Ecosystems as Unit Operations for Local Techno-Ecological Synergy: Integrated Process Design with Treatment Wetlands

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Despite the critical importance of ecological systems for sustaining all chemical and manufacturing processes, process design has kept nature outside its system boundary. Recent efforts for sustainable process design aim to reduce environmental impact, but no design method considers the capacity of ecosystems to supply the goods and services that are needed to sustain a process. Overcoming this deficiency of conventional process design is essential to transform the chemical industry into an activity that respects ecological constraints and results in a net positive societal impact. As an important step toward meeting this goal, this work expands the boundary of process design to include ecosystems as unit operations in traditional design. Similar to tasks performed by conventional unit operations, ecological processes perform ecosystem functions resulting in goods and services required by the technological system. The goal behind designing integrated techno-ecological process flowsheets is to balance the ecosystem service demand of technological systems with the ecosystem service supply of ecological systems. Systems are optimized to balance the demand and supply subject to unit operation level constraints of technological and ecological systems, and interactions between detailed process level variables and ecological variables are explored. The Techno-Ecological Synergy (TES) Design method is developed and applied to a biofuel production system, considering ecosystem services like water provisioning and water quality regulation provided by wetland ecosystems. Comparing the integrated TES design with conventional techno-centric design shows that TES design can result in net positive impact manufacturing: a case where the ecosystem service supply is equal to or exceeds the demand, with little or no compromises in process profitability. These results should encourage close integration between technological and ecological systems while designing sustainable processes, and identify many challenges for developing TES of individual processes and across the life cycle. *AIChE J*, 64: 2390–2407, 2018
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Introduction

Over the last couple of decades, several methods have been developed for designing chemical processes to meet the goal of minimizing ecological impact. Traditional process design methods include Douglas' hierarchical design procedure,[1] process integration tools such as mass and heat exchanger networks to improve energy and material efficiency,[2,3] process intensification,[4] waste minimization approaches,[5] and use of end of pipe solutions for reducing emissions from processes. Within the process integration domain, several design tools are being applied to design wastewater reduction and water conservation networks,[6] and waste interception networks with the goal of conserving resources and preventing pollution.[7] While most of these design methods focused primarily on improving and optimizing the performance of single equipment units or larger chemical plants, development and advances within the Process Systems Engineering (PSE) domain has allowed the expansion of problem boundary to larger temporal and spatial scales.

Methods such as life cycle assessment[8,9] and footprint analysis[10] have enabled expansion of the boundary of traditional process design methodologies to consider environmental impacts upstream and downstream of processes. Several efforts have combined life cycle assessment with process design and optimization with application to individual processes[11,12] and for the design of biofuel supply chains.[13] Hanes and Bakshi[14,15] developed a multiscale model that considers life cycle impacts within a national system boundary and applied this framework for minimizing environmental impacts from an ethanol plant. Several studies including Chouinard-Dussault et al.[16] and Gerber et al.[17] have extended process integration tools to include life cycle environmental impacts through the use of multiobjective optimization techniques with applications to biofuel production. In addition, methods such as eco-efficiency that maintains profitability while reducing pollution, greenhouse gas reduction methods through carbon credits and reforestation, and waste reduction algorithms

Additional Supporting Information may be found in the online version of this article.

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are other common end-of-pipe design methods to reduce environmental impact of manufacturing.

While all of these methods for designing sustainable processes have enabled minimizing ecosystem service demand through minimization of environmental impact, they fail to address a key underlying issue: the current demand for ecosystem goods and services exceeds the rate at which these services can be supplied by ecosystems. In other words, designing systems by including an environmental objective of minimizing ecosystem service demand such as carbon emissions or water use will result in more efficient processes, but may still be unsustainable due to exceeding nature's capacity to supply these services. Ignoring the role of ecosystem services and the capacity of nature to supply these services has thus been one of the major causes of ecological degradation. Going beyond the goal of minimizing environmental impact to reaching a case of absolute sustainability requires engineering to respect ecological constraints.[18] This can be enabled by identifying optimal designs that simultaneously minimize the ecosystem service demand and maximize the supply, resulting in an increase in net supply.

Existing methods that account for ecosystems typically consider these systems as a "green" alternative to conventional equipment. These include the use of ecosystems such as constructed wetlands as an ecological alternative to conventional end-of-pipe solutions for wastewater treatment,[19] vegetation as an ecological alternative for air pollution and greenhouse gas emissions control[20,21] or the use of mangroves for flood plain control and coastal erosion. These methods do not explicitly account for ecosystem services and ecosystems are referred to as methods for "fixing problems" as opposed to providing synergy and complimentary to the integrated system. López-Díaz et al. developed a model for designing eco-industrial parks[22] and biorefining systems[23] within a watershed to minimize environmental impact on the watershed through water reuse and integration methods. Even though these models integrate material flow between multiple industries and the watershed to reduce consumption of fresh water and discharge of effluents, the capacity of the watershed to support these industrial systems is ignored. Similarly, García and Ortega[24] and Garibay-Rodriguez et al.[25] developed models to identify the optimal water use strategy at a more macroscopic level accounting for different water uses, recycling, and reuse strategies as well as its effect on the surrounding watershed. While most of these studies either consider the water demand and availability within a watershed or simply rely on the economic and environmental benefits of ecosystems to meet environmental goals, none of these studies consider the *capacity* of natural systems to supply ecosystem services to support industrial activity. In all these studies, the limits imposed by nature and the interdependencies between ecosystem service demand by technological systems and ecosystem service supply by ecosystems is ignored.

The Techno-Ecological Synergy (TES) framework[26] was developed to capture the interactions between ecosystem services demanded by technological systems and services supplied by ecological systems. Demand for an ecosystem service is quantified by the total emissions generated and resources consumed by a technological system while the supply is quantified by the amount of flow of goods and services from ecological systems. The objective of TES is to design systems that maximize the net ecosystem service supply, quantified by the ecosystem service supply less the demand as opposed to the conventional design approach of minimizing only the ecosystem service demand.

Till date, the TES framework has been applied to the analysis and design of multiple systems at various scales and has shown promising results. Urban and Bakshi[27] applied the TES framework for designing a residential system at the local and life-cycle scales along with the supporting ecosystem services. Hanes et al.[28] combined the TES framework with the Process to Planet[14] framework for designing a renewable energy production system in Central Ohio, accounting for ecosystem service supply at local and regional scales, and demand at local, regional, and national scales. Previous work by Gopalakrishnan et al.[29] includes application of the TES framework to evaluate the ability of local ecosystems to meet the demand for some ecosystem services demanded by a biodiesel process with on-site power generation. Results from this study indicate that ecological systems can provide services that mitigate all criteria air pollutants while being economically feasible. Gopalakrishnan et al.[30] also expanded this analysis to the county scale to assess the economic and environmental benefits of ecosystem services and nature-based solutions. Halbe et al.[31] used a functional organizational analysis method for designing a sustainable food supply system in Canada, allowing for consideration of both technical systems and ecosystem processes. Similarly, Martinez-Hernandez et al.[32,33] developed a framework that uses a systems dynamic approach to model techno-ecological interactions in a local heathland ecosystem in the UK.

While all of these studies either include the role of ecological systems in an ad hoc manner or consider techno-ecological interactions at larger scales, none of them consider the interactions that exist between detailed process level decisions and the design of supporting ecological systems. Understanding the interactions between process level decisions and ecosystems is necessary to understand the change in environmental impacts due to process modification, and the modifications in process operation with a change in the supply of ecosystem services.

This work expands the scope of traditional process design methodologies to explicitly include the role and capacity of ecosystems, by treating ecological systems as unit operations. Similar to conventional unit operation processes such as adsorption, separation, and distillation that produce purified products and chemicals, ecological unit operations produce resources such as clean air and water by separating and distilling out pollutants and hazardous waste from ambient air and water.

Considering ecosystem functions to be analogous to unit operations allows coupling the design of technological processes and relevant ecological systems such that the supply of goods and services from ecosystems can be balanced with the input flow of natural resources and energy required by the technological system. At a manufacturing site, if ecosystem goods and services demanded by engineering activities are within the capacity of local ecosystems to supply them, then the overall techno-ecological system is locally sustainable as it can operate within local ecological constraints. Any ecosystem service beyond what is used by the technological system contributes to a corporate goal of "net positive impact" manufacturing.[34] If local ecosystems are not able to provide the needed goods and services, then the excess demand can cause negative impact on society and the environment.

Quantitative models capturing the behavior of ecological systems including operational constraints and constraints of

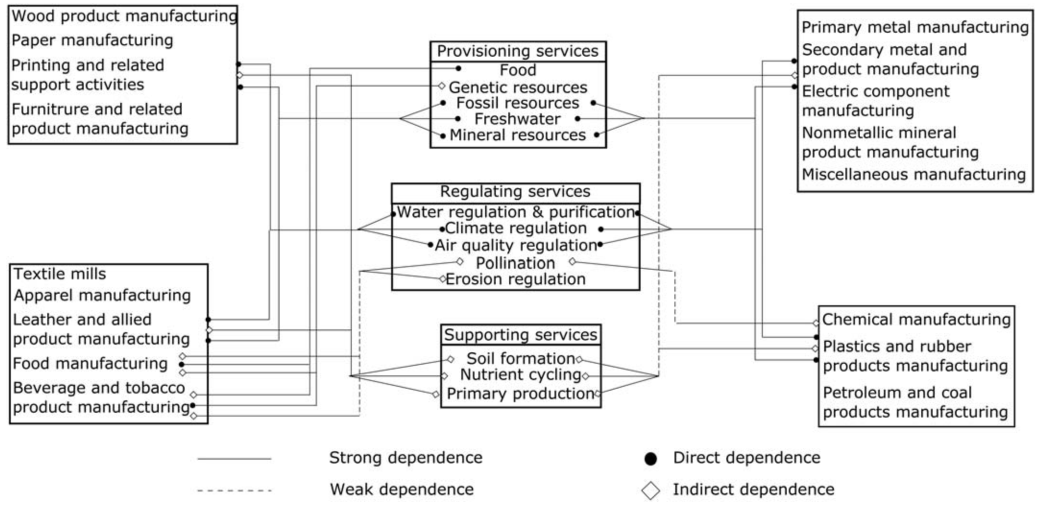

Figure 1. Dependence of industrial sectors on ecosystem goods and services.

mass, energy, and material balances are used to model ecological systems, analogous to the constraint-based representation of traditional process models. Process flowcharts are developed by establishing connections between technological and ecological systems, and interactions among multiple process units, ecological units, stream flows, resources, and objectives are considered to gain fundamental insights of the integrated process, determine attainable performance targets, and make systematic decisions for achieving these targets. Inclusion of ecological systems in the design problem will thus enable identifying designs through changes in stream flow and unit operation variables for a process as well as the ecosystem unit operation, thus resulting in designs which may have higher profitability and better performance. Adopting this holistic approach toward design and synthesis of techno-ecological systems by exploiting interactions between various unit operations and ecological systems will result in designs that minimize cost and minimize overshoot of ecological carrying capacity.

To demonstrate the practical aspects of this work at the local scale, the TES design framework with ecosystems as unit operations is developed and applied to the design of a biofuel production system. In the case study presented here, the ecological system included in the design framework is a horizontal subsurface flow wetland system for treating the wastewater and supplying a part of the treated water back to the process. This is the first effort at integrating the design of wetlands with the design of a process as most studies until now have considered wetlands as an ecological alternative to conventional wastewater treatment systems and have included wetlands only as an end-of-pipe design solution.[35] This work also conveys the economic and environmental benefits of adopting such an integrated approach. This case study is appropriate for locations where the temperature variability is not very drastic (tropical and subtropical regions) including locations between 30° degrees N and S latitudes. Benefits of adopting a TES design approach are highlighted by comparing these design solutions with a conventional techno-centric approach and by including a water cost sensitivity analysis. The problem is formulated as a multiobjective nonlinear program (Mo-NLP) and tradeoffs are identified between maximizing the net present value of the system and the net ecosystem service supply for water provisioning service. Results from this study indicate that the integrated design approach with water feedback results in systems with a higher NPV and lower ecological overshoot, with increase in water cost.

Thus, the novelty of this work is two-fold: (1) extend the concept of unit operations to ecological systems to provide a basis for characterizing ecosystems so as to integrate them in process flowsheets, and (2) demonstrate the economic and environmental benefits of adopting an integrated approach by designing a techno-ecological synergy between a biofuel production plant and a treatment wetland ecosystem.

The next section provides more details about the integrated design framework followed by a discussion on ecological unit operations relevant to industrial systems. A case study on the methanol transesterification biodiesel process is then presented followed by results demonstrating the benefits of TES design in comparison to a conventional approach. A discussion on the model limitations followed by the conclusions of this work and opportunities for future work are then presented.

Methods and Models

Ecosystem services and techno-ecological synergy

Human activities and industrial systems rely heavily on availability of goods such as fossil fuels, minerals, and so forth and services such as carbon sequestration, biogeochemical cycles of carbon and nitrogen for their sustenance. Figure 1 depicts the dependence of different industrial sectors on ecosystem goods and services and their degree of linkages. Given the strong dependence of industrial processes on ecological systems for achieving goals related to sustainability and net positive impact manufacturing, optimal spatial planning, and accounting of ecosystem capacity to provide these services to support industries is necessary.

The Techno-Ecological Synergy (TES) framework quantifies the demand and supply of ecosystem services at multiple spatial scales and determines the extent to which the demand for ecosystem services overshoots the supply. This synergy not only reduces the impact of industrial activities but it also enhances the ability of ecological systems to provide needed services. Being multiscale in nature, the TES framework can account for ecosystem services at local, regional, watershed, and global scales, depending on the type of ecosystem service. Ecosystem services like carbon sequestration supplied by vegetation and soil have a global presence while ecosystem services like air quality regulation provided by vegetation have a regional presence. Services like water provisioning and water quality remediation by constructed wetlands and bioswales are typically modeled at the watershed scale.

Sustainability metrics using the TES framework are calculated based on the degree of overshoot in demand for different ecological services as

$$V_k = \frac{S_k - D_k}{D_k} \tag{1}$$

Absolute sustainability at the serviceshed scale (V_k^*) for different ecosystem services is reached under the condition that,

$$V_k^* \geq 0 \, \forall k \tag{2}$$

where V_k represents the sustainability index, D_k and S_k represent the demand and supply of ecosystem services (k), respectively. Serviceshed (indicated by a *) is defined as the largest spatial extent or geographical area which provides the selected ecosystem service.

A negative value of the sustainability index indicates an overshoot in the demand for an ecosystem service over its supply implying that the process overshoots the ecological carrying capacity. A negative value for an ecosystem service like carbon sequestration at the local scale indicates the inadequacy of ecosystems to sequester emissions at this scale. This implies that the technological system would depend on carbon sequestration services at larger scales to close the carbon loop. A positive sustainability index would indicate a situation where the services demanded by industrial systems are within the capacity of ecological systems to supply them. This would lead to a situation of "net zero" or "net-positive" system, where the capacity of ecosystems to dissipate emissions is higher than the quantity of emissions from an industrial system. In such a situation, a net positive supply would indicate the presence of additional ecosystem services that may be available to society.

The sustainability index is used to measure the level of sustainability of multiple systems as it represents an absolute metric. This same index can also be used as an objective in optimization problems to determine an optimal system design where the process may be designed to minimize the ecosystem service demand and ecosystems may be designed to meet or exceed the demand, where possible. In this work, only the numerator of the index is used as an objective to keep the objective function less nonlinear.

Ecosystems as unit operations

The unit operation concept can be defined as a systematic functioning of individual processes in a sequential manner to achieve a desired task. This can involve individual tasks like drying of solids, distillation, evaporation, or processes like movement of solids and fluids, and transformation of heat from one substance to another. In nature too, processes such as drying, separation, heat and energy transformation occur regularly resulting in the generation of some desirable and undesirable products. For instance, the temperature on the surface of vegetation depends on the exchange of energy between the plant and the atmosphere brought about through radiative heat exchange, and through sensible and latent heat fluxes, similar to heat exchange between fluids and solids. Similarly, water purification that takes place in wetlands occurs through filtration, sedimentation, and sorption. In other words, most processes taking place within the engineering domain are directly or indirectly inspired by such processes taking place in the ecological domain. Thus, it is only appropriate to extend the concept of unit operations to the ecological domain to classify and characterize processes taking place in natural systems.

Ecosystem function defined as the capacity of a natural component to provide goods and services to satisfy human needs, directly and indirectly,[36] depends on the stocks of energy and materials like biomass and water, fluxes of energy or material processes like primary productivity and stability rates of stocks over time.[37] Thus, decomposing each ecological system into its elementary functions provide an empirical basis for classifying ecological systems based on the benefits to humans.

There are some fundamental differences between technological and ecological systems that must be accounted for. Ecological unit operations can perform multiple tasks simultaneously in contrast to technological unit operations that are designed to perform specific, individual tasks. Design of ecological systems for providing goods and services beneficial for human welfare is based on the self-designing and self-organizing ability of ecological systems. Unlike conventional unit operations where systems follow an imposed design with a high level of control and predictability, ecosystems lack such a high degree of predictability and control, and their performance can be intermittent with changes in local environmental conditions.

As ecological systems perform multiple tasks simultaneously, identifying a structured classification scheme for characterizing ecosystem functions similar to conventional unit operation systems may not be possible. In this work, the classification scheme of unit operations in the chemical engineering domain is used to draw parallels between several unit operation concepts in the chemical engineering domain with ecosystem functions and processes within the ecological domain. Some of the primary unit operation and ecosystem functions are listed below.

Mass and Heat Transfer Operations in Ecosystems. Separation processes such as adsorption and absorption take place on the surface of leaves of any vegetative surface. Leaves act as decentralized systems where gaseous particles are exchanged between the atmosphere and vegetative surfaces via their stomatal openings. These gaseous pollutants get absorbed or adsorbed on the surface of a leaf through particle diffusivity, eventually getting oxidized, or dissolved in water.

Similarly, nutrients such as nitrogen and phosphorous that get deposited into wetlands from industrial waste and storm water runoff get absorbed by the wetland soil or get absorbed by plants and microorganisms. Absorption of Carbon dioxide (CO_2) on oceans through surface-water photosynthetic microbes that dissolve CO_2 into organic carbon is another common phenomenon based on the separation process. Drying, another mass transfer operation commonly occurs in soil during the wetting-drying process for carbon and nitrogen mineralization.

Riparian buffers rely primarily on geothermal heating through conduction, and groundwater temperature exchange through advective heat transfer for regulating stream flow temperature. Riparian buffers including native grasses, trees, and shrubs act as thermal insulators for mediating stream water quality. Similarly, trees and tall grasses around buildings act

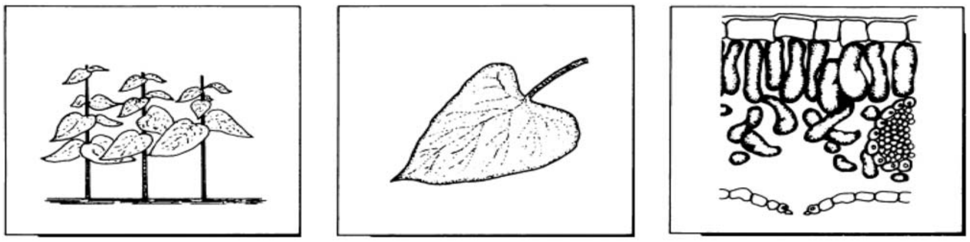

Figure 2. Sites of deposition and resistance of vegetation for different pollutant gases.

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as thermal insulators for reducing heating and cooling loads. Heat transport in soil for biological processes like germination, plant growth, microbial activity for breaking down soil organic carbon and so forth are other examples of heat transfer operations in ecological systems.

Other unit operation processes such as mechanical filtration, sedimentation and fluid flow through particle diffusivity commonly occur in wetlands and vegetative surfaces. Transport of oxygen molecules from the roots of certain tree species including mangroves onto water is an example of gas-liquid absorption. Further details on the functioning of different ecosystems and its relation to conventional unit operation processes are given in the following subsections.

Vegetation as Decentralized Absorption and Adsorption Units. Vegetation including canopy, grasses, and shrubs sequester pollutants directly from the atmosphere onto their leaf surface resulting in an improvement in air quality in the vicinity of emissions sources. These vegetative surfaces acting as a decentralized unit provide a direct sink for pollutants. The rate of pollutant transfer from the atmosphere to the interior surface of the leaf is regulated by a series of resistances through the atmosphere, the stomata surface, and the mesophyllic resistance[38] as shown in Figure 2. The friction of air mass movement creates turbulent eddies that cause the gas molecules and small particles to be entrained from the airstream over the canopy surface. Pollutants then penetrate through a boundary layer around the vegetative surface by diffusion for gasses and fine particles, and by impaction for large particles. Gas molecules like Nitrogen dioxide (NO_2), Sulfur dioxide (SO_2) and Ozone (O_3) are then absorbed onto the leaf surface or enter the leaf via the stomata. Particulate matter including PM_{10} and $PM_{2.5}$ are directly intercepted on plant surfaces. Most of the intercepted particles are retained on the leaf surface, which may eventually get washed off by rain or drop to the ground during wet periods. During dry days, these particles may get resuspended in the atmosphere, acting only as a temporary retention site for these particles before they move to the soil.

This process of dry deposition in leaves is quantified based on the deposition velocity of particles and the local pollution concentration using the i-Tree Eco model. The i-Tree Eco model developed by the United States Department of Agriculture (USDA) quantifies the dry deposition capacity of canopy to absorb pollutant molecules and sequester carbon directly from the atmosphere.[39,40] The i-Tree Eco model uses a tree's functional parameters like its height, age, diameter, along with local meteorological conditions and local ambient air concentration to calculate the pollutant flux as a function of the deposition velocity of particles on trees. Further information on the dry deposition process and the diffusion model characterizing this is given in the Supporting Information.

Tree canopies can also intercept precipitation contributing to a reduction in storm water runoff, thus increasing the total water supply within a watershed. With an impervious surface cover, about 55% of precipitation goes as run-off water while only 15% infiltrates into the ground. However, canopy cover reduces runoff to 10% of precipitation while almost 50% of precipitation infiltrates into soil.[41] Avoided water run-off due

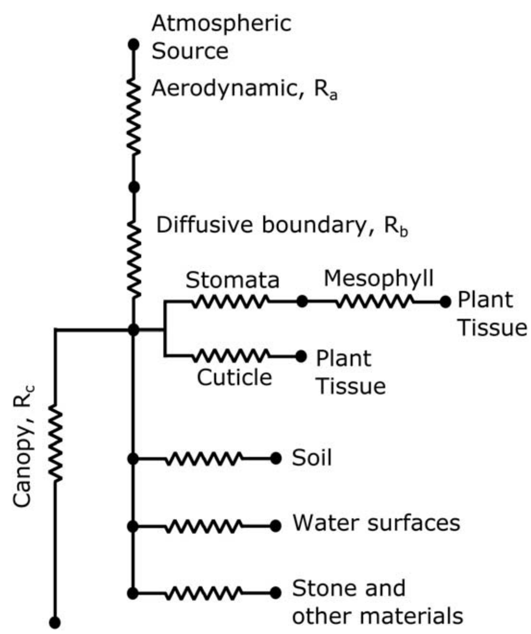

Figure 3. Resistance pathways to deposition of gaseous pollutants.

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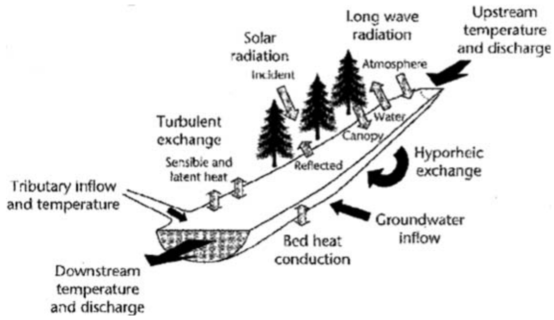

Figure 4. Factors controlling stream temperature in a riparian buffer.

Black arrows represent energy fluxes associated with water exchanges. Adapted from Ref. 65. Reprinted with permission from John Wiley and Sons.

to canopy cover is calculated based on the i-Tree Eco Precipitation Interception model.[39]

Thus, tree canopies can be considered as individual unit operations for providing ecosystem services such as carbon sequestration, air quality regulation, and water provisioning service, and these services can be quantified using the dry-deposition removal mechanism.

Riparian Buffers as Thermal Heat Exchangers. Riparian buffers that include woody vegetation along streams and rivers can have a significant influence on stream temperature due to a change in the amount of heat energy in water resulting in a significant impact on the health of aquatic ecosystems and improvement in water quality. Riparian strips may include natural and engineered zones like forests and woodlands that act as biofilters, or prevent excessive sedimentation or protect water streams from excessive surface runoff. Thus, understanding the temperature variability of rivers and streams, and the related heat exchange processes are necessary to reduce impact on aquatic population downstream due to wastewater discharge from industrial sites upstream.[42]

Wastewater discharge from multiple sources can add heat to water streams, while excessive withdrawal from streams can impair their natural ability to moderate temperatures through heat absorption. These riparian buffers can be used in addition to cooling methods for reducing heat loads from industries and manufacturing sites that generate heated wastewater. Installation of these buffers around river streams next to industrial facilities directly cools the effluent stream that is discharged into the water stream thus reducing the energy consumed in cooling wastewater streams.

Figure 4 shows the river heat exchange process and factors that affect stream water temperature. Heat flux at the air–water interface occurs primarily due to heat exchange through solar radiation, net longwave radiation, evaporative heat flux, and convective heat transfer. Further details on the relation between stream water temperature and water exchanges across the surface is described in the Supporting Information.

Several factors including canopy cover, riparian buffer width and harvest unit length have a strong influence on the stream temperature. Thus, optimal design of riparian zones as thermal insulators along rivers and streams can help in protecting aquatic health and improve water quality. Riparian vegetation also provides additional ecosystem services like carbon storage in biomass, habitat for pollinating insects, and provisioning of wood products, bush food, and pharmaceuticals.

Wetland Ecosystems as Separation Units. Ecosystems and ecological processes play important roles in the absorption and breakdown of pollutants created by human activities such as sewage wastes, oil spills, and garbage. Ecosystem components including smaller life structures like bacteria to large-scale ecosystems like forests play a significant role in the breakdown and assimilation of these pollutants. Ecosystems like wetlands have qualities that are well-suited for breaking down and absorbing pollutants like nutrients, heavy metals, suspended solids in addition to reducing the biological oxygen demand and destroying microorganisms. These ecosystems are commonly used to treat municipal wastewater and industrial wastewater. Wetland systems are nowadays being commonly adopted as an alternate or supplement to technological methods for treating wastewater. Constructed wetlands are also cost-effective options compared to many industrial wastewater treatment systems since wetlands are self-regulating, require low energy inputs and do not require a waste disposal system. Vertical or horizontal subsurface flow wetlands are most commonly used for treating industrial wastewater. Horizontal Subsurface Flow (HSSF) wetlands contain a layer of gravel or soil with selected wetland vegetation and are designed as secondary wastewater treatment systems. As the wastewater stays beneath the surface media, and water flow takes place in and around the roots of the plant, exposure to pathogenic organisms is minimized. These systems also operate better under colder conditions compared to other constructed wetlands due to the surface insulation on top of the water.[43]

A growing number of industries including paper and pulp mills, meat processing facilities, and petroleum refineries[44] are using constructed wetlands as secondary and tertiary treatment systems to remove BOD_5, COD, oil and grease, H_2S and heavy metals.

Models for constructed wetlands with an ideal plug-flow behavior based on first-order equations[45] are available that can predict the required surface area of a wetland to treat wastewater. Wetlands modeled as ideal plug flow reactors with constant conditions have an exponential profile between inlet and outlet flows with temperature effects modeled via Arrhenius equations. Further information on the steady-state first order rate equations for a HSSF that incorporate effects of precipitation and temperature are given in the Supporting Information.

Integrated Design of Technological and Ecological Unit Operations

Traditional process design procedures usually involve generating multiple process configurations or flowsheets to determine a production pathway that is most cost optimal in terms of minimum production cost or maximum Net Present Value (NPV). Multiple production pathways for an end-product are identified and a superstructure incorporating all feasible design alternatives are proposed. Typically, a Non-Linear Programming (NLP) or Mixed Integer Non Linear Programming (MINLP) optimization formulation of the superstructure is formulated and solved to identify the most optimal design configuration.

Sustainable process design concepts expand the boundary of traditional process design problems to consider an environmental objective, usually a single objective like minimizing greenhouse gas emissions or water consumption quantified by footprint methods. In such cases, the design problem will be setup as a Multi-Objective Mixed Integer Non Linear Programing problem (mo-MINLP) with the objectives of minimizing the system cost accounting for revenue from the sale of products, and minimizing the demand for an ecosystem service quantified by emissions. A Pareto-frontier is generated where each point in the Pareto-front indicates solutions that have conflicting values for different objectives. Due to the fundamental nature of this property, Pareto-optimality has played a significant role in engineering design to identify a set of optimal solutions.

Conventional sustainable process design problems are typically formulated as

$$\mathrm{Max.Z_1(x,y)} \quad \mathrm{Min.Z_2(x,y)}$$

subject to

$$\begin{gathered} f(x,y) < 0 \\ h(x,y) = 0 \\ Z_1 = Pg(x) \quad Z_2 = D_k(x) \\ D_k(x) = Eq(x) \\ x \in \mathbb{R}^n, y \in [0,1]^m \end{gathered} \tag{3}$$

Here, x represents design variables for each unit operation, $f(x, y)$ and $h(x, y)$ represent the equality and inequality constraints on the process models derived from fundamental engineering knowledge or empirical data. The economic objective function $Z_1(x,y)$ is calculated by considering economic factors such as cash flow, depreciation, labor cost, equipment related costs etc. represented by $g(x)$ and usually scaled by price data P. The environmental objective $Z_2(x,y)$ representing the ecosystem service demand ($D_k(x)$) is usually calculated as a function of the design variables $q(x)$, using fixed environmental interventions data E.

However, the conventional SPD approach does not entirely account for the fact that ecosystem services are necessary to support technological activities. The lack of ecosystem models or constraints in this formulation means that it ignores the capacity of ecological systems to assimilate emissions and provide resources. This could result in decisions that maybe *perverse* and even incorrect since they may encourage reliance on degraded ecosystem services. Such an approach will not be able to identify opportunities for protecting or restoring ecosystems, which would be the sustainable thing to do.

To address this shortcoming, the proposed integrated design framework expands the system boundary to include relevant ecological systems in the process flowsheet. Ecological unit operations are identified based on the required task and services they provide, and connections between these two systems are identified for designing a coupled Techno-Ecological system with the goal of moving toward net zero impact. The premise behind designing an integrated Techno-Ecological system is ecosystems can make a significant contribution to the integrated system by enhancing economic feasibility and environmental sustainability in a mutually beneficial manner.

The capacity of ecological systems to perform these tasks, quantified by ecosystem service supply is explicitly included in the optimization formulation. Net ecosystem service supply, quantified by ecosystem service supply less demand, which is the numerator of Eq. 1 is used as the objective in the design problem. This will help in identifying designs that simultaneously minimize ecological demand and maximize the supply, tending toward positive ecological overshoot. As a result of changes in both the unit operation variable for the process and ecological unit operation variables, significant changes in technical performance and profitability of the system can be observed in comparison to end-of-pipe designs where unit operation variables are maintained at status-quo.

In addition to mass balance constraints, spatial constraints of each ecosystem including land requirement and availability, operating constraints like retention time and flow rates, and other limiting factors like access to nutrients and water will also be considered simultaneously. Inclusion of these constraints within the optimization framework will bring out a better representation of each ecological system while making the problem more complicated. Further integration between multiple unit operations can be established by the creation of recycle loops from ecological systems, that will enhance ecosystem service supply while reducing the demand. For instance, for closing the water loop within an industrial serviceshed, wetlands can be designed to produce treated water of quality suitable for reuse within the process. Optimal operating conditions for the process and the appropriate wetland size and characteristics can be determined to design such a close-looped system.

The design problem will again be setup as a mo-MINLP with the economic objectives of maximizing NPV for the entire techno-ecological system and maximizing the net ecosystem service supply as

$$\mathrm{Max.Z_3(x,x_e,y)} \quad \mathrm{Max.Z_4(x,x_e,y)}$$

subject to

$$\begin{gathered} f(x,y) < 0 \\ h(x,y) = 0 \\ f_e(x_e,y) \le 0 \\ h_e(x_e,y) = 0 \\ Z_3 = Pg(x,x_e) \quad Z_4 = S_k(x_e) - D_k(x) \\ x, x_e \in \mathbb{R}^n, y \in [0,1]^m \end{gathered} \tag{4}$$

Here, x_e represents the ecological design variables for each ecosystem, $f_e(x_e,y)$ and $h_e(x_e,y)$ represent the inequality and equality constraints of ecological systems derived from spatial information, respectively. The new economic function $Z_3(x,x_e,y)$ is now calculated by considering economic factors of the process system and economic factors of ecosystems including establishment costs, operating costs and labor costs, once again scaled by price data P. The new environmental objective $Z_4(x,x_e,y)$ is the numerator of the sustainability index defined in Eq. 1 to avoid nonlinearity in the objective function. This objective function is calculated as the difference in ecosystem service supply (S_k) based on the ecological design variable x_e and ecosystem service demand (D_k) calculated as a function of the design variable $q(x)$ using fixed environmental interventions data (E).

The formulation for TES design in Eq. 4 can also be used for retrofitting existing processes by including decisions about small scale unit operations and material selection, to large-scale ecosystems including reuse and recycling options. Detailed quantitative information on mass, energy balance, thermodynamic principles of ecosystems and physical constraints are necessary for the proper integration of both systems. Ultimately, the TES design framework will be developed to combine data and models from multiple sources into a comprehensive modeling framework with the objective of designing processes at a local scale, such that there is minimum ecological overshoot at multiple nodes in the life cycle network.

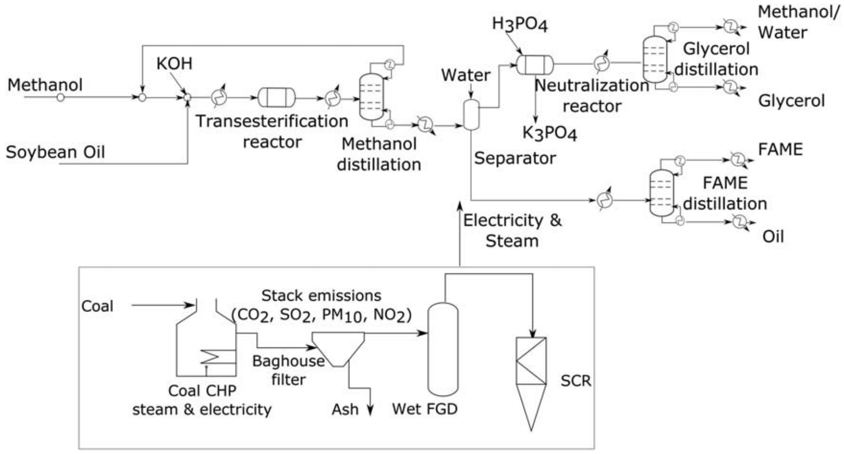

Figure 5. Biodiesel production flowsheet.

Case Study

To demonstrate the benefits of including ecological systems in traditional process design, the integrated design framework is applied to a methanol transesterification process using soybean oil as the primary feedstock. The production plant consists of an on-site coal Combined Heat and Power (CHP) unit that meets the electricity and steam demand. A closed loop cooling system is designed so as to minimize freshwater consumption in the utility system.

Figure 5 represents the process flowsheet for the alkali-catalyzed transesterification of soybean oil with potassium hydroxide (KOH) as the catalyst and alkali neutralization using phosphoric acid. The soybean oil comes from the hexane extraction process with minimum solid wastes in the stream. Methanol and oil stream undergo transesterification reaction in the transesterification reactor in the presence of KOH catalyst to produce Fatty Acid Methyl Ester (FAME), glycerol, some unconverted oil, water, and unreacted methanol. Most of the methanol is recycled back to the reactor in the methanol distillation column. FAME and glycerol produced undergo washing in the water washing unit where freshwater is added as an input. After the water washing, FAME and oil (heavier) components are separated at the bottom, and methanol and glycerol exit from the top of the separator. To remove KOH that is present in this stream, the methanol and glycerol mixture is reacted with phosphoric acid (H_3PO_4), and the potassium phosphate (K_3PO_4) that is produced is assumed to be sold as a fertilizer. All the glycerol formed as a by-product is sold in the market.

Model equations for each unit process are adopted from Martin et al.[46] All the reactor models used here are from reduced order models based on mass and energy balances over unit operations and based on design equations. All the streams undergo adiabatic mixing. The model originally developed was for cooking oil and algae oil, but all the parameters were modified to represent soybean oil. Specifically, the composition of the soybean oil stream is 27% Oleic acid, 51.4% Linoleic acid, 6.6% Linolenic acid, 10.8% Palmitic acid, and 4.2% Steric acid.[47] For modeling purposes, methyl ester from soybean oil is assumed to have a composition of 10.57% Palmitate, 22.98% Oleate, 4.09% Stearate, 54.51% Linoleate, and 7.23% Linolenate.[48]

Other components that were modified include heat capacity of the fatty acid,[49] heat of vaporization for soybean oil,[48] molecular weight of the components and the coefficients for vapor pressure calculations using Antoine's equation.[50–52]

Overall reaction yield for the transesterification reactor is calculated as[53]

$$\begin{aligned}\text{yield}=&74.6301+0.4209T+15.1582C+3.1561R-0.0019T_2^2\\&-0.2022T_2C-0.01925T_2R-4.0143C^2-0.3400CR-0.1459R^2\end{aligned} \tag{5}$$

where T is the temperature of the transesterification reactor, C is the catalyst concentration (%), R is the methanol to oil molar ratio, T_2 is the temperature of the stream entering the transesterification reactor.

Fatty Acid Methyl Ester produced by the alkali-catalyzed transesterification of soybean oil is produced at the rate of 0.532 kg/s. Soybean oil is assumed to be produced by the hexane extraction process and directly supplied to the transesterification plant without any transportation costs.

The total heat energy requirement in the process is calculated by summing up all the positive energy inputs in the network.[54] Methanol recycle step is the most energy intensive process in the entire network and this is one of the main factors in deciding the overall energy consumption and design of the CHP system. The CHP is designed to meet the steam and electricity demand for the production plant. 10% of the total electricity produced is consumed *in situ* and the excess electricity produced by the CHP is sold back into the grid. Initial water withdrawn for the CHP is based on the model in[55] and is assumed to come from a river next to the production facility. The make-up water consumed is assumed to be directly supplied to the plant or this comes from the water recycled from the treatment system.

For the CHP system, make-up water consumption (T_{mw}) is calculated as,

$$T_{mw}=mw_{\text{evap}}+mw_{bd}+mw_{\text{drift}} \tag{6}$$

where mw_{evap} is the evaporative loss, mw_{bd} is the blowdown loss and mw_{drift} is the drift loss calculated from empirical correlations.[56]

The objective of this study is to include ecological systems, like a wetland ecosystem within the design framework and identify optimal network topologies between technological and ecological systems to enhance the level of sustainability of a process, with respect to water provisioning ecosystem

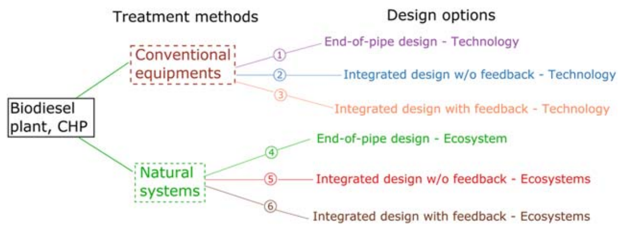

Figure 6. Super structure of wastewater treatment options.

[Color figure can be viewed at wileyonlinelibrary.com]

service. For the case study here, network topologies are identified by redesigning an existing methanol transesterification process flowsheet. In addition, to highlight the benefits of including ecological systems, these integrated design networks are compared to the case of a purely techno-centric design. Sensitivity of water cost toward design parameters, net present value, and net water provisioning supply are also evaluated. Net present value and system operation costs are calculated over a 20-year period and represented on an annualized basis.

Figure 6 shows the superstructure for different water treatment and reuse pathways. Currently, the facility includes a coagulation-flocculation (CF) pretreatment unit. We considered an Anaerobic Baffled Reactor (ABR) as a technological alternative to the wetland ecosystem, for treating wastewater. Figure 7 represents the process flowsheet with the ABR or wetland ecosystem. A total of six different treatment pathways were considered as shown in the figure. Pathways 1 and 4 are designed as end-of-pipe treatment methods where the transesterification flowsheet is optimized based on an economic objective (maximizing NPV) and an environmental objective of minimizing water demand, and the technological or ecological options are considered as an add-on treatment option. This method of designing a production process with water treatment systems as end-of-pipe solutions is currently the most prevalent practice in industries. Pathways 2 and 5 marked as "Technological design" in brown and "Techno-ecological design" in green represent the design where the ABR and wetland are included in the design framework but with no feedback or water supply from the treatment systems. Pathways 3 and 6 represented by "Technological design with feedback" and "Techno-ecological design with feedback" represent a truly integrated system where the treated water from the ABR and wetland is supplied back to the production process and CHP for continuous reuse. All the six pathways are optimized for maximizing the net present value for the entire system, minimizing water provisioning demand for pathways 1, 2, 4, and 5, and maximizing net water provisioning supply for pathways 3 and 6.

A generic component balance over each unit operation equipment in the integrated flowsheet is represented as

$$F_j = \sum_{i \in \text{components}} f_{j,i} \; ; \forall j \in \text{streams} \tag{7}$$

where F_j is the total stream flow rate through each equipment. Individual component stream flow rates $f_{j,i}$ were calculated as,

$$f_{j,i} = \frac{F_j}{x_{j,i}} \; ; \forall i \in \text{components}, \; j \in \text{streams} \tag{8}$$

and component stream mole fraction is represented by

$$\sum_i x_{j,i} = 1 \tag{9}$$

An overall enthalpy (H) and energy balance (Q) over equipment (k) is represented as

$$\sum_j (F_j H_j)^{\text{in}} + Q_k^{\text{in}} = (F_j H_j)^{\text{out}} + Q_k^{\text{out}} \tag{10}$$

$$Q_k = \sum_j f_{j,i} Cp_j (T_j^{\text{out}} - T_j^{\text{in}}) \tag{11}$$

where T_j represents the stream temperature.

Design of ABR and wetland modules

Figure 8 shows the water flow through the ABR and wetland in pathways 2, 3, 5, and 6. For pathways 2 and 5, the treated water from the ABR or wetland is released into the river while in pathways 3 and 6, part of the water is recycled to the process and CHP, while the remaining water is released into the river. Water input to the CF unit includes blow-down water from the CHP (mw_{bd}) and wastewater from the process collected at a common point. The main source of wastewater from the plant comes from the water washing step from purifying the crude biodiesel after methanol distillation. Water is added to the water washing stage where the heavier fractions of FAME and oil separate from the glycerol and excess methanol. This process, known as wet washing is most commonly used in industrial treatment systems. The wastewater contains some amount of unreacted oil and fats, methanol, and a high concentration of COD. There are additional sources of wastewater in the entire plant including water from the steam condensate, wastewater from process water softening, water used for washing the equipment and floors, and sanitary wastewater. However, here we focus only on treating the wastewater from the production plant.

The CF unit uses powdered aluminum sulfate as the coagulant and is effective in removing about 99% of all the oil and grease, and about 53% of COD.[57] The ABR and wetland are designed so as to achieve the desired COD level of 75 mg/L before being released into the river or recycled back to the process. Design of the CF unit, ABR Unit and wetland is given in Supporting Information. For pathways 3 and 6 that include a water recycle stream, a reservoir system collects water from the wetland or ABR, and from the external water supply from where the water is sent to the biodiesel and CHP facilities, as shown in Figure 9. Water balance for the reservoir system (represented with wetland here) is determined as,

$$f_{(\text{Wa,Wet,Res})} + f_{(\text{Wa,Ext,Res})} = f_{(\text{Wa,Res,CHP})} + f_{(\text{Wa,Res,Sep})} \tag{12}$$

where $f_{(\text{Wa,Wet,Res})}$ represents the flow of water (Wa) into the reservoir (Res) from the wetland (Wet) ecosystem, $f_{(\text{Wa,Ext,Res})}$ represents the external (Ext) water supply into the reservoir system, $f_{(\text{Wa,Res,CHP})}$ is the water flow from reservoir to CHP and $f_{(\text{Wa,Res,Sep})}$ is the water flow from the reservoir to separator.

The current cost of process water assumed to be \$0.0005 per kg[58] accounting for price scaling[59] and a future water cost 100 times the original cost is considered. The rationale behind considering the high-water cost scenario is because currently negative externalities are not included in market prices of goods. However, most industries are trying to make decisions while taking the true cost of water into account by considering their own water pricing strategies. Considering a larger price

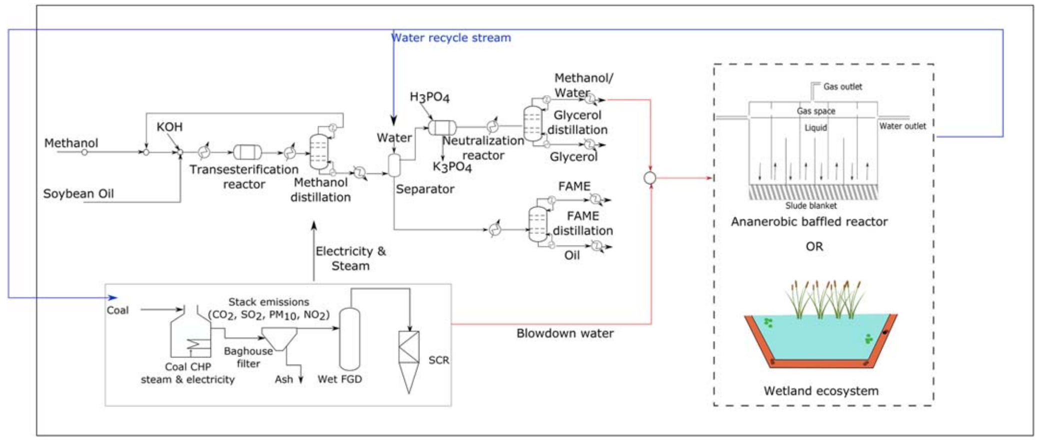

Figure 7. Process flowsheet for the biodiesel-CHP system with either an ABR or wetland ecosystem.
(a) Pathways 2 and 5 (b) Pathways 3 and 6. [Color figure can be viewed at wileyonlinelibrary.com]

for water than the current market price will aid in water risk analysis and calculation of financial implications.

Decision variables and description

Design variables used within the optimization problem primarily include process-level decision variables for the biodiesel process and design variables for the CHP and water treatment systems are then derived for each optimal solution. Design variables for the wetland include the area of wetland and, amount of water feedback from wetland and the design variables for ABR include the volume of ABR reactor, the compartment up flow area and amount of water feedback. Design variables for the two systems can be found in column 2 in Tables 1 and 2.

Optimization formulation

The set of objective functions for the conventional and techno-ecological design cases are given in Eqs. 13–15. Both the objective functions in all scenarios are calculated on an annualized basis, in a manner that the NPV is annualized assuming a 20-year life time, and water demand and supply are calculated on a yearly basis. As we are assuming the revenue, manufacturing and depreciation costs to be constant every year, the generic annual NPV objective function for all pathways is given by[60]

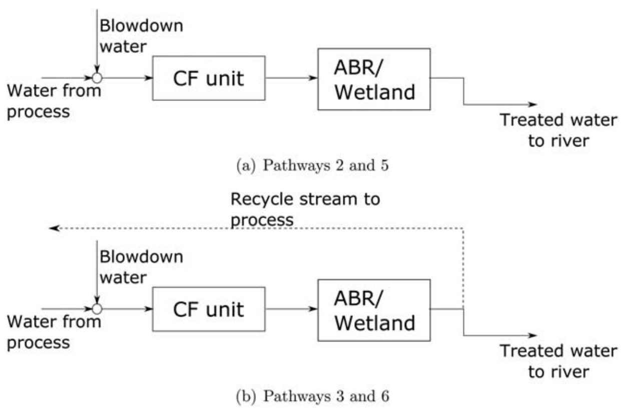

Figure 8. Water flow scheme through ABR and wetland for integrated designs without and with water recycle.

$$Z_{NPV}=\frac{\left(-(C_I+C_w)+\frac{(((C_R-C_M)(1-t))(1-(1+i)^{-20}))}{i}+\frac{(C_D*t)(1-(1+i)^{-20})}{i}+\frac{C_w}{(1+i)^{20}}\right)i}{(1-(1+i)^{-20})} \tag{13}$$

where C_I is the investment cost which includes the cost of equipment and CHP for the conventional designs, and additional land cost and wetland capital cost for the techno-ecological designs. C_w is the working capital calculated as 15% of the investment cost, C_R is the system revenue from the sale of products, by-products and electricity to the grid, C_M is the overall manufacturing costs for both the technological and ecological systems. Depreciation is calculated using the straight-line method with a salvage cost of zero. As land value does not depreciate, depreciation costs excluding land costs are used. The interest rate is assumed to be 7% with a tax rate of 5%.

The total water demand is calculated as the sum of water consumed in the biodiesel process, annual water withdrawn for the coal CHP and the make-up water lost during CHP operation. The water provisioning demand objective function (Z_W) for pathways 1,2,4, and 5 is calculated as,

$$Z_W=f_{(\mathrm{CHP,Wa})}+f_{(\mathrm{Sep,Wa})}+f^W_{(\mathrm{CHP,Wa})} \tag{14}$$

where $f_{(\mathrm{CHP,Wa})}$ represents the CHP (CHP) water demand, $f_{(\mathrm{Sep,Wa})}$ represents the water demand in the separator (Sep) and $f^W_{(\mathrm{CHP,Wa})}$ represents the annual water withdrawal for the coal CHP process.

The net water provisioning supply objective function ($Z_{\Delta W}$) for pathways 3 and 6 is calculated as,

$$Z_{\Delta W}=f_{(\mathrm{Wet,Wa})}-(f_{(\mathrm{CHP,Wa})}+f_{(\mathrm{Sep,Wa})}+f^W_{(\mathrm{CHP,Wa})}) \tag{15}$$

where $f_{(\mathrm{Wet,Wa})}$ represents the water supply from the wetland or ABR system. Each NLP problem for the pathway is implemented in GAMS and solved using the BARON global optimization solver.[61,62] Linear approximations to several equations

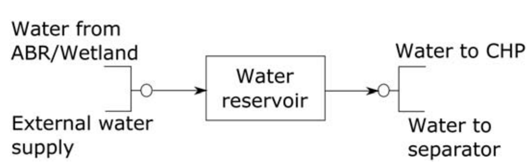

Figure 9. Water flow scheme through reservoir.

Table 1. Design Variables for Different Pathways for Maximizing NPV for the Low Water Cost Scenario

Variable	Description	Pathway 1 (L_{1a})	Pathway 4 (L_{4a})	Pathway 2 (L_{2a})	Pathway 5 (L_{5a})	Pathway 3 (L_{3a})	Pathway 6 (L_{6a})	Pathway 6 (L_{6c})	Units
Low Water Cost									
x_1	Mass flow of MeOH input stream	0.176	0.176	0.166	0.165	0.176	0.176	0.142	kg/s
x_2	Mass flow of oil input stream	1.256	1.256	1.165	1.153	1.257	1.254	0.952	kg/s
x_3	Mass flow of KOH input stream	0.278	0.278	0.287	0.288	0.278	0.278	0.31	kg/s
x_4	Mass flow of H_3PO_4 input stream	0.217	0.217	0.203	0.201	0.217	0.217	0.168	kg/s
x_5	Temperature of transesterification reactor	52.67	52.67	52.234	52.373	52.677	52.838	48.88	°C
x_6	Catalyst fraction in mass of H_2SO_4	0.015	0.015	0.005	0.014	0.015	0.005	0.005	
x_7	Ratio of methanol to oil	7.5	7.5	7.5	7.5	7.5	7.359	7.49	
x_8	Recovery of methanol in distillation column	0.987	0.987	0.986	0.985	0.987	0.986	0.975	
x_9	Recovery of water in distillation column	0.75	0.75	0.75	0.75	0.75	0.75	0.75	
x_{10}	Recovery of FAME in distillation column	0.338	0.338	0.359	0.361	0.339	0.339	0.425	
x_{11}	Recovery of Glycerol in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
x_{12}	Recovery of KOH in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
x_{13}	Recovery of oil in distillation column	0.75	0.75	0.793	0.75	0.75	0.75	0.983	
x_{14}	Recovery of FFA in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
x_{15}	Reflux ratio of methanol distillation column	1.203	1.203	1.287	1.3	1.203	1.241	1.538	
x_{16}	Reflux ratio of FAME distillation column	2	2	2	2.27	2	2	3	
x_{17}	Reflux ratio of Glycerol distillation column	0.75	0.75	0.75	0.75	0.75	0.75	0.755	
x_{18}	Size of CHP	0.324	0.324	0.316	0.316	0.325	0.327	0.299	Mwh
x_{19}	Total water demand	0.183	0.183	0.179	0.179	0.184	0.185	0.171	kg/s
x_{20}	Total external water supply	0.183	0.183	0.179	0.179	0.064	0.068	0.001	kg/s
x_{21}	Feedback water supply	0	0	0	0	0.119	0.116	0.17	kg/s
x_{22}	Area of wetland	–	10,457	–	10,246	–	9,145	13,395	m^2
x_{23}	Volume of ABR	43.49	–	38.42	–	38.76	–		m^3

in the process models are applied to reduce the problem complexity. The multiobjective optimization problem for different pathways is solved using the ϵ-constraint method with constraints placed on the system NPV.

Results

Figure 10 summarizes the results for six different design pathways, under the low and high-water cost scenarios. All points in these graphs represent the single objective optimization results for maximizing net present value, net water provisioning supply, and minimizing water provisioning demand objectives. The net water provisioning supply objective is associated with pathways 3 and 6 that include water supply from the environmental treatment processes, while the water provisioning demand objective is associated with pathways 1, 2, 4, and 5. Large solid points represent optimization results for the system with high water cost while small hollow points represent optimization results for the systems with low water cost.

System performance

Optimal Design Pathways—Existence of Win–Win Designs. Different optimal designs were observed for each objective and for each water cost. As expected, all design

Table 2. Design Variables for Different Pathways for Maximizing NPV for the High-Water Cost Scenario

Variable	Description	Pathway 1 (H_{1a})	Pathway 4 (H_{4a})	Pathway 2 (H_{2a})	Pathway 5 (H_{5a})	Pathway 3 (H_{3a})	Pathway 6 (H_{6a})	Pathway 6 (H_{6c})	Units
High Water Cost									
x_1	Mass flow of methanol input stream	0.166	0.166	0.164	0.176	0.176	0.178	0.143	kg/s
x_2	Mass flow of oil input stream	1.153	1.153	1.151	1.257	1.257	1.256	0.902	kg/s
x_3	Mass flow of KOH input stream	0.287	0.287	0.289	0.278	0.278	0.278	0.309	kg/s
x_4	Mass flow of H_3PO_4 input stream	0.201	0.201	0.200	0.217	0.217	0.215	0.161	kg/s
x_5	Temperature of transesterification reactor	52.93	52.93	51.12	52.66	52.66	52.78	51.291	°C
x_6	Catalyst fraction in mass of H_2SO_4	0.015	0.015	0.013	0.005	0.005	0.005	0.006	
x_7	Ratio of methanol to oil	7.5	7.5	7.5	7.5	7.5	7.492	7.5	
x_8	Recovery of methanol in distillation column	0.985	0.985	0.983	0.987	0.987	0.978	0.94	
x_9	Recovery of water in distillation column	0.75	0.75	0.75	0.75	0.75	0.75	0.99	
x_{10}	Recovery of FAME in distillation column	0.356	0.356	0.366	0.339	0.339	0.339	0.432	
x_{11}	Recovery of Glycerol in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
x_{12}	Recovery of KOH in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.989	
x_{13}	Recovery of oil in distillation column	0.75	0.75	0.988	0.75	0.75	0.754	0.756	
x_{14}	Recovery of FFA in distillation column	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
x_{15}	Reflux ratio of methanol distillation column	1.305	1.305	1.203	1.289	1.203	1.207	1.654	
x_{16}	Reflux ratio of FAME distillation column	2	2	2	2.14	2	2	2.321	
x_{17}	Reflux ratio of Glycerol distillation column	0.75	0.75	0.767	0.75	0.75	1.218	0.313	
x_{18}	Size of CHP	0.316	0.316	0.316	0.325	0.325	0.338	0.313	Mwh
x_{19}	Total water demand	0.179	0.179	0.179	0.184	0.184	0.19	0.178	kg/s
x_{20}	Total external water supply	0.179	0.179	0.179	0.184	0.064	0.007	0.001	kg/s
x_{21}	Water supply—recycle loop	0	0	0	0	0.119	0.183	0.177	kg/s
x_{22}	Area of wetland	–	12,464	–	9145	–	14,447	13,921	m^2
x_{23}	Volume of ABR	46.11	–	40.04	–	38.76	–	–	m^3

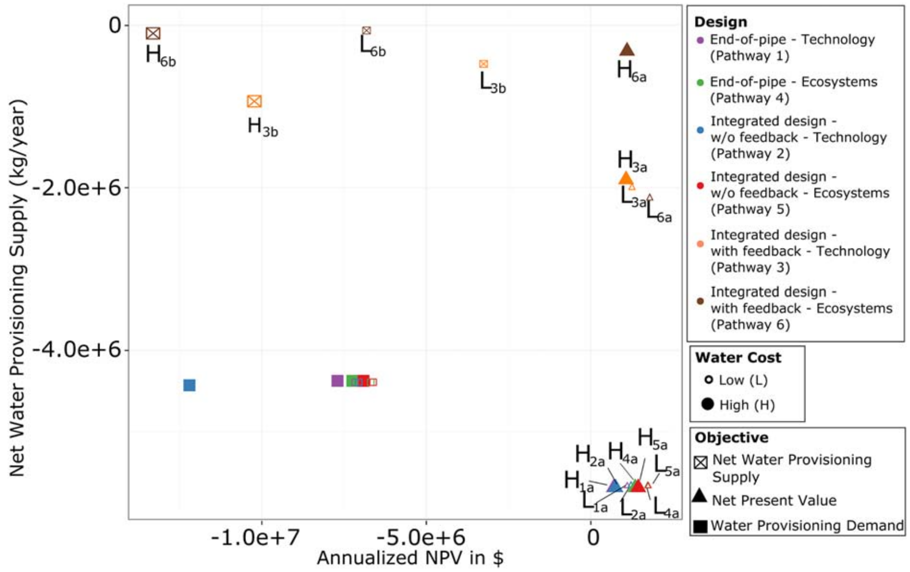

Figure 10. Single objective optimization for different designs.

Designs with subscript "a" are obtained by solving the NPV objective and designs with subscript "b" are obtained by solving the water provisioning demand objective function or net water provisioning supply objective function, depending on the pathway. These results indicate that integrated design with feedback with ecosystems (pathway 6) have a large NPV and highest net water provisioning supply value, indicating that this design results in a more sustainable solution, especially with high water cost. [Color figure can be viewed at wileyonlinelibrary.com]

pathways have a higher NPV for the low water cost scenario as compared to the high-water cost scenario. Note, however, that the effect of water cost on the NPV is quite small. The overall net water provisioning supply for the integrated design with feedback is larger for the case with high water cost, indicating that systems designed by accounting for both demand and supply of ecosystem services result in a more sustainable solution. This is of particular relevance as the cost of process water will increase in future. Further discussion on the benefits of integrated design with an increase in water cost is discussed in detail later.

Points marked in brown and orange in Figure 10 in the left end of the graph (with negative NPV) represent designs obtained for the net water provisioning supply objective for high and low water cost scenarios with ecosystems (H_{6b} and L_{6b}) and technology (H_{3b} and L_{3b}), respectively. One trade-off to observe here is the lower NPV for the case with ecosystems (H_{6b} and L_{6b}) compared to the designs with technology (H_{3b} and L_{3b}) for the objective of maximizing net water provisioning supply, even though the designs with ecosystems have a larger net water provisioning supply value. This is because the design solutions with technology have a higher energy demand due to higher input stream flow rates and higher energy consumption in the transesterification reactor resulting in a significantly larger water demand. The total electricity generated in the CHP for these designs is also larger than the overall energy consumption resulting in excess energy being sold back to the grid, generating a higher revenue. The optimal reflux ratio for the glycerol distillation column is 2.05 compared to 0.75 for the design with wetland resulting in a larger energy consumption in the heat exchangers. This increases the overall utility load, resulting in a higher electricity production beyond what is consumed. Thus, even though the manufacturing and operating costs for the integrated design with technology with feedback case are higher than its ecological counterpart, the additional revenue generated from the sale of electricity results in a larger NPV for the designs with technology. However, for the designs obtained by maximizing net water provisioning supply with ecosystems (points H_{6b} and L_{6b}), the designed wetland for the techno-ecological synergy case can supply 99% of the water demanded by the system.

Points H_{3a} and L_{3a} represent designs for the NPV objective for pathway 3, and points H_{6a} and L_{6a} represent designs for pathway 6 for maximizing NPV. Detailed design and unit operation variables for these four points are given in columns 7 and 8 in Tables 1 and 2. For the low water cost scenario, the optimal design with ABR (L_{3a}) can meet 64% of the process water demand compared to the case with ecosystems (L_{6a}), that can meet 62% of the water demand. The overall energy consumption and water demand for the design with ABR are lower than the design with wetlands. In addition, the concentration of COD in the wastewater stream leaving the system with wetland (L_{6a}) is significantly higher resulting in a wetland design that satisfies the required water quality over providing water supply as feedback. This results in a system with a lower net water provisioning service but larger NPV for the design with ecosystems (L_{6a}). A low water cost also results in higher external water consumption as opposed to modifying the design of the wetland to meet process water demand.

However, a different trend is observed for the high-water cost scenario. As the cost of water increases, water feedback from the treatment systems increase significantly for the case with ecosystems (H_{6a}) compared to the design with technological systems (H_{3a}). The designed wetland ecosystem can meet 96% of the water demand compared to 64% for the case with ABR. Lower external water consumption and lower cost of ecological systems result in a higher NPV and high net ecosystem service supply for this case, resulting in a "win-win" solution. This system also has a higher NPV and high net water provisioning service compared to the end-of-pipe solution (H_{4a}) and the integrated design without feedback (H_{5a}). Similarly, this solution also outperforms the designs obtained with technology (H_{3a}). Even though this design solution has the highest energy consumption and process water demand among all the designs obtained by maximizing NPV for the high-water cost scenario, the optimal wetland design can meet both the water quality and water provisioning services. These results demonstrate that an integrated design with water feedback with ecosystems results in a more sustainable solution, that is also economically feasible, especially when the cost of water is high. Such a solution is obtained only due to the inclusion of ecosystems, and cannot be obtained under a purely techno-centric approach. In addition, the win–win solution is obtained only when the cost of water is high.

Integrated TES Designs with Feedback Allows More Water Use Compared to End-of-Pipe Designs. Comparing across the different design scenarios, points marked in purple, green, blue and red in the lower end of Figure 10 represent the end-of-pipe designs (pathways 1 and 4) and integrated designs without water feedback (pathways 2 and 5) respectively. From this figure, we can see that integration of the wetland and ABR in the design problem as opposed to an end-of-pipe design, as is the practice in industry at present, results in solutions with a higher net present value and lower water demand. For the low water cost scenario, the reduction in water demand for the integrated design without water feedback cases (pathways 2 and 5) was mainly due to a reduction in energy consumption in the transesterification reactor due to a lower optimal value for the input streams of methanol, oil, and phosphoric acid. Comparing these design solutions with the integrated design cases with feedback (pathways 3 and 6), the overall energy and water consumption for the design with feedback is higher than the energy and water consumption for the end-of-pipe design and integrated design without water feedback case, particularly for the high water cost scenario as shown in Tables 1 and 2. The higher energy consumption for the designs with feedback (H_{6a}, H_{3a}, L_{6a}, L_{3a}) is due to an increase in the input consumption streams of methanol, oil and KOH, resulting in an increase in energy consumption of the transesterification reactor even though the energy consumption in the methanol distillation column reboiler is lower. This is however counter-intuitive to the argument that stronger integration of environmental technologies in the design problem will result in design solutions with a lower water demand. However, since the objective for pathways 3 and 6 is to maximize net water provisioning supply, the optimal design of the ABR and the wetland is enough to supply most of the water demanded by the process. This is particularly the case for designs with ecosystems (pathway 6) for the high-water cost scenario as mentioned earlier. Thus, the TES design with feedback allows for a system design with a larger ecosystem service demand compared to the designs obtained by the end-of-pipe and integrated design without feedback cases (with ecosystems and technology), but the availability of water provisioning ecosystem service due to the wetland ecosystem is sufficient to meet a significant portion of the process water demand.

Existence of Innovative Designs. Figures 11 and 12 depict the multi-objective optimization results for different pathways. Each point on the Pareto curve is found by optimizing for the ecosystem service demand and NPV objectives for pathways 1, 2, 4, and 5, and between net ecosystem service supply and NPV for pathways 3 and 6. The ϵ-constraint method is used to generate points on the Pareto curves, by constraining the system NPV. Each point on this curve is obtained by generating designs for a fixed value of NPV ranging between the two extreme points on the curve. Discontinuity in points maybe due to the absence of an optimal solution for a given NPV. Design solutions to the right of the y-axis (NPV = 0) represent designs that have a positive system NPV. Comparing the curves in the figure, we can see that for each design option, inclusion of ecosystems in the process design framework as opposed to an end of pipe solution results in an expansion of the solution space resulting in novel solutions that are ecologically and economically better. This is evident from the Pareto curves for pathways 5 and 6, where ecosystems outperform conventional technologies (pathways 2 and 3) in most aspects. These curves are located in a region that is favorable from both an economic and environmental point of view and are unattainable from a purely techno-centric approach.

Analyzing the Pareto-optimal solutions for pathway 6, some design solutions in the integrated case that has feedback with ecosystems, also have a positive net present value with a large net water provisioning supply value ($V_k = -0.006$). Compared to the two extreme points on the curve generated by maximizing NPV (H_{6a}) and maximizing net water provisioning supply (H_{6b}), this represents a design that is "win-lose," where the system has a lower NPV compared to the maximum NPV design point (H_{6a}) but with a larger net water provisioning supply. This design with lower NPV and larger net ecosystem service supply (H_{6c} in Figure 12) has different operating conditions and design variables compared to the maximum NPV design (H_{6a}). The input flow rates of methanol, oil and phosphoric acid for this design are lower than the maximum NPV design case, while the overall recovery of methanol in the distillation column is 94% compared to the maximum NPV design case (98%). The optimal reflux ratio for the distillation column is 1.65 compared to maximum NPV design case of 1.207. This increase in reflux ratio results in a higher energy consumption in the reboiler. However, the lower input flow streams for this design results in a decrease in energy consumption of the transesterification reactor resulting in a lower energy and water demand for the system. The low recovery of methanol affects the quality of wastewater leaving the system with a higher COD concentration than the maximum NPV design case but the optimal wetland size is 13,921 m^2, only slightly smaller than the maximum NPV design case of 14,447 m^2. The lower NPV for this design is primarily due to a lower revenue generated from the sale of products and by-products, even though the manufacturing cost is smaller. Detailed design parameters for this design can be found in column 9 in Table 2.

Such a trend can also be observed for the compromise design L_{6c} under the low water cost scenario. Once again, this design has a lower NPV than the maximize NPV design (L_{6a}) but a larger net water provisioning supply ($V_k = -0.005$). The input flow rates of methanol, oil and phosphoric acid for this design solution are lower than the maximum NPV design, resulting in a lower energy consumption. Methanol recovery for this design (97%) is slightly lower than the maximum NPV design case (99%) but the optimal reflux ratio for the distillation column is 1.53 compared to 1.241 for the maximum NPV design case. Higher reflux ratio results in a larger reboiler energy demand, but the energy consumption and optimal temperature of the transesterification reactor are larger for the NPV design ($T = 52°C$) than the compromise design ($T = 48°C$). This results in a lower energy and water demand for this system (L_{6c}). Water leaving the production plant has a

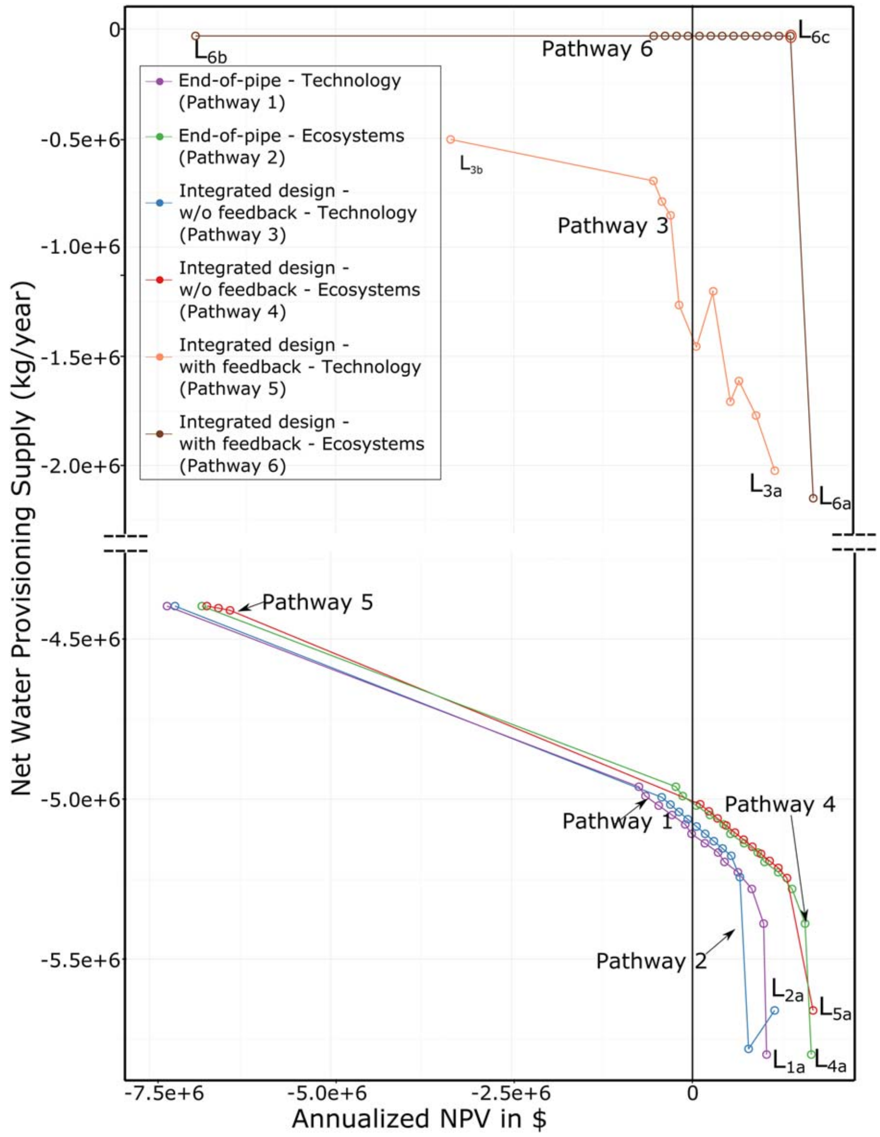

Figure 11. Multi objective optimization for the low water cost scenario.

Results indicate that inclusion of ecosystems as unit operations in conventional design problem expands the solution to result in innovative solutions that are "win-win." One such solution is the compromise design marked by L_{6c}. [Color figure can be viewed at wileyonlinelibrary.com]

higher COD concentration for the compromise design, resulting in an optimal wetland size of 13,395 m^2 compared to 9,415 m^2 for the maximum NPV design case. This also increases the amount of water feedback from the wetland for the compromise design case. Detailed design parameters for this design can be found in column 9 in Table 2. Thus, with minor changes in the process operating conditions and compromises in the system NPV, it is possible to identify designs that have a much smaller ecological overshoot compared to a system designed by purely techno-centric methods.

Comparison between Low and High Water Cost Scenarios. As mentioned before, different design trends were observed for the scenarios with low and high-water costs. We compared the optimal design points for the maximum NPV case across all design pathways between the high (Table 2) and low (Table 1) water cost scenario. For the end-of-pipe designs (pathways 1 and 3), a reduction in water demand or external water consumption was observed as the price of water increased. Comparing the optimal designs for the maximize NPV case for pathway 2 (L_{2a} and H_{2a}), the overall water demand remained constant. However, for the same design scenario with ecosystems (pathway 5, L_{5a}, and H_{5a}), water demand and the total external water supply increased by 2.7% as the water cost increased. This increase in water consumption may be attributed to the increase in energy consumption in the transesterification reactor, with an increase in input consumption of methanol, oil, and phosphoric acid. However, a different trend was observed for the integrated designs with water feedback. Specifically, for the integrated design with feedback with technology case (pathway 3, H_{3a}, and L_{3a}), external water consumption remained at 34.7% relative to the demand, as water cost increased. For the integrated design with feedback with ecosystems case (pathway 6), external water consumption reduced from 37% (L_{6a}) to 4% (H_{6a}) of demand as the water cost increased. This significant reduction in water consumption with increase in water cost for the TES case is due to an

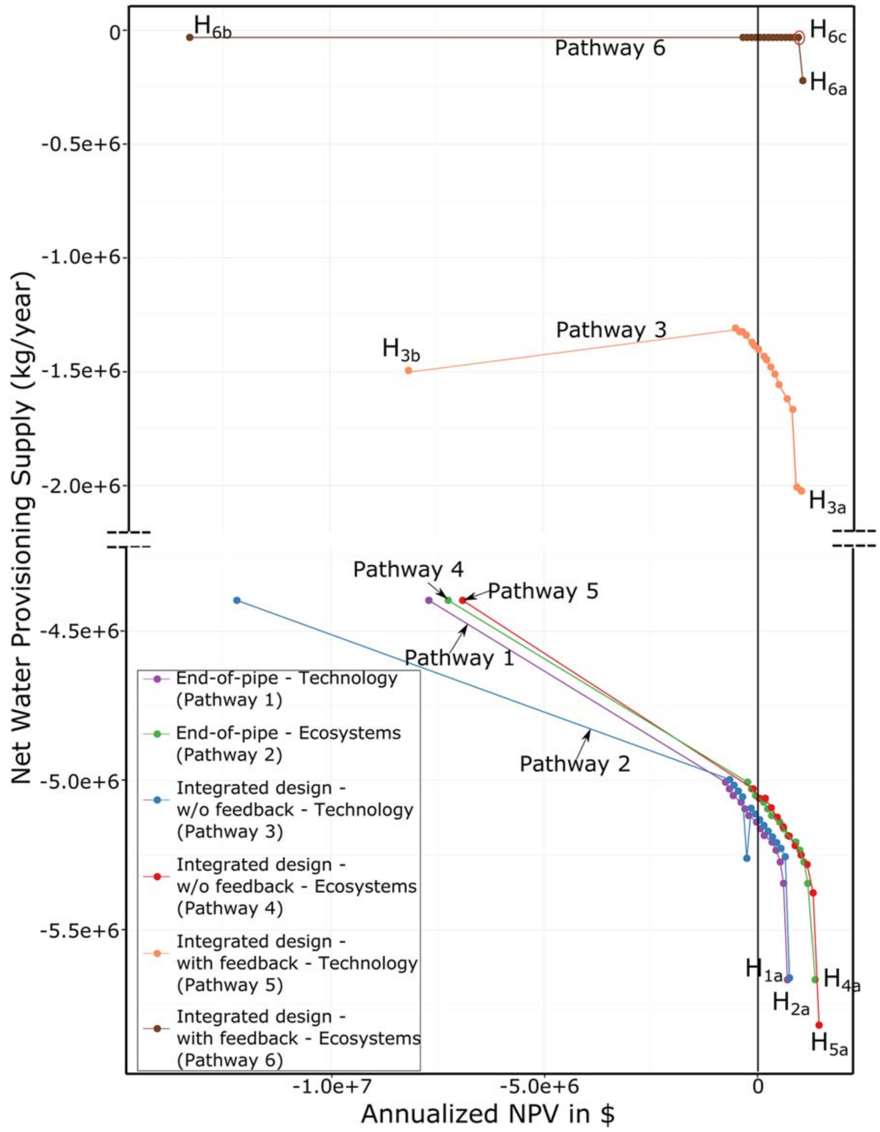

Figure 12. Multiobjective optimization for the high-water cost scenario.

With increase in water cost, a significant improvement in net present value and net water provisioning supply was observed for the integrated design with feedback with ecosystems case compared to conventional designs. [Color figure can be viewed at wileyonlinelibrary.com]

increase in the size of the wetland from 9,145 m^2 to 14,447 m^2 resulting in a higher water feedback, and a reduction in water demand with lower energy consumption in the transesterification reactor. This indicates that it is cheaper to redesign the wetland to recycle more water than consuming process water from an external source as the price of water increases. These results indicate that, as the water cost increases, a significant improvement in objectives can be observed for the integrated design with feedback with ecosystems case, indicating that a TES approach results in a system with a higher net ecosystem service supply and a high NPV compared to conventional design approaches.

Model limitations

All the results presented in the previous sections are based on steady state models of the production process, ecosystems and pollution control equipment. The ecosystem service demand including demand for water provisioning and water quality regulation service is also assumed to be a constant. However, wastewater concentration from industrial sites will vary with time depending on performance of each unit operation in the production process. Similarly, the quality of water leaving the wetland system after treatment (COD, Oil concentration, etc.) may not always meet the desired value due to external disturbances to the wetland system. Even though the horizontal subsurface flow wetland system has limited exposure to the outside environment and the design of this system accounts for precipitation and evapotranspiration effects, intermittency in the performance of wetlands may arise due to water infiltration to the ground, changes in surface water temperature during extreme cold and performance of vegetation for water treatment. The surface water temperature is assumed to be 25°C throughout the year. In addition, presence of other possible contaminants in water like nitrogen and ammonia present in the soybean oil were not considered in the study here. This may affect area of wetland, depending on the quantity of impurities present. Changes in retention time of water on an hourly basis, depending on fluctuations in temperature were also not considered in the study here. Given that this is the first TES process design study of its type, these approximate models were used to evaluate feasibility of this idea.

Discussion and Future Work

This work introduces and discusses the concept of ecosystems as unit operations and characterizes several ecosystem functions similar unit operation processes in chemical engineering. The goal behind characterizing ecosystems as unit operations similar to chemical processes is to couple the design of technological and ecological systems, to balance the flow of goods and services between the two systems, for sustainability. Till date, most methods for designing sustainable systems consider only the ecosystem service demand quantified by environmental emissions and their impact while ignoring the ecosystem service supply and interactions that exists between the processes and surrounding ecological systems that they depend on. Ignoring the ecosystem service supply within the process design boundary has resulted in decisions that result in ecological overshoot of natural goods and services and lost opportunities for innovation.

To account for the role of ecosystems and ecological carrying capacity, a generic design framework that explicitly includes the ecosystem service supply in the objective function as opposed to conventional methodologies that consider only the demand was developed. The design framework also directly incorporates the mass and energy balance constraints of ecological systems quantified by unit operation models of ecosystems in order to identify the synergies and inter-dependencies that exists between technological and ecological systems.

The benefits of expanding the scope of traditional process design boundaries to include ecosystems as unit operations were demonstrated by application to a biodiesel production system. Ecosystems incorporated in the design framework include a treatment wetland that provides water quality regulation and water provisioning services. Several different process design configurations for water conservation, reuse, and treatment were synthesized including the use of an anaerobic baffled reactor as a conventional method and wetland as an ecological option. Design pathways included consideration of these treatment methodologies as an end-of-pipe solution as is the common practice today, integration of these environmental control strategies within the design problem but without water recycle, and integration with water recycle. Sensitivity of each design configuration to water cost was also analyzed. Results from the case study demonstrated that expanding the scope of traditional process design to include interactions with ecosystems resulted in designs that have a higher sustainability index than those obtained from a purely techno-centric approach. Absolute sustainability, wherein the supply of ecosystem service exceeds the demand was never reached in the TES design (with and without feedback) and in the end-of-pipe designs. However, only the integrated design with feedback (pathways 5 and 6) resulted in designs that tend toward absolute sustainability with ecosystems outperforming conventional technologies.

Results also showed that the integrated design with water recycle had the highest energy and water consumption compared to the end-of-pipe and integrated design without recycle options, and for this design the wetland ecosystem outperformed the ABR. These systems also have the highest ecosystem service demand for water provisioning service but the highest NPV and lowest external water consumption. It may seem counter-intuitive that systems that have the highest energy and water demand are best in terms of NPV and net water use. This is because, simultaneous design of the wetland ecosystem leads to system designs that have a larger ecosystem service demand, but the design of wetland can balance this demand, resulting in systems with higher absolute sustainability (largest possible index -0.04). In addition, for some specific designs in the integrated design with feedback with ecosystem case (L_{6c} in Figure 11 and H_{6c} in Figure 12), a small sacrifice in system economics compared to the max NPV case resulted in designs with a much smaller ecological overshoot for water provisioning service. Such solutions may not be obtained by adopting a traditional techno-centric design methodology.

Another major finding from this work is that, as the cost of water increases, a significant improvement in both the objectives were observed for the integrated Techno-Ecological design case. This design scenario (H_{6a}) had the highest NPV with 96% of the water demand being supplied by the wetland ecosystem. However, for the integrated design with feedback from the ABR, no increase in water feedback was observed as the cost of water increased. As the cost of freshwater is very likely to increase in the future due to a reduction in availability of clean water resources, this approach toward designing systems will be of greater significance. In addition, including wetlands as ecological alternatives to conventional technology would enhance resilience to scarcities.

While the results presented here are specific to a biodiesel production system with a treatment wetland, insights from this case study may develop into general design heuristics or rules of thumb for sustainable process design. One major aspect ignored in this work is consideration of other ecosystem services like carbon sequestration and air quality regulation. Future work will include these two ecosystem services by considering a forest ecosystem as a unit operation model in the process flowsheets, along with water provisioning service at the watershed scale through reduction in storm water run-off with restoration. Demand for carbon sequestration and air quality regulation service is created by stack emissions from the CHP and emissions from the biodiesel production process. Trade-offs and synergies between the three ecosystem services and system economics will be explored using multiobjective optimization techniques to identify design solutions that may be "win-win" solutions for cost and multiple ecosystem services.

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