the inventory generated here represents a specific process, and all of the included emissions can be explained by the process chemistry. The market-average ecoinvent inventory(15) is an average of three process technologies and relies on a combination of operations data from nearly two decades earlier and numerous assumptions about process chemistry and waste treatment. Thus, the simulated inventory provides an increased quality of data, especially when including modeled emissions.

The ultimate utility of LCIs is their application in life cycle impact assessment. Therefore, a key concern when considering multiple data sets for the same process is understanding how the resulting impact assessment may be affected. As shown in Table S2, this was accomplished qualitatively by comparing the five sets of air emissions against the characterization factors for nine impact categories in the U.S. EPA's Tool for the Reduction and Assessment of Chemical and other Impacts (TRACI).(45) All five of the LCIs would yield impacts in six of the categories (smog formation, global warming, human health (HH) criteria respiratory effects, HH cancer, HH noncancer, and ecotoxicity), although the magnitude of impacts would vary based on the distribution of the total flows within each category. The data mining method could yield additional impact for ozone depletion based on the emission of bromomethane, while the U.S. LCI inventory could generate acidification and eutrophication impacts from the emission of ammonia. Even so, these additional impacts arising from single flows should not deter the use of the simulated inventories, particularly when considering their potential data quality benefits. Instead, future inventory methods may benefit from a hybridization that incorporates the strengths of both approaches given their complementary nature. Such hybridization is the subject of future work.

Although simulation and modeling can provide a more accurate qualitative LCI based on process chemistry and real-world plant phenomenon like fugitive emissions, some LCA practitioners may consider this approach to be limited by the engineering knowledge required to apply it. The added complexity of simulation can be balanced against the improved data quality and completeness of the resulting LCI as well as the reduced time that may be needed to generate the inventory. Furthermore, the suggested emission modeling techniques are relatively simple given that they were developed to assist industry with regulatory reporting and compliance. These aspects make LCI modeling based on simulation and modeling applicable to both regulatory and industrial decision needs, covering a range

of applications such as alternative chemical assessment and sustainable chemical or process design.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

References

1. U.S. EPA TSCA. <https://www.epa.gov/tsca-inventory/about-tsca-chemical-substance-inventory> (accessed August 31, 2016).
2. U.S. EPA CDR. <https://www.epa.gov/chemical-data-reporting/chemicals-commerce-reported-2012-cdr-cycle>(accessed August 31, 2016).
3. National Research Council. Sustainability and the U.S. EPA; National Academies Press: Washington, D.C., 2011.
4. International Organization for Standardization. *ISO 14040: Environmental Management, Life Cycle Assessment, Principles and Framework*; International Organization for Standardization: Geneva, Switzerland, 2006.
5. International Organization for Standardization. *ISO 14044: Environmental Management, Life Cycle Assessment, Requirements and Guidelines*; International Organization for Standardization: Geneva, Switzerland, 2006.
6. National Research Council. A Framework to Guide Selection of Chemical Alternatives; National Academies Press: Washington, D.C., 2014.
7. National Research Council. Sustainability Concepts in Decision-Making: Tools and Approaches for the US Environmental Protection Agency; National Academies Press: Washington, D.C., 2014.
8. Guinée JB; Heijungs R; Huppes G.; Zamagni A; Masoni P; Buonamici R; Ekvall T; Rydberg T. Life Cycle Assessment: Past, Present, and Future *Environ. Sci. Technol.* 2011, 45 (1) 90–96 DOI: 10.1021/es101316v [PubMed: 20812726]
9. Cashman SA; Meyer DE; Edelen A; Ingwersen WW; Abraham JP; Barrett WM; Gonzalez MA; Randall P; Ruiz-Mercado GJ; Smith RL Mining Available Data from the United States Environmental Protection Agency to Support Rapid Life Cycle Inventory Modeling of Chemical Manufacturing *Environ. Sci. Technol* 2016, 50, 9013 DOI: 10.1021/acs.est.6b02160 [PubMed: 27517866]
10. Suh S Developing a sectoral environmental database for input-output analysis: the comprehensive environmental data archive of the US Economic Systems Research 2005, 17 (4) 449–469 DOI: 10.1080/09535310500284326
11. Sengupta D; Hawkins TR; Smith RL Using national inventories for estimating environmental impacts of products from industrial sectors: a case study of ethanol and gasoline *Int. J. Life Cycle Assess.* 2015, 20(5) 597–607 DOI: 10.1007/s11367-015-0859-x
12. Weidema BP; Cappellaro F; Carlson R; Notten P; Palsson A-C; Patyk A; Regalini E; Sacchetto F; Scalbi S. Procedural Guideline for Collection, Treatment, and Quality Documentation of LCA Data; Italian National Agency for New Technologies, Energy and the Environment: Rome, Italy, 2004.
13. Global Guidance Principles for Life Cycle Assessment Databases: *A Basis for Greener Processes and Products*; United Nations Environment Programme, Sustainable Consumption and Production Branch: Paris, France, 2011.
14. Jimenez-Gonzalez C; Kim S; Overcash MR Methodology for Developing Gate-to-Gate Life Cycle Inventory Information *Int. J. Life Cycle Assess.* 2000, 5 (3) 153–159 DOI: 10.1007/BF02978615
15. Wernet G; Bauer C; Steubing B; Reinhard J; Moreno-Ruiz E; Weidema B. The ecoinvent database version 3 (part I): overview and methodology *Int. J. Life Cycle Assess.* 2016, 21 (9) 1218–1230 DOI: 10.1007/s11367-016-1087-8

16. Hischer R; Hellweg S; Capello; Primas. Establishing Life Cycle Inventories of Chemicals Based on Differing Data Availability Int. J. Life Cycle Assess. 2005, 10 (1) 59–67 DOI: 10.1065/lca2004.10.181.7
17. Wernet G; Hellweg S; Hungerbuhler KA Tiered Approach to Estimate Inventory Data and Impacts of Chemical Products and Mixtures Int. J. Life Cycle Assess 2012, 17, 720–728 DOI: 10.1007/s11367-012-0404-0
18. Bojarski AD; Guillén-Gosálbez G; Jiménez L; España A; Puigjaner L Life Cycle Assessment Coupled with Process Simulation under Uncertainty for Reduced Environmental Impact: Application to Phosphoric Acid Production Ind. Eng. Chem. Res 2008, 47 (21) 8286–8300 DOI: 10.1021/ie8001149
19. Morais S; Mata TM; Martins AA; Pinto GA; Costa CAV Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils J. Cleaner Prod 2010, 18(13) 1251–1259 DOI: 10.1016/j.jclepro.2010.04.014
20. Petrescu L; Fermeglia M; Cormos C-C Life Cycle Analysis applied to acrylic acid production process with different fuels for steam generation J. Cleaner Prod 2016, 133, 294–303 DOI: 10.1016/j.jclepro.2016.05.088
21. Office of Air Quality Planning and Standards. Protocol for Equipment Leak Emission Estimates; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1995.
22. Emission Estimation Protocol for Petroleum Refineries, version 3; RTI International: Research Triangle Park, NC, 2015.
23. Allen DT; Shonnard DR; Prothero S Evaluating Environmental Performance During Process Synthesis In Green Engineering: Environmentally Conscious Design of Chemical Processes; Prentice-Hall: Upper Saddle River, NJ, 2002.
24. Douglas JM. Conceptual Design of Chemical Processes; McGraw-Hill: Boston, 1988.
25. Biegler LT; Grossmann IE; Westerberg AW Systematic Methods of Chemical Process Design; Prentice-Hall: Upper Saddle River, NJ, 1997; pp 61–70.
26. Seider WD; Seader JD; Lewin DR; Widagdo S Product and Process Design Principles: Synthesis, Analysis and Design; John Wiley & Sons: Hoboken, NJ, 2008.
27. U.S. EPA Emission Inventory Improvement Program. Methods for Estimating Air Emissions from Chemical Manufacturing Facilities; Mitchell Scientific: Westfield, NJ, 2007; Vol. 2, Chapter 16.
28. Compilation of Air Pollutant Emission Factors, AP-42; U.S. EPA, Office of Air Quality Planning and Standards: Research Triangle Park, NC, 2016.
29. Peress J Estimate Storage Tank Emissions Chem. Eng. Prog 2001, 44–45
30. TANKS 4.09 Software Program; U.S. EPA, Office of Air Quality Planning and Standards: Research Triangle Park, NC <https://www3.epa.gov/ttnchie1/software/tanks/> (accessed July 7, 2016).
31. Qu M; Wan J; Hao X Analysis of Diurnal Air Temperature Range Change in the Continental United States Weather and Climate Extremes 2014, 4, 86–95 DOI: 10.1016/j.wace.2014.05.002
32. Control of Volatile Organic Compound Emissions from Batch Processes—Alternative Control Techniques Information Document; U.S. EPA, Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1994.
33. Hatfield JA A Model for Estimating Process Emissions from Gas Sweep Operations in Batch and Continuous Chemical Operations Environ. Prog 2004, 23 (1) 45–51 DOI: 10.1002/ep.10006
34. Detection Leak and Repair—A Best Practices Guide; Office of Enforcement and Compliance Assurance, U.S. Environmental Protection Agency: Washington, D.C., 2007.
35. Turton R; Bailie RC; Whiting WB; Shaeiwitz JA *Analysis, Synthesis, and Design of Chemical Processes*; Prentice Hall: Upper Saddle River, NJ, 2009.
36. Couper JR; Penney WR; Fair JR; Walas SM. Chemical Process Equipment: Selection and Design, 3rd ed; Elsevier: Waltham, MA, 2012.
37. Bausbacher E; Hunt R Process Plant Layout and Piping Design; Prentice Hall: Edgewood Cliffs, NJ, 1993.
38. Cheung H; Tanke RS; Torrence GP Acetic Acid. In *Ullmann's Encyclopedia of Industrial Chemistry*; Elvers B Ed.; John Wiley and Sons: Hoboken, NJ, 2001; pp 209–237.

39. Zhu Y; Jones SB. Techno-economic Analysis for the Thermochemical Conversion of Lignocellulosic Biomass to Ethanol via Acetic Acid Synthesis, PNNL-18483; U.S. Department of Energy, Pacific Northwest National Laboratory: Richland, WA, 2009.
40. Scates MO; Trueba DA Process for Producing Acetic Acid, U.S. Patent 7,208,624; 2007.
41. Sunley GJ; Watson DJ High Productivity Methanol Carbonylation Catalysis using Iridium: The Cativa Process for the Manufacture of Acetic Acid *Catal. Today* 2000, 58, 293–307 DOI: 10.1016/S0920-5861(00)00263-7
42. Jones JH The Cativa Process for the Manufacture of Acetic Acid Platinum Metals Rev 2000, 44 (3) 94–105
43. Morris GE; Sunley JG Iridium-Catalyzed Carbonylation Process for the Production of a Carboxylic Acid, U.S. Patent 5,932,764; 1999.
44. CHEMCAD, version 7.0.1; Chemstations: Houston, TX, 2016; <http://chemstations.com/>.
45. Bare JC Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI): User's Guide. *EPA/600/R-12/554*; U.S Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory; Cincinnati, OH, 2012.

Synopsis

A methodology is described for developing life cycle inventories for chemical manufacturing processes using simulation, land use, and emission modeling.

Figure 1. Elements of a life cycle inventory for a process. Infrastructure includes steel for unit operations, land use, etc. Water discharges and solid waste release inventories are not developed in this work but are included for a complete representation.

Figure 2.
ChemCAD(44) flowsheet for the simulated acetic acid manufacturing process.

Table 1.

Numbers of Fugitive Sources for Various Types of Unit Operations

unit operations		compressors	connectors	pressure relief valves	pumps	sampling connections	valves
absorption columns			57	1			12
compressors		1	16				7
decanters			87	1			19
distillation columns			142	1			30
flash vessels			56	1			11
heat exchangers	energy fluid		30				6
	process fluid		34				6
mixers					1		
pumps			16		1		7
tank reactors			129	1		1	25
storage vessels	gas		13				4
	liquid		28	2			7

Table 2.

SOCMI Average Emission Factors(21)

equipment type	service	emission factor (kg/h/source)
pumps ^a	light liquid ^b	0.0199
	heavy liquid ^c	0.00862
compressors	gas	0.228
valves	gas	0.00597
	light liquid ^b	0.00403
	heavy liquid ^c	0.00023
connectors (e.g., flanges)	all	0.00183
open-ended lines	all	0.0017
sampling connections	all	0.0150
pressure relief valves	gas	0.104

^aThe light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

^bLight liquid is defined as a fluid with vapor pressure greater than 0.3 kPa at 20 °C.

^cHeavy liquid is defined as a fluid with vapor pressure less than 0.3 kPa at 20 °C.

Table 3.Life Cycle Inventory Inputs for Acetic Acid Production^a

LCI inputs	units	simulation	simulation with emission models	percent change
carbon monoxide	kg/kg	5.088×10^{-1}	5.092×10^{-1}	0.08
methanol	kg/kg	5.389×10^{-1}	5.394×10^{-1}	0.12
methyl iodide	kg/kg	1.225×10^{-2}	1.350×10^{-2}	10.32
steel	kg/kg	3.095×10^{-4}	3.097×10^{-4}	0.08
land use	m ² /kg	not included	1.023×10^{-4}	not applicable
steam	MJ/kg	1.751	1.752	0.08
	kg/kg	7.785×10^{-1}	7.791×10^{-1}	
cooling water	MJ/kg	3.058	3.060	0.08
	kg/kg	4.361×10^1	4.365×10^1	
electricity	MJ/kg	5.598×10^{-3}	5.602×10^{-3}	0.08

^aTable values have multiple significant figures only so that differences in results are shown.

Table 4.

Uncontrolled Air Emissions from the Acetic Acid Manufacturing Process Per Kilogram of Product

emitted species (kg/kg acetic acid product)	simulation			simulation with emission models		
	fugitive	storage	vents	fugitive	storage	vents
carbon monoxide			2.2×10^{-2}	1.8×10^{-5}		4.4×10^{-2}
carbon dioxide			1.7×10^{-3}	7.9×10^{-7}		3.5×10^{-3}
methane			6.4×10^{-4}	2.9×10^{-7}		1.3×10^{-3}
methanol			1.9×10^{-3}	1.5×10^{-5}	1.1×10^{-4}	1.9×10^{-3}
acetic acid				3.2×10^{-5}	3.2×10^{-5}	7.2×10^{-4}
methyl iodide			6.9×10^{-3}	2.8×10^{-5}	1.4×10^{-5}	8.1×10^{-3}
hydrogen iodide			2.0×10^{-3}	1.1×10^{-6}		2.1×10^{-3}
methyl acetate			1.3×10^{-3}	1.1×10^{-5}		2.2×10^{-3}
water			5.2×10^{-7}	2.6×10^{-5}		6.9×10^{-6}
propionic acid				1.8×10^{-8}		3.1×10^{-7}