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Multiobjective Optimization of Product and Process Networks: General Modeling Framework, Efficient Global Optimization Algorithm, and Case Studies on Bioconversion

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A comprehensive optimization model that can determine the most cost-effective and environmentally sustainable production pathways in an integrated processing network is needed, especially in the bioconversion space. We develop the most comprehensive bioconversion network to date with 193 technologies and 129 materials/compounds for fuels production. We consider the tradeoff between scaling capital and operating expenditures (CAPEX and OPEX) as well as life cycle environmental impacts. Additionally, we develop a general network-based modeling framework with nonconvex terms for CAPEX. To globally optimize the nonlinear program with high computational efficiency, we develop a specialized branch-and-refine algorithm based on successive piecewise linear approximations. Two case studies are considered. The optimal pathways have profits from −\$12.9 to \$99.2M/yr, and emit 791 ton CO_2-eq/yr to 31,571 ton CO_2-eq/yr. Utilized technologies vary from corn-based fermentation to pyrolysis. The proposed algorithm reduces computational time by up to three orders of magnitude compared to general-purpose global optimizers. *AIChE J*, 61: 530–554, 2015
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Introduction

As the risk of global warming and future climate change continues to grow with fossil fuel combustion, biofuels and biochemicals (hereafter referred to as bioproducts) have been focal points of discussion in the energy and environmental spaces over the past decade. When implemented correctly, bioproducts processes are seen as a potential strategy toward weaning ourselves off of fossil energy.[1,2] Much like its chief competitive feedstock—petroleum—biomass has the potential to be converted into a plethora of different products, ranging from fuels to high-value or commodity chemicals.[3–11] Unlike petroleum, biomass has the potential to be a carbon-neutral feedstock, meaning that the amount of carbon emitted into the environment is equal to the carbon captured during biomass cultivation. However, in many cases, making a process more environmentally sustainable increases production costs, diminishing profitability. Thus, a complex tradeoff of environmental sustainability and economics arises when considering a bioproducts process.[12–14] Further tradeoffs can include social issues such as the number of local jobs accrued when building a biofuels facility.[15,16] An ideal bioproduct process is one that is both environmentally and economically sustainable. Indeed, this must be the case to compete with and eventually out-perform current petroleum-based processes.[17]

Further complicating the issue is the sheer variety of biomass feedstocks, conversion technologies, and potential products.[6,11,18,19] Noncellulosic fermentation-based bioethanol processes make up the bulk of the United States biofuel sector, and are among the most well-understood technologies at a commercial scale.[20,21] Lignocellulosic bioethanol technologies have been in development for decades, but their economics remain a challenge.[4–7] In general, current lignocellulosic bioethanol processes have high energy costs and might not generate enough coproducts to be economical.[7] Algal and thermochemical conversion technologies are, for the most part, still in the development and planning stages. However, these technologies boast a huge potential to produce a wide array of different products. For example, one can convert the biomass to synthesis gas (gasification), pyrolyze it (pyrolysis), or liquefy it (hydrothermal liquefaction [HTL]), all leading to different pathways and products.[8–11] At this stage of technological development, however, key economic and environmental questions must be answered to determine if new bioconversion processes can be commercially viable. A comprehensive strategy that optimizes the environmental and economic tradeoff at all levels of the bioproduct value chain could be a valuable tool to help answer these questions.

In addition to the motivators of diminishing quantities and declining volumes of global oil production predicted in the future, some governments around the world have mandated that a certain amount of their fuels must be derived from biomass. Brazil's government gives strong incentives to use domestic ethanol produced from sugarcane as an automotive

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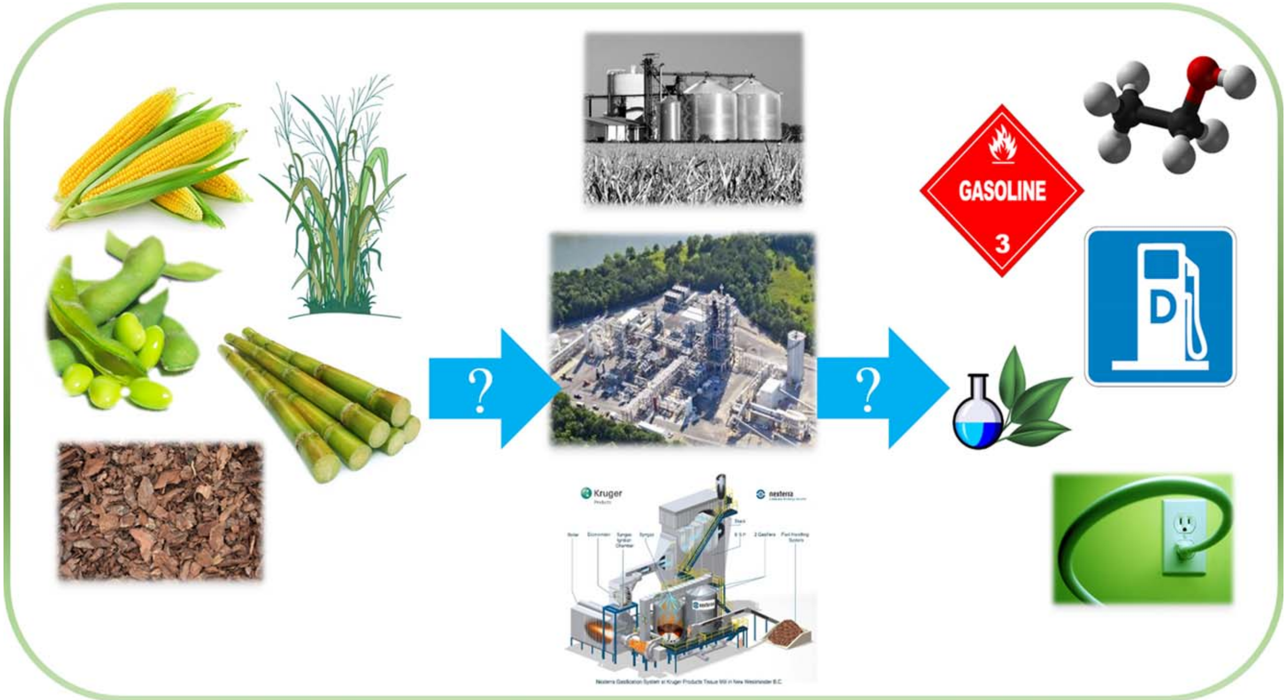

Figure 1. Which feedstock is best to use through which pathway to make which product?

The present work aims to narrow in on the answer to this question. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fuel. The program has been successful in reducing the quantity of petroleum consumed in Brazil, as around 40% of the nation's vehicles are flex fuel vehicles with engines that can take up to 100% ethanol.[21] Brazil produced 21.1 billion L of ethanol in 2011, representing approximately one quarter of global production at the time. The United States Environmental Protection Agency (EPA) also set mandates on minimum volumes of biofuels to be incorporated into the nation's fuel supplies. Termed the Renewable Fuel Standards (RFS) these standards stem from the Energy Independence and Security Act of 2007 (EISA), and mandate the production of four types of biofuels—conventional biofuel, biomass-based diesel, cellulosic biofuel, and other advanced biofuels. The goal of these standards was to galvanize firms to meet the lofty goals set in the EISA legislation. However, advanced biofuel production in the United States is anemic at best and is nowhere near the RFS goals for advanced biofuels. Thus, the EPA recently revised the RFS, slashing targets for advanced biofuel production.[22] Additionally, existing advanced biofuel producers are struggling. A promising producer, KiOR, announced in their 10-K in March 2014 that they elected to cancel continuing operations to complete a series of optimization projects to try to return to profitability.[23] At the time, they were unsure of their ability to continue as an operating firm, and had to procure a huge boost of $25M to stay in business. Clearly, optimization of bioproduct systems must be performed to ensure the profitability of these complex technologies.

However, the development and subsequent optimization of a comprehensive bioconversion technology network is not without its challenges. There is an enormous variety of potential biomass feedstocks to use, such as switchgrass, corn, corn stover, hard- and soft-woods, Jatropha, rapeseeds, timber, and paper wastes. These feedstocks all have different compositions and properties. Some are high in oil precursors, such as Jatropha, algae, and palm. Others are high in lignocellulosic material, such as woody biomass. Similar feedstocks can be processed through the same family of technologies, but the processing conditions, pretreatment, and postconversion upgrading steps will all depend on the feedstock. Further complicating the matter is the number of different biomass processing options at each step of the bioconversion pathway, including pretreatment, conversion, and upgrading. The intricacies and quantities of bioconversion technology choices have posed significant problems in choosing which product to make, how to make it, and which feedstock to use (Figure 1). It is likely that there is no single technology pathway or feedstock that is ultimately the superior choice. A combination of economic and environmental factors on local, regional, or global levels will all impact the choice of technology pathway and feedstock utilization. A base model for the representation of these complexities and underlying factors must be constructed if uncertainties regarding bioconversion technology deployment are to be minimized or understood.

It is the aim of this work to develop a general, network-based model to select the optimal conversion pathways while considering both pathway economics (e.g., the tradeoff between capital expenditures [CAPEX] and operating expenditures [OPEX]) and environmental sustainability. While we focus on applying this network model to a bioconversion case, the model is general enough to apply to a wide variety of product and process network problems. A technology network is constructed from a myriad of technical and literature sources, and key economic and environmental constraints and calculations are included. Multiobjective optimization is performed via the augmented ε-constraint method over the optimal pathway's annual profit and annual Global Warming Potential (GWP).[24] Capital costs for each technology in the pathway are assumed to scale with capacity in a nonlinear fashion, resulting in a nonlinear program (NLP) with nonconvex terms. An efficient global optimization algorithm based on successive piecewise linear approximations using specially ordered set variables (SOS1) is developed, resulting in significant computation efficiency increases, illustrated in two bioconversion case studies. A small case study seeks to identify the optimal processing pathway for 860,000 ton/yr of hardwood feedstock under a demand of 3.05 Mgal/yr of gasoline. A larger case study identifies optimal processing pathways for a feedstock portfolio of 8,600,000 ton/yr of all biomass feedstocks and a demand portfolio of 2.88 Mgal/yr of ethanol, 2.73 Mgal/yr of diesel, and 3.05 Mgal/yr of gasoline. The model presented in this work represents a key step toward the development of a comprehensive bioconversion optimization model.

In summary, this work presents the most comprehensive multiobjective bioconversion optimization model to date. A global optimization strategy that uses a novel branch-and-refine algorithm based on successive piecewise linear approximations of nonconvex terms is implemented. It should be reiterated that the modeling framework and solution strategies within this work are general enough to describe a variety of processing networks. The proposed branch-and-refine algorithm can be used in other similarly structured nonconvex optimization problems to increase computational efficiency and quickly find global optima. The case studies provide a novel view into the interconnectivity of a multitude of bioconversion pathways and provide a new understanding of profitable and environmentally responsible bioconversion pathway selection.

This article is organized as follows: first, a literature review on the optimization space will be provided, followed by the problem statement, methodology, model formulation, and case studies. Finally, a discussion on the results will be presented.

Literature Review

It is certainly true that much progress has been made toward solving the bioproducts optimization problem. On the product optimization side, a reaction network generator called RING (short for Rule Input Network Generator) can generate large networks of possible thermochemical biomass conversion routes.[25,26] Additional reaction pathway identification networks using reaction network flux analysis were also extended to the biofuels case.[27] Such network generators might be double-edged swords: certainly, they provide foundations for the development of novel biotechnologies and bioconversion pathways, but such tools also provide a plethora of new options, potentially making it more difficult to find the best pathway from feedstock to product (Figure 1). To that end, several economic optimization studies have been performed for a variety of bioconversion systems. Several bioethanol economic optimization studies considering biomass transportation costs, capital costs, and operating costs can be found in the literature.[28,29] Gasification-based integrated biorefineries have also been optimized under economic constraints using multiple-cascade automated targeting approaches.[30] Significant previous work has been done in bioconversion process and network modeling, and these works are now highlighted.

Kim et al. performed a thorough overview of economic optimization of a multitude of biofuels technologies.[31] As in many large-scale economic network studies, various technoeconomic factors were understandably neglected, such as biomass transportation cost, scaling capital cost with plant size, and emissions throughout the process. Additionally, the capacities of the upstream biomass feedstock processing steps were fixed to a predetermined value. Thus, all that was to be determined was the bioconversion pathway—the capital and operating costs of the pathway were constants. While certainly useful if the facility is to be built to a prespecified size, it is possible that the proposed facility size and capacities of each process would be allowed to vary during the planning phase. Facility planning done in this fashion allows local, regional, or even global economic and environmental considerations. Additionally, capital and operating costs typically scale differently with capacity, with CAPEX tending to follow a nonlinear, nonconvex scaling, and OPEX following a more linear scaling. Pathways selected only on CAPEX or OPEX scaling criterion might not be truly optimal—it is crucial to treat each concept explicitly. If the end goal is to produce as much biofuel or bioproduct as possible both economically and in an environmentally sustainable way, allowing the facility size to vary while considering the tradeoff between CAPEX and OPEX scaling is critical. Thus, one of the goals of the work is to address this issue in a network-based optimization model.

Gong et al. developed a highly detailed process model for algal-based processes.[32] Similarly to the current work, a large number of processing options and pathways were considered for algae processing. The addition of detailed mass and energy balances led to a complex fractional mixed-integer nonlinear programming (MINLP) problem with a structure strongly specific to the algal-based processes considered. The aim of this work, however, is to develop a general network-based model that is independent of the specific processes modeled within. Thus, to ensure that the network-based optimization of a bioconversion pathway that includes but is not limited to algal-based processes is computationally tractable, each technology pathway in the network should be represented more broadly compared to a process-based model. While we emphasize modeling and algorithmic development, the key focuses of this work are to construct the most up-to-date bioprocessing pathway network and to efficiently solve a general network optimization model for bioconversion pathways.

Other methods have developed recently to optimize bioconversion pathways over a bioprocessing technology network. Quaglia et al. developed an integrated business and engineering optimization method to simultaneously generate a bioprocessing technology superstructure and optimize the design of a bioethanol plant from that superstructure.[33] The methodology takes advantage of a series of logic-based expressions to relate variables and parameters to each other, reducing the amount of time it takes to formulate and specify a model. Our approach will instead focus on taking advantage of the underlying mathematical structure of the problem, which will lend itself well to solving the problem more efficiently, especially as the network/problem size increases. Additionally, our goal is to optimize a bioconversion pathway over all available pathways including but not limited to bioethanol-producing routes.

Other approaches have also been developed for the optimization of biofuel processing pathways. Bao et al. developed a method to rapidly and systematically identify process-technology pathways, with a focus on biofuel production.[34] This approach has been further explored by

Figure 2. Biomass processing and utilization network superstructure for the current work.

Light red indicates intermediate processes, yellow indicates processes that produce a final product/byproduct, blue indicates a final fuel product, green indicates a biomass feedstock, and orange indicates a byproduct. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

several subsequent contributors to account for sustainability metrics.[35,36] A key feature of these models revolves on carefully accounting for the chemistry involved in each process. Our approach is a broader one; we aim to develop a model that can efficiently screen and optimize over a network of hundreds of candidate processes for economic and environmental performance. Thus, we adopt a black box approach to represent each process to focus more on the optimization of the resulting process pathway network.

Even with this progress, however, there remain many gaps in network-based analysis and optimization of bioproduct process systems, and there is a strong need for a suitable computational infrastructure to solve such problems.[37] Little algorithmic work exists that aims to optimize bioconversion pathways over the gamut of available biomass feedstocks and conversion technologies. Specifically and to the best of our knowledge, no works exist that perform multiobjective optimization over the entire portfolio of bioproduct technologies while taking into account economic and environmental objectives. Multiobjective optimization (e.g., economic and environmental) studies that aim to study choices between all known bioconversion pathways are, as of yet, few and far between. Additionally, many of these studies are concerned with large-scale supply chain problems. Rizwan et al. studied process network optimization specifically for the production of biodiesel from algae.[38] Santibañez-Aguilar et al. explored an economic and environmental multiobjective optimization of biomass-to-fuels processes.[12] However, each process was

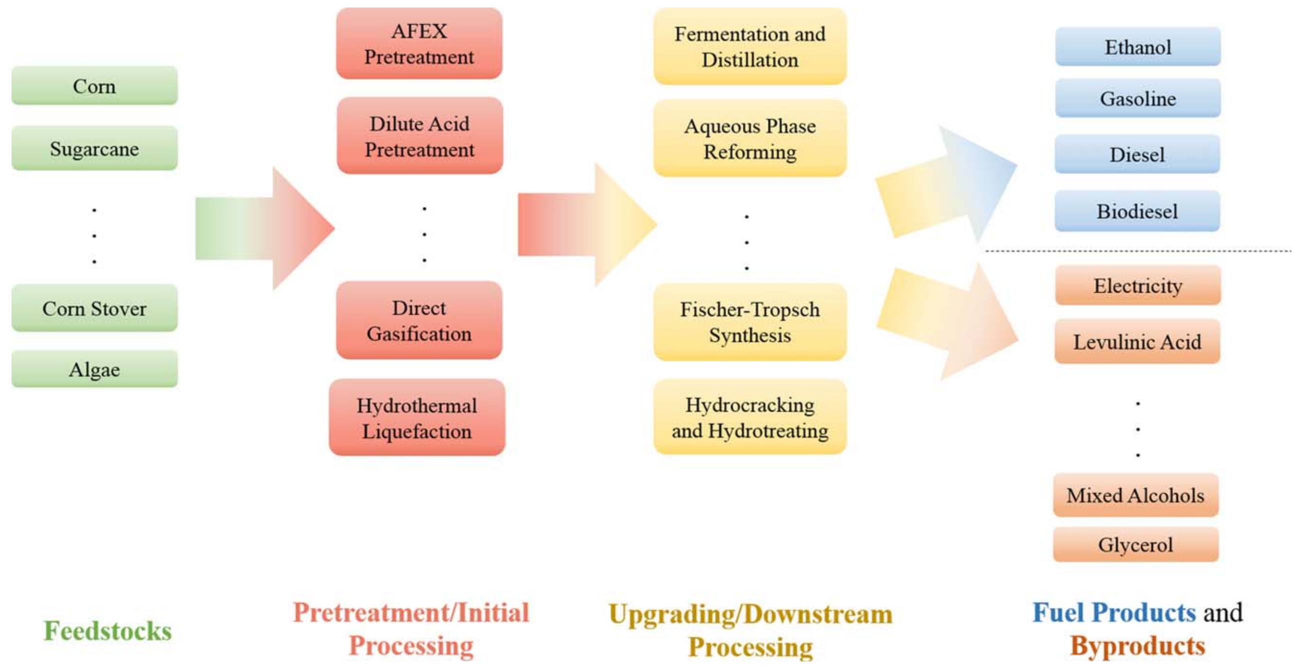

Figure 3. Simplified sample of the bioconversion network.

Feedstocks can be processed through a variety of technologies to produce fuels and byproducts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modeled as a block pathway. For example, the production of ethanol from sugarcane was represented as one block technology with one conversion factor that represented all inner processes such as pretreatment, acid hydrolysis, and fermentation. One goal of this work is to demonstrate the interconnectivity of bioconversion technologies. Thus, more detail compared to the aforementioned study is incorporated.

This work aims to narrow several knowledge gaps and address pertinent challenges in both network modeling and bioconversion pathway optimization. A general network process model is presented that is amenable to a variety of different network problems, and includes important considerations such as capital costs that scale in a nonconvex fashion with capacity. The model can take in a host of data, including conversion values, supply and demand constraints, and emissions from feedstock transportation and processing, allowing for the modeling of a large number of process network problems. The model is a nonconvex NLP, so a specialized branch-and-refine algorithm based on successive piecewise linear approximations is developed for efficient global optimization of the proposed problem. Much like the presented model, the algorithm is general enough to be utilized under a variety of different models and applications, adding another tool for optimizing large network models. Finally, the largest bioconversion network to date of 193 technologies and 129 compounds/materials is constructed (Figure 2) and then optimized within the presented modeling framework. The case studies evaluated over this bioconversion network give novel insights into bioconversion pathway choices when considering all available options.

Background

This work amalgamates data from a host of previous process studies and bioconversion literature, resulting in the most comprehensive biomass to fuels modeling network to date, with 193 technologies and 129 materials/compounds.[4–9,18–20,39–93] Some of the data comes from process design reports, where the processes were carefully simulated in well known and widely used chemical engineering simulation software (e.g., data for the biodiesel processes).[19] Other data for the present model was retrieved from pilot plant designs or other designs in the field (e.g., other algal processes).[18] At a very minimum, data concerning all processes involved in the superstructure are based on a technoeconomic analysis and were not extrapolated from solely lab-scale data.

Figure 2 represents the entire network; a simpler representation is given in Figure 3. In this section, a brief overview of recently published data, technologies, and where they fit into the bioconversion landscape is given. The compilation of such a variety of biomass processing pathways and technologies posed a significant challenge. Care was taken to ensure that chosen technologies met a relatively high level of technological maturity. For example, technologies with only lab-scale data were usually not included, as many key parameters can change during scale-up studies. This decision criterion had to be put in place to ensure meaningful results from the optimization problems, as unit processes could have capacities of hundreds of thousands of tons per year.

Pretreatment of biomass is an important and potentially costly component of the bioconversion process.[40] When pretreating lignocellulosic material for the production of bioethanol, one of the aims of the process is to increase the enzymatic accessibility of the biomass, allowing for greater yields downstream. Pretreating woody biomass reduces recalcitrance in the wood—serving essentially the same purpose as pretreatment for general lignocellulosic materials. Various methods of pretreatment have been under investigation for use in bioconversion processes, including dilute acid pretreatment, hot water pretreatment, and ammonia fiber expansion-based pretreatment, as well as physical pretreatments such as milling, shredding, and chopping. New pretreatment methods are always being developed and refined, including a recent idea to use white rot fungi to reduce recalcitrance in woody biomass[94]; this particular technology, however, is not ready for commercialization.

However, other pretreatment technologies are nearing commercial readiness. In recent years, a new biomass pretreatment process using an ionic liquid at moderate temperatures—ionic liquid pretreatment (ILP)—has been developed.[39] Much like other pretreatment technologies, ILP is known to dissolve cellulose and lignin as well as hard- and softwoods, switchgrass, and corn stover. The use of ILP followed by acidolysis is appealing due to the lower temperatures needed for ILP operation (160°C or lower for half an hour to 6 h). Thus, ILP provides lower operating costs compared to other pretreatment techniques, such as hot water pretreatment. The technology is still in its developmental infancy relative to other pretreatment techniques, but some initial steps in technoeconomic performance evaluation for corn stover pretreatment have been taken.[39] Thus, the technology is added to the current model.

HTL of biomass is another promising technology in the bioconversion portfolio.[8,9] HTL, much like pyrolysis, produces a bio-oil that must undergo further upgrading via hydrotreating and hydrocracking to produce a fuel product. Unlike pyrolysis, however, HTL produces a bio-oil with a much lower oxygen content, on the order of 10–20% instead of around 40%, reducing downstream upgrading costs. Likewise, HTL bio-oil has a significantly higher heating value at approximately 35 MJ/kg compared to pyrolysis oil (16–19 MJ/kg), a value much closer to the heating value range for petroleum-based fuels (40–45 MJ/kg). However, the process requires high temperatures of 250–380°C and high pressures of 5 to 30 MPa. A technoeconomic analysis has recently been performed on HTL as the technology moves closer to commercialization, and this advancement has been incorporated into the present model.[9]

Algal processes provide perhaps the most promising production pathways for bioconversion processes.[38,41–43] Similarly to some thermochemical biomass conversion processes, algal conversion processes can result in a bio-oil that can be subsequently upgraded to fuels or other useful products. Thus, in this work, a variety of algae cultivation, extraction, and harvesting methods are included to incorporate these high-potential technologies. To the best of our knowledge, algal-based bioconversion processes have not yet been compared to other biomass conversion technologies in such a comprehensive multiobjective economic and environmental framework. As algal-based conversion processes are relatively new compared to other types of biomass conversion technologies considered in this work, only a few thoroughly examined algal technologies have been added to the bioconversion network. For cultivation, raceway (or open) pond growth, bubble column photobioreactors, and flat panel airlift photobioreactors were added to the network. Algae harvesting methods include electrocoagulation and dissolved air flotation with centrifugation. Extraction methods are limited to butanol solvent extraction or HTL of the algae. In both cases, the extracted lipids or bio-oils are further upgraded to fuel products. An option to anaerobically digest the spent algae is also provided in the network.

Problem Statement

This work focuses on optimal processing pathway selection within the bioconversion product and process network. As such, many parameters are retrieved, calculated, or estimated from the most up-to-date literature sources, design reports, or commodity and chemical markets.[95,96] Such parameters include:

- The average electricity mix of the United States,
- The emission factors for each source of electricity,
- Emissions associated with transportation by truck of biomass to the facility,
- Biomass feedstock prices,
- Prices of all other inputs,
- Selling prices of byproducts and products,
- A base capacity for each technology,
- An initial capital cost corresponding to the base capacity for each technology,
- An initial operating cost corresponding to the base capacity for each technology,
- The yields for each process output.
- The average trucking distance to transport the biomass feedstock to the processing facility,
- The variable transportation and fixed transportation costs for biomass,
- The availability for each biomass feedstock/input,
- The demand for each final product,
- The minimum purchase quantity of each feedstock/input.

Noteworthy assumptions include:

- All purchased feedstock is successfully converted at the facility (no spoilage, unreacted feedstock, etc),
- The fuels produced are drop-in ready, and are sold to the end users,
- All biomass feedstock is transported to the facility solely by diesel-burning trucks,
- The facility will be able to sell all products produced from the pathway,
- Fixed costs and some components of the variable operating costs are set fractions of the capital cost,
- Capital costs scale with capacity in a nonconvex fashion,
- Variable operating costs are assumed to scale linearly with capacity,
- There are no dramatic variations in operating costs over the life of the facility,
- A tax rate is assessed on all gross margins at the facility.

Finally, the ultimate goal of this model is to determine the optimal bioconversion processing network based on economic and environmental constraints as well as mass balances. Thus, major decision variables in this optimization model include:

- Technology pathway selection,
- Sizing of technologies in the pathway,
- The quantity of feedstock to purchase,
- The quantity of product(s) to produce,
- Capital and operating costs,
- Environmental impacts from transporting and processing biomass.

Model Formulation

We formulate a general NLP model that simultaneously maximizes the profit and minimizes the environmental impact of a conversion pathway from an expansive technology network. Nonlinear terms arise within the economic constraints, namely the relation between the facility's capital cost and its capacity. The operating costs of the technology pathway and transportation costs of the required feedstock are calculated.

Indirect emissions from process energy sources and direct emissions from diesel truck transportation of feedstock to the facility are calculated following the life cycle approach. Varying parameter values, such as the final product demand mix or the mix of available feedstocks gives the model flexibility to optimize over a range of possible scenarios. A list of indices, sets, parameters, and variables is given in the Nomenclature section. Parameters are denoted with lower-case symbols, and variables are denoted with upper-case symbols. The model is general in the sense that it can be applied to many types of process-product networks. Values of parameters, such as demand, prices, and yields can be tuned to the specific problem. We focus on a bioconversion network model in this study.

Mass balance, supply, and demand considerations

For each technology in the network (Figure 2), the standard mass balance relationship constraint must hold

$$P_i+\sum_j \mathrm{py}_{ij}\cdot X_j=S_i-\sum_j \mathrm{dy}_{ij}\cdot X_j,\quad \forall i \tag{1}$$

where P_i is the quantity of material/compound i purchased, py_{ij} is the productive yield of compound i processed in technology j, X_j is the capacity of technology j, S_i is the quantity of compound i sold, and dy_{ij} is the destructive yield of compound i consumed in technology j (note that this quantity is negative in sign). In other words, the quantity of a given compound purchased and produced must equal the quantity of that compound sold and consumed. Similar mass balance equations have been previously formulated for process network planning problems.[97]

Supply and demand constraints are the only inequality economic constraints considered in this work. The remaining economic considerations involve calculating the capital and operating costs of the conversion pathway. The quantity sold of each product i must be greater than or equal to the demand d_i

$$d_i\leq S_i,\quad \forall i \tag{2}$$

There are two constraints on the feedstock supply, one for a minimum purchase quantity mpq_i

$$mpq_i\leq P_i,\quad \forall i \tag{3}$$

and another for the maximum availability of each feedstock i, ma_i

$$P_i\leq ma_i,\quad \forall i \tag{4}$$

Economic considerations

The capital cost of technology j in the model is calculated from both a base capital cost and base year from either the scientific literature or design reports scaled by Chemical Engineering Plant Cost Indices.[98] Next, the capital cost must be scaled according to its calculated capacity X_j. This is performed by assuming the capital cost scales with capacity like so

$$CC_j=icc_j\left(\frac{index_j}{index_{base,j}}\right)\left(\frac{X_j}{refcap_j}\right)^{sf_j},\ \forall j \tag{5}$$

where CC_j is the capital cost of technology j, icc_j is the initial (base) capital cost of technology j, $index_j$ is the CEPC Index for the current year, $index_{base,j}$ is the base CEPC Index taken from the basis year, sf_j is the scaling factor of technology j and $refcap_j$ is some reference capacity of technology j. For this work, it is assumed that the scaling factor of each technology is 0.6, following the six-tenths rule.[98] Note that Eq. 5 adds a nonlinear, nonconvex term in the capacity X_j to the model, resulting in computational challenges for global optimization.

Production costs are calculated as the Total Annual Processing Cost ($TAPC_j$) and include terms for an annualized capital cost, variable annual operating costs, and fixed annual operating costs

$$TAPC_j=\left(\frac{r(1+r)^n}{(1+r)^n-1}\right)\cdot CC_j+\left(\frac{X_j}{refcacp_j}\right)\cdot ioc_j+fcf\cdot CC_j,\ \forall j \tag{6}$$

where the first term in parenthesis is a capital charge factor, calculated by assuming an interest rate r of 10% and a plant lifetime n of 20 years. The variable operating cost is assumed to scale linearly with capacity with an initial operating cost represented by ioc_j. Finally, a fixed cost factor fcf is introduced to estimate the fixed variable costs. This factor is taken as 5% of the capital cost of technology j.[98]

Both variable and fixed transportation costs are considered in this work, based on previous estimations concerning biomass transportation costs.[99,100] Thus, the variable transportation cost of biomass was taken to be \$0.456/ton/km, and the fixed transportation cost was taken to be \$4.839/ton. The annual variable transportation cost associated with biomass transport is calculated by

$$VTC_i=vtcc\cdot dist\cdot P_i,\ \forall i \tag{7}$$

where VTC_i is the variable transportation cost, $vtcc$ is the variable transportation cost coefficient, and $dist$ is the average distance for biomass transportation. Note that all variables and parameters in the above equation are general and the values can be tuned to specific network problems. For the bioconversion case explored in this article, an average transportation distance was calculated assuming the biorefinery is located in the middle of a biomass cultivation circle of radius 50 miles. This distance is regarded as a critical distance in order for a typical biorefinery to be cost-competitive.[101] As the average distance from the center of a circle to a point within the circle can be taken as one third of twice its radius, the average biomass transport distance within a circle of radius 50 miles was estimated to be 33.3 miles, or 53.6 km. Thus, the term $vtcc\cdot dist$ in Eq. 7 was taken as \$24.442/ton.[99,100]

The fixed transportation costs were similarly calculated

$$FTC_i=frcc\cdot P_i,\ \forall i \tag{8}$$

where FTC_i is the fixed transportation cost and $ftcc$ is the fixed transportation cost coefficient with a value of \$4.839/ton.[99,100]

Gross annual revenue can then be calculated as the sum of all sales minus all operating, processing, and transportation costs

$$Gross=\sum_i sp_i\cdot S_i-\sum_i fp_i\cdot P_i-\sum_j TAPC_j-\sum_i FTC_i-\sum_i VTC_i,\ \forall i,j \tag{9}$$

where $Gross$ is the gross revenue of the pathway.

Any positive gross revenue is taxed by federal, state, and local governments, and a total tax rate tr of 40% of earnings is taken as a rule of thumb assumption[98]

$$Taxes = tr \cdot Gross \tag{10}$$

Finally, the economic objective function of overall annual profit can be defined

$$OBJ_{profit} = Gross - Taxes \tag{11}$$

Life cycle-based environmental objective

The environmental component of the present model incorporates a gate-to-gate life-cycle assessment (LCA) methodology to calculate the GWP from both process and transportation emissions, as in several other publications concerning biomass/biofuel process optimization.[102,103] The current system boundary includes the transportation of biomass from the farm to the biorefinery, the processing of biomass and other inputs at the biorefinery, and the production of the final product portfolio. Thus, the model includes both direct (biomass transportation) and indirect (process) emissions. Biofuel transportation from the facility to an end use location is not considered for several reasons. Unlike transportation of biomass where an ideal transportation radius is relatively clear,[101] there is no straightforward method to calculate a standard distribution distance. This distance is more closely related to optimization of biofuel supply chains, which is outside the scope of the current study. Additionally, the bulk of transportation emissions are likely to come on the biomass transportation end, as the final liquid fuel has a much higher energy density than the incoming biomass. Finally, the mass of the transported fuel is necessarily significantly less than that of the transported biomass; so in comparison, the emissions due to transportation of the final products can be neglected with a likely low error rate. The goal of the current LCA-based approach is to provide a cursory perusal into the implementation of this life-cycle framework within the context of a complex bioconversion technology network, achieved by considering one life cycle impact category—the GWP—from biomass transportation and process operations. In other words, the GWP is taken as a representative environmental impact to demonstrate the validity and efficacy of the current model.

Direct transportation emissions are to be calculated assuming that biomass transportation is achieved via diesel-burning trucks. According to the Energy Information Agency (EIA), diesel fuel combustion emits approximately 73.15 kg CO_2 per MMBTU of energy.[104] Data compiled for the energy usage per ton per kilometer for biomass transportation by Börjesson et al[99] allows the calculation of the total amount of ton CO_2 emitted per ton of feedstock delivered to the facility

$$Tem = \sum_i tremf \cdot P_i \tag{12}$$

where *tremf* is a transportation emissions factor that reflects the CO_2 emission rate of a diesel burning truck per ton of feedstock delivered, and *Tem* is the total transportation emissions. Note that *Tem* is also GWP per annum, as CO_2 has a GWP factor of 1.

The electricity generation mix used to calculate the indirect emissions from the bioconversion pathway technologies was assumed to come from the national average mix of electricity generated, compiled in the EIA Electric Power Annual 2001–2013 database, taken from 2013 data.[105] Carbon dioxide–equivalent GWP factors (in units of mass of CO_2-eq per unit energy usage) for each source of electricity generation were also obtained from the EIA.[104] Combined with the unit energy consumption, these factors allow the calculation of the annual rate of GWP (ton CO_2-eq per year)

$$em_j = uec_j \sum_e ef_e \cdot emf_e \tag{13}$$

where the set e is the set of all sources of electricity generation to the bioconversion facility, uec_j is the unit energy consumption of technology j, ef_e is the fraction of the electricity generation mix of electricity source e, and emf_e is the emissions factor associated with generating electricity from source e. A total annual GWP for all processes within the bioconversion pathway(s), then, is simply

$$Pem = \sum_j em_j \cdot X_j \tag{14}$$

where *Pem* is the total emissions related to all processes within all selected bioconversion pathways.

Thus, the environmental objective function will be the sum of the direct transportation emissions and the indirect process emissions

$$OBJ_{GWP} = Tem + Pem \tag{15}$$

Model summary

Equations 1 through 15 represent a nonlinear, nonconvex, economic and environmental multiobjective optimization problem describing a bioconversion network with 193 technologies and 129 compounds, denoted as (P1) throughout the rest of this article, represented below:

$$\max\ OBJ_{profit} = Gross - Taxes$$
$$\min\ OBJ_{GWP} = Tem + Pem$$

(P1). s.t. mass balance, supply, and demand considerations (1)–(4)
economic evaluation considerations (5)–(10)
life cycle-based environmental considerations (12)–(14)

In summary, the model considers the tradeoff arising between CAPEX and OPEX due to the different ways in which these quantities scale with capacity, supply and demand market forces, annualized costs, and GWP from both direct (transportation) and indirect (process energy) sources. The model is a nonconvex NLP and is solved by several solution strategies, as discussed in the following section.

Solution Strategies

Multiobjective optimization procedure

A common method to solve multiobjective optimization problems is the ε-constraint method.[24] Essentially, the method holds one of the objective equations as a constraint less than or equal to some ε, while optimizing over the other objective. However, the method as it is most often used may not produce a set of wholly Pareto-efficient solutions—that is to say that there is no guarantee that all solutions will lie on the Pareto-optimal curve.[24] Thus, a modified version of the standard ε-constraint method, the augmented ε-constraint method pioneered by Mavrotas, is used in this work that can more efficiently handle multiobjective optimization problems

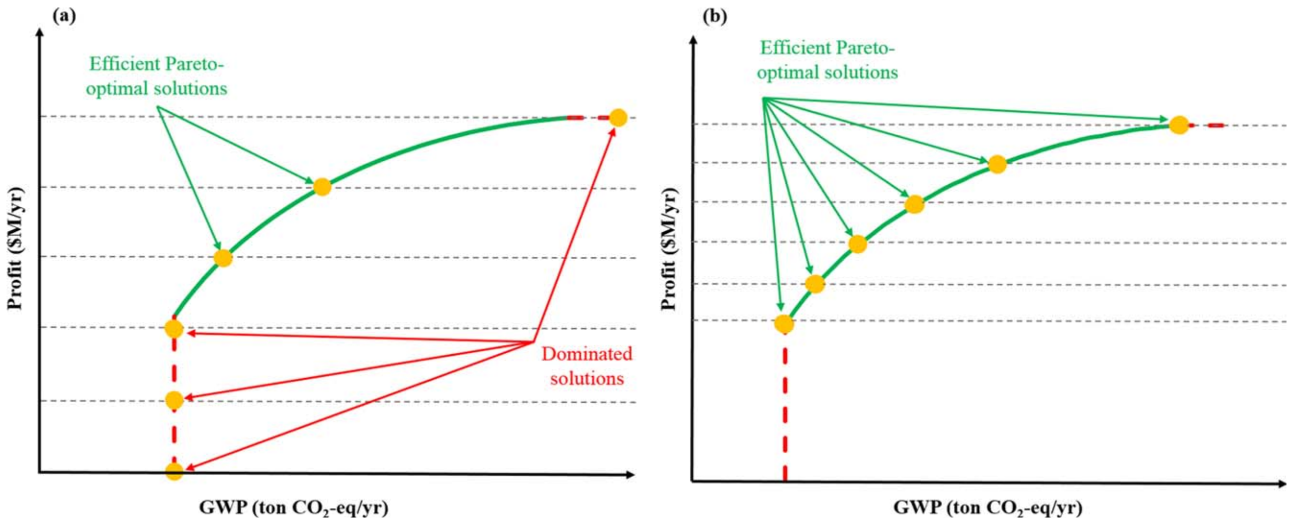

Figure 4. Potential solution generating scenario for (a) a traditional ε-constraint method and (b) the augmented ε-constraint method.

In each case, the solutions are evenly spaced along the vertical axis but only in the augmented ε-constraint method case are all solutions efficient and nondominated by Pareto-optimal solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and guarantee a set of efficient Pareto-optimal solutions (see Figure 4).[24] The main difference between the two methods is the construction of a "payoff table" in the augmented ε-constraint method, which calculates all extreme points on the Pareto-optimal curve. A set of evenly spaced, efficient solution points can be subsequently calculated, ensuring no inferior/inefficient points are calculated. Considering the large size of the present bioconversion network, such computation efficiency could be quite valuable.

Global optimization algorithm based on successive piecewise linear approximation

The NLP problem (P1) can be directly solved by off-the-shelf global optimizers, such as BARON 12.7.3 or SCIP 3.1.0. It should be noted that problem (P1) has only one type of nonlinearity. Thus, we can take advantage of this problem's mathematical structure and globally optimize (P1) with a branch-and-refine algorithm based on successive piecewise linear approximations. Considering the size and complexity of the technology network in this work, such a specialized global optimization algorithm could provide significant computational benefit. A discussion of the linearization procedure and the proposed solution algorithm is given below.

Piecewise Linear Approximation. In this work, the nonlinearity in capital cost calculations associated with Eq. 5 is approximated by a piecewise linear underestimator using special ordered sets (SOS), in particular special ordered sets of type 1 (SOS1). These sets allow at most one variable within the set to take a positive value, usually 1—all other variables in the set are set to zero. The nonlinearity in problem (P1) can be underestimated by successively solving an inner piecewise linear branch-and-refine approximation algorithm, giving a valid upper bound for the annualized profit in (P1).[106–108] This particular method was chosen as it has been shown to be faster than other linearization methods due to an increase in efficiency. GAMS has a variety of solvers that can work with SOS1 variables, including the CPLEX solver, allowing for efficient computation and rapid solving times.

Much like a typical piecewise linear approximation algorithm, the basic idea is to estimate a nonlinear variable term, X_j^{sf} in this study, with a linear approximation. In this case, the original nonlinearity for the capital cost in Eq. 5 is underestimated by an inner linear approximation (Figure 5). Note that by underestimating the capital cost, the algorithm provides an upper bound for the profit objective in the original problem (P1). If the capital cost is underestimated, then the annualized profit of the objective function OBJ_{profit} will be overestimated, thus providing an upper bound. An algorithm incorporating this underestimation will update the upper and lower bounds upon successive iterations, and, if the problem is feasible, the bounds will converge to the same answer found in the nonlinear case. A flowchart for the proposed solution algorithm compared to the NLP case is shown in Figure 6. Note that while directly solving the nonconvex problem (P1) provides a globally optimal solution, global solvers may not be able to converge to the optimum in a reasonable time frame. However, each iteration of the

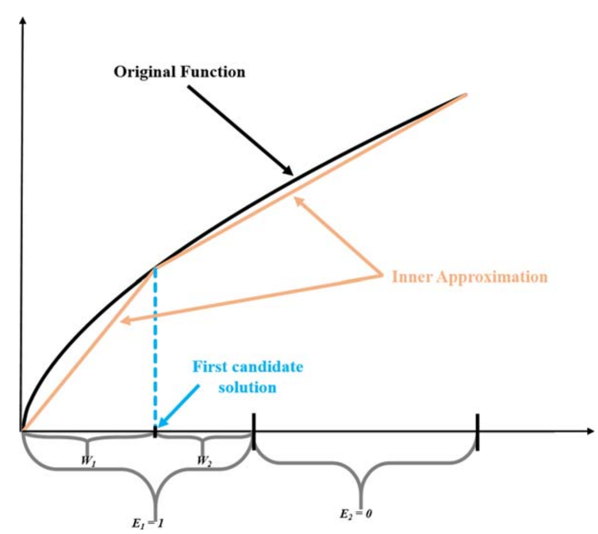

Figure 5. Piecewise inner approximations of a nonlinear, nonconvex function.

This figure shows the SOS1 method after the first iteration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

branch-and-refine algorithm in Figure 6b should be fast and efficient.

To approximate (P1) with SOS1 variables, first the capacity X_j is substituted with the following

$$X_j=\sum_{n=1}^{N} W_{j,n} \cdot u_{j,n},\ \forall j \tag{16}$$

and

$$\sum_{n=1}^{N} W_{j,n}=1,\ \forall j \tag{17}$$

where the total number of horizontal points on the grid in the piecewise linear approximation is given by n with N being the total number of grid points, resulting in $N-1$ intervals and line segments, $u_{j,n}$ are the values of the grid points in the X_j space, and $W_{j,n}$ are continuous, positive weighting terms for each $u_{j,n}$ in each interval. For example, if a point is exactly between grid points 2 and 3, $W_{j,2} = 0.5$ and $W_{j,3} = 0.5$. $W_{j,n}$ can be related to SOS1 variables through the following series of equations and constraints

$$\sum_{n=1}^{N} E_{j,n}=1,\ \forall j \tag{18}$$

$$W_{j,1} \le E_{j,1},\ \forall j \tag{19}$$

$$W_{j,n} \le E_{j,n-1}+E_{j,n},\ \forall j, 2 \le n \le N-1 \tag{20}$$

$$W_{i,N} \le E_{j,N-1},\ \forall j \tag{21}$$

$$0 \le W_{j,n} \le 1, E_{j,n} \in \{\text{SOS1}\} \tag{22}$$

where $E_{j,n}$ are SOS1 variables and serve as the position indicators—each $E_{j,n}$ has a value of 1 when the value of X_j lies in the nth interval and 0 otherwise. A graphical representation of a SOS1-based piecewise linear approximation with three grid points and two intervals is shown in Figure 5.

The nonlinear term X_j^{sf} can be approximated by some RX_j

$$RX_j=\sum_{n=1}^{N} W_{j,n} \cdot val_{j,n},\ \forall j \tag{23}$$

where $val_{j,n} = u_{j,n}^{0.6}$ is equal to the value of the nonconvex function at the grid point $u_{j,n}$ and serves as an estimator of X_j^{sf}. The new equation for the capital cost thus becomes

$$CC_j=icc_j\left(\frac{index_j}{index_{base,j}}\right)\left(\frac{RX_j}{refcap_j^{sf_j}}\right),\ \forall j \tag{24}$$

which is linear in the only variable in the equation, RX_j. Finally, a constraint must be added to ensure the value of RX_j is always greater than or equal to the linear approximation for X_j^{sf}

$$RX_j \ge \sum_{n} W_{j,n} \cdot val_{j,n} \tag{25}$$

Equations 1–4 and 6–24 result in an MILP problem, denoted as (P2) for the remainder of this article and represented more succinctly as:

$$\max\ OBJ_{profit} = Gross - Taxes$$

$$\min\ OBJ_{GWP} = Tem + Pem$$

(P2). s.t. mass balance, supply, and demand considerations (1)–(4)
economic evaluation considerations (6)–(10)
life cycle-based environmental considerations (12)–(14)
SOS1 piecewise linearization approximation constraints (16)–(25)

Since the capital cost is underestimated in the proposed piecewise linear approximation, the profit objective of (P2) is an overestimator of the true profit objective of (P1), providing a valid upper bound for (P1). The two problems (P1) and (P2) have the same feasible region, so a lower bound for (P1) can be found by substituting the solution of (P2) into (P1) and evaluating the objective functions. The final remaining challenge is iteratively solving (P2) until the gap between the upper and lower bounds is sufficiently small to satisfy a stopping criterion. In this work, a specialized branch-and-refine solution algorithm is proposed to handle this task, and a discussion of this algorithm is given next.

MILP-Based Branch-and-Refine Solution Algorithm. As this is a multiobjective optimization model, a choice must be made to determine the convergence criteria for the branch-and-refine algorithm. The profit objective function was chosen for this duty, as the profit depends more heavily on the nonlinear Eq. 5 than the environmental criterion. The algorithm begins with an upper bound of positive infinity and a lower bound of negative infinity (profits are allowed to be negative). At first, the piecewise linear approximation for each technology's capital cost is divided into only one interval, resulting in a straight line estimation of Eq. 5. This interval is constructed with a point at the origin, and another at a capacity *capmax* far larger than could be reasonably constructed for all technologies in the database, ensuring the solution exists in the approximation space. A candidate solution is found on this linear approximation by solving (P2). Updated upper and lower bounds must be calculated at this point to decide whether to add a grid point in the next iteration or if the approximation is good enough. The upper bound is taken as the economic objective function OBJ_{profit}, calculated from solving (P2). The lower bound for each iteration is calculated from the profit objective function of Eq. 11, with capital costs calculated by Eq. 5 using the value of X_j obtained from solving (P2). A gap between the upper and lower bounds can then be calculated

$$gap=\left|\frac{ub-lb}{ub}\right| \tag{26}$$

Note that the gap parameter is strictly positive, in case the profit is negative (net loss). If the gap is smaller than some tolerance level *tol*, then another grid point is added, refining the structure of the piecewise linear approximation. Another iteration on this new approximation is then performed. Refer to Figure 6 for a flowchart of the branch-and-refine algorithm.

An opportunity arises at this point in the algorithm to choose where to place the next grid point. In this work, the new grid point for each iteration is placed at the previous candidate solution of the linear approximation.[109–111] For example, Figure 5 shows how the piecewise linear approximation would look after one iteration of the algorithm,

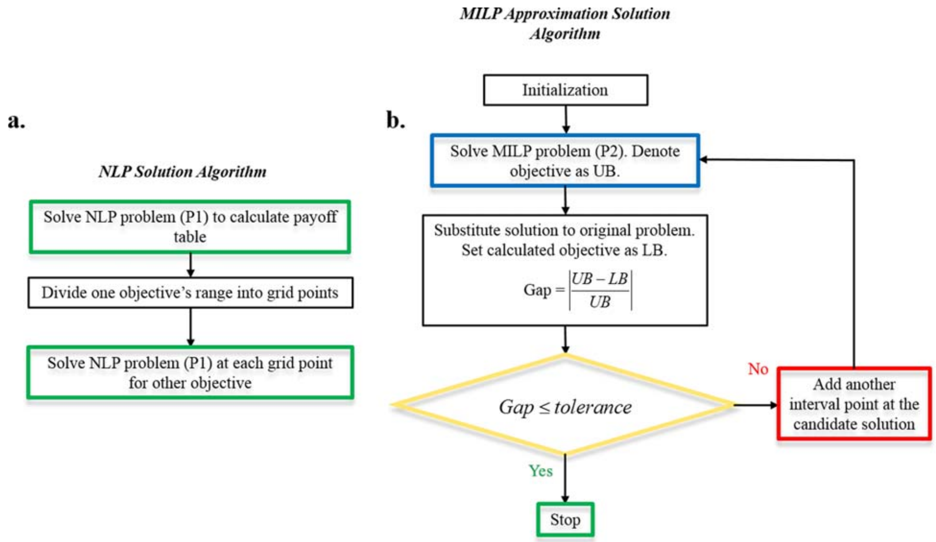

Figure 6. Algorithm flowcharts for generation of all Pareto-optimal points in the NLP problem (a) and the generation of one solution in the branch-and-refine algorithm (b).

Green steps denote final solution steps, yellow denote checking steps, red steps denote that another iteration is needed, and blue denotes solving an MILP with the SOS1 formulation. UB = upper bound, LB = lower bound. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resulting in two line segments, and three grid points. Technologies that are not selected in the bioconversion pathway will have their capacity $u_{j,n}$ set to zero. Thus, the linear approximation for these technologies will not change, as the "new" grid point will be placed at the origin. More grid points are added with successive iterations until the gap between the upper and lower bounds on the profit is smaller than the tolerance *tol*.

Case Studies

Two case studies are presented in this section and subsequently solved under both formulations (P1) and (P2). A small, illustrative case study demonstrates the validity of the model, and a larger case study reflects the complexity of the model and the efficiency of the branch-and-refine algorithm. The two case studies will be referred to as the small-scale case study and the large-scale case study, respectively, for clarity. The results of each case study are analyzed, with the bulk of the analysis focused on the large-scale case study results. Major differences between the case studies include the type and quantity of feedstock available and the type and quantity of products demanded. Prices for feedstocks that are listed on the Chicago Board of Trade were taken from average June 2014 prices on the exchange.[95] Prices for hardwood, softwood, sugarcane, and switchgrass were taken from a variety of sources[112–114] and converted to 2014 prices via a US price inflation calculator.[115] The prices for all fuel products were taken from the EIA to reflect prices as of June 2014.[116] The price of ethanol was assumed to be \$2.50/gal.[96] All figures shown in this discussion are based off of results obtained from solving (P2) with the specialized branch-and-refine algorithm, unless otherwise specified.

All computational experiments are performed on a DELL OPTIPLEX 790 desktop with an Intel(R) Core(TM) i5-2400 CPU @ 3.10GHz and 8 GB RAM. All models and solution procedure are coded in GAMS 24.2.1.[117] The MILP problems are solved using CPLEX 12.6. The nonconvex NLP problems are solved using BARON 12.7.3[118] and SCIP 3.1.0 with an optimality gap of 10^{-5}.

Small-scale case study

The small-scale case study involves a supply of a single feedstock, hardwood, and demand for a single product, gasoline. Specifically, an optimal bioconversion pathway is found for an available supply of 860,000 ton/year of hardwood feedstock to meet a gasoline demand of 3.05 million gal/year. A Pareto-optimal curve is generated from this scenario and is shown in Figure 7. Three points of interest are circled on the curve. One point denotes the most environmentally sustainable solution (lowest GWP), another a near break-even point (making a small profit), and the third identifies the most profitable solution (highest profit).

The most environmentally sustainable pathway (Figure 8) involves producing only gasoline and utilizes a pathway that begins with direct gasification after handling and chopping. Direct gasification is likely chosen by the model over indirect gasification as the yields for direct gasification are higher, despite a higher capital cost. Higher yields mean less biomass will be transported to the facility, meaning fewer transportation emissions, and a lower GWP. Only gasoline is made from this pathway in the methanol to gasoline process after synthesizing methanol from syngas. It is clear that an environmentally sustainable solution focuses on the pathway that can most efficiently convert as much of the original feedstock (hardwood) into the desired product (gasoline). Exactly 3,053,869 gal/yr of gasoline is produced in the process, just enough to meet the required demand. As a result, the capacity is quite small, processing only 83,902 ton/yr of hardwood feedstock out of the available 860,000 ton/yr. The small size of the facility and the focus on a single product does not permit the full advantages of economies of scale, so the profit, a loss of \$12.9M/yr, is the lowest of all Pareto-optimal solutions.

The most profitable solution focuses on a pyrolysis-based processing network, shown in Figure 9. Pyrolysis is likely chosen as more products can be made and sold from the

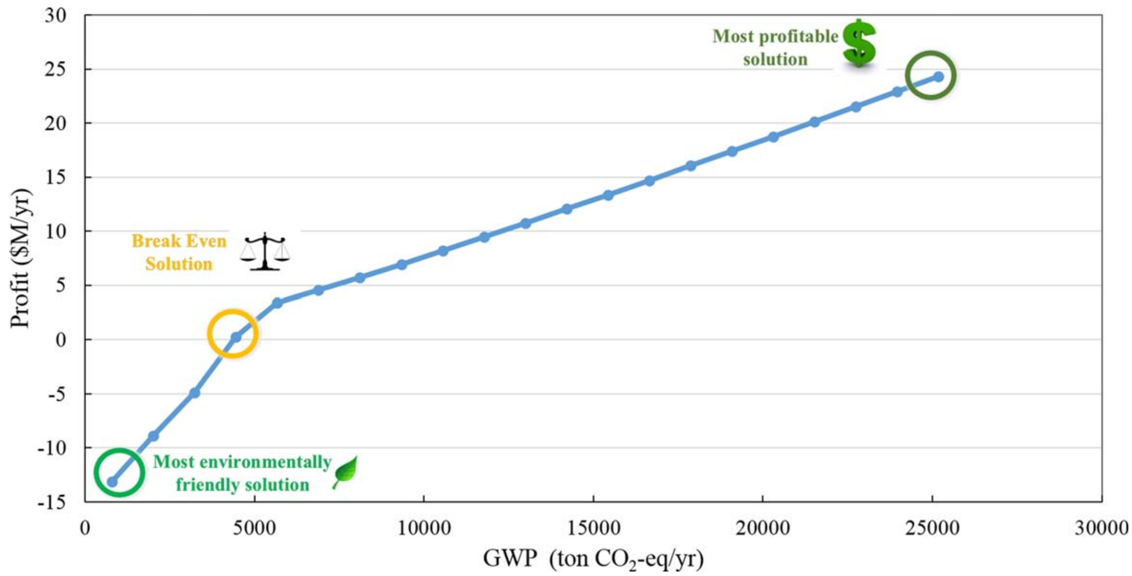

Figure 7. Pareto curve for the small-scale case study.

A supply of 860,000 ton/yr of hardwood feedstock is available under a demand of 3.05 Mgal/yr of gasoline. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resulting pyrolysis oil (in this case, diesel). Approximately 16.3 million gal/yr of gasoline and 19.5 million gal/yr of diesel are produced, well above the simulated demand of either product. The pathway takes advantage of economies of scale, processing over 589,000 ton/yr of hardwood feedstock of the available 860,000 ton/yr. It is noted that the pyrolysis process uses significantly more energy than the direct gasification pathway in the most environmentally sustainable solution, so its GWP is two orders of magnitude larger (over 24,900 ton CO_2-eq/yr compared to only around 791 ton CO_2-eq/yr), while posting a much greater profit (over $24.8M/yr compared to a loss of over $12.9M/yr). Thus, the results show a clear tradeoff between the profitability and environmental sustainability of a proposed bioconversion pathway.

A break-even solution was also selected for comparison between the two previous solutions, and this technology pathway is shown in Figure 10. This break-even solution results in a profit of about $292,000/yr and a GWP of around 4455 ton $CO_{2\text{-eq}}$/yr. Both quantities are significant increases from the most environmentally sustainable case and significant decreases from the most profitable case. The GWP of the pathway is dominated by transportation emissions over process emissions. Two technology pathways are combined in this solution—pyrolysis to produce gasoline and diesel, and indirect gasification leading to methanol synthesis and gasoline production. Figure 11 shows the capital and operating cost distribution of the break-even solution.

Formulation (P1) results in a problem with 841 continuous variables and 919 constraints. Formulation (P2) results in a problem with 193 SOS1 variables, 1716 continuous variables, and 2485 constraints. The objective value for the profit obtained by BARON 12.7.3 directly solving problem (P1) was $0.29M/yr. The branch-and-refine algorithm calculated the same profit. SCIP 3.1.0 also produced the same objective value. The CPU times taken by BARON to solve (P1) and by CPLEX with the branch-and-refine algorithm to solve (P2) were quite similar at 0.51 and 0.59 s, respectively. At a problem of this size, the increased number of constraints and variables introduced in the MILP formulation (P2) might be the cause of the higher computation time compared to that of BARON in solving (P1). SCIP took slightly longer at 2.02 s to calculate the solution. The branch-and-refine algorithm converged to the solution in only four iterations, resulting in a speed of 0.148 s per iteration.

Large-Scale Case Study. The large-scale case study involved a scenario in which all feedstocks were available at 8,600,000 ton/yr each, and the demand for gasoline, ethanol, and diesel were 3.05, 2.88, and 2.73 Mgal/yr, respectively. The Pareto-optimal curve generated from this case study is

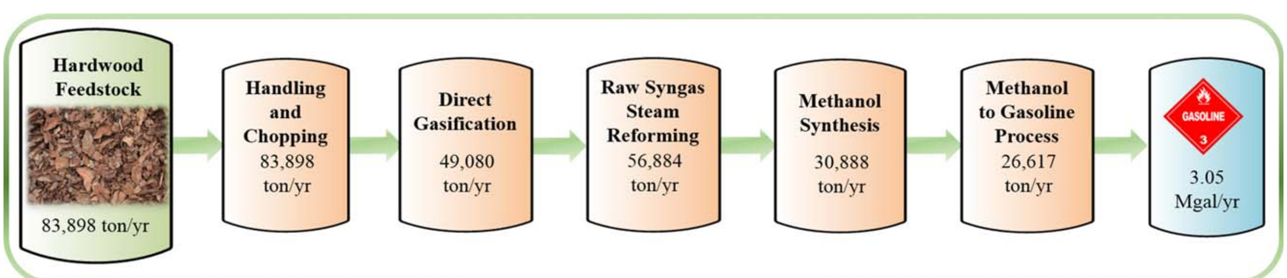

Figure 8. Technology pathway and capacities for the most environmentally sustainable point in the small-scale case study.

Hardwood is converted via gasification and subsequent upgrading to gasoline. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

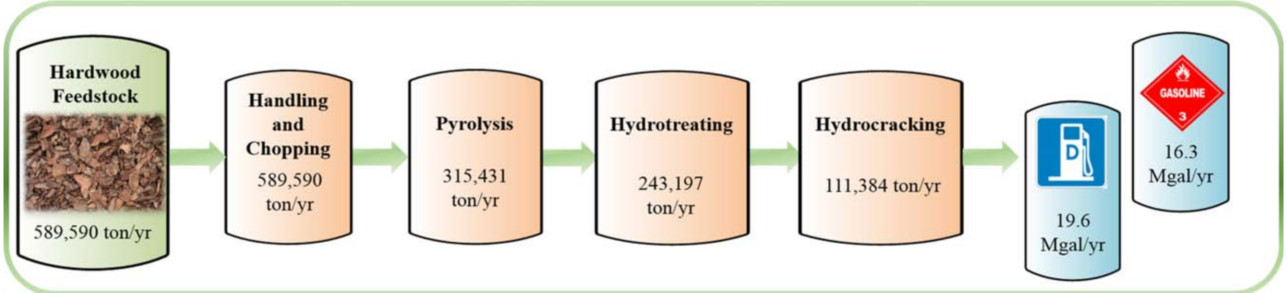

Figure 9. Technology pathway and capacities for the most profitable point in the small-scale case study.

Hard wood feedstock is converted by pyrolysis and subsequently upgraded to gasoline and diesel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Figure 12. Three points of interest are circled on the plot—the most environmentally sustainable solution, the most profitable solution, and a good-compromise solution that has objective values between the other two. The good-comporomise solution might be chosen if the goal is to be both reasonably profitable while reducing the environmental impact. Compared to the small-scale case study, there are more significant differences between these three bioconversion pathways. These differences are likely due to a larger portfolio of available feedstocks and higher demand.

The processing scenario of the most environmentally sustainable solution is shown in Figure 13. Corn stover is used to make diesel and gasoline through pyrolysis. Soft wood is used to make gasoline, diesel, and ethanol via direct gasification syngas production followed by the Fischer–Tropsch process, the methanol to gasoline process, and acetic acid hydrogenation to ethanol. Similarly to the most environmentally sustainable solution in the small-scale case study, only a small fraction of the available biomass is put to use. Approximately 36,550 ton/yr of corn stover and 99,072 ton/yr of soft wood is processed out of the available 8,600,000 ton/yr for each feedstock. Also as in the previous case study, the demand for all products is met exactly.

The economic loss of the facility, −\$4.35M/yr, is likely due to the relatively small size of the facility—sized only to meet demand and not to maximize profitability. The GWP amounts to 3065 ton CO_2-eq/yr. A breakdown of the capital and operating costs for this scenario is shown in Figure 14. Some of the technologies used, such as direct gasification of soft wood, hydrogenation of acetic acid, and the Fischer–Tropsch process have large operating costs. Hydrogenation of acetic acid, the preparation of the soft wood for direct gasification, and the conversion of methanol to acetic acid all incur large capital costs, but have higher yields compared to other alternatives (such as indirect gasification or preparing the feedstock for pyrolysis instead). These higher yields allow the use of smaller quantities of biomass feedstock, lowering transportation emissions. This solution does not take advantage of economies of scale, so the capital cost of the facility is relatively high, making the pathway unprofitable, and, in reality, unviable. While most of the emissions from the small-scale break-even point came from transportation of the hardwood feedstock, most of the emissions from the most environmentally sustainable scenario in the large-scale case study come from process emissions. This is likely due to the conversion efficiencies associated with hardwood for gasoline compared to those of corn stover or softwood conversion to gasoline, diesel, and ethanol. Hardwood processes in general have a lower conversion rate than the other two feedstocks, resulting in a need to use more feedstock to produce the same amount of product—raising transportation demand and, thus, transportation emissions relative to process-based emissions.

As in the previous case study, the processing network for the most profitable solution, shown in Figure 15, is significantly different than that of the most environmentally sustainable solution. Three feedstocks of soybeans, switchgrass, and softwood are used in this case compared to the two

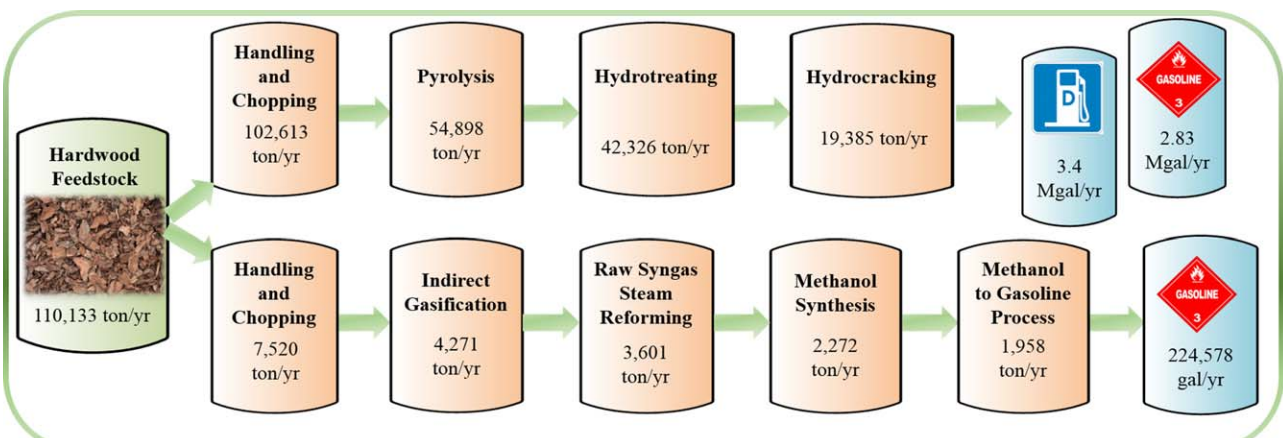

Figure 10. Technology pathway and capacities for the break-even point in the small-scale case study.

Hardwood is converted by gasification to produce gasoline, and by pyrolysis to produce gasoline and diesel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

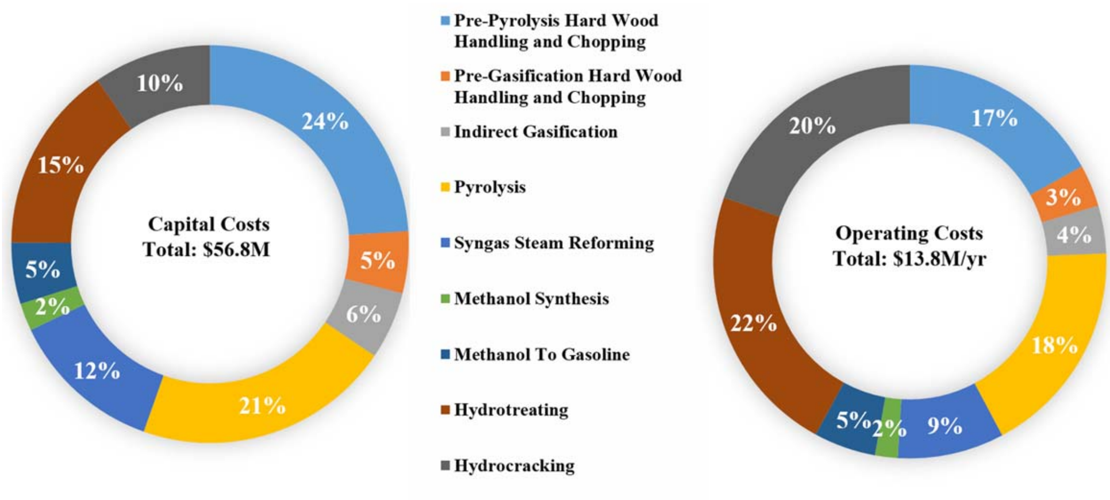

Figure 11. Capital and operating cost distribution for the small-scale study break-even point.

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

feedstocks in the most environmentally sustainable solution. In addition, more products are produced, with biodiesel from soybeans in particular being produced on a large scale. Soybeans are used to make biodiesel via traditional methods. Switchgrass is pyrolyzed and upgraded to make diesel and gasoline. Finally, syngas is made from softwood through direct gasification, followed by methanol synthesis, acetic acid synthesis, and acetic acid hydrogenation to make ethanol. All told, about 90,205 ton/yr of soybeans, 777,560 ton/yr of softwood, and 402,738 ton/yr of switchgrass is purchased and converted in the most profitable scenario, and 27 Mgal/year of biodiesel, 117.2 Mgal/yr of ethanol, 25.4 Mgal/yr of gasoline, and 19.6 Mgal/yr of diesel is produced and sold. A breakdown of the capital and operating costs of the most profitable solution is given in Figure 16. As one might suspect, the capacity is much larger compared to the most environmentally sustainable solution, and the capital and operating costs reflect this: both are an order of magnitude larger in comparison. The benefit of having a larger facility is to take advantage of economies of scale, following the scaling cost with capacity relationship of Eq. 5: the larger the facility is, the cheaper it becomes to make one extra unit of product.

The most profitable solution makes a profit of $99.2M/yr and has a GWP of 31,566 ton CO_2-eq/yr. Note that profitability increases dramatically compared to the most environmentally sustainable solution, but the GWP does not increase quite as much. The profit increases by several orders of magnitude and undergoes a sign change, but the GWP increasess by a factor of about 10. It is clear from these results and the Pareto-optimal curve of Figure 12 that decreasing the emissions of the bioconversion pathway incur larger and larger costs. Ultimately, the only scenario in which there will be no net GWP increase will be when all transportation and process energy comes from renewable sources. The breakdown of emissions between transportation and process-based sources is also different in the most profitable case compared to the most environmentally sustainable

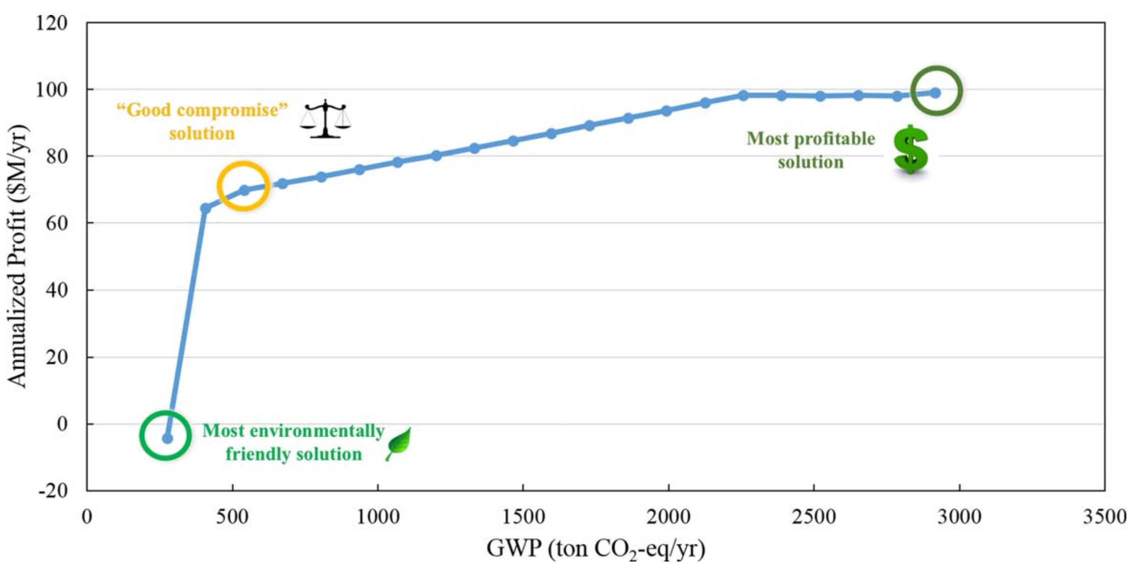

Figure 12. Pareto curve for the large-scale case study.

A supply of 8,600,000 ton/yr of all feedstocks is available under a demand of 3.05 Mgal/yr of gasoline, 2.88 Mgal/yr of ethanol, and 2.73 Mgal/yr of diesel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

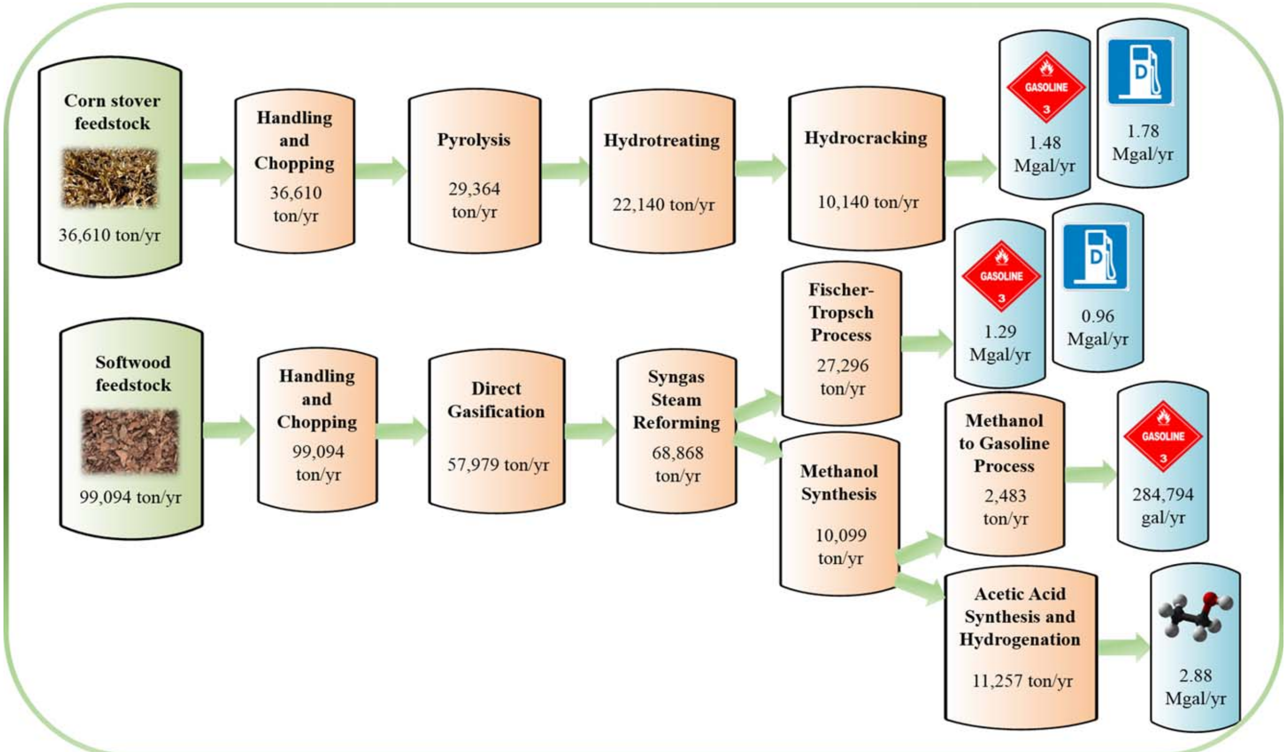

Figure 13. Technology pathway selection and capacities for the most environmentally sustainable solution from the large-scale case study.

Gasoline and diesel are made from corn stover via pyrolysis, and gasoline, diesel, and ethanol are made from gasification and subsequent upgrading of softwood. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

case. A larger portion of the emissions stem from indirect (process) sources. This is likely due to the technology choices involved. If the sole objective is to produce as much as possible, it is likely that one will lean toward utilizing technologies that have lower capital and operating costs, but use more energy. Indeed, the soybean pathway is quite energy intensive, but has relatively low operating and capital costs due to technology maturity, making it an attractive option when pursuing the bottom line.

While all of the points on the Pareto-optimal curve of Figure 12 are efficient and optimal, the curve still provides the user with a variety of bioconversion pathway options. A third solution between maximum profitability and maximum environmental sustainability is now analyzed and termed the good-compromise solution (see Figure 12). This solution has a profitability and environmental score that is between those of the aforementioned solutions, and provides some insight into how the technology pathway might change along the

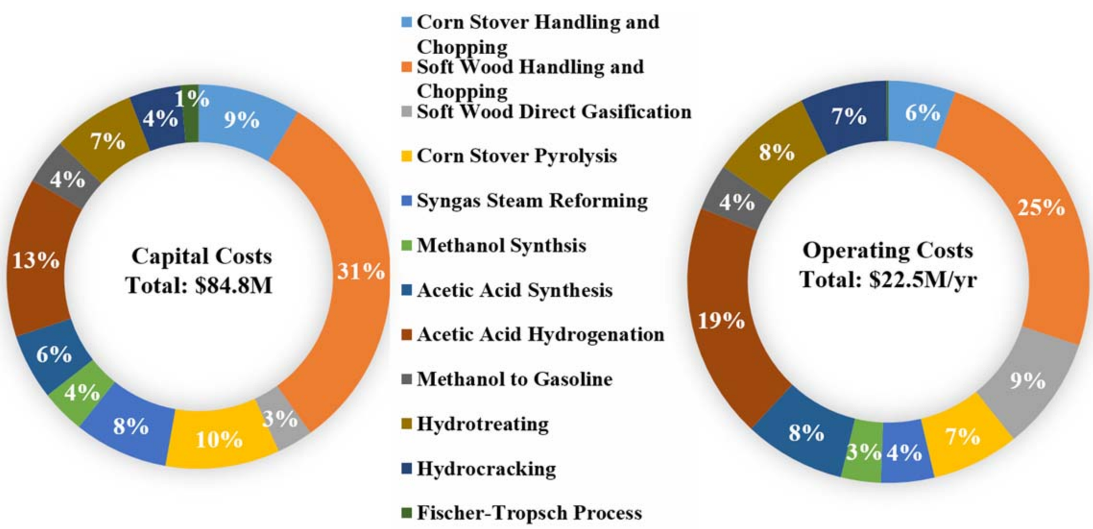

Figure 14. Capital and operating cost distributions for the most environmentally sustainable solution for the large scale case study.

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

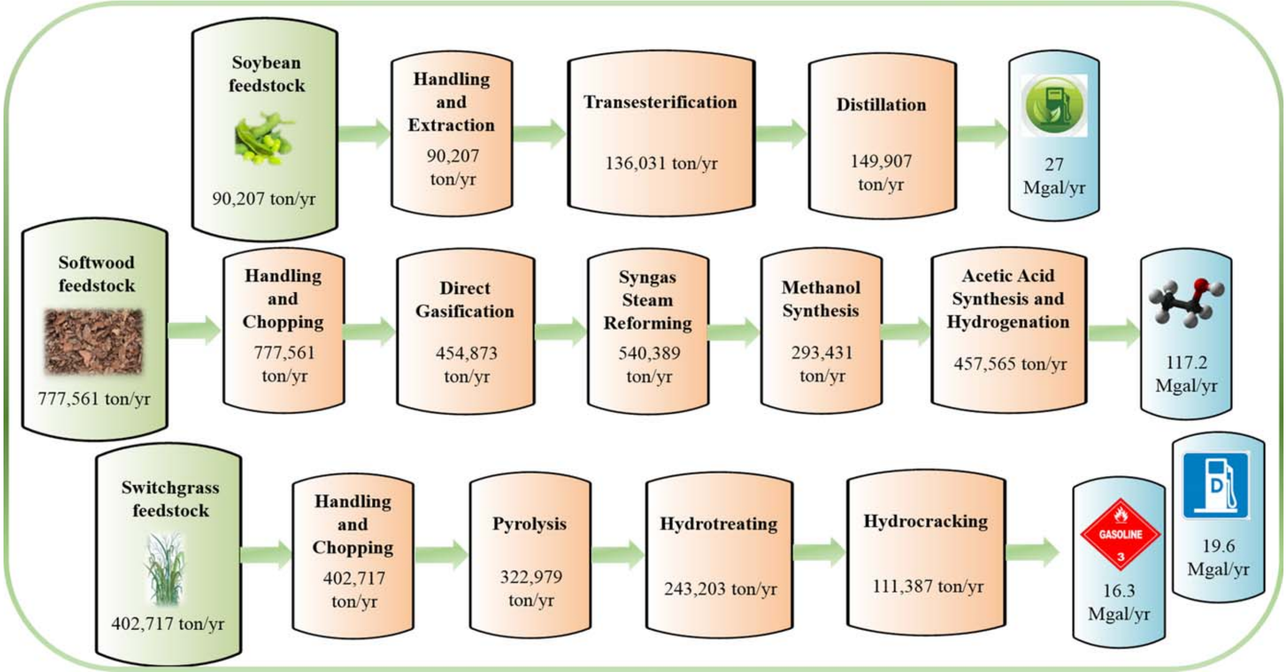

Figure 15. Technology pathway and capacities for the most profitable solution in the large-scale case study.

Soybeans are converted to biodiesel, switchgrass is pyrolyzed to gasoline and diesel, and softwood is gasified and upgraded into ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Pareto front. The processing network for the good-compromise solution is shown in Figure 17. Similarly to the most profitable solution, a variety of products are made: biodiesel from soybeans, ethanol from traditional corn fermentation, and gasoline and diesel from pyrolysis and upgrading of switchgrass. In this solution, 90,205 ton/yr of soybeans, 26,823 ton/yr of corn, and 82,302 ton/yr of switchgrass is purchased to make 27.3 Mgal/yr of biodiesel, 3.32 Mgal/yr of gasoline, 2.88 Mgal/yr of ethanol, and approximately 4 Mgal/yr of diesel.

From these results, one can glean which processes are the most economical and which ones might be more environmentally sustainable. It is clear that biodiesel production from soybeans is the most economical option, as this pathway appears in both the most profitable solution and the good compromise solution. This result is likely due in some sense to technology maturity. Conversion of soybeans to biodiesel is a relatively mature technology compared to some other options in this network, and it appears to provide some reliable income to help finance other technological options. To a lesser extent, pyrolysis of switchgrass appears to be a reasonably economical way to produce gasoline and diesel, as this process appears in both the most profitable scenario and the good comporomise scenario, although at a significantly smaller scale. Exactly 2.88 Mgal/yr of ethanol is produced to meet the demand via traditional corn kernel fermentation methods, signaling that producing ethanol from biomass is in general the least economically viable option when also considering environmental criteria. As a whole, the good compromise solution makes a profit of \$69.9M/yr with a GWP of 5915 ton $CO_{2\text{-eq}}$/yr. A capital and operating cost breakdown for the good-compromise case is shown in

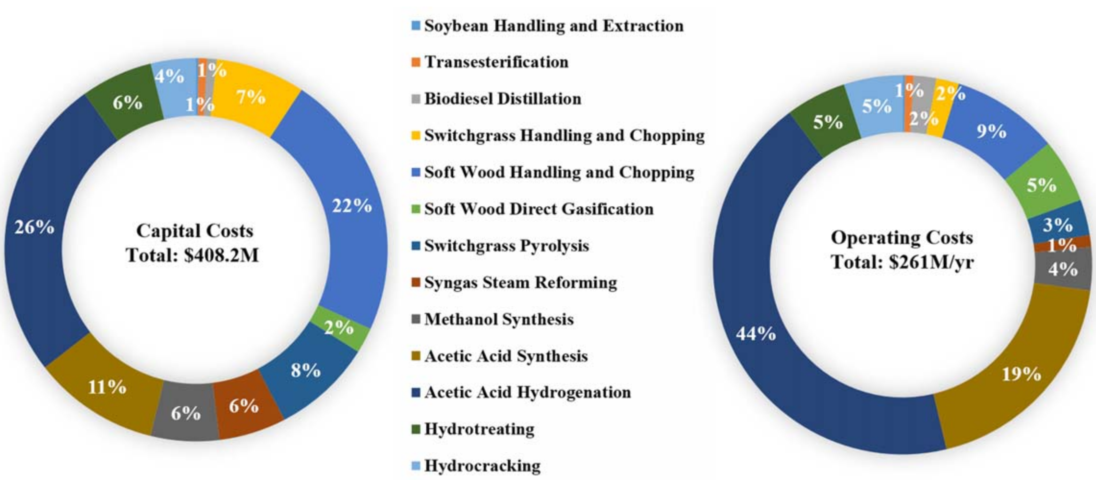

Figure 16. Breakdown of operating and capital costs of the most profitable solution in the large-scale case study.

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

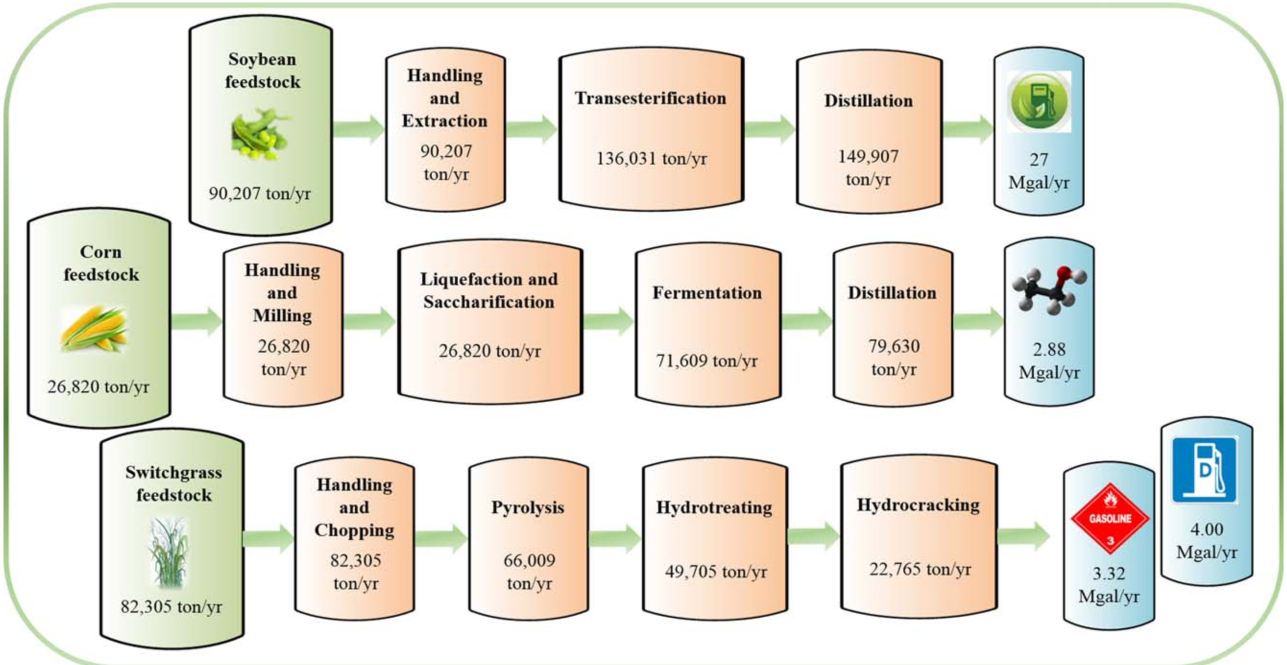

Figure 17. Technology pathway and capacities for the good-compromise solution.

Soybeans are converted to biodiesel by transesterification, corn is converted to ethanol by fermentation, and switchgrass is converted to gasoline and diesel through pyrolysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 18. It should be noted that this facility has the lowest capital cost of the three analyzed. The capacity is not as large as that of the most profitable solution, and the technologies are less expensive compared to those of the most environmentally sustainable solution. Pyrolysis and switchgrass handling and chopping are the two most capital-intensive units. Operating costs are between those of the other two solutions. Operation of the distillation columns accounts for large proportions of the overall operating cost. Hydrotreating and hydrocracking of the pyrolysis oil are also expensive processes to operate.

In all of the large-scale case studies, process emissions were a larger part of the emissions profile than transportation emissions. Process emissions accounted for 68% of emissions in the good-compromise solution, 62% in the most profitable solution, and 59% in the most environmentally sustainable solution. The environmentally sustainable solution likely had the lowest overall GWP due to purchasing and transporting just enough feedstock to make enough product to meet demand. Emissions increased with increasing capacity, with the most profitable solution having almost six times the emissions of the good-compromise solution and approximately 10 times the emissions of the most environmentally sustainable solution. Thus, the results show that a bioconversion pathway planning team can cut GWP emissions by around 80% while taking a profit hit of only around 30% by choosing the good-compromise solution pathway instead of the most profitable technology pathway. It should be noted that this does not mean that a healthy profit will not be made—recall the good-compromise facility provides a profit of almost $70 million dollars per year. While these results reiterate the trade-off between profits and the environment, the approach taken in this article provides a framework to identify different strategies to find solutions that make sense from both an economic and environmental standpoint.

The profit, emissions, and technology selections of all points in the Pareto-optimal curve of Figure 12 are shown in the Appendix in Table A1. It is clear that as the solutions move from more sustainable to more profitable, tried and true biofuel production methods (in particular soybean to biodiesel) contribute more to the resulting economics and environmental performance of the pathway. In general, fewer feedstocks are consumed and fewer products are produced as the solutions move from more profitable to more sustainable. Such characteristics could help designers of future biofuel facilities to better understand how type and quantity of each feedstock choice and technology selection affects the economic and environmental properties of a biofuel production pathway.

Sensitivity analyses were performed on the large scale case study to determine how sensitive the results were to changes in feedstock prices and the yields of key technologies. In four different experiments solving (P2) with the MILP-based branch and refine algorithm, the prices of the feedstocks were all changed at rates of $\pm$10% and $\pm$20%. The change in total profit, emissions, and technology choices are shown in Tables A2 through A5 in the Appendix.

Pathway selection appears to be sensitive to changes in feedstock prices. As a general rule, as feedstock prices increased, pathway selection became less varied, and the feedstock mix became more homogeneous. The only exception to this trend was the most environmentally sustainable solution, which was the same in all four cases. The profitability of the most environmentally friendly process varied nonlinearly with the change in feedstock costs compared to the base case. That is, the process became 12.7% less profitable when rising feedstock costs by 10%, 22.5% less profitable when increasing prices by 20%, 14.3% more profitable when costs fall by 10%, and 28.7% more profitable when biomass costs fall by 20%. Making biodiesel from soybean

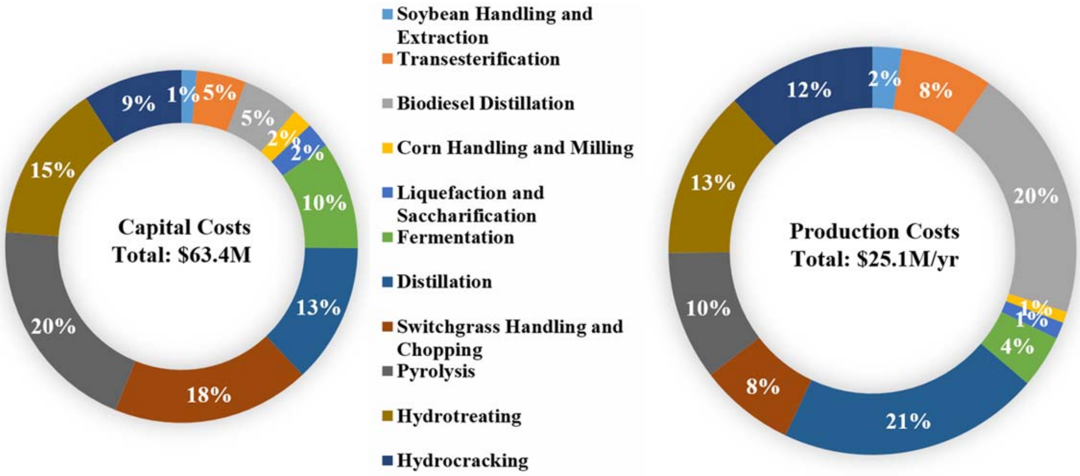

Figure 18. Breakdown of operating and capital costs of the good compromise solution in the large-scale case study.

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

still appears to be an important technology in all additional experiments, as it was still chosen in many solutions.

Direct gasification of softwood was identified as an important technology in the optimal process networks of both the most sustainable and the most profitable solution in the large-scale case study. Thus, the yield of this process was allowed to change by ±10% in two different experiments to determine the sensitivity of the solution to yields of important conversion technologies. Profit, emissions, and process pathway results of the Pareto-optimal results of these experiments are shown in the Appendix in Tables A6 and A7. The solutions appear to be far more sensitive to changes in important process yields than they are to changes in feedstock costs. For just a 10% decrease in the yield of the direct gasification of soft wood, the annual economic loss of the most environmentally sustainable pathway more than doubled. Much like the trends seen in the increasing feedstock cost cases explored above, a decrease in the yield of an important technology results in solutions with significantly less feedstock and process selection variety. Also, as expected, the augmented technology appeared in more solutions than in the base case.

Other important parameters that could affect the results, such as the variation in the chemical composition of the given feedstocks and rates of each reaction in each process are not explicitly accounted for in the present model. Thus, fruitful sensitivity analyses concerning such parameters could not be performed and is outside the scope of this communication. We recognize the potential importance of this variance, and look to future work to further investigate this question.

The computational results for solving the overall Pareto-optimal curve of Figure 12 are shown in Table 1. Overall, the branch-and-refine algorithm reproduces the results from directly solving the original NLP problem. The overall time taken to calculate the Pareto-optimal curve of Figure 12 with BARON via formulation (P1) was 54.7 h. In comparison, the entire set of Pareto-optimal points was generated by the branch-and-refine algorithm through CPLEX in only 127 s, a reduction in time by three orders of magnitude. Thus, the results clearly show that the branch-and-refine algorithm not only can reliably reproduce the results from the global NLP solver BARON but also do it significantly faster. As the network becomes more complex in the future with the addition of more technlogies and more environmental considerations, it will become critical to continue to use and improve such

Table 1. Computational Results for Calculating All 21 Pareto-Optimal Points in the Large-Scale Case Study

	Direct Solution of (P1)	Direct Solution of (P1)	Proposed Branch-and-Refine Algorithm with iterative solution of (P2)
SOS1 Variables	0	0	193
Continuous variables	841	841	1716
Constraints	919	919	1485
Problem type	Nonconvex NLP	Nonconvex NLP	MILP
Solver	BARON 12.7.3	SCIP 3.1.0	CPLEX 12.6
CPU time (s)	197,068	239	127
Average iteration count	N/A	N/A	9.81

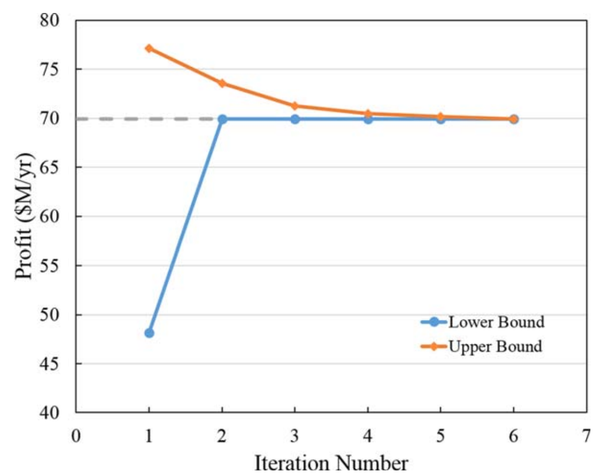

Figure 19. Upper and lower bounds calculated at each iteration in the MILP reformulation (P2) for the good compromise case.

The optimal value, $69.93M/yr is found in only six iterations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

algorithms to obtain globally optimal solutions in a timely manner. The SCIP solver performed intermediately between BARON and the proposed branch-and-refine algorithm with an overall solving time of 239 s. This computation time is a significant improvement on that of BARON, but is still almost twice as long as that of the proposed algorithm. Thus, the results show that the proposed branch-and-refine algorithm performs significantly better than two other powerful global solvers when solving large network-based modeling problems.

The iterations' upper and lower bounds for the good-compromise solution from the MILP formulation (P2) are shown in Figure 19. All of the solution points were solved with a gap tolerance *tol* between the two bounds of 0.00001 (10^{-5}). If the tolerated gap was set to be larger, it is possible that the number of iterations would decrease, as the gap between the lower and upper bound decreases the most in the first three iterations, and then slowly narrows in to the solution. The six iterations used to calculate the good-compromise point take only 1.12 s of CPU time to compute altogether, or approximately 0.19 s per iteration.

Conclusions

A foundation for a comprehensive economic and environmental multiobjective network optimization model for a general conversion pathway network was presented. A bioconversion network of 193 technologies and 129 materials/compounds was established. Key technoeconomic factors such as nonlinearly scaling capital costs with equipment capacity, process emissions, transportation emissions, and transportation costs were included in the model. An NLP model was formulated and subsequently solved. To improve the computational efficiency, a piecewise linear approximation MILP model using specially ordered set (SOS1) variables was constructed and solved by a specialized branch-and-refine algorithm. This method improved computational efficiency by up to three orders of magnitude compared to off-the-shelf solvers. For a large-scale case study in bioconversion, BARON took 54.7 h and SCIP took 239 s to solve the original NLP, respectively. The proposed algorithm, however, solved the MILP-based approximation model in only 127 s. Under the MILP model, each solution was found in at most 40 s.

Two case studies were considered in this work: a small-scale case study, and a large-scale case study. The small-scale case study involved producing at minimum one product (gasoline) from only one feedstock (hard wood), while the large-scale case study involved the production of several products (gasoline, diesel, and ethanol) from any feedstock in the network. In either case, the most environmentally sustainable solution satisfied the demand exactly, keeping the capacities and, thus, the environmental footprints small. However, these solutions resulted in economic losses of up to \$12.9M/yr. The most profitable solutions always resulted in technologies with larger capacities than the most environmentally sustainable solutions in addition to a wider product portfolio. Profits from these solutions ranged from approximately \$24M/yr in the small-scale case to \$99M/yr in the large-scale case study. A break-even solution was analyzed in the small-scale case study with a profit of \$0.29M/yr and GWP of 4455 ton CO_2-eq/yr. A good-compromise solution form the large-scale case study had a profit of \$69.9M/yr and GWP of 5915 ton CO_2-eq/yr.

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Notation

Sets/Indices

e = set of possible sources for electricity provided to the plant
i = set of materials/compounds
j = set of technologies
n = set of intervals in the SOS1 piecewise linear approximation algorithm

Parameters

$capmax$ = maximum upperbound on the capacity for all technologies
ccf = capital cost factor
d_i = demand for a given product i
$dist$ = average biomass transportation distance
dy_{ij} = destructive yield of material/compound i in technology j
ef_e = fraction of electricity source e in the electricity mix delivered to plant
em_j = CO_2 emissions emitted by technology j in ton CO_2 per ton capacity of technology j
emf_e = emission factor of electricity source e in ton CO_2 per MMBTU generated
fp_i = price of feedstock i
$ftcc$ = fixed transportation cost coefficient
gap = the gap in the upper and lower bounds for each iteration in the MILP algorithm
icc_j = initial capital cost of technology j for the base capacity
$index_j$ = 2014 chemical engineering plant cost index
$index_{j,base}$ = basis chemical engineering plant cost index
ioc_j = initial operating cost of technology j for the base capacity
lb = the lower bound used for calculating the gap for each iteration in the MILP algorithm
ma_i = maximum availability of feedstock i
mpq_i = minimum purchase quantity of compound i
n = estimated plant life in years
py_{ij} = productive yield of compound i in technology j
r = interest rate for capital cost amortization
$refcap_j$ = reference capacity of technology j
sf_j = scaling factor for technology j
sp_i = selling price of compound i
tol = a tolerance for the gap in each iteration in the MILP algorithm
tr = income tax rate
$tremf$ = emission factor for diesel transportation in ton CO_2 per ton feedstock processed
$u_{j,n}$ = horizontal grid points for technology j with n grid intervals
ub = the upper bound used for calculating the gap for each iteration in the MILP algorithm
uec_j = energy requirement of technology j in Wh per ton
$val_{j,n}$ = estimated capital cost for technology j calculated at the nth grid interval based on $u_{j,n}$
$vtcc$ = variable transportation cost coefficient

SOS1 variables

$EX_{j,n}$ = SOS1 variable describing in which interval the current solution candidate is located

Variables

CC_j = capital cost of technology j
FTC_i = fixed transportation cost of the biomass feedstock i
Gross = total revenues minus operating costs and purchases
OBJ_{GWP} = the total amount of global warming potential of the processing network
OBJ_{profit} = total gross less the taxes of the processing network
P_i = the amount of feedstock/input i purchased
Pem = emission associated with all processes at the facility
RX_j = substitute variable for nonlinear term in the SOS1 formulation

S_i = the amount of compound i sold
TAPC_j = total annual processing cost of technology j
Taxes = total taxes based on gross revenue
Tem = emissions associated with diesel burning trucks transporting biomass feedstock
VTC_i = variable transportation cost of the biomass feedstock i
$W_{j,n}$ = the weighting of the point within interval n for technology j
X_j = capacity of technology j in ton per year

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Appendix

Table A1. Profit, Emissions, and Technology Path Data for the Base Case in the Large-Scale Cases Study

Point	Profit ($M/yr)	GWP (ton CO2-eq/yr)	Technology Pathways
1	−4.35	3065	Pyrolysis of corn stover, direct gasification of soft wood
2	64.31	4490	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover, indirect gasification of soft wood
3	69.82	5915	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
4	71.81	7340	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
5	73.85	8764	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
6	75.95	10189	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
7	78.07	11614	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
8	80.23	13039	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
9	82.41	14464	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
10	84.61	15889	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
11	86.84	17313	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
12	89.07	18738	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
13	91.32	20163	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
14	93.59	21588	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
15	95.86	23013	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
16	98.15	24438	Soybeans to biodiesel, corn to bioethanol, pyrolysis of corn stover
17	98.87	25862	Soybeans to biodiesel, corn to bioethanol, hot water pretreatment of soft wood, pyrolysis of corn stover
18	98.57	27287	Soybeans to biodiesel, corn to bioethanol, hot water pretreatment of soft wood, pyrolysis of corn stover
19	98.32	28712	Soybeans to biodiesel, corn to bioethanol, hot water pretreatment of soft wood, pyrolysis of corn stover
20	98.1	30137	Soybeans to biodiesel, corn to bioethanol, hot water pretreatment of soft wood, pyrolysis of corn stover
21	99.09	31562	Soybeans to biodiesel, pyrolysis of corn stover, direct gasification of soft wood