Sustainable Process Design by the Process to Planet Framework

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Sustainable process design (SPD) problems combine a process design problem with life cycle assessment (LCA) to optimize process economics and life cycle environmental impacts. While SPD makes use of recent advances in process systems engineering and optimization, its use of LCA has stagnated. Currently, only process LCA is utilized in SPD, resulting in designs based on incomplete and potentially inaccurate life cycle information. To address these shortcomings, the multiscale process to planet (P2P) modeling framework is applied to formulate and solve the SPD problem. The P2P framework offers a more comprehensive analysis boundary than conventional SPD and greater modeling detail than advanced LCA methodologies. Benefits of applying this framework to SPD are demonstrated with an ethanol process design case study. Results show that current methods shift emissions outside the analysis boundary, while applying the P2P modeling framework results in environmentally superior process designs. Future extensions of the P2P framework are discussed. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 3320–3331, 2015
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Introduction

Increasing environmental regulations have driven a shift in chemical process design from the traditional, process economics-oriented methods toward methods that consider a process' environmental impacts. The earliest such environmentally conscious process design methods strongly resembled economics oriented methods in that a single process was considered and optimized for efficiency, thereby reducing resource consumption and waste production. Such methods include procedures for increasing process efficiency through process integration[1–10] and designing for waste reduction (WAR).[11–14]

Process integration, intensification, and WAR methods include only a single process in the analysis boundary. The narrow analysis boundary makes for a tractable design problem but neglects many relevant systems connected to the process of interest, including upstream activities such as feedstock processing and downstream activities such as wastewater treatment. Because these connected systems are neglected, design decisions that appear optimal when only the process of interest is considered may in fact be suboptimal or incorrect, due to the effects of those decisions on systems outside the process of interest.[15–17] For instance, a process design that shifts some processing stages off-site will appear to have lower environmental impacts due to the smaller energy and resource consumption, but in reality the net environmental impacts attributable to the process have not necessarily decreased and may have increased.

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A broad analysis boundary, encompassing the process of interest and relevant connected systems, is thus necessary to ensure optimal and correct design decisions.[18,19] Environmentally conscious process design methods developed after the design-for-process-efficiency methods considered upstream and downstream processing stages as well as the process of interest in the analysis boundary. The WAR algorithm designed for pollutant and waste reduction, considering both the physical amount of waste produced[20–23] and the environmental impacts, particularly toxicity, of the waste.[24] Various applications of the WAR algorithm considered, in addition to the process of interest, processes such as raw materials extraction, power generation,[25,26] production of intermediate inputs and waste treatment.[27,28]

Life cycle assessment (LCA), a method to account for impacts throughout the life cycle of a product, was developed and standardized roughly in parallel with early environmentally conscious process design methodologies.[29,30] LCA offered a standardized and rigorous methodology for further expanding the analysis boundary of process design, and was formally integrated with process design in the Method for Environmental Impact Minimization (MEIM).[31,32] The MEIM applied LCA to quantify environmental impacts attributable to the process of interest throughout its life cycle. This and subsequent sustainable process design (SPD) methods designed for reduced environmental impacts throughout the life cycle rather than at the process of interest alone. The existence of trade-offs between process economics and life cycle impacts led to the widespread use of multiobjective optimization techniques.[33–36]

Recent developments in SPD methods have relied on advances in process systems engineering (PSE), particularly the

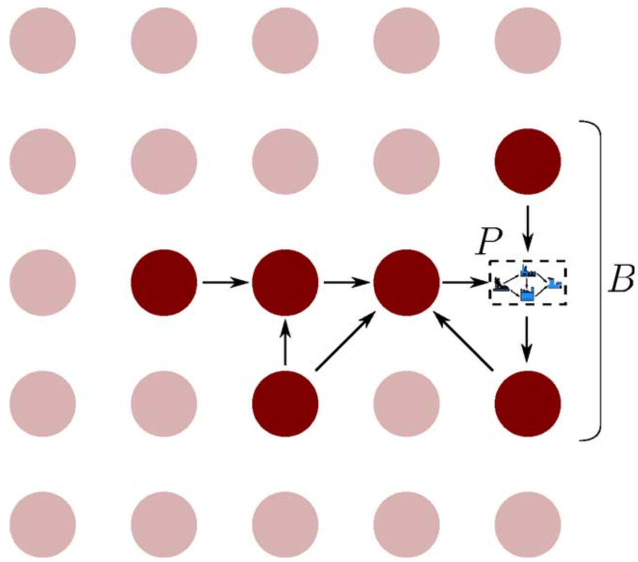

Figure 1. A complete life cycle is infinite due to the interconnections between industries and cannot be modeled feasibly using process LCA.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ability to formulate and solve large optimization problems, and on the increased availability and reliability of life cycle inventory data.[37] SPD methods now account for uncertainties in life cycle data,[38–40] consider the "triple bottom line" by combining economic, environmental, and social objective functions,[41–44] and account for spatial and temporal variations.[45,46] Advancements in sustainable supply chain design include techniques for making planning and logistics decisions[47–50] and designing for risk management.[51]

These advanced SPD methods rely on the latest developments in mathematical programming, optimization algorithms, and PSE modeling. However, the techniques used to perform a LCA and utilize the results within a design problem have not substantially changed since the MEIM was first developed. Process LCA[52] or, more commonly, a life cycle modeling tool based on process LCA,[53] is used to define the system boundary. The resulting inventory commonly excludes contributing processes past second or third order as well as a portion of the inputs, particularly those for which no life cycle data is available. The life cycle itself is modeled with fixed vectors of inputs and outputs that scale linearly.[54,55] Environmental interventions such as pollutants generated within the life cycle are likewise modeled with fixed "emissions factors."[56–58]

Figure 1 illustrates the scope of a typical process LCA utilized in SPD, indicated by the dark circles which represent life cycle processes. Each of these processes captured by LCA has at least one upstream process that provides material inputs, one that provides energy or fuel, a process that produced the equipment being used, the manufacturing and construction processes that produced the plant or factory itself, and so forth. The full life cycle more closely resembles the entire system shown in Figure 1 (both dark and light circles), in which the life cycle processes captured by process LCA are indicated by dark circles and the neglected processes by light circles. Process LCA as used in SPD applications, thus, excludes potentially significant processes from the inventory and chronically under-represents environmental interventions and impacts. The error in life cycle impact accounting incurred by using process LCA rather than a more comprehensive inventory technique is estimated to be 20–50%.[59] Hybrid LCA methods[60,61] which expand the boundary to the national or planetary scale have been developed and applied in the field of LCA, but thus far have not been applied to SPD.

The assumption of fixed emissions factors used to model a process LCA inventory is valid for applications that deal with fixed systems, including straightforward LCA. When a system involves variables, for instance in a design problem, the emissions factors are in reality *dependent on the design solution*. The dependence is caused by avoided production of coproducts utilized in the life cycle and the aggregated nature of the life cycle inventory and economy scale models. Avoided production is the situation where an input to a process is displaced by an equivalent by-product of another process, thereby avoiding the production of the original input. For example, the production and sale of lignin electricity as a by-product of cellulosic ethanol production induces avoided production of grid electricity. Avoided production results in changes in the emissions factors for the affected life cycle process(es), and is particularly significant for large-scale design problems such as those in Refs. 45 and 62. Failing to account for variable emissions factors results in inaccurate life cycle models which in turn cause potentially suboptimal or infeasible process designs.

The level of aggregation in the life cycle and economy models can also lead to inaccurate emissions factors. "Processes" modeled in life cycle inventories do not represent individual processes or plants but rather aggregates of several production technologies for one type of process in a given region. Industrial sectors in economic models are even more highly aggregated, generally by the type of commodity each sector produces. In the case that only some of the production technologies in a life cycle process or industrial sector are utilized by the system of interest, these production technologies may be modeled in greater detail at a smaller scale, necessitating disaggregation of the larger scale models. Disaggregation separates system components into two portions, one which is modeled at a smaller scale and the remainder of the original component, which is modeled at the original scale.[63,64] Both technological interventions and environmental interventions, represented by emissions factors, are disaggregated, resulting in emissions factors for large scale models that are dependent on smaller scale models and in particular on engineering design variables.

As a step toward overcoming these shortcomings, the process to planet (P2P) framework[63] integrates models of individual processes, life cycle activities and economies to capture the full life cycle. This framework combines the large scope of national and global economic models at the economy scale, with relatively accurate life cycle activity models at the value chain scale, and highly accurate fundamental models at the equipment scale. This work focuses on practical aspects of the P2P framework by applying it to a SPD problem. Benefits of this framework over the existing SPD approach are demonstrated by application to a corn ethanol production system that is modeled and optimized for minimum carbon dioxide emissions at the equipment, value chain, and economy scales. The equipment scale consists of fundamental linear and nonlinear models of ethanol manufacturing, the value chain scale includes models obtained from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) life cycle model, and the economy scale model captures the U.S. economy.

Table 1. Submatrices that Make Up the P2P Transactions Matrix $\underline{\bar{\mathbf{X}}}(\{\mathbf{z}\})$

Economy model $\bar{\mathbf{I}}-\bar{\mathbf{A}}^*(\{\mathbf{z}\})$	Value chain upstream cutoffs $-\underline{\mathbf{X}}_u(\{\mathbf{z}\})$	Equipment-economy upstream cutoffs $-\mathbf{X}_u^E(\{\mathbf{z}\})$
Value chain downstream cutoffs $-\underline{\mathbf{A}}_d(\{\mathbf{z}\})$	Value chain model $\underline{\mathbf{X}}^*(\{\mathbf{z}\})$	Equipment-value chain upstream cutoffs $-\mathbf{X}_u^V(\{\mathbf{z}\})$
Equipment-economy downstream cutoffs $-\mathbf{A}_d^E(\{\mathbf{z}\})$	Equipment-value chain downstream cutoffs $-\mathbf{X}_d^V(\{\mathbf{z}\})$	Equipment scale models $\mathbf{X}(\{\mathbf{z}\})$

While conventional SPD studies claim to design processes within the process' life cycle, in reality the life cycle being considered is that of the primary product. Significant inputs such as process equipment, maintenance services, construction of plants, and others are rarely included in the inventory. A probable reason for the exclusion of process equipment and other inputs is the lack of life cycle inventory data for their production. The P2P framework offers a convenient way to include neglected flows without accurate life cycle inventory data: the flows are modeled as inputs originating in the economy. The only data required is the purchase cost of the input flows and knowledge about in which economic sector the inputs were produced.

The rest of the article is organized as follows. First, a brief review of current SPD techniques is given. The next section gives an overview of the multiscale P2P modeling framework developed in Ref. 63. In the same section, an optimization formulation of a SPD problem utilizing the P2P modeling framework is compared to an optimization formulation of the same problem using conventional SPD methods. The following section gives details of the corn ethanol production system case study, states the optimization problem using the P2P framework and contains results, discussion, and significant findings of the case study. Finally, the article is concluded with a discussion of future work in this area, including planned extensions to the existing framework.

Existing Methods for SPD

As discussed in the Introduction, SPD differs from traditional process design in its expanded system boundary. The boundary of a purely profit-oriented design problem includes only the system of interest. The profitability of processing stages upstream and downstream of the process of interest is of no concern, as it has no effect on the primary process' profitability except indirectly through input prices. In contrast, the environmental performance of upstream and downstream processes has a large effect on the environmental performance of the process of interest. When inputs are purchased from upstream processes and products are sold to downstream processes, the process of interest is assigned responsibility for the environmental impacts incurred in the production of inputs and the further processing of its products.[65] SPD, therefore, relies on the system boundary shown in Figure 1, which includes the system of interest (within the dotted rectangle) and its life cycle (dark and light circles).

Given the system shown in Figure 1, a generic SPD problem consists of optimizing the system within the dotted rectangle with respect to both economic and environmental objectives[66]

$$\begin{aligned} &\text{maximize } Z_1; \qquad \text{minimize } Z_2 \\ &\text{subjectto } f(z) \geq 0; \qquad Z_1 = Pg(z); \qquad Z_2 = Bh(z) \end{aligned} \tag{1}$$

$f(z)$ represents process models derived from fundamental engineering knowledge, empirical data, or holistic guidelines; these models constrain the design variables z to feasible values. The function $g(z)$ represents quantities involved in calculating a process' cash flow, including input and output amounts, annual hours of labor, process equipment parameters, and so forth; these quantities are scaled by price data P to calculate the economic objective function Z_1. In a similar manner, the function $h(z)$ represents quantities that are scaled by environmental intervention data B to calculate the environmental objective function Z_2.

P and B are quantified at different scales: P consists of price data for inputs and outputs of the system of interest, while B consists of data on emissions and environmental impacts for the system of interest and its life cycle. In practice, B consists of emissions factors, assumed to be fixed and linearly scalable, obtained from life cycle inventory data available from a commercial database or LCA modeling software.

The exact forms of Z_1 and Z_2 vary from problem to problem. Process or production cost[67] and net present value[68] are commonly used economic objective functions. Early SPD studies frequently used multiple environmental objectives, including global warming potential (GWP), water pollution, and acidification.[31–34] The majority of more recent SPD studies consider single environmental objectives, with the most common being Eco-Indicator 99,[69–73] greenhouse gas emissions,[44,62,74–77] and GWP.[78,79] Multiobjective optimization techniques are used to locate designs that offer compromises between the economic and environmental objectives[80–86] and are occasionally applied to identify trade-offs between multiple environmental objectives.[87,88]

P2P Framework for SPD

Overview of P2P framework

Exchanges within a P2P production system are represented with the P2P transactions matrix $\underline{\bar{\mathbf{X}}}(\{\mathbf{z}\})$, defined as

$$\underline{\bar{\mathbf{X}}}(\{\mathbf{z}\}) = \begin{bmatrix} \bar{\mathbf{I}}-\bar{\mathbf{A}}^*(\{\mathbf{z}\}) & -\underline{\mathbf{X}}_u(\{\mathbf{z}\}) & -\mathbf{X}_u^E(\{\mathbf{z}\}) \\ -\underline{\mathbf{A}}_d(\{\mathbf{z}\}) & \underline{\mathbf{X}}^*(\{\mathbf{z}\}) & -\mathbf{X}_u^V(\{\mathbf{z}\}) \\ -\mathbf{A}_d^E(\{\mathbf{z}\}) & -\mathbf{X}_d^V(\{\mathbf{z}\}) & \mathbf{X}(\{\mathbf{z}\}) \end{bmatrix} \tag{2}$$

Submatrices on the diagonal model exchanges between components at a single scale, and off-diagonal submatrices model exchanges between scales, called cutoff flows. Descriptions of the submatrices in $\underline{\bar{\mathbf{X}}}(\{\mathbf{z}\})$ are given in Table 1, with details in Ref. 63. In Eq. 2, an overbar, $\bar{X}$, indicates an economy scale model, an underbar $\underline{X}$ indicates value chain scale models, and no bars indicates equipment scale models. A superscript star indicates models that have been disaggregated.

Each column of $\underline{\bar{\mathbf{X}}}(\{\mathbf{z}\})$ is a multiscale input–output vector for one component in the P2P system. Columns on the left describe economic sectors, columns in the middle describe value chain activities, and columns on the right describe equipment scale processes. Each row represents the production and consumption of a commodity (top rows), value chain product (center rows), or equipment scale product (bottom rows). The differences between system components and product exchanges modeled at different scales are the level of aggregation and the type of model used to represent components. Economy scale models are highly aggregated, value chain models are somewhat aggregated, and equipment scale models are completely disaggregated. Economy and value chain models are derived from empirical data, do not involve design variables and are assumed to be linearly scalable, while equipment scale models are derived from fundamental engineering knowledge, are generally nonlinear with design variables, and can benefit from economies of scale. The $(\{\mathbf{z}\})$ after each submatrix in Eq. 2 indicates that equipment scale design variables appear throughout the P2P system; this is due to the disaggregation of the larger scale models. These variables may be continuous, integer-valued or both, depending on whether the equipment scale models are parametric or represent superstructures of potential unit operation configurations. The design variables are constrained by fundamental engineering models for each equipment scale process n

$$\left\{ \begin{array}{c} \mathbf{h}_1(\mathbf{z}_1) \geq \mathbf{0} \\ \vdots \\ \mathbf{h}_N(\mathbf{z}_N) \geq \mathbf{0} \end{array} \right\} \tag{3}$$

which are alternatively written as

$$\mathbf{H}(\{\mathbf{z}\}) \geq 0 \tag{4}$$

Two additional components of the P2P modeling framework are the scaling vector $\underline{\bar{\mathbf{s}}}$

$$\underline{\bar{\mathbf{s}}} = \begin{bmatrix} \bar{\mathbf{s}} \\ \underline{\mathbf{s}} \\ \mathbf{s} \end{bmatrix} \tag{5}$$

and final demand vector $\underline{\bar{\mathbf{f}}}$

$$\underline{\bar{\mathbf{f}}} = \begin{bmatrix} \bar{\mathbf{f}} \\ \underline{\mathbf{f}} \\ \mathbf{f} \end{bmatrix} \tag{6}$$

$\underline{\bar{\mathbf{s}}}$ is a vector that scales the level of production of each component in the P2P system such that the final demand $\underline{\bar{\mathbf{f}}}$ on the entire system is met, as shown in Eq. 12. In general, the elements of $\underline{\bar{\mathbf{s}}}$ are variable; however, in the case that the capacity of one or more equipment scale processes is already fixed, the corresponding elements of $\underline{\bar{\mathbf{s}}}$, $\mathbf{s}$, can be constants. For processes with variable capacity, $\mathbf{s}$ can contain nonlinear elements such as $s^{0.7}$ to capture the effects of economies of scale. The value chain and economy scale elements of $\underline{\bar{\mathbf{s}}}$ are always linear and, along with $\{\mathbf{z}\}$ and any variable elements of $\mathbf{s}$, are decision variables in the design problem. $\underline{\bar{\mathbf{f}}}$ is a vector of constants. The value chain and economy scale elements in $\underline{\bar{\mathbf{f}}}$ will generally be zero; only the final demand on the processes of interest will be nonzero.

Equation 2 models product exchanges within the P2P system. The final component of the P2P modeling framework, the P2P interventions matrix, captures exchanges between the P2P system and the environment called environmental interventions

$$\underline{\bar{\mathbf{B}}}(\{\mathbf{z}\}) = \left[\bar{\mathbf{B}}^*(\{\mathbf{z}\}) \quad \underline{\mathbf{B}}^*(\{\mathbf{z}\}) \quad \mathbf{B}(\{\mathbf{z}\}) \right] \tag{7}$$

The equipment scale interventions matrix $\mathbf{B}(\{\mathbf{z}\})$ relates the unit operation variables for each process to interventions generated by that process. For instance, one column of $\mathbf{B}(\{\mathbf{z}\})$ could model carbon dioxide and nitrous oxide emissions resulting from fuel combustion in a combined heat and power (CHP) unit. The amount of each type of emission produced would depend on the operating parameters of the CHP unit: one or more variables in $\{\mathbf{z}\}$. Similarly, the value chain scale interventions matrix $\underline{\mathbf{B}}(\{\mathbf{z}\})$ models average interventions generated by the production technologies at that scale. Nonlinearities and design variables appear in $\underline{\mathbf{B}}(\{\mathbf{z}\})$ through the disaggregation process; the original matrix $\underline{\mathbf{B}}$ contains only linear elements or "emissions factors". The economy scale interventions matrix $\bar{\mathbf{B}}^*(\{\mathbf{z}\})$ likewise contains nonlinearities due to the disaggregation process.

A SPD problem can now be stated, using the P2P modeling framework, as a nonlinear program with multiple possible objective functions. The economic objective function Z_1 remains unchanged: although the P2P modeling framework captures a more comprehensive system compared to conventional SPD, only the economics of the equipment scale are of interest in typical SPD problems. Z_1 is defined as

$$Z_1 = \sum_{n=1}^{N} Z_{1n}(\{\mathbf{z}_n\}) \tag{8}$$

with the economic objective for each process n given by

$$Z_{1n} = \mathbf{p}(\{\mathbf{z}\}) \cdot \mathbf{s}, \qquad \forall n \in N \tag{9}$$

The environmental objective function for intervention r

$$\underline{\bar{Z}}_{2r} = \underline{\bar{\mathbf{B}}}_r(\{\mathbf{z}\}) \cdot \underline{\bar{\mathbf{s}}} \tag{10}$$

contains interventions generated at the economy scale as well as at the process and value chain scales captured by

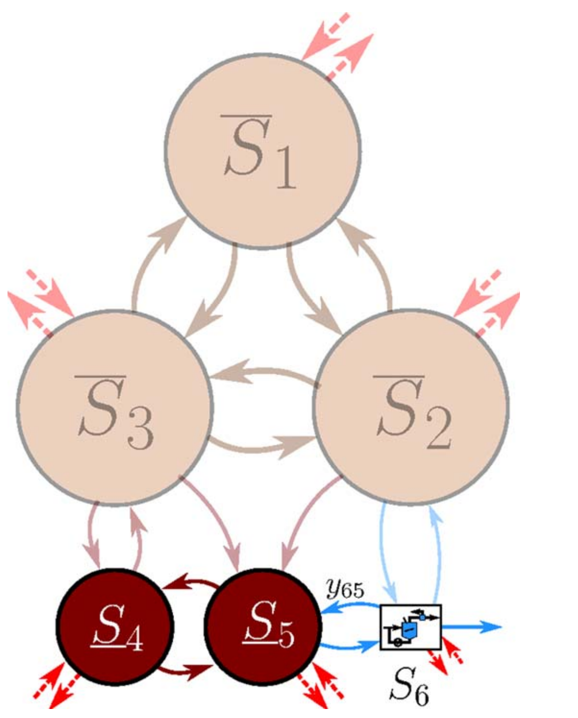

Figure 2. Conventional SPD accounts only for the process(es) of interest (S_6) and select processes in the value chain ($\underline{S}_4$ and $\underline{S}_5$).

Feedback to the value chain (y_{65}) is rarely accounted for, and all exchanges with the economy ($\bar{S}_1$, $\bar{S}_2$, and $\bar{S}_3$) are neglected. The P2P approach for SPD accounts for all the components and exchanges shown in this figure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

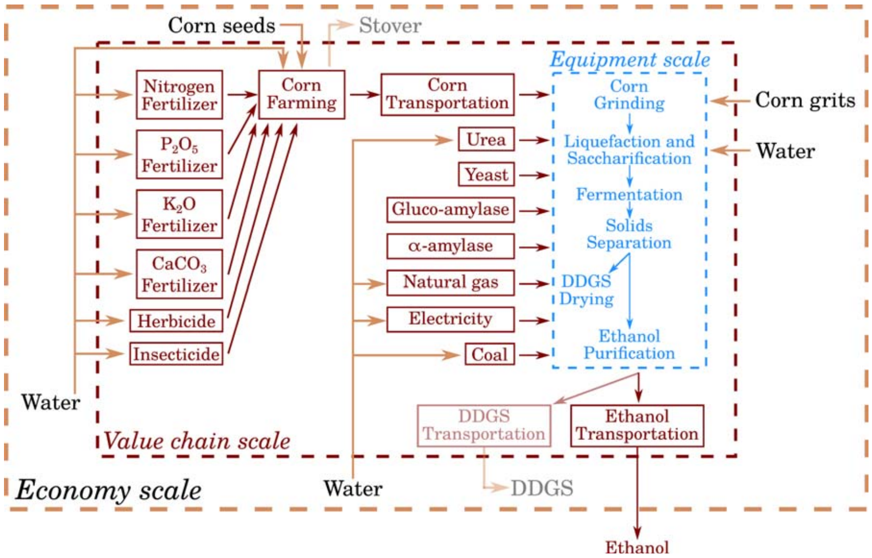

Figure 3. P2P model of the dry-grind corn ethanol process and its value chain, showing upstream connections to the economy.

Downstream connections to the economy that were not captured in the P2P model are shown in lighter colors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conventional SPD methods. To see this more clearly, Eq. 10 is rewritten as

$$\underline{Z}_{2r} = \bar{\mathbf{B}}_r^*(\{\mathbf{z}\})\cdot\bar{\mathbf{s}} + \underline{\mathbf{B}}_r^*(\{\mathbf{z}\})\cdot\underline{\mathbf{s}} + \mathbf{B}_r(\{\mathbf{z}\})\cdot\mathbf{s} \tag{11}$$

Emissions factors $\underline{\mathbf{B}}$ and $\bar{\mathbf{B}}$, which are fixed in conventional SPD, are now functions of unit operation design variables due to the disaggregation procedure.

The decision variables $\underline{\bar{\mathbf{s}}}$ and $\{\mathbf{z}\}$ are constrained with Eqs. 2 and 3. Equation 2 is used to define a set of system-wide balance equations on production and consumption

$$\begin{bmatrix} \bar{\mathbf{I}} - \bar{\mathbf{A}}^*(\{\mathbf{z}\}) & -\underline{\mathbf{X}}_u(\{\mathbf{z}\}) & -\mathbf{X}_u^E(\{\mathbf{z}\}) \\ -\underline{\mathbf{A}}_d(\{\mathbf{z}\}) & \underline{\mathbf{X}}^*(\{\mathbf{z}\}) & -\mathbf{X}_u^V(\{\mathbf{z}\}) \\ -\mathbf{A}_d^E(\{\mathbf{z}\}) & -\mathbf{X}_d^V(\{\mathbf{z}\}) & \mathbf{X}(\{\mathbf{z}\}) \end{bmatrix} \begin{bmatrix} \bar{\mathbf{s}} \\ \underline{\mathbf{s}} \\ \mathbf{s} \end{bmatrix} = \begin{bmatrix} \bar{\mathbf{f}} \\ \underline{\mathbf{f}} \\ \mathbf{f} \end{bmatrix} \tag{12}$$

The engineering process models in Eq. 4 further constrain the unit operation design variables $\{\mathbf{z}\}$ to feasible values.

Due to the integrated nature of the modeling framework, the decision variables are optimized *simultaneously* and *in the context of the entire system*. There are no sequential decisions, and each decision variable within the system affects all other decision variables regardless of scale.

Conventional SPD as a special case of P2P SPD

A conventional SPD problem was stated as an optimization formulation in Eq. 1. This problem is restated using the notation introduced in the P2P framework for SPD section as

$$\begin{aligned} &\text{maximize} \quad && Z_1 = \sum_{n=1}^{N} Z_{1n}(\{\mathbf{z}_n\}) \\ &\text{minimize} \quad && Z_2(\{\mathbf{z}\}, \underline{\mathbf{B}}, \mathbf{B}(\{\mathbf{z}\})) \\ &\text{subject to} \quad && \mathbf{H}(\{\mathbf{z}\}) \geq \mathbf{0} \end{aligned} \tag{13}$$

The economic objective function Z_1, which is identical to that used in the P2P SPD problem, is a function of price data $\mathbf{p}$ and the unit operation design variables $\{\mathbf{z}\}$. Z_2 is a function of the value chain and equipment scale environmental interventions matrices $\underline{\mathbf{B}}$ and $\mathbf{B}(\{\mathbf{z}\})$.

Conventional SPD problems such as the one stated in Eq. 13 consider only the equipment and value chain scales. Figure 2 compares the system boundary of a conventional SPD problem, in dark colors, to the boundary of the P2P modeling framework which encompasses the entire figure. Interactions with system components outside these scales, including inputs purchased from the economy and environmental interventions generated at the economy scale, are neglected. The design problem consists of choosing the optimal values of the unit operation design variables $\{\mathbf{z}\}$. As in the P2P framework, value chain activity models are empirical and fixed while process models are theoretical and are functions of unit operation variables. However, under conventional SPD no disaggregation of the value chain models is performed, thus all environmental interventions at the value chain scale are constant and independent of the design solution.

Case Study: Corn Ethanol Plant Design

The P2P framework was applied to the optimization of an ethanol production system consisting of a dry-grind corn ethanol plant and its life cycle, shown in Figure 3. Detailed engineering models for the ethanol production process were obtained from Ref. 89 and were implemented in the Python language. The original model was simplified from a MINLP superstructure optimization to a NLP parametric optimization with fifteen independent design variables, defined in Table 2. The process capacity was set by fixing the input rate of corn grain at 18 kg/s; only the operating conditions of the process were variable.

Empirical models for value chain activities were obtained from the GREET 2014 fuel life cycle model.[53] Environmental interventions for corn farming, corn transportation and ethanol transportation included vehicle production and distribution, and all activities included interventions from upstream fuel production and distribution activities back to fossil resource extraction. Data on the use of corn seeds in the corn farming activity was not included in GREET and was obtained from Ref. 90. Water consumption data was included in GREET for

Table 2. List and Description of Unit Operation Design Variables Present in the Ethanol Process Model

Variable	Description
z_1	Mass flow of water stream entering mixer after corn is ground
z_2	Mass flow of water (steam) stream entering jet
z_3	Temperature (C) of jet stream
z_4	Mass flow of water entering mixer upstream of fermentation vessel
z_5	Mass flow of urea entering mixer upstream of fermentation vessel
z_6	Temperature of stream entering mixer upstream of fermentation vessel
z_7	Fraction of water from the incoming stream that goes into the liquid stream outlet of the mechanical press
z_8	Fraction of water in the feed solids that goes to the vapor stream
z_9	Fraction of stream leaving solids separation that is discarded
z_{10}	Temperature of stream entering the beer column
z_{11}	Recovery of water in beer column
z_{12}	Recovery of water in rectification column
z_{13}	Split fraction of impure ethanol stream sent to rectification column
z_{14}	Split fraction of impure ethanol stream sent to adsorption operation
z_{15}	Fraction of water removed from the mixture entering the adsorption operation

all value chain activity models of interest except for the production and distribution of α-amylase, gluco-amylase, and yeast; the water use by these activities was therefore not included in the P2P model. Emissions associated with water supply and distribution were not included in GREET, thus water supply and distribution was modeled at the economy scale and water inputs were upstream cutoff flows originating at the economy scale. Default values were used for all GREET input parameters.

Both the ethanol plant and the corn farming activity provide by-products: the ethanol plant produces both ethanol and dried distiller's grains and solubles (DDGS) while the corn farming activity produces both corn grain and stover. For simplicity, these by-products are neglected. Were they to be included in the model, by-products would be modeled as downstream cutoff flows. The corn stover would be a value chain downstream cutoff and the DDGS an equipment-economy downstream cutoff. Figure 3 accordingly shows the flow of by-products back to the economy in lighter colors, indicating that these flows were not captured in the model.

The equipment and value chain scales were expanded to a P2P model by using the economy scale to model the production and distribution of inputs for which value chain scale data was not included in GREET 2014. For this case study, only the production and distribution of corn seeds, water and corn grits could not be modeled at the value chain scale. The P2P model includes these inputs as upstream cutoffs, flows from the economy to the value chain and the equipment scales.

Make and use tables (producer's prices, after redefinitions) from the 2002 benchmark input–output model developed by the U.S. Bureau of Economic Analysis were used to derive the economy scale model.[91] The tables were obtained at the detailed level of aggregation and originally consisted of 426 sectors and 430 commodities. The tables were transformed into square matrices by removing rest-of-world inputs and redistributing scrap production proportional to commodity production.[92] Sectors that were to be disaggregated and sectors that provided inputs to the value chain and the ethanol process were kept at the detailed level of aggregation, the most disaggregated level possible. Remaining sectors were aggregated to the summary level, with the exception of the four retail sectors (441000, Motor vehicle and parts dealers; 445000, Food and beverage stores; 452000, General merchandise stores; and 4A0000, Other retail) which were aggregated into a single retail sector. The resulting make and use tables were square and consisted of 74 sectors and 74 commodities. Environmental intervention data was obtained from Eco-LCA[93,94] and consisted of fossil CO_2 emissions per sector for the year 2002. Sources for price data used to model products purchased from the economy are listed in Table 3; prices for inputs not listed in Table 3 were obtained from online retailers. When prices for 2002 were not available for a product, the most current price was found and converted to 2002 levels using commodity-specific producer's price indexes obtained from the U.S. Bureau of Labor Statistics.[106] Further information can be found in Ref. 107.

No disaggregation was necessary at the value chain scale because the ethanol plant was modeled at the equipment scale rather than using GREET's default ethanol production model. The ethanol plant model, thus, did not overlap with any of the value chain activity models. As a result, the value chain technology and environmental interventions matrices were fixed instead of being functions of unit operation design variables. The economy scale was disaggregated to remove the value chain activities and the ethanol production process, resulting in parent sectors having emissions factors that were dependent on the equipment scale design variables.

Optimization formulation

The objective of the case study is to optimize the ethanol plant design for minimum life cycle CO_2 emissions. To compare the results of a conventional SPD optimization with the results of the proposed P2P approach, the ethanol production system was optimized under two CO_2 objective functions. The objective function that corresponds to the conventional SPD approach includes CO_2 emissions from the value chain and equipment scales

$$Z_{\text{conventional}}(\{\mathbf{z}\}) = \underline{\mathbf{b}} \cdot \underline{\mathbf{s}} + \mathbf{b}(\{\mathbf{z}\}) \cdot \mathbf{s} \tag{14}$$

The objective function that corresponds to the proposed P2P approach includes CO_2 emissions from the economy scale as well as the value chain and equipment scales

Table 3. Sources for Price Data Used in the P2P Ethanol Production System Model

Product	Source(s)
Fuels (all)	95–99
Electricity	100
Fertilizer	101
Herbicide and insecticide (approx.)	102
Corn seed	90
Corn grits	103
α-amylase	104
Gluco-amylase	104
Yeast	104
Urea	104
Water	105

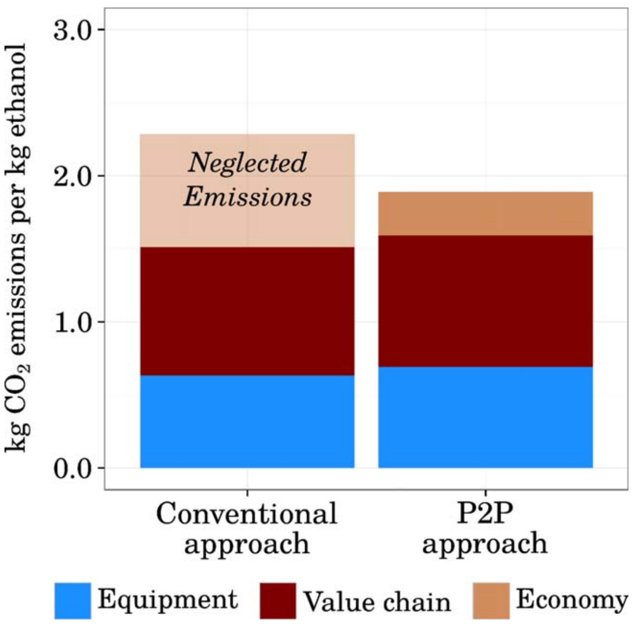

Figure 4. Results of the ethanol production system case study.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$Z_{\mathrm{P2P}}(\{\mathbf{z}\}) = \bar{\mathbf{b}}^{*}(\{\mathbf{z}\}) \cdot \bar{\mathbf{s}} + \underline{\mathbf{b}} \cdot \underline{\mathbf{s}} + \mathbf{b}(\{\mathbf{z}\}) \cdot \mathbf{s} \tag{15}$$

Plant economics are not considered as an objective function in this case study; as discussed previously, the economically optimal plant designs will be identical under the conventional and P2P approaches.

The P2P model contains two sets of constraints. The first set consists of the P2P product balance, expressed as

$$\bar{\underline{\mathbf{X}}}(\{\mathbf{z}\})\bar{\underline{\mathbf{s}}} = \bar{\underline{\mathbf{f}}} \tag{16}$$

In Eq. 16, the equipment scale element of $\bar{\underline{\mathbf{f}}}$ was set equal to the mass flow rate of ethanol produced by the ethanol process. This ensured that the scaling factor for the ethanol process was always equal to 1, and nonlinear effects of scaling the ethanol process did not need to be accounted for in the P2P model.

The P2P scaling vector $\bar{\underline{\mathbf{s}}}$ was calculated by inverting the P2P transactions matrix as follows

$$\bar{\underline{\mathbf{s}}} = \bar{\underline{\mathbf{X}}}^{-1}(\{\mathbf{z}\})\bar{\underline{\mathbf{f}}} \tag{17}$$

This has the effect of reducing computational time by reducing the number of decision variables in the optimization, as the elements of $\bar{\underline{\mathbf{s}}}$ are calculated from and, therefore, are entirely dependent on the values of $\{\mathbf{z}\}$. Inverting $\bar{\underline{\mathbf{X}}}(\{\mathbf{z}\})$ was possible due to the corn stover and DDGS by-products being neglected. Had these by-products been included, the P2P transactions matrix would be rectangular rather than square. Calculating $\bar{\underline{\mathbf{s}}}$ via Eq. 17 would still be possible, but an additional allocation step would be necessary to convert the rectangular transactions matrix to a square matrix. In the case that inverting the P2P transactions matrix is not possible, Eq. 16 would remain as constraints in the optimization problems and the elements of $\bar{\underline{\mathbf{s}}}$ would remain decision variables.

The second set of constraints are those imposed on the unit operation design variables by the ethanol process models, expressed as

$$\{\mathbf{h}_{1,\ldots,173}(z_1,\ldots,z_{15}) \geq \mathbf{0}\} \tag{18}$$

Results and discussion

The optimization problem contained 15 continuous decision variables ($z_1,\ldots,z_{15}$), 5 equality constraints and 63 inequality constraints. The ALGENCAN optimizer in the pyOpt package[108] was used to optimize the P2P model under both the conventional SPD objective function of Eq. 14 and the P2P objective function of Eq. 15, resulting in two optimal designs for the ethanol plant. Although an economic objective function was not considered in this case study, the different environmentally optimal designs indicate that different trade-offs between economics and the environment exist under the conventional and P2P approaches. Figure 4 shows CO_2 emissions from the equipment, value chain and economy scales of the P2P model for both designs.

The process design obtained using the conventional approach to SPD has lower *equipment and value chain* emissions. However, this comes at the expense of much higher emissions at the economy scale, which are neglected under the conventional approach. Neglecting emissions attributable to the system of interest defeats the purpose of taking a life cycle approach to design. The process design obtained using the P2P approach has lower *total system-wide* emissions. This result was expected based on the nature of the different objective functions used in each approach, as discussed in the Optimization formulation section. The P2P process design has total system-wide emissions that are 17% lower than emissions for the conventional process design.

Optimal values of the unit operation design variables for the conventional and P2P process designs are given in Table 4, with variables that changed under the different approaches indicated in bold. The amounts of variable process inputs for the two designs are given in Table 5. Variables z_{13} and z_{14} control the fraction of the ethanol-water stream going through each of the three drying unit operations. In the conventional process design, 7.8% by mass of the ethanol/water stream is sent to the rectification column (z_{13}), 27% to corn grits adsorption (z_{14}), and 65.2% ($1-z_{13}-z_{14}$) to the molecular sieve operation. In the P2P process design, 37% of the ethanol/water stream is sent to rectification, 0.1% to adsorption (the minimum allowable by the process model), and 62.9% to the

Table 4. Values of Unit Operation Design Variables for the Two Process Designs

Variable	Units	Optimal Values	
		Conventional Approach	P2P Approach
z_1	kg/s	0.00	0.00
z_2	kg/s	1.04	1.04
z_3	°C	120.0	120.0
z_4	kg/s	8.17	8.17
z_5	kg/s	0.086	0.086
z_6	°C	25.0	25.0
z_7	–	0.92	0.92
z_8	–	0.97	0.97
z_9	–	0.011	0.011
z_{10}	°C	94.6	94.6
z_{11}	–	0.20	0.20
z_{12}	–	0.14	0.14
$\mathbf{z_{13}}$	–	**0.078**	**0.37**
$\mathbf{z_{14}}$	–	**0.27**	**0.001**
$\mathbf{z_{15}}$	–	**0.92**	**0.08**

Variables without specified units are unitless. Differences between the two designs are indicated in bold.

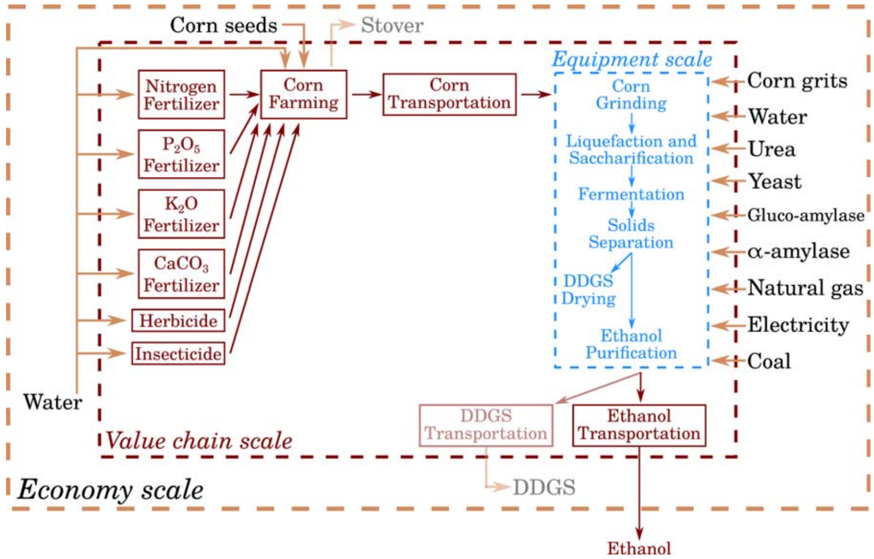

Figure 5. Alternative P2P model of the dry-grind corn ethanol process and its value chain, showing upstream connections to the economy.

Downstream connections to the economy that were not captured in the model are shown in lighter colors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular sieve. This change seems counter-intuitive at the equipment scale due to the high energy intensity of rectification; as seen in Table 5, the P2P process design consumes more energy and, therefore, produces more equipment scale CO_2 emissions than the conventional design. However, when emissions from the entire P2P system are considered in the objective function, the environmental effect of purchasing corn grits from the economy outweighs the effect of an increase in process energy consumption, and the adsorption unit becomes virtually unused in favor of the rectification column and molecular sieve. This is an example of a design decision that shifts emissions outside the analysis boundary, resulting in a decrease in emissions within the boundary but a net increase in emissions outside the boundary.

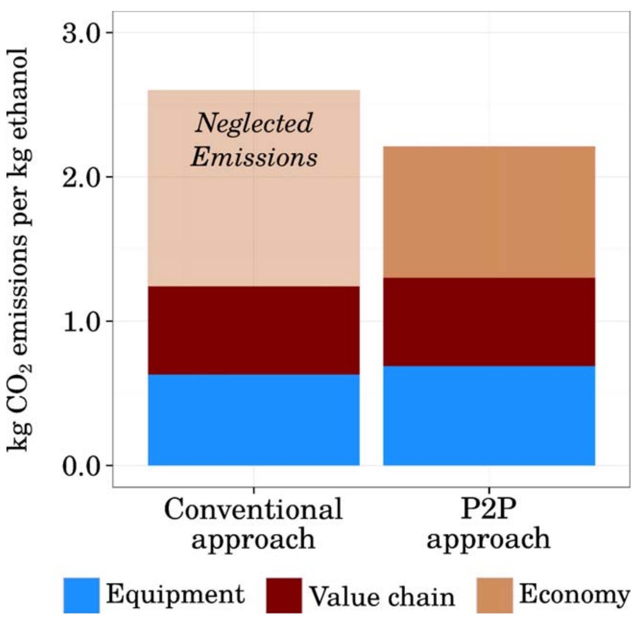

Figure 6. Results of the ethanol production system case study obtained using the alternative P2P model.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Alternative P2P model of the ethanol production system

GREET is a process based life cycle modeling tool that is more detailed and comprehensive than many life cycle models, particularly in accounting for greenhouse gases. As discussed in the previous sections, when GREET is used at the value chain scale there are relatively few remaining inputs that must be captured at the economy scale. However, modeling a life cycle entirely at the value chain scale is not practical for all systems. The time and effort required to construct a comprehensive process-based inventory is quite large, and for any new technologies it is unlikely that the necessary data will be readily available. In this section, an alternative P2P model of the ethanol production system is developed, based on the assumption that reliable value chain scale data was not available for the production of several ethanol process inputs. For this particular case study, this assumption is completely artificial, but for the majority of SPD problems it is unlikely that a value chain scale model with the level of detail and comprehensiveness of GREET will be available. In fact, even GREET has a very limited scope for environmental impacts other than greenhouse gases.

The alternative P2P model, shown in Figure 5, includes fewer value chain activity models. Several process inputs that

Table 5. Summary of Variable Process Input Amounts for the Two Optimal Process Designs

Input	Conventional approach	P2P approach	Units
Water	1.13	1.13	kg/s
Process energy	6.568×10^4	7.168×10^4	kJ/s
α-amylase	9.567×10^{-3}	9.567×10^{-3}	kg/s
Gluco-amylase	2.297×10^{-2}	2.297×10^{-2}	kg/s
Urea	8.634×10^{-2}	8.634×10^{-2}	kg/s
Corn grits	7.372	0.124	kg/s

Corn grain and yeast were modeled as fixed flow rates and are not shown here.

Table 6. Values of Unit Operation Design Variables for the Optimal Process Designs Obtained from the Alternative P2P Model

Variable	Units	Optimal values: Conventional approach	Optimal values: P2P approach
z_1	kg/s	0.00	0.00
$\mathbf{z_2}$	**kg/s**	**1.04**	**0.90**
$\mathbf{z_3}$	**°C**	**120.0**	**300.0**
$\mathbf{z_4}$	**kg/s**	**8.17**	**8.31**
z_5	kg/s	0.086	0.086
z_6	°C	25.0	25.0
z_7	–	0.92	0.92
z_8	–	0.97	0.97
z_9	–	0.011	0.011
z_{10}	°C	94.6	94.6
z_{11}	–	0.20	0.20
z_{12}	–	0.14	0.14
$\mathbf{z_{13}}$	–	**0.078**	**0.37**
$\mathbf{z_{14}}$	–	**0.27**	**0.001**
$\mathbf{z_{15}}$	–	**0.92**	**0.08**

Variables without specified units are unitless. Differences between the two designs are indicated in bold.

Table 7. Summary of Variable Process Inputs for the Optimal Process Designs Obtained Using the Alternative P2P Model

Input	Conventional Approach (Alternative Model)	P2P Approach (Alternative Model)	Units
Water	1.13	0.99	kg/s
Process energy	6.568×10^4	7.171×10^4	kJ/s
α-amylase	9.567×10^{-3}	9.497×10^{-3}	kg/s
Gluco-amylase	2.297×10^{-2}	2.280×10^{-2}	kg/s
Urea	8.634×10^{-2}	8.634×10^{-2}	kg/s
Corn grits	7.372	0.124	kg/s

Corn grain and yeast are not shown.

were previously modeled as equipment-value chain upstream cutoffs (process energy, water, α-amylase, gluco-amylase, yeast, urea, and corn grits) are now modeled as equipment-economy upstream cutoffs. In doing so, the alternative model takes advantage of the comprehensive economy scale model and reduces the amount of data needed to build the P2P model. When inputs are modeled as upstream cutoffs, the only necessary data are the physical magnitude of the flow and market price data to convert the flow from physical to monetary units. The production of upstream cutoffs is then captured by the economic input–output model, rather than the value chain model for which additional data on material and energy inputs to production are required. Replacing equipment-value chain upstream cutoffs with equipment-economy upstream cutoffs therefore reduces the size of the P2P model, as fewer value chain activity models are required. However, although the alternative P2P model requires less data to build, it is likely to be less accurate than the original P2P model. The economy scale model is much coarser than the equivalent value chain model and is, therefore, likely to have greater uncertainty than the original P2P model of the previous section.

The alternative P2P model, like the original model, was optimized under both the conventional SPD approach and the P2P approach. The optimization formulation stated previously remains unchanged except for the dimensions of the P2P transactions matrix, final demand vector, and scaling vector, all of which are smaller compared to the original model due to the reduced value chain model size. The original P2P transactions matrix was 91 × 91, and the alternative P2P transactions matrix is 84 × 84. Figure 6 shows equipment, value chain and economy CO_2 emissions for conventional, and P2P process designs obtained using the alternative P2P model.

Overall conclusions of the original case study do not change when the alternative P2P model is optimized: the P2P approach still results in a significant (15%) reduction in CO_2 emissions compared to the conventional approach. Economy scale emissions for both the conventional and P2P designs are significantly higher under the alternative model, due to this model containing more equipment-economy upstream cutoff flows. This increases the economic activity necessary to supply inputs and, as a result, increases emissions produced by the economy.

Table 6 gives the optimal design variable values for the conventional and P2P process designs under the alternative model. The conventional process designs obtained using the original and alternative models are identical. However, the P2P process designs are different under the two models, although the difference (variables z_2 through z_4) represents a

Table 8. Disaggregating the EIO Model Resulted in Changes in Emissions Factors (Elements of the Environmental Interventions Matrix) for Parent Sectors

Sector	Change in Emissions Factors, $\bar{b}_j - \bar{b}_j^*(\{\mathbf{z}\})$ (kg CO_2/\$): Conventional	P2P
Original P2P Model		
Grain farming	6.60×10^{-4}	6.60×10^{-4}
Coal mining	7.68×10^{-6}	8.39×10^{-6}
Electric power generation, transmission and distribution	1.50×10^{-5}	1.64×10^{-5}
Natural gas distribution	1.01×10^{-4}	1.01×10^{-4}
Other basic organic chemical manufacturing	8.56×10^{-4}	1.04×10^{-3}
Fertilizer manufacturing	4.59×10^{-3}	4.59×10^{-3}
Pesticide and other agricultural chemical manufacturing	7.42×10^{-5}	7.42×10^{-5}
Rail transportation	5.39×10^{-4}	5.39×10^{-4}
Truck transportation	-8.93×10^{-4}	-8.85×10^{-4}
Alternative P2P Model		
Grain farming	-4.44×10^{-4}	-4.44×10^{-4}
Other basic organic chemical manufacturing	8.13×10^{-4}	9.97×10^{-4}
Fertilizer manufacturing	4.59×10^{-3}	4.59×10^{-3}
Pesticide and other agricultural chemical manufacturing	7.42×10^{-5}	7.42×10^{-5}
Rail transportation	5.39×10^{-4}	5.39×10^{-4}
Truck transportation	-9.77×10^{-4}	-9.76×10^{-4}

relatively small effect on the overall process design. Variables z_2 through z_4 controlled the corn cooking step prior to fermentation. The decrease in z_2 and increase in z_3 implies that a smaller quantity of higher temperature steam was used to cook the corn prior to fermentation in the P2P design compared to the conventional design. The total amount of water added to the corn prior to fermentation is unchanged: the increase in z_4 (water added to mixer just upstream of the fermentation vessel) is the same magnitude as the decrease in z_3 (steam used to cook the corn). However, as seen in Table 7, the amount of water added elsewhere in the process has decreased as a result of the changing design variables, as the total water input to the process is reduced in the P2P process design.

Table 7 compares amounts of ethanol process inputs for the conventional and P2P process designs obtained using the alternative model. The P2P design under the alternative model has drastically decreased consumption of corn grits, just as the P2P design under the original model did. Consumption of water and enzymes has also decreased, and consumption of process energy has increased. These changes have the effect of reducing the economic activity compared to the conventional process design and both of the process designs obtained using the original P2P model.

As discussed in the P2P framework for SPD section and in Ref. 63, the disaggregation procedure caused the economy-scale emissions factors to become dependent on the plant design. Table 8 shows that the disaggregation procedure can either increase or decrease a sector's emissions factors; the direction of change is determined by the constituent activity or process and whether that constituent has higher or lower emissions relative to the rest of the parent sector.

Conclusions and Future Work

Based on the results of this case study, it can be concluded that the larger P2P analysis boundary reduces the chance of unintended harm caused by shifting of emissions and other environmental impacts outside the smaller system boundary used in conventional SPD. That this result is apparent even for this relatively small-scale design problem holds promise for future, larger-scale applications of the P2P modeling framework. For larger design problems such as regional supply chains, the effect of including emissions from the economy scale and the resulting net savings in emissions are both expected to be more significant than for this case study. This study shows that in addition to using sophisticated optimization methods, as is quite common in current work, it is also critical to define the proper system boundary and objective function to obtain the true optimum result.

The results of this case study represent designs that do not account for the production and sale of by-products. Including the sale of by-products will reduce the total emissions for all designs due to avoided production. This is because displacement in a P2P model is captured throughout the entire economy, thus, there will likely be significant indirect effects from accounting for displacement effects. Therefore, when by-products of the ethanol system are included in the P2P model, the conclusions of this case study are not expected to change.

While the P2P modeling framework improves on the limited boundary of process LCA, it fails to capture the effects of international imports and exports. Outsourced manufacturing and processing stages have become extremely common, resulting in situations where one nation's consumption results in another nation's environmental impacts. While the P2P model used in this work did not go beyond the national scale, the P2P framework is capable of including models at larger scales such as a global scale or world input–output model[109,110] that can either replace the national scale EEIO model or be integrated into the framework as a fourth scale.

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