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A Process Systems Framework for Rapid Generation of Life Cycle Inventories for Pollution Control and Sustainability Evaluation

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Abstract

Life Cycle Assessment (LCA) is a tool that aids in sustainable decision-making among product and process alternatives. When implementing LCA, the efficient and accurate modeling of chemical processes for Life Cycle Inventory (LCI) generation is still challenging. Challenges include a lack of systematic design and simulation tools and approaches to develop chemical process models for obtaining and analyzing more realistic LCI results. In this contribution, a novel process systems framework is proposed for estimating LCI results when implementing pollution control technologies. This framework involves the development and incorporation of pollution control unit (PCU) modules into process simulation and generation of LCI data associated with the PCUs for use in a sustainability evaluation. Different pollution control modules are designed for rapid LCI estimation and applied to obtain emissions, utility consumption, material, and land footprint results related to waste streams of a process simulation. Then, the LCI results are analyzed with the objectives of minimizing the environmental impact and utility consumption. The proposed framework is illustrated via a biomass/coal gasification process for syngas production with the end goal of acetic acid manufacturing. Results associated with this case study show that the developed framework can provide guidelines for sustainable decision-making based on generated LCI results.

Keywords

Life Cycle Inventory; Sustainability; Biomass; Coal; Process Systems; Pollution Control; Gasification

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Introduction and Background

over the past several decades, the United States and many other countries have enacted legislation and regulations to limit releases to the environment as well as to alleviate the adverse effects of pollution by human activity. The U.S. Environmental Protection Agency (U.S. EPA) has made important progress to advance environmental protection strategies from end-of pipe treatment to pollution prevention (Freeman et al. 1992). The Clean Air Act (CAA) of 1970 and the Clean Water Act (CWA) of 1977 are regulatory foundations used to mitigate the environmental and human health concerns associated with air and water quality. In addition, the Toxic Substances Control Act (TSCA) of 1976 provides EPA the authority to demand reporting, record-keeping and testing requirements, and restrictions relating to chemical substances and/or mixtures manufactured or processed, including imports, in the United States and in the chemical industry. For example, as part of the CAA, EPA is charged with setting the National Ambient Air Quality Standards (NAAQS). These standards limit the ambient concentrations of six criteria air pollutants: ground-level ozone (including volatile organic compounds, VOCs), carbon monoxide (CO), sulfur dioxide (SO₂), particulate matter (PM), nitrogen oxides (NO_x), and lead (Pb). Therefore, as stationary sources of air, solid, and water pollutants, chemical processes are subject to federal, state, and local air quality regulations. Such regulations require chemical plants to undertake several emission-permitting procedures during construction and operation. However, feasibility-level designs typically do not consider the impacts associated with emission control technologies in process sustainability analysis for real-world decision making.

Life Cycle Assessment (LCA) is a standard tool for sustainable decision-making among product and process alternatives (Hellweg and Milà Canals 2014). Specifically, LCA takes into account mass and energy flows as well as environmental releases in the life cycle of a product, from the extraction of raw materials, production, and use to disposal/recycling (Guinée et al. 2011). LCA is increasingly applied to identify and quantify the far-reaching impacts of a process/product within its life cycle. For example, an integrated framework of LCA and pollution control/prevention can provide holistic results beyond a single process and thus help to identify those alternatives that enhance sustainability in addition to environmental protection (Ghassemi 2001). Additionally, the information LCA provides can guide decision-makers (e.g., individual facility, environmental policy makers) to improve decisions in terms of sustainability. Although many contributions have been made in LCA recently, the efficient and accurate modeling of chemical processes for rapid Life Cycle Inventory (LCI) generation is still challenging. LCI, as a fundamental step of LCA, is used to quantify the energy use and raw material inputs as well as environmental releases accurately throughout a product's life cycle.

Currently, there are about 85,500 chemicals reported in the EPA's TSCA Chemical Substance Inventory (U.S. Environmental Protection Agency 2017a), with 9,626 of those being active in commerce (U.S. Environmental Protection Agency 2017b). However, in contrast, substances included in the most common LCA databases represent only a portion of these chemicals. In addition, there is a lack of consistency, transparency, and available procedures for finding reliable LCI data. Particularly, obtaining consistent LCI data is one of the most time consuming steps of an LCA. Poor data availability and inconsistency of data

may lead to unrealistic results and conclusions. Some of the existing challenges in LCI generation are due to the lack of systematic process systems (e.g., design and simulation) tools to develop chemical process models for rapidly obtaining and analyzing LCI results at early development stages.

Typically, there are two methods to generate LCI data for a product, process or activity. The top-down approach relies on facility-level data (Cashman et al. 2016), while the bottom-up approach depends on process design approaches for sets of unit operations (Smith et al. 2017). Some benefits of the top-down approach are that the data reported by companies can be more realistic. However, some adverse issues regarding the top-down method include large data gaps related to variations in reporting requirements, potential lack of transparency regarding the underlying process technology production rates represented in databases, allocation of facility-level emissions, material and energy inputs to a single chemical process within multi-process facilities, and limited coverage of reported substances (Smith et al. 2017). In contrast, the bottom-up approach possesses some benefits and limitations as well. Some benefits include estimates of material and energy inputs for a direct LCI connectivity with the life cycle stages beyond the process of interest and process specificity. In addition, there is no need to apply allocation to the collected LCI and the inventory can be tracked down to process equipment unit allocation. However, process modeling assumptions and extensive process systems engineering (PSE) knowledge in process design and simulation are required to develop a full chemical production process and apply a bottom-up approach for LCI modeling.

As described by Subramanian and Golden (2016), there are several bottom-up methodologies to deal with LCI estimation data gaps/modeling: molecular structure-based neural network modeling (Wernet et al. 2008), input–output schema for calculation of mass and energy flows using heuristics and on-site data (Geisler et al. 2004), estimating gate-to-gate life cycle using chemical process design techniques (Jiménez-González et al. 2000), LCI estimation using the inherent burden approach (Bretz and Frankhauser 1996), obtaining inventory data using stoichiometric equations from technical literature (Hischier et al. 2005), and proxy LCI data. Along the same lines, Yao and Masanet (2018) developed generic unit operation models to estimate the life cycle energy and greenhouse gas (GHG) emissions for chemical processes at early or R&D stages. Another study conducted by U.S. EPA combined the Environmentally-Extended Input-Output (EEIO) analysis with LCA methods based on more recent economic and environmental data of U.S. goods and services (Yang et al. 2017). In addition, other bottom-up approaches employ computer-aided process simulation for estimating LCI data (Villalba et al. 2006; Bojarski et al. 2008; Sugiyama et al. 2008; Kiruchi et al. 2010; Petrescu et al. 2016). The bottom-up methods in literature can be roughly grouped in two types: process flow approaches and matrix-based methods (Ling-Chin et al. 2016). LCI results from process flow methods are calculated based on process balance models and thus more accurate when compared to matrix-based methods that employ a set of simultaneous simple equations for each unit. Also, matrix-based LCI (Heijungs and Suh 2006) can be easily applied for advanced LCI analysis with the limited application to single-output processes.

However, none of these approaches address PCUs as part of the LCI. In addition, controlled emission values were calculated as fractions of the mass of each substance in the process step (Geisler et al. 2004; Hischer et al. 2005), total emissions were obtained as the sum of estimated fugitive losses, global mass balance fractions, and flue gas emissions from controlled combustion units (Jiménez-González et al. 2000), and generic modules were derived from yields and elemental balances (Bretz and Frankhauser 1996) for assessing direct emissions for energy generation (Morales-Mendoza and Azzaro-Pantel 2017). In considering some examples of pollution control equipment modeling for inclusion in a LCI, Bojarski et al. (2008), described the modeling of process units for the treatment of waste streams (air and liquid) based on black box models and distribution function values. Another example includes equipment modeling and simulation focused on air emissions (flue gas) treatment for carbon capture (Petrescu et al. 2016; Eberle et al. 2017). In addition, Bhatt et al. (2016) evaluated the techno-economic impacts of emission controls to comply with air quality regulations of a bio-refinery and its location and production scale. Therefore, these limitations of controlled emissions data, pollutant-of-interest targeting (i.e., carbon capture), and cost analysis approaches demonstrate the need to develop methods and frameworks for handling controlled emission modeling when simulating LCIs given the importance of emission streams and regulations in environmental impact evaluations. Moreover, performing a more detailed material and energy balance when implementing pollution control systems will allow designers to consider additional material input flows, accessory equipment, and the energy consumption required for emission controls. In addition, the footprint (construction material (e.g., carbon steel) and land use) associated with these system changes will affect the overall profile of emission controls. At this level of detail through LCI modeling, the importance of considering emission controls for rapid LCI modeling of a chemical manufacturing process can be demonstrated.

To bridge the gap between PSE, LCI methods, and pollution control needs identified in the reported studies, this contribution corresponds to the development of a process systems framework that involves the incorporation of PCU modules into process simulation and LCI data generation associated with the PCUs and the entire process. The parameterized PCU modules are developed employing a user-friendly Excel interface with the goal of making the models easier to use by decision-makers with little process data or limited knowledge on specific waste treatment technologies, including non-engineer LCA practitioners. In essence, the proposed PCU reduced models are intended to augment existing capacity of commercial process simulators. Thus, some distinguished features included in the PCU modules are: 1) parameterized input variables with default/suggested values; 2) easy customization for application to different cases; and 3) ability for integration with different commercial process simulation software.

Processes to manufacture acetic acid starting from biomass and coal gasification are employed to illustrate the application of the proposed framework. This case study is selected for analysis as a representative technology that is described in various forms of literature. Currently, there are numerous works published that describe the acetic acid production process (Sunley and Watson 2000; Cheung et al. 2001; Scates and Trueba 2007; Zhu and Jones 2009), which include its LCI modeling using the top-down (Cashman et al. 2016) and bottom-up (Smith et al. 2017) approaches. Therefore, this study will analyze the LCI

modeling implications of implementing technologies to reduce pollutant emissions from chemical manufacturing. A key output of this work is a set of parameterized pollution control modules that can be used by LCA practitioners to include pollution control in their LCI models by specifying a set of key operational parameters. The current baseline design will consider multiple control devices to reduce emissions. However, additional controls are necessary to ensure compliance with all applicable federal regulations and thus are part of ongoing work.

Process Systems Framework for Rapid LCI Generation

An overview of the proposed process systems framework is given in Figure 1. In this framework, a chemical process manufacturing simulation is built while considering the different approaches to manufacture the desired product from different feedstocks. Unit operation infrastructure (e.g., steel consumption, land use, etc.) and utility (e.g., heating, cooling, and electricity) requirements change for different feedstocks and product(s) quality. Even though the current framework includes more meticulous bottom-up inventory modeling based on process simulation, the PCU modules could just as easily be applied if a practitioner already has information on a waste stream to be treated and can specify the necessary parameters, i.e., skip process simulation and proceed directly to PCU module application. The outputs of the LCI modeling are the desired product, side products, and waste streams. These waste streams are then sent to the developed parameterized (simplified) modules for various PCUs that could append the production LCI with pollution abatement based on user inputs. In this way, the boundaries of the PCU LCI are specific to the control device and not the entire manufacturing process (red box in Figure 1). These narrow boundaries enable the control device models to become modular in nature and support plug-and-play application for LCA projects in general. The composition of the waste streams dictates the type of unit operation infrastructure, utility and ultimately the PCU used to remediate such waste streams.

In this contribution, LCI will be generated for the inputs to the process: feedstock, utility and infrastructure as well as outputs: emissions and by/co-product(s). Emissions associated with process energy use (e.g., utility) are outside the boundary of this study as shown in Figure 1. Note that PCUs for water discharges and solid waste release inventories are not developed in this work, but are also included for a complete representation. These units are part of ongoing work.

Pollution Control Units and LCI Generation

The design and implementation of PCUs require the evaluation of many aspects such as the waste stream to be treated, physicochemical properties of the pollution streams, selection of control equipment, and evaluation of the exhaust to meet expected outcomes and performance. The quality and quantity of the pollutants directly influence the size of the PCUs. Therefore, any upstream process modification that either can eliminate or minimize the amount of pollutant to be treated will reduce the needs and cost for pollution control. For example, replacing the feedstock and changing process operating conditions can be considered if an important reduction in pollution generation can be achieved.

For air pollution control, four representative pieces of equipment are developed for obtaining their input/output mass and energy performance and their infrastructure needs (material of construction and land use). However, there are many types of equipment depending on the pollutant characteristics, which can be classified into two main categories: control equipment for removal of pollution particulate and those for the removal of noxious gases (Peters et al. 2003). In addition, the EPA (U.S Environmental Protection Agency 2002) for techno-economic evaluation purposes classifies pollution controls (recapture, destruction, pre-combustion, combustion, post-combustion) according to some of the pollutants that must be in compliance with an air quality standard: CO, volatile organic compounds (VOCs), PM, oxides of nitrogen (NO_x), and some acid gases (primarily SO₂ and HCl).

In this contribution, the focus is placed on demonstrating the needs and benefits of adding the effects of pollution control for rapid LCI modeling of a chemical manufacturing process by designing, modeling, and simulating four PCUs for noxious gas removal. The four air PCUs are designed using Microsoft Visual Basic for Applications (VBA) in Microsoft Excel®. These PCUs simulate the purification of gas-phase waste streams from a chemical process, and provide rapid LCI estimates for the corresponding process. For accessing the PCU modules, see the Supporting Information file. The PCUs considered in this study are described below.

Scrubbers

Scrubbers (U.S. Environmental Protection Agency 1995), or gas absorbers, as pollution control devices, are used widely in industry for the purification of waste gas streams containing inorganic contaminants, such as HCl, H₂S, and NH₃ and organics such as CO₂ (see scrubber schematic in Figure 2). Some applicable pollutants removed include PM less than or equal to 10 μm in aerodynamic diameter (PM₁₀), PM less than or to equal 2.5 μm in aerodynamic diameter (PM_{2.5}), precursors of secondary PM from hazardous air pollutants (PM_{HAP}), inorganic gases (e.g., SO₂, ammonia, chlorides), and VOCs. Scrubbers can employ a variety of techniques including packing materials, perforated trays, and sprayers to force close contact between the polluted gas and the gas scrubbing liquid flowing through the scrubber. The liquid solvents used to achieve this removal are water, mineral oils, or non-volatile hydrocarbons. Removal efficiencies typically range from 90% to 99.9% and can be attained with higher solvent surface areas, for example, the use of spray nozzles in spray scrubbers. The physical properties of the pollutant and solvent dictate the physical absorption process taking place. The parameters for a wet scrubber (i.e., size, flowrate of solvent) are then determined by the physical properties, removal efficiency, and equilibrium data (U.S Environmental Protection Agency 2002; Theodore 2008). For the full detail of design equations and parameters of this unit, see Supporting Information, Section S1.

Boilers

Contaminated streams that have no chemical recovery value and are combustible (some VOCs) can be treated with boilers. Fire tube and water tube boilers both use waste gas as an auxiliary fuel to produce steam that can be utilized for power or heating needs in a process (see boiler schematic in Figure 3). For pollution control purposes, the waste gas is typically combined with natural gas or other fuels, but high combustion temperature and additional

pollution controls may be needed to achieve a complete combustion (U.S. Government Publishing Office 1991). In a fire tube boiler, the hot gases from the combustion of the waste gas-fuel mixture move through the tubes while the water is heated in the shell of the boiler. Here the hot gases are passed multiple times through the tubes. Design of fire tube boilers are limited by regulations on diameter and operating pressures. In a water tube boiler, water entering the boiler moves through tubes exposed to the heat generated from the waste gas-fuel combustion. The heated water is circulated, while the steam is withdrawn. For the full detail of design equations and parameters of the boiler when employed as a noxious gas removal unit, see Supporting Information, Section S2.

Flare Units

Flare units (U.S. Environmental Protection Agency 2002) are used to completely combust compounds introduced into the unit, typically VOCs (except halogenated compounds), via an open flame (see flare schematic in Figure 4). The combustion is considered complete if the products are carbon dioxide and water, while incomplete combustion results in the formation of carbon monoxide or other partially oxidized organic compounds. A flare can achieve VOC destruction greater than 98%. There are three different types of flares in terms of the method for increasing mixing at the flare tip: steam-assisted, air-assisted, and non-assisted. Steam-assisted flares inject steam in the combustion zone to generate turbulence and induce air into the flame. The steam requirements for smokeless burning depends on the composition and flowrate of the mixture (please refer to Supporting Information, Section S3 for detailed calculation information). Air-assisted flares increase the mixing required for smokeless operation using compressed air provided by a compressor placed at the bottom of the unit. The amount of compressed air entering the unit is about 1.2 times the steam flowrate since steam is more efficient in preventing smoke formation. This configuration is usually used when steam is not available, or the flare unit is small (when it is not economically feasible for an air-assisted flare with large vent gas flowrate) (U.S. Environmental Protection Agency 2017c). A non-assisted flare essentially burns the vent gas without the aid of steam/air. Its use is limited to handle waste gas streams with a low carbon/hydrogen ratio (such as methane) that can burn without producing smoke (Stone et al. 1992). For the full detail of design equations and parameters of flare units for VOC destruction, see Supporting Information, Section S3.

Thermal Oxidizers

Thermal oxidizers (U.S. Environmental Protection Agency 2002), or incinerators, are one of the best-known methods for industrial waste gas disposal (see thermal oxidizer schematic in Figure 5). Thermal oxidizers are used to control the release of VOCs and CO through thermal or catalytic incineration, and are generally used when the waste gases are diluted mixtures of combustible gases and air (air content should be greater than 98%). The advantage of using a thermal oxidizer is that almost any VOCs can be oxidized to CO₂ and water safely and cleanly in the presence of high temperature and enough oxygen. This unit incinerates compounds and typically requires natural gas as an auxiliary fuel to aid in the combustion process. The amount of natural gas required can be decreased by recovering heat from the effluent stream of the combusted products. Heat exchange between the flue gas and inlet stream prior to entering the combustion chamber can achieve this with typical energy

recovery as high as 70%. For the full detail of design equations and parameters of the thermal oxidizer PCU, see Supporting Information, Section S4.

As mentioned above, the objective of the proposed PCU simulators is to introduce a method for estimating the LCI, including mass, energy, material, and footprint of air pollution control technologies to reduce or eliminate the emissions of potentially hazardous air pollutants from industrial waste streams. Table 1 provides a summary with brief descriptions, strengths and limitations associated with the different PCUs, which may serve as guidelines for users on how to select the PCUs for particular applications of interest. In general, the scrubber and thermal oxidizer are typically chosen for diluted waste streams, while the boiler and flare systems are more flexible w.r.t. concentrations of the waste streams to be treated.

Table 2 describes a summary of user input parameters required for each PCU module. In the modules, users just need to adjust operational parameters and perform process design for integration if necessary, as the modules provide guidelines and default values that facilitate the functionality of the framework in generating LCI data for non-engineer users. In particular, the developed PCUs can serve as a plug-and-play role for LCA projects only requiring the information on the waste stream to be treated. Note that many of these data entries have suggested default values, which can be found (in parenthesis) in Table 2. For more detailed information on these parameters, please refer to Supporting Information. Waste gas flowrate and composition are key parameters for obtaining the LCI results. In addition, the user would need to enter more data if the pollutants of interest are not listed in the internal database. After describing the set of PCUs developed for LCI modeling, and to demonstrate the objectives of this work, the above PCU modules are applied to an acetic acid from biomass/coal simulation case study. The acetic acid case study was chosen due to previous work on applications of the top-down (Cashman et al. 2016) and bottom-up (Smith et al. 2017) approaches for approximating LCI.

Chemical Process Simulation

Due to the increasing projected global energy demand and the needs to move away from fossil fuels, biomass has received considerable attention as a feedstock and energy input. Biomass is a renewable feedstock alternative with the potential for ameliorating the environmental effects of using fossil fuels (e.g., coal). However, the utilization of biomass is facing some challenges, such as limited and intermittent availability/supply, as well as its low energy density. Two scenarios associated with acetic acid manufacturing from coal/biomass are analyzed. In this work, Aspen Hysys (AspenTech 2017) and ChemCAD (Chemstations 2016) are used to model the acetic acid production process from coal/biomass. As described in Figures 6–8, the entire biomass/coal to acetic acid process consists of three subprocesses: (i) the biomass/coal to syngas section which includes gasification, water-gas-shift reaction, and sour gas treatment; (ii) the methanol synthesis; and (iii) the methanol-to-acetic acid subprocess. Note the gasification-to-methanol simulation that includes gasification, water-gas-shift reaction, sour gas treatment, and methanol synthesis step is modelled in Aspen Hysys due to the software capabilities for working with different fluid packages, as well as different sour gas treatment options. Using a previously developed

simulation as a reference (Smith et al. 2017), the methanol-to-acetic acid process with a production rate of 300,000 t of end product per year is simulated in ChemCAD.

Methanol Synthesis Process Simulation

Figure 6 presents the Aspen Hysys flowsheet setup used for methanol synthesis process from coal/biomass. The flowsheet is built and conditions are obtained based on previously published literature (Robinson 2011; Worley and Yale 2012). In this flowsheet, coal and biomass are approximately simplified using pseudo components based on the atomic ratio of hydrogen to carbon. Biomass in this work is assumed to be comprised of wood chips, with the typical composition of 55 wt% carbon, 32 wt% oxygen, and 10 wt% hydrogen, 2 wt% sulfur and 1 wt% of other species (Fout et al. 2015). Coal is represented by a pseudo component hydrocarbon (Robinson and Luyben 2008) ($C_{18}H_{20}$) based on the weight of C and H in the coal. With the assumed biomass and coal raw materials as well as oxygen and water, an entrained flow gasifier is used to convert the hydrocarbon feed into raw synthesis gas. In addition, as shown in Figure 6, the gasifier island step includes three parts: partial oxidizer (POX) (CSTR100–102), radiant synthesis gas cooler (RSC) (E100) and water quench (MIX-101).

High temperature conditions in the POX can improve the conversion rate to syngas (typical conversion rates for biomass/coal to syngas are 50 wt% / 65 wt%, respectively) and the RSC helps to recover part of the heat via steam generation while cooling the process syngas to around 800°C. Then the quench water drops the water temperature in the syngas to around 200°C. The downstream units from the gasifier are mostly standard gas phase processes, including the sour water gas shift (SWGS) reactor and acid gas removal (AGR) process, followed by the methanol synthesis (MS) step. Before entering the SWGS part, particles and traces of acid gas in raw syngas are removed through a wet scrubber (Scrubber). In the SWGS part, the ratio of hydrogen/carbon in the syngas required for methanol synthesis can be adjusted to 2 even if only biomass is used as feedstock. Then, as shown in Figure 7, monoethanolamine (MEA) is used to remove acid gases (H_2S and CO_2) and the sweet syngas from the top of the absorber (T-103) goes to the methanol reactor, while the rich MEA solvent is regenerated by the stripper (T-101). To reach high conversion rate to methanol (~90 %) as well as ensure high methanol purity (99.5 wt%) required by the AA production process, most of the gas stream (in Stream 25) from the top of the separator (V-103) is recycled back to the methanol reactor (GBR-100). The methanol synthesis reaction is exothermic and the optimal reaction temperature for this process is around 200°C.

Acetic Acid Process Simulation

The simulation of the acetic acid process, as illustrated by the CHEMCAD process flow diagram in Figure 8, includes the calculated temperatures, pressures, and compositions for each stream and unit operation throughout the process flow diagram.

A description of the streams and unit operations begins with the fresh methanol and methyl iodide (MI) streams (Streams 1 and 9) being mixed and preheated by passing through a heat exchanger integrated unit (Unit 6) which transfers the excess heat from the reactor outlet

stream (Stream 14). This stream is mixed with a fresh stream of CO (Stream 26) and a recycling stream (Stream 25) from downstream operations (flash vessel and absorption column). The resulting stream then enters the isothermal methanol carbonylation reactor (Unit 10) at temperature of 189°C, where the reaction mechanism shown below occurs. In order to achieve a methanol conversion of 98.5% in the simulation, 91.5% of the carbon monoxide is reacted. The outlet reactor stream pressure is reduced using an adiabatic flash valve (Unit 11). The stream is cooled and the resulting vapor-liquid mixture is flashed in Unit 19 to remove non-condensable compounds. The flashed stream (Stream 18), which is rich in acetic acid is then sent to the distillation column (Unit 16) for further purification of the final acetic acid product. The rigorous multi-stage vapor-liquid equilibrium multicomponent column is designed to produce a bottom product stream (Stream 19) with a content of 98 mol% acetic acid. The product stream is depressurized and cooled enough to produce acetic acid (Stream 21) at 45 °C and 101.325 kPa, i.e., ready for storage. In addition, the gas stream from the distillation column (Stream 22) is conditioned in a heat exchanger and sent to the absorption column (Unit 24) where a portion of the valuable condensable compounds are absorbed by using part of the fresh methanol as solvent (Stream 5). The liquid stream from absorber Unit 24 (Stream 24) recovers part of the methyl iodide, methyl acetate, and hydrogen iodide, which are recycled back into the reactor unit. The gas leaving the absorption column (Stream 6) is vented as Gas Releases of uncontrolled air emissions. This stream, along with the Gas Releases from Stream 27, may contain hydrogen iodide, methyl iodide, methanol, methyl acetate and methane (see full list in Table 4), some of which may cause skin and lung irritation, digestive disorders in addition to being an asphyxiant (in the case of methanol) (Worley and Yale 2012). The pollution control units developed in this work previously described are used next to simulate the remediation process of these waste streams, as well as to provide more realistic LCI results for use in a sustainability evaluation.

Results and Discussion

Incorporation of PCUs into Acetic Acid Process Simulation Results

As mentioned above, many researchers and engineers are trying to reduce or control pollution and emissions from chemical processes, in addition to making their product competitive in terms of cost. The proposed approach of integrating process simulation with PCU modules for LCI generation can be employed across a wide range of applications, for both new product design as well as retrofit/upgrade scenarios. The acetic acid manufacturing process is employed here to illustrate how the developed PCU simulators can enable the rapid estimation of controlled emissions, utility and construction material consumption as well as land footprint information for LCI generation. The calculations of construction material and footprint are typically based on the plant life time (20 years in this case study), as shown in equations (1–2).

$$LCI \text{ Material Index} = \frac{\text{total material weight}}{\text{product yearly flowrate} \times \text{plant life time(years)}} \quad 1$$

[kg/kg product per year]

$$LCI \text{ Footprint Index} = \frac{\text{total area}}{\text{product yearly flowrate}} \quad \left[m^2/kg \text{ product per year} \right] \quad 2$$

Tables 3 and 4 show the LCI input/output results from the application of three PCUs (scrubber, boiler and flare) to the methanol-to-acetic acid (AA) sub-process. In Table 4, the stream compositions are shown without PCUs (under “Simulation”) as well after application of each PCU (with their respective name), in which the LCI outputs include the exit concentration of chemicals from the emission streams (streams 6 and 27 in Figure 9) after implementing each PCU as shown in Figure 9. The “Emission with PCUs” column depicts the releases after applying the three in-series PCUs (see Figure 9) while the LCI inputs show the electricity, utility consumption, facility material and land use associated with the construction and operation of the selected PCUs. Note that the percentage change for inputs (in Table 3) is calculated by dividing the PCU subtotal by the simulation inputs (under “Simulation” in Table 3) and then multiplying the result by 100%. Also, the percentage change for outputs (in Table 4) is calculated by the emissions with PCUs minus the simulation emissions (under “Simulation” in Table 4), and then dividing the resulting quantity by the simulation emissions (multiplied by 100%). In addition, as described in Table 2, the collection of some waste stream data and the selection of equipment parameters were required for the implementation of the PCU modules for obtaining the corresponding LCI results.

After performing an engineering evaluation of the complete system, the decision regarding the appropriate pollution control technologies to use needs to be made based on the analysis of the source, component and flowrate of the emission(s). A systematic analysis may be required if a sequence of pollution control technologies should be employed to treat the waste streams. Therefore, it was found for the acetic acid sub-process, waste streams 27 and 6 (see Figure 8) should be combined for treatment by the developed PCU modules as shown in Figure 9. In addition, as described in Table 4, the waste streams from the acetic acid process (denoted as “Simulation”) consists of inorganic acids, VOCs (e.g., methyl acetate, acetic acid, methanol and methane) as well as CO. To effectively treat this stream, the first step is to remove hydrogen iodide (HI) by employing a scrubber, which is the most widely used pollution control device for soluble inorganic contaminants from gas streams. In the developed scrubber module, solvent, packing material, size and operating conditions can be set based on the pollutant of interest and its inlet concentration. For HI, the scrubber is simulated as a packed column containing 2’ Raschig Rings, and a shell material of 304 Stainless Steel. From Table 4, it can be observed that HI has been effectively removed by the scrubber with an efficiency of 100%. The scrubber unit was designed based on the required HI removal efficiency (99%). However, 5.3 times the solvent flowrate demanded by the

required HI removal efficiency was required to soak the whole packing material of the scrubber tower (U.S. Environmental Protection Agency 2002), resulting in a higher removal efficiency of 100%. Water, methanol, acetic acid, and propionic acid are more soluble in water than HI, thus after scrubber, all of them are zero. In addition, the utility consumption, construction material and footprint results are calculated by the scrubber simulator, as shown in Table 3 (see Supporting Information, Section S1, for calculation procedures).

The output from the scrubber mainly consists of CO and methyl acetate and thus can be fed to the boiler to recover the combustion heat value. Since the heat input in this stream is low, a small sized boiler (10 MW) is used with an uncontrolled burner type (see Supporting Information, Section S2, for calculation procedures). It is important to note that waste gas is mixing with natural gas as the fuel for the boiler and the heat input of waste gas should not be larger than that of natural gas. In the design case for boiler simulator, the percentage of waste gas heat input can be adjusted by changing the size of the boiler. In this work, boiler is considered as a pollution control unit that processes all the emissions from the scrubber. However, it might be the case in reality that only part of the waste emissions can be treated by the existing boiler at a specific facility and the rest of the waste stream has to go through other PCUs. For the purpose of demonstrating all the designed PCUs, the outlet stream from the boiler is released to the environment through the flare unit, which causes a large construction material need for the flare unit.

The pollution control devices are thus able to produce a resulting stream after treatment that is more environmentally-friendly. Table 4 shows the detailed LCI output results for scrubber, boiler, and flare. Please note that boilers are initially rated for a specific fuel (e.g., natural gas), and operational performance can degrade, heat transfer equipment can be damaged, and emissions can increase with changes in fuels burned (NGC+ Interchangeability Work Group 2005). In addition, there are some restrictions on burning hazardous waste that is not categorized as a fuel in industrial boilers (U.S. Government Publishing Office 1991). Those restrictions describe a minimum heating value requirement for the waste, prohibiting their blending to augment the heating value of the waste, and exclusion of burning dioxin-listed wastes. In summary, this table clearly shows the scrubber has the capability to remove those species which have a large solubility in the solvent, such as HI, methanol, and acetic acid, while bringing down the boiler net steam consumption by 36.5%. The large amount of CO₂ released to the environment is due to the boiler and flare converting all combustible species to CO₂. The resulting CO₂ could be sent to carbon capture and storage units for further processing.

An LCI for acetic acid synthesis from methanol has been reported in commercial LCI databases. A model for the European production process is available in Ecoinvent (Wernet et al. 2016), while a US production process is available from the USLCI (National Renewable Energy Laboratory). The Ecoinvent data is based on theoretical process modeling with an assumption that 50% of waste gas is converted to CO₂ by combustion. The USLCI LCI dataset represents industry average data reported by a non-government organization and includes the upstream transport of materials to the manufacturing site. A comparison of the emission results with/without PCUs simulated here with the commercially available data is shown in Table 5. When compared to the theoretical Ecoinvent process, the quantities of

carbon dioxide emitted for the case with PCUs is nearly triple while the carbon monoxide is reduced by one order of magnitude. The Ecoinvent data contains residual organics because of the assumption to only treat 50% of the gas-phase stream. When compared to the USLCI data, the simulation data with PCUs again predicts more carbon dioxide and less carbon monoxide because of the choice to model complete gas-phase waste treatment. The comparison between “Simulation without PCUs” and Ecoinvent/USLCI shows that emissions without PCUs are closer to the USLCI results for methanol and carbon dioxide species. Carbon dioxide emission is only 1.5% of the amount of Ecoinvent and 31% of USLCI while carbon monoxide is as high as 7 times of Ecoinvent and 11 times of USLCI. This can be explained by the fact that industry might have pollution control units (e.g., flare) to convert carbon monoxide to carbon dioxide with efficiency higher than 50%, which is much lower than the efficiency considered here for simulation with PCUs, which is around 98%. Interestingly, ammonia is reported by the USLCI while not being predicted by either the simulated or theoretical inventories. In addition, the PCU LCI reported NO_x and PM values as opposed to the commercial databases; that is due to their assumptions, thereby omitting these important pollution categories. Based on the performed comparisons, the simulated inventory appears to overpredict the level of pollution control when compared to the commercial databases that show a lower pollution control efficiency. Therefore, additional research is necessary to develop guidance for how to best apply and customize the PCU modules in LCI modeling and improve their accuracy.

Incorporation of PCU models into Methanol Synthesis Simulation Results

The synthesis of methanol, as the main feedstock for acetic acid production, is analyzed through the comparison of gate-to-gate LCI data modeling under two cases: 1) methanol produced from coal; 2) methanol produced from biomass. In addition, the methanol synthesis for both scenarios are studied in order to fulfill the production demand of acetic acid. Both processes have waste streams that are sent to the external PCU modules for treatment. The proposed method provides rapid yet accurate LCI data estimates of controlled emissions that could be used by non-engineer LCA practitioners when the LCI information is not readily available from industry, literature, or commercial software.

Coal-Based Simulation

For this case of coal as the feedstock to generate methanol, a summary of the LCI inputs, with and without the PCUs, including the raw materials and utilities, is presented in Table 6. Oxygen, as one of the required resources for the methanol production process, is assumed to be obtained from air separation units that are considered outside of the process LCI boundary. In addition, the boundary does not include pretreatment of raw material (e.g., coal/biomass grinding/drying). The steam reported in Table 6 is the steam produced by recovering the heat within the process after the deduction of the steam needed for the process heating duty, as provided by the process simulator. The electricity requirements in this table are estimated based on the assumption that efficiencies for pumps and compressors are 75% and 70%, respectively.

Concerning emissions from the process, as described in Figure 6, there are two waste streams that need to be treated prior to release: 1) the waste stream from mixer-106 (waste

stream 1), which is composed primary of CO and methanol; and 2) the waste stream from mixer-105 (waste stream 2), comprised mostly of CO₂ and H₂S (Worley and Yale 2012). Waste stream 2 is assumed to be sent to absorption units to separate CO₂ from H₂S, followed by Carbon Capture and Storage (CCS) and Claus unit technologies to handle the two acid gases, respectively. The developed thermal oxidizer module (see Supporting Information, Section S4, for calculation procedures) unit is employed to treat the VOCs present in waste stream 1 as shown in Figure 9, with the generated LCI output results described in Table 7. Please note that N₂ and O₂ in the emission stream (in Table 7) are calculated based on the excess air required by the thermal oxidizer. By adjusting the operating temperature and residence time of the thermal oxidizer, the destruction efficiency of the VOCs obtained reached as high as 99.5%. Although estimated utility use is reported, the inputs (and emissions) related to fuel used to generate the steam and electricity are assumed to occur in upstream processes.

Biomass-Based Simulation

The flowsheet for the biomass case study was kept as similar as possible to the coal case study to allow for direct comparison. The operating conditions, such as the oxygen and water flowrates as well as the bypass fraction to the water-gas shift reactor, were adjusted according to the biomass conversion rate and syngas composition, in order to produce a methanol with similar purity and production rate needed for the subsequent acetic acid synthesis sub-process. For generating LCI results, the considered LCI boundary and assumptions on the efficiencies of pumps and compressors still hold. When compared to the coal case study, the LCI results, reported in Table 8, for the oxygen and water inlets are less than those for the coal case study, due mainly to the fact that biomass is richer in oxygen content and consists of 15% water. However, the LCI results for biomass for steam and cooling water usage are greater than those in the coal case study. This can be attributed to the biomass' lower energy density and a larger quantity of biomass being needed to generate the same amount of syngas.

In addition, the syngas quality from the biomass, in terms of H₂/CO, is much lower than that generated from coal. Thus, greater quantities of utilities, such as steam and cooling water, for the biomass are consumed when compared to coal. Electricity estimates for the two cases studies were found to be equivalent. When referring to waste streams, both waste streams exist for the two cases studies: 1) waste stream from mixer-106 (waste stream 1), which is mainly composed of CO and methanol; 2) waste stream from mixer-105 (waste stream 2), including mostly CO₂ and H₂S. The result of treating waste stream 1 employing the thermal oxidizer PCU is shown in Table 9, which is similar to the results from the coal case study. However, the acid gases in waste stream 2 that would be sent to downstream units as described above is much lower than that for the coal case study, as shown in Table 10. This table depicts the comparison of the results of the uncontrolled emissions from both the coal and biomass-based case studies.

Analysis of Coal to AA Production Process

As described in the process simulation section, the entire process can be separated in two parts (methanol synthesis and acetic acid production) and the previous LCI results were

obtained and analyzed separately. The LCI input and output results in this section are based on the same functional unit (kg AA) using coal as feedstock, as shown in Tables 11 and 12. Note the results for the two parts are for the scenario including pollution control unit simulations. Specifically, a thermal oxidizer was used in the coal to methanol part for treating the gas phase waste from the methanol synthesis reactor, while a scrubber, boiler and flare were used for treatment in the methanol to acetic acid process. As shown in Table 11, greater quantities of utilities (cooling water, electricity, and steam) were used in the methanol synthesis part when compared to the utility values needed for the methanol to acetic acid process. This can be attributed to the complexity of the methanol synthesis process, which includes gasification, sour water gas shift reaction, acid gas cleaning part and methanol reactor process steps. In addition, this result highlights the potential to further improve the LCI results, which will be addressed in future research in process optimization and control.

For the LCI output results, the first part of the process releases CO, CO₂, H₂S, and small amounts of CH₄, CH₃OH, as well as H₂. While the acetic acid process portion generates CO₂ with small quantities of NO_x, CO and PM. It is important to note the source for each species as this can guide further investigation on how to handle and treat such emissions. For example, the sources of CO₂ emissions, from the two parts of the process, are different even though both release a high quantity of CO₂. More specifically, CO₂ from the methanol process, which is primarily generated by the water gas shift reaction, can be separated from other species present in the stream and then go to carbon capture and storage (CCS). Additional processing steps are required to collect the CO₂ generated from the acetic acid process, as the majority of CO₂ originates from the combustion in the boiler and flare.

Conclusions

The objective of this work was to develop a generic and integrated framework for rapid LCI generation of PCU modules by adopting systematic methods for process modeling, simulation, and design. Specifically, process simulation that included mass and energy balances was employed for providing LCI data which otherwise may be incomplete without considering the impacts of implementing pollution control systems for process waste streams. The developed PCUs were comprised of modules for treating gas releases that provide LCI information regarding land footprint and utility and material use.

The effectiveness of the proposed framework was demonstrated on the acetic acid manufacturing process from a coal/biomass feedstock. The outputs from the acetic acid simulation were used as input streams to the respective PCU modules. Those suitable PCUs were successfully implemented to remove process pollutants and recover the combustion heat. A comparison between LCI results with and without application of the developed PCU modules demonstrated considerable variations in material compositions, energy demand, and infrastructure that cannot be omitted when generating a suitable LCI.

For the current case study, the LCI results, when comparing methanol production from biomass vs. coal, showed the biomass case requires more utility demand (steam and cooling water), while generating less CO₂ and H₂S. In the future, co-gasification of coal and

biomass will be investigated as a potentially economically attractive and technically viable alternative to the conversion of biomass to energy and chemicals while improving the sustainability performance of the coal gasification process.

Furthermore, the authors will investigate an advanced process control strategy, such as a biomimetic approach (Li et al. 2016; Lima et al. 2016), as a potentially optimal and clean approach for the utilization of biomass and coal. From this investigation, it is anticipated a determination on the optimum combination of coal and biomass to balance the raw material input to reduce emissions without sacrificing desired production rate and profitability that can be achieved.

This contribution demonstrates the needs and benefits of adding the effects of pollution control units for rapid LCI modeling of a chemical manufacturing process by designing, modeling, and simulating PCUs for noxious gas removal. These parameterized PCU modules can simplify pollution control modeling when compared to fully simulating the units by providing rapid LCI estimates that could be used by non-engineer LCA practitioners when LCI information is not readily available from industry or literature.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Process systems framework for pollution control and LCI generation

Figure 2.
Counter-current packed spray scrubber schematic (U.S Environmental Protection Agency 2002)

Figure 3.
A simplified diagram of a gas-fired boiler system

Figure 4.
Schematic diagram of a flare system (U.S Environmental Protection Agency 2002)

Figure 5.
Block flow diagram of a thermal oxidizer system

Figure 6.
Aspen Hysys flowsheet for methanol synthesis

Figure 7.
Aspen Hysys flowsheet for the sour gas treatment process

Figure 8.
CHEMCAD flowsheet for the simulated acetic acid manufacturing process

Figure 9.
Incorporation of PCUs into acetic acid process simulation results for rapid LCI modeling

Table 1.

Summary on brief descriptions, strengths and limitations of developed PCUs

PCUs	Brief Descriptions	Strengths	Limitations
Scrubber	<ul style="list-style-type: none"> Absorption is widely used as a pollution control technique for inorganic emissions 	<ul style="list-style-type: none"> Good for inorganic acid gases Raw material and/or product can be recovered 	<ul style="list-style-type: none"> Need suitable solvents that should be easily regenerated or disposed in an environmentally acceptable manner
Boiler	<ul style="list-style-type: none"> Existing boilers can be used to control emission streams containing organic compounds 	<ul style="list-style-type: none"> High destruction efficiency (98%) Small capital cost with no fuel cost High recovery of the combustion heat 	<ul style="list-style-type: none"> Limited in dealing with emission streams with corrosive compounds and variations in terms of flowrate and contents Only applied for low flowrate waste gases (less than 20% of the natural gas volumetric flowrate) with high heating values (higher than 5,589 kJ/m³ (at 1 atm, 20 °C))
Flare	<ul style="list-style-type: none"> Flare is commonly used for disposal of waste gases for chemical plants Flares can be used for controlling almost any VOC emission stream 	<ul style="list-style-type: none"> High destruction efficiency Can handle fluctuations in emitted VOC and inert contents and flow rates 	<ul style="list-style-type: none"> No organics can be recovered Large flowrate of waste streams only No combustion heat can be recovered
Thermal Oxidizer	<ul style="list-style-type: none"> Thermal oxidizer (TO) is used to control a wide variety of continuous emission streams containing dilute VOCs 	<ul style="list-style-type: none"> High destruction efficiency Wide applicability Possible to recover heat energy 	<ul style="list-style-type: none"> No organics can be recovered Capital intensive It is not suitable for streams with highly variable flows

Table 2.

A summary of user input parameters required for applying each PCU module for LCI modeling

	Pollution Control Unit			
	Scrubber	Boiler	Flare	Thermal Oxidizer
User Input Parameters	Waste gas flowrate			
	Waste gas composition			
	Inlet temperature (30 °C)	Inlet temperature (40 °C)	Inlet temperature (40 °C)	Inlet temperature (40 °C)
	Pressure (~101.325 kPa)	Pressure (101.325 kPa)	Pressure (>101.325 kPa)	Pressure (~101.325 kPa)
	Fresh solvent composition (100% solvent)	Excess of air (5%)	Liquid mass fraction (0.05)	Designed control efficiency (99%)
	Designed removal efficiency (99%)		Liquid density (795 kg/m ³)	Designed energy recovery (70%)
	Waste gas viscosity and pollutant diffusivity in air (if not listed in the internal database)	Boiler size in terms of heat content of fuel gas: small size (<29.3 MW) and large size (>29.3 MW). Heat content of waste gas should be smaller than 50% of boiler's heat needs and > 11,630 kJ/kg.	Flare type (steam-assisted)	Operation temperature (871.1 °C)
			Designed combustion efficiency (98%)	Fan efficiency (70%)
			Designed Mach number (0.2)	
	Pollutant diffusivity in air and solvent properties (if not listed in the internal database)	Burner type: the amount of CO, NO _x , VOCs emissions are related to burner type. For smaller size boilers, uncontrolled burners might be able to meet the environmental standards. Controller-Low-NO _x burner is recommended for larger size boilers.	Maximum allowable thermal radiation (1.58 kW/m ²)	
			Radiation fraction (0.3)	
	Packing size and properties: (Raschig rings ceramic, 2'')		Wind velocity (yearly average wind velocity of local area)	
	Equilibrium data: equilibrium line data and saturation solubility data are required for the primary pollutant; solubility data for other components are needed if it is a multi-component system		Recommended horizontal distance to the stack center (50 m). For this recommendation, a typical stack height value can be calculated (30 m).	

Table 3.

LCI input results before and after waste streams have been processed by PCUs

LCI Inputs	Units	Simulation	Simulation with emission control units				Percentage change
			Scrubber	Boiler	Flare	PCU Subtotal	
Air	kg/kg AA	0	0	1.63E-1	1.36E-2	1.76E-1	∞
Natural Gas	scm/kg AA	0	0	9.16E-3	1.43E-2	2.34E-2	∞
Purge Gas (Nitrogen)	scm/kg AA	0	0	0	1.24E-3	1.24E-3	∞
Steam	kg/kg AA	7.79E-1	0	-2.84E-1	0	-2.84E-1	-37%
Solvent (Water)	kg/kg AA	0	2.47E+0	0	0	2.47E+0	∞
Electricity	kW/kg AA	5.60E-3	5.90E-5	8.11E-5	0	1.40E-4	3%
Construction Material	kg/(kg AA per year)	2.03E-6	8.43E-8	4.88E-7	1.43E-5	1.49E-5	733%
Footprint	m ² /(kg AA per year)	1.02E-4	4.47E-8	7.73E-7	1.60E-6	2.42E-6	2%

A negative sign (–) represents decrease (in percentage) or generation (for steam in the boiler), while “∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream).

Table 4.

LCI output results before and after waste streams have been processed by PCUs

LCI Output	Units	Simulation	Simulation with emission control units			Emissions with PCUs	Percentage change
			Scrubber	Boiler	Flare		
Carbon Monoxide	kg/kg AA	4.39E-2	4.36E-2	7.15E-4	8.73E-4	8.73E-4	−98%
Carbon Dioxide	kg/kg AA	5.45E-4	5.42E-4	9.68E-2	1.36E-1	1.36E-1	24868%
Methane	kg/kg AA	1.97E-4	1.97E-4	2.18E-6	1.09E-9	1.09E-9	−100%
Water	kg/kg AA	1.55E-4	0	6.81E-3	3.21E-2	3.89E-2	25015%
Methanol	kg/kg AA	3.10E-5	0	0	0	0	−100%
Acetic Acid	kg/kg AA	5.89E-4	0	0	0	0	−100%
Methyl Acetate	kg/kg AA	2.14E-3	2.13E-3	0	0	0	−100%
Hydrogen Iodide	kg/kg AA	1.84E-3	0	0	0	0	−100%
Propionic Acid	kg/kg AA	1.57E-7	0	0	0	0	−100%
NOX	kg/kg AA	0	0	2.07E-5	1.96E-5	1.96E-5	∞
PM (< 1 μm)	kg/kg AA	0	0	1.63E-6	1.63E-6	1.63E-6	∞
Nitrogen	kg/kg AA	0	0	1.24E-1	1.34E-1	1.34E-1	∞
Oxygen	kg/kg AA	0	0	1.89E-3	4.50E-4	4.50E-4	∞

A negative sign (−) represents decrease (in percentage) or generation (for steam in the boiler), while “∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream).

Table 5.

A comparison of LCI results with commercially available data

Substance	Units	Simulation without PCUs	Simulation with PCUs	Ecoinvent	USLCI
Acetic Acid	kg/kg AA	5.89E-4	0	5.00E-3	–
Ammonia	kg/kg AA	–	–	–	5.70E-4
Carbon Dioxide	kg/kg AA	5.46E-4	1.36E-1	3.71E-2	1.76E-3
Carbon Monoxide	kg/kg AA	4.39E-2	8.73E-4	6.32E-3	3.97E-3
Hydrogen	kg/kg AA	–	–	2.96E-4	–
Hydrogen Iodide	kg/kg AA	1.84E-3	0	–	–
Methane	kg/kg AA	1.97E-4	0	4.99E-3	–
Methanol	kg/kg AA	3.10E-5	0	2.52E-3	4.00E-5
Methyl Acetate	kg/kg AA	2.14E-3	0	–	–
Total Organic Carbon	kg/kg AA	–	–	–	2.71E-3
Water	kg/kg AA	1.55E-5	0	–	–
NO _x	kg/kg AA	0	1.96E-5	–	–
PM (< 1 µm)	kg/kg AA	0	1.63E-6	–	–

“–” means the substance was not included in the reported inventory

Table 6.

Life cycle inventory inputs for methanol production from coal

LCI Inputs	Units	Simulation	Simulation with	Percent change
			Thermal Oxidizer	
Oxygen	kg/kg MeOH	2.62E+0	2.62E+0	0
Water	kg/kg MeOH	1.11E+0	1.11E+0	0
Coal	kg/kg MeOH	1.61E+0	1.61E+0	0
MEA	kg/kg MeOH	1.33E-5	1.33E-5	0
Steam (Flowrate/Duty)	kg/kg MeOH	4.57E+1	4.57E+1	0
	MJ/kg MeOH	9.78E+1	9.78E+1	0
Cooling Water (Flowrate/Duty)	kg/kg MeOH	7.19E+2	7.19E+2	0
	MJ/kg MeOH	1.32E+2	1.32E+2	0
Electricity	MJ/kg MeOH	3.20E-1	3.51E-1	9.7%
Air	kg/kg MeOH	0	8.21E+0	∞
Natural Gas	scm/kg MeOH	0	8.49E-2	∞
Construction Material	kg/(kg MeOH/yr)	5.76E-4	5.79E-4	0.5%
Footprint	m ² /(kg MeOH/yr)	–	1.85E-7	∞

“ ∞ ” represents division by zero in calculation of percentages (for cases without corresponding inlet stream), while “–” means the inventory data is not calculated for the methanol synthesis process footprint

Table 7.

LCI outputs before and after waste streams have been processed by PCUs per kilogram of methanol produced from coal

LCI Outputs	Units	Simulation	Simulation with Thermal Oxidizer	Percentage change
Methane	kg/kg MeOH	1.41E-3	0	−100%
Carbon Dioxide	kg/kg MeOH	7.03E-3	9.43E-1	13313%
Carbon Monoxide	kg/kg MeOH	5.88E-1	9.18E-3	−98%
Hydrogen	kg/kg MeOH	8.65E-2	0	−100%
Methanol	kg/kg MeOH	2.04E-2	1.02E-4	−99.5%
Nitrogen	kg/kg MeOH	0	6.30E+0	∞
Oxygen	kg/kg MeOH	0	1.91E+0	∞

“∞” represents division by zero in calculation of percentages

Table 8.

Raw material and utility life cycle inventory for methanol production from biomass

LCI Inputs	Units	Simulation	Simulation with Thermal Oxidizer	Percent change
Oxygen	kg/kg MeOH	8.01E-1	8.01E-1	0
Water	kg/kg MeOH	1.00E-1	1.00E-1	0
Biomass	kg/kg MeOH	2.74E+0	2.74E+0	0
Steam (Flowrate/Duty)	kg/kg MeOH	4.57E+1	4.57E+1	0
	MJ/kg MeOH	9.78E+1	9.78E+1	0
Cooling Water (Flowrate/Duty)	kg/kg MeOH	7.19E+2	7.19E+2	0
	MJ/kg MeOH	1.32E+2	1.32E+2	0
Electricity	MJ/kg MeOH	3.20E-1	3.54E-1	10.8%
Air	kg/kg MeOH	0	8.21E+0	∞
Natural Gas	scm/kg MeOH	0	5.38E-2	∞
Construction Material	kg/(kg MeOH/yr)	5.76E-4	5.81E-4	0.9%
Footprint	m ² /(kg MeOH/yr)	–	8.55E-7	∞

“ ∞ ” represents division by zero in calculation of percentages (for cases without corresponding inlet stream) while “–” means the inventory data is not calculated for methanol simulation case

Table 9.

LCI before and after waste streams have been processed by PCUs for biomass case

LCI Outputs	Units	Simulation	Simulation with Thermal Oxidizer	Percentage change
Methane	kg/kg MeOH	1.03E-2	0	–100%
Carbon Dioxide	kg/kg MeOH	1.28E-3	8.76E-1	68337%
Carbon Monoxide	kg/kg MeOH	5.44E-1	8.53E-3	–98.4%
Hydrogen	kg/kg MeOH	7.97E-2	0	–100%
Methanol	kg/kg MeOH	2.04E-2	3.84E-5	–99.8%
Nitrogen	kg/kg MeOH	0	6.30E+0	∞
Oxygen	kg/kg MeOH	0	1.91E+0	∞

“∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream)

Table 10.

Uncontrolled emissions from coal and biomass-based methanol process

LCI Output	Units	Coal Case	Biomass Case
Methane	kg/kg MeOH	6.39E-6	6.51E-5
Carbon Dioxide	kg/kg MeOH	3.09E+0	2.13E+0
Hydrogen Sulfide	kg/kg MeOH	5.86E-2	5.60E-4
Carbon Monoxide	kg/kg MeOH	5.31E-3	9.96E-3
Water	kg/kg MeOH	3.97E-2	2.69E-2
Nitrogen	kg/kg MeOH	7.03E-5	3.26E-5
Hydrogen	kg/kg MeOH	8.37E-4	1.20E-3

Table 11.

LCI input for entire process from coal to AA

LCI Input	Units	Coal to Methanol Simulation	Methanol-to-Acetic Acid Simulation	Total
Oxygen	kg/kg AA	1.42E+0	0	1.42E+0
Water	kg/kg AA	5.98E-1	0	5.98E-1
Coal	kg/kg AA	8.70E-1	0	8.70E-1
Carbon Monoxide	kg/kg AA	0	5.09E-1	5.09E-1
Methanol	kg/kg AA	0	5.39E-1	5.39E-1
Methyl Iodide	kg/kg AA	0	2.03E-3	2.03E-3
Steam (Flowrate/Duty)	kg/kg AA	2.47E+1	4.95E-1	2.52E+1
	MJ/kg AA	5.28E+1	1.75E+0	5.46E+1
Cooling Water (Flowrate/Duty)	kg/kg AA	3.88E+2	4.37E-1	3.89E+2
	MJ/kg AA	7.16E+1	3.06E+0	7.46E+1
Electricity	MJ/kg AA	1.90E-1	6.65E-2	2.56E-1
Air	kg/kg AA	4.44E+0	1.76E-1	4.61E+0
Natural Gas	kg/kg AA	4.59E-2	2.34E-2	6.93E-2
Purge Gas (Nitrogen)	kg/kg AA	0	1.24E-3	1.24E-3
Solvent (water)	kg/kg AA	0	2.47E+0	2.47E+0
Construction Material	kg/(kg AA/yr)	3.13E-4	1.49E-5	3.28E-4

Table 12.

LCI output for entire process from coal to AA

LCI Output	Units	Coal to Methanol Simulation	Methanol-to-Acetic Acid Simulation	Total
Carbon Monoxide	kg/kg AA	7.83E-3	8.73E-4	8.71E-3
Carbon Dioxide	kg/kg AA	2.18E+0	1.36E-1	2.32E+0
Methane	kg/kg AA	3.45E-6	0	3.45E-6
Water	kg/kg AA	2.15E-2	0	2.15E-2
Methanol	kg/kg AA	5.51E-5	0	5.51E-5
Acetic Acid	kg/kg AA	0	0	0
Methyl Acetate	kg/kg AA	0	0	0
Hydrogen Iodide	kg/kg AA	0	0	0
Propionic Acid	kg/kg AA	0	0	0
NO _x	kg/kg AA	0	1.96E-5	1.96E-5
PM (< 1 µm)	kg/kg AA	0	1.63E-6	1.63E-6
Hydrogen Sulfide	kg/kg AA	3.17E-2	0	3.17E-2
Hydrogen	kg/kg AA	4.52E-4	0	4.52E-4