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Network-Based Life Cycle Optimization of the Net Atmospheric CO_2-eq Ratio (NACR) of Fuels and Chemicals Production from Biomass

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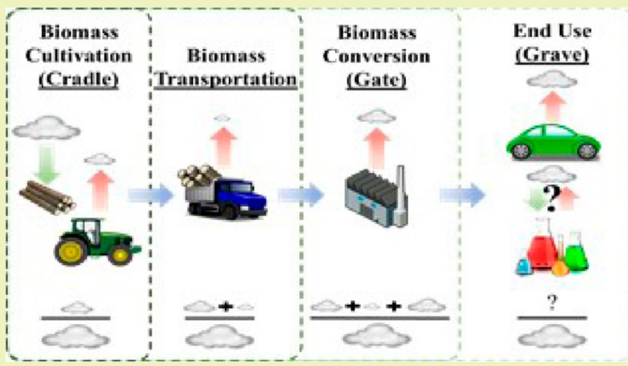
Supporting Information

ABSTRACT: A biofuels and bioproducts conversion network is optimized over unit cost and unit greenhouse gas emissions objectives. We use a multiobjective, functional unit approach based on the life cycle analysis methodology with simultaneous consideration of capital budget constraints. A novel functional unit of mass of input biogenic CO_2-eq is proposed to capture common benefits of bioproducts and biofuels. A novel dimensionless net atmospheric carbon ratio (NACR) for bioconversion processes is defined that captures the life cycle carbon footprint of the process from feedstock cultivation to product end use. The model is formulated as a nonconvex multiobjective mixed integer nonlinear fractional programming problem. We address computational complexity by developing a novel global optimization algorithm that incorporates the parametric algorithm and successive piecewise linear approximations to estimate nonconvex terms, and we introduce nonlinear programming subproblems to ensure global convergence under capital cost budget constraints. We consider large-scale case studies of a bioconversion network of 200 technologies and 142 materials/compounds where fuels and chemicals can be made from biomass. Unit costs range from −\$0.27 to −\$0.43/kg input CO_2-eq, and the NACRs range from 0.17 to 0.25. An optimal NACR that includes biofuel combustion emissions over a network where only biofuels are produced was found to be 1.90.



KEYWORDS: *Network optimization, Life cycle optimization, MINLP, Biofuels, Bioproducts*

INTRODUCTION

Sustainability is a topic of increasing attention and importance. Renewable energy is often jointly discussed with sustainability, as they share several qualities. For example, it is difficult to imagine a sustainable society that heavily if not largely relies on nonrenewable energy sources for everyday activities. Clearly, developing and implementing renewable energy technologies is a necessary undertaking if the goal of sustainability is to be reached. More nations, communities, and industries realize that both concepts are desirable if not vital to continuing many aspects of today's society, if not all of society itself.[1,2] Biofuels have been identified as a key component of the renewable energy portfolio.[3,4] Thus, we must consider developing and implementing biofuel systems that are sustainable.

To reach this goal, bioconversion systems must be designed with both economic and environmental sustainability in mind. Certainly, the question of economics has been discussed, addressed, and studied at length. Economic metrics of sustainability include familiar terms such as net present value, return on investment, profits, etc. However, some key economic concerns of emerging renewable energy technologies and systems must still be addressed. For example, if novel, sustainable technologies such as biofuel production processes are to be designed, constructed, and operated, the capital cost of these processes should not be prohibitively high. An important reason biofuel investment has decreased in recent years is due to the high capital costs associated with this sector.[5] It will be critical during planning stages to ensure that the capital cost of novel, proposed processing pathways will not be larger than a threshold capital cost. If process designers can ensure this will be the case, uncertainty associated with the project will decrease, possibly leading to more investment in the sector. However, incorporating a capital cost budget into process pathway design and optimization models poses mathematical challenges owing to how capital costs typically scale nonconvexly with capacity. While capital budgeting modeling has been studied[6] and some approaches considered,[7] much of the work has come from a financial research perspective and does not take into account scaling capital costs with capacity or other process attributes. It is necessary to

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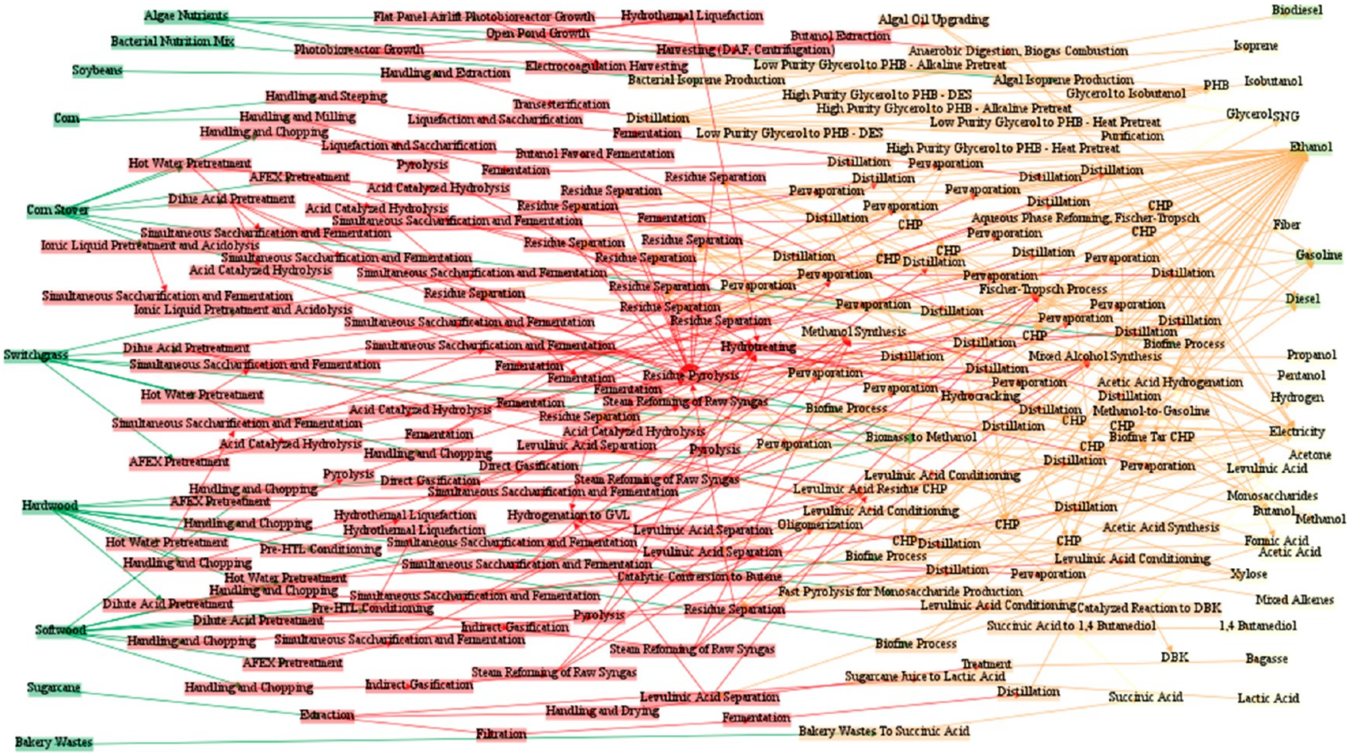

Figure 1. Bioconversion product and process network used in this study. Biomass feedstocks are colored in dark green in the left side of the figure, pretreatment/primary processing stages are colored in dark red (middle-left area of the figure), upgrading and final processing stages are colored in tan (middle-right area of the figure), biofuels are colored in light green (right side of the figure), and bioproducts are colored in light yellow (right side of the figure). The colors of the arrows are based on that of their source nodes.

consider scaling capital costs under a capital budgeting constraint when optimizing novel processing pathways to ensure their viability and practical feasibility.

An intriguing aspect of biofuels is that, much like petroleum, there is an option to process the biomass into other value-added chemicals and compounds, referred to as bioproducts throughout this work.[8−10] Examples of bioproducts that have received attention recently include biopolymers such as poly-3-hydroxybutyrate,[11] succinic acid,[12] and isobutanol.[13] Since economic investment in biofuels has decreased recently, at least in the United States,[5] there exists a prime opportunity to either produce bioproducts directly or co-produce them with biofuels to make biofuels more economically sustainable. Thus, there is also a research opportunity to incorporate bioproducts into bioconversion product and process network models. While chemicals process and product networks for natural gas and natural gas liquids have been studied and optimized,[14] bioconversion product and process networks that include bioproducts have not been investigated. Additionally, using bioproducts to replace other petroleum-based chemicals could provide an environmental benefit.[8] Therefore, producing or co-producing bioproducts with biofuels could augment both economic and environmental sustainability. However, quantifying environmental sustainability or impacts of biofuels and bioproducts with appropriate metrics is a challenge. A commonly used environmental metric has been the greenhouse gas (GHG) emissions of a process to determine its environmental footprint.[15,16] Other metrics are continually being developed and implemented, such as the nitrogen footprint or other climate impacts.[17] When co-producing bioproducts and biofuels, however, there must be some quantitative measure to fairly determine the environmental impact of both biofuel and bioproducts production.

It is the aim of this paper to provide a novel, bioconversion-targeted approach to quantitatively understand and optimize biofuel and bioproducts process and product networks over economic and environmental objectives. Thus, our goal is not to optimize bioconversion pathways at the process level but at the processing pathway level. We first construct a bioconversion product and process network of 200 technologies and over 140 materials/compounds that includes both biofuels and bioproducts, as opposed to previous works that studied exclusively biofuels,[18,19] resulting in the most comprehensive bioconversion network to date. Next, we propose a novel functional unit of kilograms of input carbon dioxide equivalent (or kg input CO_2-eq) from the biomass feedstock. Such a functional unit is required in order to fairly measure the environmental impact of both biofuels and bioproducts and has not been used in previous works. We then introduce a new ratio, the Net Atmospheric CO_2-eq Ratio (NACR), to determine the net overall CO_2-eq emitted to the atmosphere, calculated as the CO_2-eq emissions throughout the processing pathway divided by the input CO_2-eq in the input biomass. Optimizing the NACR of a bioconversion processing pathway can provide a novel perspective into the trade-off of producing more biofuels and bioproducts against increasing emissions throughout the processing pathway. Such a perspective has not been provided by minimizing bulk GHG emissions as in previous works.[18] We formulate multiobjective optimization models using this network and functional unit to find optimal processing pathways with minimum NACR and minimum unit cost. An overall processing pathway capital cost budget constraint is also considered, the first time such a constraint

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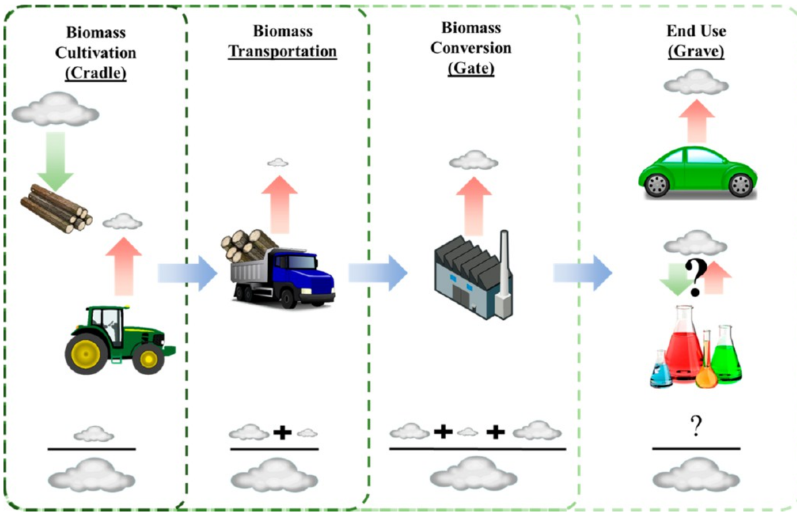

Figure 2. Demonstration of different system boundaries for bioconversion processing pathways, with cumulative NACR calculations in the bottom of each system boundary. Cumulative emissions are shown in the numerator and inputs of CO_2-eq are shown in the denominator in the bottom of each system boundary. The quantity of CO_2-eq emitted or consumed in the end uses of any bioproducts produced is unclear.

has been considered in network/superstructure optimization models.[15,18,19] We develop a novel solution method to handle the nonconvexities and difficulties presented from the capital cost budget constraint to increase computational efficiency. Finally, we apply these two models to a case study under biofuels demand with the option to produce bioproducts and another under biofuel demand with no option for bioproducts production. The NACR calculations in the latter case study account for biofuel combustion emissions. Results are presented and discussed, followed by the conclusion.

MATERIALS AND METHODS

The model formulation provided in the Appendix and used in this work is a general process and product network optimization model that can be applied to a number of process and product networks. We focus on the specific case of a biofuels and bioproducts network; thus, the following subsections deal with the specifics of data collection, life cycle analysis (LCA) and optimization, and other details of bioconversion networks. Information on data sources and data collection methods can be found in the Supporting Information (SI) for the interested reader.

Some of the network data, particularly for the biofuel technologies, carries over from the authors' previous work.[18] More biofuels and new bioproducts technologies were added, including methods for the production of biopolymers, isobutanol, monosaccharides, etc.[11−13,20−25] The bioconversion product and process network used in this study is shown in Figure 1. Altogether, 200 technologies and 142 materials/compounds are present in the network model. Full details of the data used in this study for each technology, including reference capacities, reference operating costs, reference capital costs, inputs, outputs, yields, etc. can be found in the SI. All data sources (journal articles, government reports, etc.) and corresponding information within each source (process flow diagrams, tabulations of data, etc.) are also noted for each technology in the SI. Thus, each technology in our network model has not necessarily been optimized on the process level (depending on the data source), but some form of simulation or data collection method used in each data source (for example, from pilot studies) ensures the data is of good quality and is taken from state-of-the-art process design studies.

Life Cycle Optimization. LCA has developed into a well-known and generally accepted methodology for determining the environmental impact or impacts of a product or process.[26] Environmental impacts are identified and quantified within predefined system boundaries. For example, one might investigate environmental impacts from cradle-to-gate or from feedstock procurement to the production of the final product. While LCA can help us make comparisons between products or pathways, this information is only available *a posteriori* or after the processing pathways are set and production is underway. Life cycle optimization is a trending methodology that integrates the tenets of LCA with optimization models to *a priori* estimate the life cycle impacts of novel or proposed processes.[27−30] Thus, decision makers now have more insight into the environmental impacts that their designs will have before large sums of capital must be invested in construction, allowing for more educated and better decisions. This new understanding of the environmental effects of a process will be critical in the development and implementation of biofuels and bioproducts technologies. Thus, we develop a life cycle optimization approach for a bioconversion product and process network. In this work, we aim to quantify and minimize the 100-year global warming potential (GWP) in terms of greenhouse gas emissions (kg CO_2-eq) from the fourth assessment report of the IPCC: CO_2 was given a GWP of 1, CH_4 a GWP of 24, and N_2O a GWP of 298.[31] Climate carbon feedbacks are not included. We narrow our focus to the GWP in this study so as to allow for development of the novel, fundamental ideas proposed in this work. The GWP is certainly not the only environmental concern that should be characterized in a thorough life cycle optimization; land use changes, eutrophication potential, and the nitrogen footprint are all important environmental concerns that can be addressed in future works using the foundational framework presented herein.

System Boundaries. As in a typical LCA, we consider the system boundaries for life cycle optimization. This is a critical step, as different system boundaries can give different results. In the case where production of both biofuels and bioproducts are

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allowed, the system boundaries are defined as cradle-to-gate (Figure 2). GHG emissions will be tallied in biomass cultivation, transportation of the biomass, and production of the biofuels and bioproducts. GHG emissions from biomass cultivation were taken from the GREET model.[32] However, while it is clear that the biofuels will undergo combustion as an end use, the end use for bioproducts is not as straightforward. Some bioproducts could be used for energy, such as hydrogen. Others, such as the biopolymer poly-3-hydroxybutyrate, have primary functions that will not include combustion, but rather have uses in the chemicals manufacturing industry. Thus, we limit the system boundary to a cradle-to-gate boundary rather than a cradle-to-grave one in order to allow a more focused discussion on the environmental effects of bioconversion to any product (Figure 2). However, in the case where only biofuels are allowed to be produced, we consider a cradle-to-grave boundary (Figure 2). In this case, we assume that all of the produced biofuels are consumed after being produced in the processing pathway, and all combustion emissions are attributed to the processing pathway.[33]

Functional Unit. Another key aspect of LCA is the choice of functional unit. Functional units are meant to be a quantitative basis that determines how the results of the LCA could be interpreted. They can lead to more insightful results as opposed to bulk numbers that might be difficult to understand in context. For example, an LCA of an automobile manufacturing facility might consider emissions per vehicle produced instead of the facility's total emissions. This can help decision makers by providing a more tangible understanding of their operations' environmental impacts. More importantly, however, results from the functional unit approach can be used to compare the environmental impacts with those of other facilities and products from within their organization, their competition, and around the globe.

The process systems engineering field has responded to the importance of the functional unit in LCAs by integrating the concept into life cycle optimization techniques. Pioneering work by Osman and Ries[34] optimized and compared electrical and thermal energy systems for commercial buildings based off of a functional unit of 1 kWh of energy. However, they used the functional unit to constrain the optimization problem; each type of electrical/thermal energy system was optimized under a constraint to produce the functional unit of 1 kWh of energy. More recently, functional units have alternatively been directly integrated into the objective functions of optimization models. For example, Yue et al. optimized a biofuels supply chain using a functional unit of gasoline-equivalent gallon, an energy-based metric.[35] Gong et al. optimized a microalgae processing technology superstructure to produce biodiesel in a similar vein.[36] Life cycle optimization of a cellulosic bioelectricity supply chain employed a functional unit of 1 kWh of electricity produced.[37] Integrating the functional unit into the objective functions of life cycle optimization models instead of implementing the functional unit as a constraint allows optimization of those objectives with respect to the functional unit, allowing for more flexible and diverse optimization models. These choices of functional units are relatively straightforward—fuels and electricity are both primarily used as sources of energy, so an energy basis for each functional unit is immediately intuitive.

When only biofuels can be produced from the processes under consideration, as in the previous studies, the choice of an energy-based functional unit, such as gasoline-equivalent gallon, serves the life cycle optimization model well. However, when bioproducts that are not meant to serve as a source of energy are also produced, the choice of functional unit is not as clear. To confront this dilemma, thought was directed toward commonalities between bioproducts and biofuels. To that end, we noted that the benefit of these processes, indeed the impetus behind their development, is to increase society's use of renewable ones (e.g., biomass). Thus, these products' functions are to use renewable carbon-based feedstocks, leading to the definition and introduction of a novel functional unit of "mass of input biogenic CO_2-eq " This functional unit aims to capture the quantity of atmospheric carbon dioxide absorbed by the biomass during its growth. Thus, it symbolizes the CO_2 sequestering effect of biomass. Since CO_2 is not directly present in the biomass, all of the carbon content of the biomass in its various forms (carbohydrates, proteins, cellulose, hemicellulose, lignin, etc.) was assumed to be derived from CO_2 absorption. Therefore, the amount of input CO_2-eq was calculated from the chemical composition of each biomass feedstock.

As this is a new functional unit, some justification and explanation is required. Consider the case where the objective is to minimize the unit costs of a bioconversion processing pathway with this functional unit. The units of the solution could for example be \$/kg input CO_2-eq Conceptually, this cost could be interpreted as the cost that the decision maker pays or the value the decision maker creates when using specifically renewable feedstocks to produce traditional fuels and/or chemicals. Alternatively, when minimizing unit greenhouse gas emissions of the pathway, use of this functional unit will result in a dimensionless ratio. We term this ratio the "Net Atmospheric CO_2-eq Ratio" (NACR), as it can convey the relation between the input CO_2-eq in the biomass and the total CO_2-eq emissions throughout the products' lifecycles:

$$NACR = \frac{\textit{total kg } CO_2 - \textit{equivalent emitted throughout processing pathway}}{\textit{kg } CO_2 - \textit{equivalent absorbed by inputs from atmosphere}}$$

To clarify, the numerator of the NACR as it is defined here reflects total GHG emission throughout the processing pathway and does not account for CO_2-eq uptake at any point in the processing pathway. CO_2-eq uptake throughout the processing pathway is calculated in the denominator. We note that the kg CO_2-eq absorbed by inputs in a bioconversion processing pathway (the biomass) is the same as the kg CO_2 absorbed. However, the NACR as it is defined allows for flexibility of other processes that need not use biomass but that might absorb other GHGs from the atmosphere, such as methane or nitrous oxide. This ratio can be less than one when bioproducts are also produced and when combustion emissions of any biofuels are omitted. In a case where only biofuels are produced and combustion emissions are counted when calculating overall processing pathway emissions, this number should be expected to be greater than one, with unity holding only when the processing pathway produces neither indirect nor direct emissions. It is noted that the information within the NACR depends on the temporal and spatial system boundaries; examples of this dependence are depicted in each system boundary in Figure 2. As another example, consider petroleum fuel production and combustion. If considering short time frames, the NACR approaches infinity (essentially zero atmospheric carbon is absorbed in the formation of the feedstock in the short term). However, if the temporal system boundary stretches from when the ancient input biomass began

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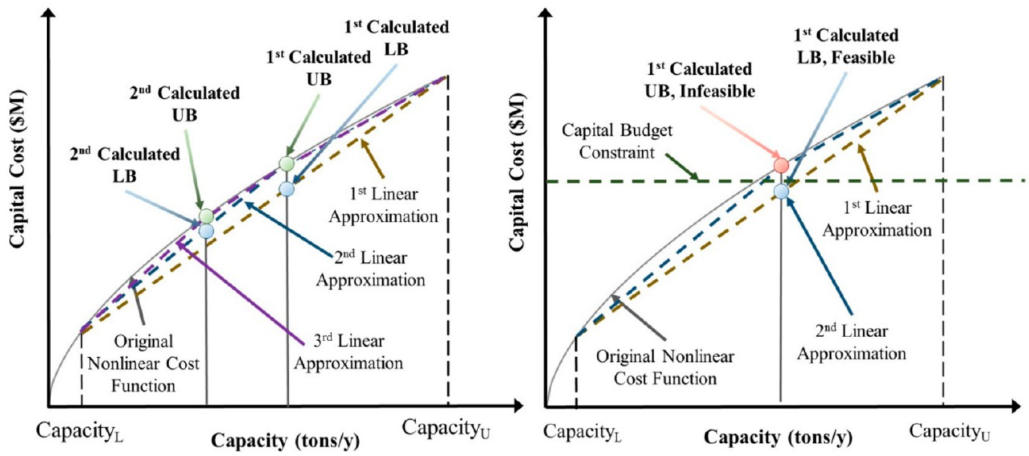

Figure 3. Traditional branch-and-refine algorithm with successive piecewise linear approximations (left) can become infeasible if capital budget constraints are considered in the model (right).

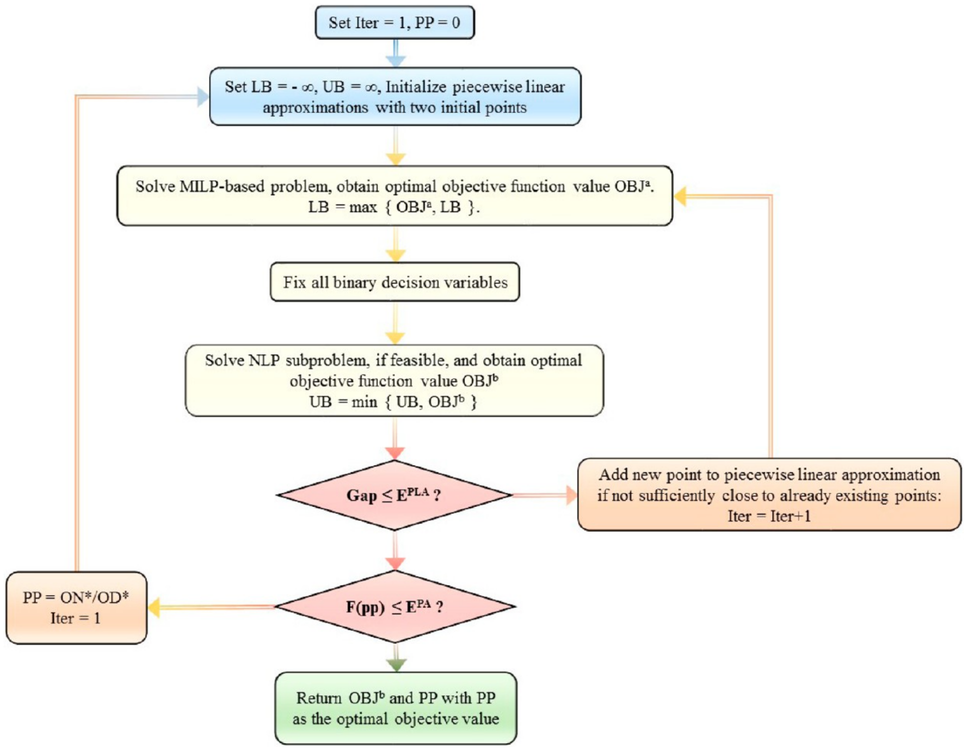

Figure 4. Algorithm flowchart for the proposed solution method in this study.

conversion to fossil fuels into the present day, then the NACR of fossil fuels could approach unity. This paper focuses on the practical case of the present to near future usage of the feedstock and any end products. The power of this functional unit lies in its flexibility to account for the use of input biomass for any purpose—fuel or otherwise, assuming appropriate and clear system boundaries are drawn—and is based on the reason for using biomass as a fuel or chemical precursor—its renewability. However, there are some key potential drawbacks of this functional unit. In the case where it is used as a denominator of an objective function that is to be minimized in an optimization model (such as in the NACR above), then the objective could be minimized by maximizing the mass of input CO2-eq In the specific case of a bioconversion processing pathway optimization study, for example, this would equate to using as much input biomass as possible. When considering other environmental objectives, such as land use, nitrogen consumption, etc., this result might be disagreeable. However, such an analysis is outside of the scope of this particular study, but should be investigated moving forward.

Model Formulation and Solution Method. A multi-objective mixed integer nonlinear fractional programming (MINLFP) problem is formulated to determine the minimum unit cost and minimum NACR for a processing pathway from a bioconversion process and product network. Additionally, a single objective MINLFP is formulated in this work to minimize the NACR for a biofuels-only process and product network. The general problems, as well as all sets, variables, and equations, are provided in the Appendix.

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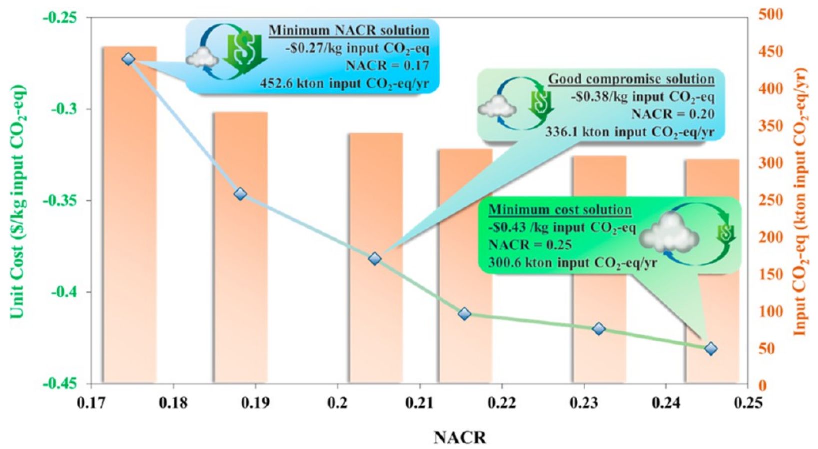

Figure 5. Pareto-optimal curve for the simultaneous minimization of unit cost and NACR; this curve can be read using the left and bottom axes (Unit Cost versus NACR). The orange bars correspond to the right axis and the input CO_2-eq/y of each solution.

As MINLFP problems can be difficult to solve directly with general global solvers, three steps were taken to increase computational efficiency. First, we incorporate the ε-constraint method to handle the multiobjective component of the problem.[38] Next, the fractional form of the objective function results in nonlinear terms that can be computationally difficult to handle. We circumvent this complication by implementing the parametric algorithm.[39−41] The resulting problem is still a nonconvex mixed integer nonlinear programming (MINLP) model with separable concave terms. We note that these concave terms arise in the calculation of the capital cost terms that follow the "six-tenths rule" scaling with capacity.[42] These nonlinear, nonconvex terms can increase the computational difficulty of the problem. Therefore, we implement piecewise linear approximations with SOS1 variables instead of these nonlinear, nonconvex terms to find a valid global lower bound for the objective function,[43] resulting in a mixed integer linear programming (MILP) problem that is much easier to solve. A valid global upper bound for the production cost could be calculated from using the optimal solution of the MILP problem to calculate the value of the original MINLP objective function. These piecewise linear approximations are successively updated in a branch-and-refine algorithm until a predefined gap between the objective function's upper and lower bound is met.[44−46]

However, the introduction of a capital cost budget in this work may make this approach infeasible, shown in Figure 3. To confront this problem, we develop a novel approach to retain both the solving efficiency of the piecewise linear approximations and global convergence to a feasible solution. In all of the models presented in this work, the only binary variable introduced is the variable that determines whether a technology will be incorporated into the processing pathway or not. Thus, when this variable is fixed as a parameter, the resulting problem is reduced from an MINLP to a nonlinear programming (NLP) model. Any feasible solution of this NLP (local or global) is a feasible upper bound to the problem's global solution. Thus, the piecewise linear approximations of Figure 3 can still be used to determine a feasible lower bound, the binary design decision variable can be fixed, and the resulting NLP subproblem can then be solved to obtain a feasible upper bound. This global optimization strategy is outlined in Figure 4 and is further detailed in the Appendix. This method shares some similarities to the outer approximation method,[47] but in this case, the underlying NLP has nonconvex terms, requiring the presented novel approach. In summary, the MILP is first solved to find a feasible lower bound with the branch-and-refine algorithm with successive piecewise linear approximations. The binary variables are then fixed, and the resulting NLP subproblem is solved to find a valid global upper bound to the original MINLFP. This process is iterated within the context of the parametric algorithm until some gap threshold of the relative difference between the bounds is met.

All computational experiments are performed on a DELL OPTIPLEX 790 desktop with an Intel(R) Core(TM) i5-2400 CPU @ 3.10 GHz and 8 GB RAM. All of the models and solution procedures are coded in GAMS 24.4.2.[48] The MILP problems within the proposed algorithm are solved with CPLEX 12.6, and the NLP subproblems are solved using CONOPT 3. The original MINLFP formulation is solved with BARON 14.4.0[49] with an optimality gap of 10^{-2}. The results shown in this section were obtained with the proposed algorithm.

■ RESULTS AND DISCUSSION

In each case study, demands of ethanol, gasoline, and diesel (10.9, 11.5, and 10.3 ML/y, respectively) are to be met. These demands are based on the production rate of a recently constructed representative POET cellulosic biorefinery with a starting production capacity of 20 Mgal/y of ethanol.[50] This representative facility has an estimated capital cost of \$275M, providing an appropriate capital cost budget for the demand levels of each fuel to be satisfied in the following case studies.[50] Major decision variables in these models include technology pathway selection and sizing of the chosen technologies. Other model variables include quantity of feedstock to purchase, quantity of product(s) to produce, capital and operating costs, and environmental impact throughout the pathway. Direct and indirect emissions (including from electricity consumption and fuel use on-site) are accounted for with direct emission factors (see Appendix). The simultaneous unit cost and NACR minimization case study has a system boundary drawn from cradle to gate, and the case study for NACR minimization over a biofuels-only network has a cradle to grave system boundary (Figure 2). As detailed in the Appendix, the cost is calculated as the summation of the various costs incurred throughout the processing pathway (feedstock costs, annualized capital costs, operating costs, etc.) with the sales of products (fuels and

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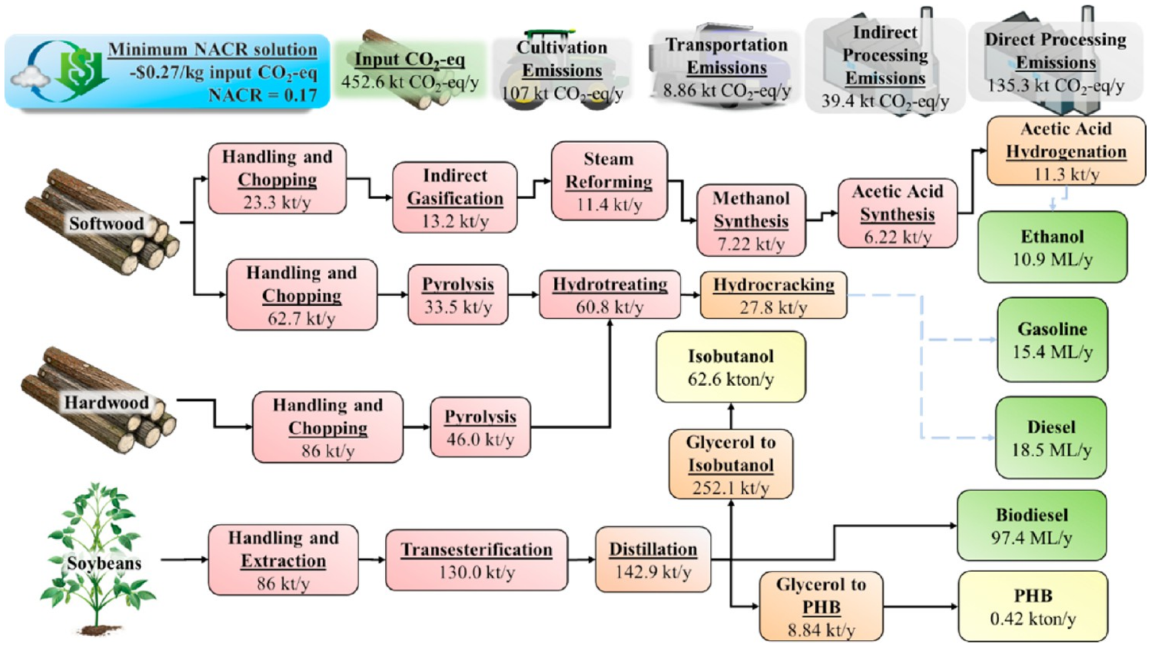

Figure 6. Optimal processing pathway results at the minimum NACR solution.

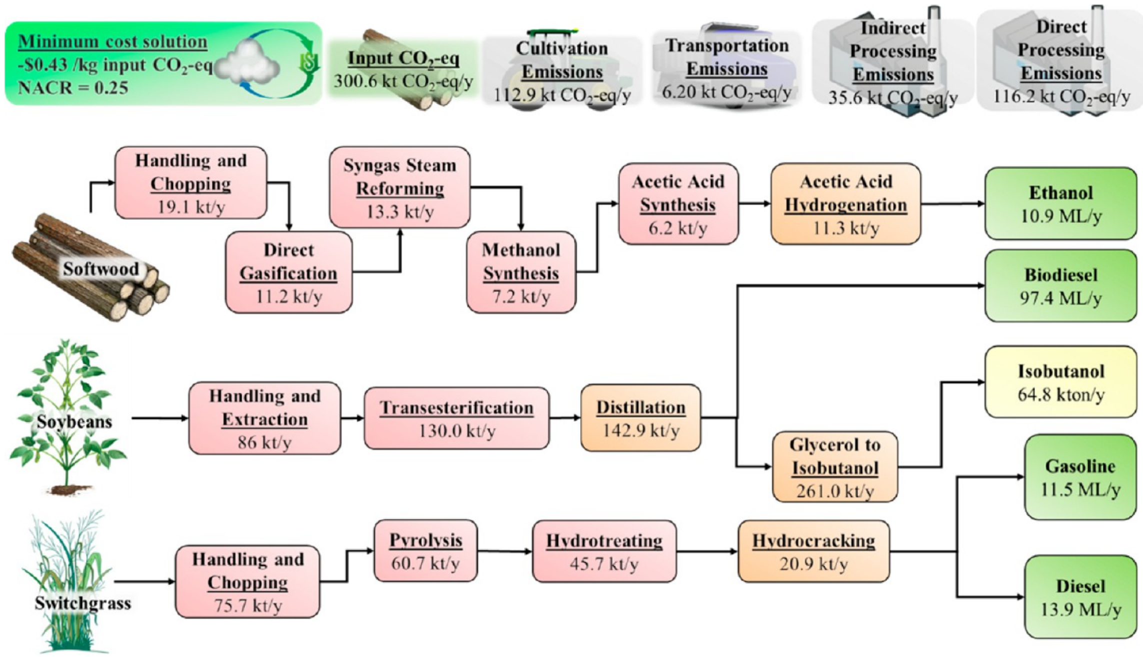

Figure 7. Optimal processing pathway for the minimum unit cost solution.

bioproducts) taken as a negative credit. Thus, the unit cost is allowed to be negative, implying the revenue from sales is larger than the cost; in other words, this would mean the processing pathway is profitable. Ultimately, the goal of the model is to identify optimal biomass processing pathways with biofuel demands to be satisfied. Thus, the problem is not to optimize the design and operations of a biorefinery or biorefineries that will utilize the processes identified, but to determine an ideal processing pathway of biomass to fuels and, perhaps, chemicals. Such a focus allows the model to focus on a more fundamental question of identifying an overall optimal bioconversion processing pathway.

Simultaneous Unit Cost and NACR Minimization. The Pareto-optimal curve for the simultaneous minimization of unit cost and NACR over the entire bioconversion network is shown in Figure 5 The input CO_2-eq of each solution is also indicated as a bar chart in the figure. Unit costs range from −\$0.27 to −\$0.43/kg input CO_2-eq, and the NACRs ranges from 0.17 to 0.25. It should be noted that the NACRs calculated in this case study do not include postprocessing combustion of product biofuels. Bioproducts are also allowed to be produced, and it is unclear how to determine any postprocessing emissions to them. Thus, the case study focuses on a cradle-to-gate analysis. The minimum NACR solution, the minimum unit cost solution, and a good compromise solution

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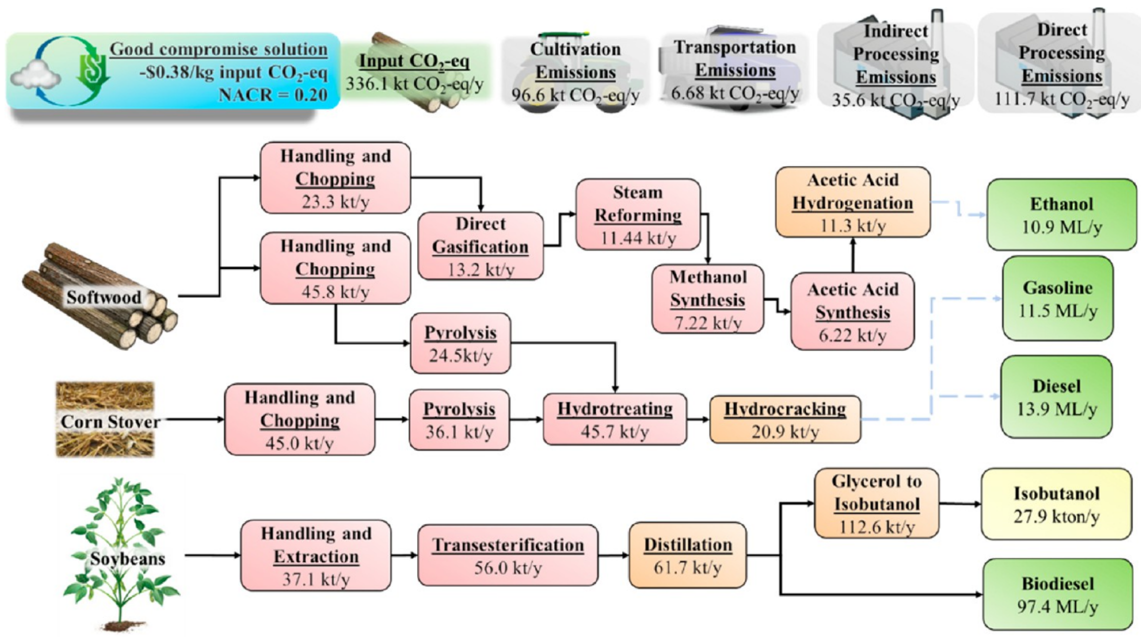

Figure 8. Optimal processing pathway for the good compromise solution.

are highlighted in Figure 5, and their corresponding processing pathways are shown in Figures 6, 7, and 8, respectively.

Demand for ethanol is met exactly in the minimum NACR solution (Figure 6), which is profitable with a unit cost of −\$0.27/kg input CO_2-eq and has a NACR of 0.17. Gasoline and diesel are produced in excess of their respective demands, indicating the process to produce them (pyrolysis and upgrading of softwood and hardwood) is profitable. All of these products are made from softwood and hardwood using the relatively inefficient thermochemical pathways of pyrolysis and gasification. When considering the minimization of overall greenhouse gas emissions throughout the processing pathway, it might be expected that product demand would be met exactly with no other processing. This strategy avoids feedstock transportation emissions and direct and indirect processing emissions. However, not only are the demands for gasoline and diesel exceeded, but a large amount of soybeans is used to make poly-3-hydroxybutyrate (PHB), isobutanol, and biodiesel at this minimum NACR solution. Furthermore, relatively inefficient (from a mass yield perspective) softwood and hardwood pathways are utilized, requiring large amounts of softwood and hardwood feedstocks. Indeed, according to Figure 5, this solution uses the most input CO_2-eq of all solutions. The addition of the functional unit of kg input CO_2-eq to the model serves to introduce a balancing act of environmental harm with perceived environmental benefit. This trade-off is between the benefit of using renewable feedstocks to make fuels and chemicals, while the harm would be emissions incurred by processing the biomass. Thus, minimizing the NACR for bioconversion product and process networks provides results from a novel perspective. It should be noted that this processing pathway is profitable, in part due to the production of bioproducts in addition to biofuels. Therefore, it is possible that the production of bioproducts is, in effect, subsidizing the production of the biofuels in the processing pathway. Such information can be utilized by decision makers to adjust their production targets accordingly depending on their goals (economic, environmental, or otherwise).

The processing pathway for the minimum unit cost solution is shown in Figure 7. As in the minimum NACR pathway, softwood and soybeans are used. However, switchgrass is also used in this pathway. Overall, the processing pathway is more streamlined and less integrated than the minimum NACR solution. Ethanol and gasoline demands are met exactly, indicating that the marginal economic cost to produce ethanol or gasoline via any processing pathway in the network is higher than the producer's marginal economic benefit. Large amounts of biodiesel and isobutanol are produced, indicating that these processes are profitable. This result gives credence to the proposal that bioproducts can aid the economics of a biofuels process. The NACR of this process is 0.25, an increase of almost 50% over the minimum NACR solution, despite consuming approximately half of the input CO_2-eq. Pathways with higher yields are favored in this solution to avoid the purchase of more biomass, decreasing the unit cost and increasing the NACR.

The good compromise solution has a unit cost of −\$0.38/kg input CO_2-eq and a NACR of 0.20; the processing pathway of this solution is shown in Figure 8. Thus, this good compromise solution is profitable with 25% fewer unit emissions than the minimum unit cost solution and utilizes an amount of input biomass that is intermediate between the two. Thus, this solution represents a good compromise on a number of levels between the two extreme points. As in the previous two pathways, this pathway utilizes soybeans and softwood. However, corn stover is also pyrolyzed to make more gasoline and diesel—products with higher margins for the producer. Co-production of bioproducts is important to achieving a low NACR in all cases; isobutanol is produced in all of the solutions. With low NACRs across all of the Pareto-optimal solutions, there could be a large environmental benefit to producing bioproducts in tandem with biofuels.

Sensitivity analyses were also performed. The yield of a key technology (indirect gasification of softwood) was allowed to vary, and the prices of the biomass feedstocks were also allowed to vary (refer to the SI for the results of the sensitivity

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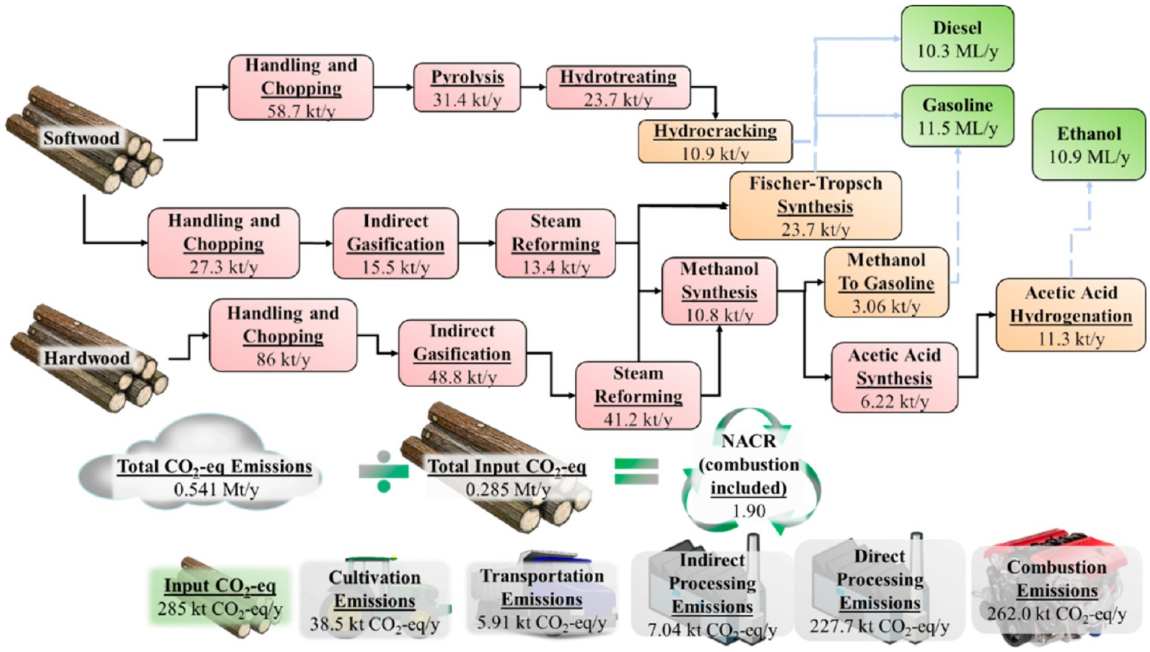

Figure 9. Optimal processing pathway for NACR minimization of the biofuels-only product and process network. Calculation of the NACR is also shown.

analyses). Overall, these changes did not change the objective values or processing pathways of the solutions along the Pareto curve dramatically. This is likely due to the fractional nature of the objective function; only significantly large deviations in the results will cause large fluctuations in the value of fractional objectives. We note that in order to truly assess the robustness of the results presented here, dedicated future studies employing techniques such as stochastic programming or robust optimization will be required.

NACR Minimization in a Biofuels-Only Network. The NACR is minimized in this case study with a different system boundary than the previous case study. Only biofuels are allowed to be produced—thus, the CO_2-eq emissions incurred from biofuel combustion are considered. The optimal processing pathway with minimum NACR is shown in Figure 9. As expected, the resulting NACR of 1.90 is well over 1, as emissions are produced from biofuel combustion and throughout the processing pathway. The process is highly integrated and uses 285 kt/y of biomass to exactly meet fuel demand. Thus, the trade-off between the benefit of using renewable biomass inputs for fuel and the environmental costs of biomass cultivation and processing is optimized. These results show that the NACR serves to succinctly display this trade-off and shows promise as an environmental indicator for biofuels processing pathways within a variety of system boundaries.

We note that across all case studies, transportation and indirect processing emissions were significantly smaller than GHG emissions stemming from biomass cultivation and direct processing. These results might indicate that reductions in emissions from biomass cultivation and bioconversion processing will be key to lessening the GWP of bioconversion processes as a whole. Furthermore, use of woody biomass is almost unilaterally preferred in all cases above, and thermochemical conversion technologies are largely favored over traditional biochemical methods. Indeed, the traditional corn to bioethanol process is absent from all solution methods (including results from the sensitivity analyses in the SI). These results might indicate that later generation technologies, such as pyrolysis and gasification might not only be more economical, but might also result in lower levels of GHG emissions. Further work should also be performed comparing optimization results obtained with the proposed functional unit of kg CO_2-eq and an energy-based functional unit (e.g., MJ) of a biofuels only product and process network optimization problem.

A comparison of the computational performance of solving this case study with the proposed solution algorithm and solving the problem directly with BARON 14.4.0, a general purpose MINLP solver is shown in Table 1. Despite the increase in problem size due to the addition of more constraints and binary variables, the proposed solution method demonstrated significant performance improvements compared to BARON 14.4.0. The proposed solution method found an optimal NACR of 1.899 in 1.68 s, while BARON 14.4.0 could not find an optimal solution within the computational limit of 10,000 CPUs. Furthermore, few iterations on the parametric

Table 1. Computational Results of the NACR Minimization in the Biofuels-Only Case Study

	original MINLFP problem	MILP with NLP subproblem
objective value (NACR)	[1.59828,1.94335]	1.899
constraints	1514	2913 (1513 in NLP subproblem)
continuous variables	1091	1890 (890 in NLP subproblem)
discrete variables	200	400 (0 in NLP subproblem)
solver	BARON 14.4.0	CPLEX 24.2.1/CONOPT 3
solution time (CPU s)	10,000*	1.68
outer loop iteration count	N/A	4
average inner loop iteration count	N/A	1.25

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algorithm (the outer loop) were needed, and the average iteration count of the inner loop was also small. Thus, the proposed solution method shows promise to find globally optimal solutions for product and process network optimization problems with capital budget constraints.

■ CONCLUSION

A bioconversion network of 200 technologies and 142 compounds/materials was constructed, the largest compiled to date. This network includes processing pathways for both biofuels and bioproducts. A functional unit of "kg input CO_2-eq" was defined to perform life cycle optimization over the network. A general multiobjective MINLFP model was constructed to optimize product and process networks over economic and environmental criteria. The parametric algorithm was employed to handle the fractional component of the problem. The ε-constraint method was implemented to handle the multiobjective optimization. Piecewise linear approximations were used to provide a valid, global lower bound for the objective function. A novel NLP subproblem method to obtain feasible upper bounds within the context of capital budget constraints was implemented to increase computational solving efficiency. This model was then applied to a variety of case studies.

A multiobjective case study was performed for the simultaneous minimization of unit cost and the Net Atmospheric CO_2-eq Ratio (NACR), defined as the amount of CO_2-eq emissions relative to the input CO_2-eq of the biomass. The NACR ranged from 0.17 to 0.25 with unit costs ranging from −\$0.27 to −\$0.43/kg input CO_2-eq A single objective case study was also performed under a scenario where only biofuels were allowed to be produced for the minimization of the NACR, which included biofuel combustion emissions. In this case, the NACR was found to be 1.90. The proposed algorithm was found to perform significantly faster than the off-the-shelf global solver BARON 14.4.0 and shows promise for finding globally optimal solutions for product and process network optimization problems with fractional objectives and capital budget constraints.

Overall, the new functional unit of "kg input CO2-eq" was shown to produce insightful results in the case of bioconversion product and process network optimization. The proposed NACR was shown to have potential in capturing the environmental benefit not only in producing bioproducts in tandem with biofuels, but also in reducing the relative greenhouse gas emissions produced to make products from a biomass feedstock. In the case of co-production of biofuels and bioproducts, the system boundary for life cycle optimization was drawn as cradle-to-gate, as the end-life destinies of the various bioproducts were uncertain. Future studies could investigate this key aspect for a more thorough life cycle optimization of biofuels and bioproducts co-production. Further steps should be taken to refine and implement this functional unit and the NACR when analyzing bioconversion systems. Similar refinement must be considered for other environmental and social impacts.

■ APPENDIX: MODEL FORMULATION

This appendix details the construction of the MINLFP model used in this study. A new model is developed for this study that includes fractional objectives for network-based optimization problems and also contains a novel capital cost budget constraint. This model provides a novel perspective on unit costs and environmental impacts of bioconversion processes and allows the user to set a maximum capital cost for the processing pathway. These features are not present in previous works and network optimization models. The goal is to simultaneously minimize the unit cost and NACR objective functions under economic, mass balance, and greenhouse gas emissions constraints. Variables are denoted in capital case, and parameters are denoted in lower case. Multiobjective, MINLFP model results that can be represented compactly as (P1) are shown below:

$$\begin{aligned} &\min OBJ_{NACR} \text{ in (A.1)} \\ &\min OBJ_{uc} \text{ in (A.2)} \end{aligned} \tag{P1}$$

s.t. economic evaluation constriants A.3−A.7
mass balance constraints A.8−A.10
greenhouse gas emissions constraints A.11−A.14

Implementation of the ε-constraint method, parametric algorithm, and piecewise linear approximations is demonstrated in the Supporting Information.

Objective Functions

The goal of the model is to minimize the NACR:

$$OBJ_{NACR} = \frac{GHG}{IC} \tag{A.1}$$

where GHG is a variable for the amount of greenhouse gas emissions, measured in kg CO_2-eq, that are emitted throughout the processing pathway's system boundaries, and IC is a variable that denotes the amount of input CO_2-eq in the form of biomass to the processing pathway. In the multiobjective case, the NACR is simultaneously minimized along with the unit cost of the processing pathway:

$$OBJ_{uc} = \frac{\cos t}{IC} \tag{A.2}$$

Economic Constraints

Cost is the variable that captures all aspects of the processing pathway's costs:

$$\begin{aligned} cost = &\sum_j (fcf_j + cchf_j)\cdot CC_j + \frac{X_j}{refc_j}\cdot refoc_j \\ &+ \sum_{i\in B} P_i\cdot(fp_i + vtc_i + ftc_i) + ec\sum_j ue_j\cdot X_j \\ &- \sum_{i\in F,P} S_i\cdot sp_i \end{aligned} \tag{A.3}$$

where fcf_j is the fixed cost factor for technology j, $cchf_j$ is the capital charge factor for technology j, CC_j is the capital cost of technology j, X_j is the capacity of technology j, $refc_j$ is the reference capacity for technology j, $refoc_j$ is the reference operating cost for technology j, P_i is the quantity purchased of material/compound i, fp_i is the feedstock price of compound i, vtc_i is the variable transportation cost of feedstock i, ftc_i is the fixed transportation cost of feedstock i, ec is the cost of electricity, ue_j is the unit energy consumption of technology j, S_i is the quantity sold of biofuel or bioproduct i, and sp_i is the selling price of biofuel or bioproduct i. The fixed transportation costs ftc_i are distance-fixed and not mass-fixed parameters; thus, these costs must be multiplied by the feedstock quantity purchased, P_i. The capital cost can be calculated as follows:

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$$CC_j = refcc_j \cdot ccf \cdot X_j^{sf_j},\ \forall\ j \tag{A.4}$$

where $refcc_j$ is the reference capital cost of technology j corresponding to $refc_j$, and ccf is the capital cost factor that takes into account the chemical engineering plant cost index (CEPCI) from the year the technology was reported to the current year. The capital charge factor $cchfj$ is calculated by assuming an interest rate of 10% and a plant lifetime of 20 years, as previous works have assumed.[18] The fixed cost factor fcf_j is taken as 5% of the capital cost of technology j.[42]

The denominator IC in each objective is calculated as follows:

$$IC = -\sum_{i\in B}\sum_j X_j \cdot dy_{ij} \cdot caco_i \tag{A.5}$$

where dy_i is the destructive yield of technology i in process j, and $caco_i$ is the CO_2-eq content of the input biomass i. Thus, only biomass that is both purchased and processed is counted in the calculation for input CO_2-eq

We implement a novel capital cost budget ccb:

$$\sum_j CC_j \le ccb \tag{A.6}$$

We then add upper and lower bounds on the capacity for each technology:

$$BD_j \cdot lcap_j \le X_j \le BD_j \cdot ucap_j,\ \forall\ j \tag{A.7}$$

where $lcap_j$ is the lower bound on capacity for technology j, BD_j is the binary decision variable that determines whether technology j is chosen to be in the pathway or not, and $ucap_j$ is the upper bound on capacity for technology j.

Mass Balance Constraints

There must be mass balance constraints in the model. Mass is balanced over each technology in the pathway:

$$P_i + \sum_j py_{ij} \cdot X_j = S_i - \sum_j dy_{ij} \cdot X_j,\ \forall\ i \tag{A.8}$$

where py_{ij} is the productive yield of compound/material i in technology j (positive if compound/material i is produced in technology j), and dy_{ij} is the destructive yield of compound/material i in technology j (negative if compound/material i is consumed in technology j).

Biofuel demand must be met:

$$dem_i \le S_i,\ \forall\ i \in F \tag{A.9}$$

where dem_i is the demand for biofuel i.

Biomass feedstocks are subject to minimum and maximum availabilities:

$$mna_i \le P_i \le mxa_i,\ \forall\ i \in B \tag{A.10}$$

where mna_i is the minimum availability of feedstock i, and mxa_i is the maximum availability of feedstock i. In this study, the minimum availability of each feedstock was set to zero. The maximum availability was made large enough to ensure that feedstock availability would not constrain the model such that demands for the biofuels could not be satisfied and optimal processing pathways could be found.

Greenhouse Gas Emissions Constraints

Next, environmental constraints that are used to calculate the NACR must be considered. GHG from eq A.1 can be calculated as follows:

$$GHG = E + T + \sum_{i\in B} cuem_i \cdot P_i + \sum_j pcee_j \cdot \left(\frac{X_j}{refc_j}\right),\ \forall\ j \tag{A.11}$$

where E accounts for the emissions of the process due to electricity usage, T accounts for emissions of the process due to transportation of the biomass feedstock, $cuem_i$ accounts for emissions from the cultivation of feedstock i, and $pcee_j$ accounts for the CO_2-eq emissions associated with processing through technology j. E can be calculated:

$$E = \sum_j em_j \cdot X_j \tag{A.12}$$

where em_j is the rate of CO_2 emitted due to electricity demand of technology j:

$$em_j = ue_j \cdot \left(\sum_e elf_e \cdot emf_e\right),\ \forall\ j \tag{A.13}$$

where elf_e is the electricity fraction for electricity source e, and emf_e is the emf_e is the emission factor of nonrenewable CO_2 emitted by electricity source e.

T can also be calculated:

$$T = \sum_{i\in B} tref_i \cdot P_i \tag{A.14}$$

where $tref_i$ represents the emissions associated with transporting feedstock i.

ASSOCIATED CONTENT

Supporting Information

A full list of the technologies used in this work along with all relevant data (inputs, outputs, yields, reference capacities, reference operating costs, reference capital costs, fossil-based process CO_2-eq emissions, and primary data sources). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00262.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

Sets

- B Set of biomass feedstocks indexed by i
- E Set of all possible sources of electricity used in processing pathway indexed by e
- F Set of biofuels indexed by i
- I Set of all compounds and materials indexed by i
- J Set of processing technologies indexed by j
- N Set of grid points for piecewise linear approximations to capital cost indexed by n

P Set of bioproducts indexed by i

Parameters

$caco_i$ CO_2-eq content of biomass i
ccb Capital cost budget for the processing pathway
ccf Capital cost factor (accounts for inflation, the Chemical Engineering Plant Cost Index, etc.)
$cchf_j$ Capital charge factor for technology j (accounts for interest rate and project lifetime)
$cuem_i$ GHG emissions from cultivation of feedstock i
dem_i Demand for compound/material i
dy_{ij} Destructive yield of compound/material i in technology j
ec Cost of electricity
elf_e Electricity fraction for electricity source e
em_j Rate of CO_2 emitted due to electricity demand of technology j
emf_e Emission factor of nonrenewable CO_2 emitted by electricity source e
enc_i Energy content of material/compound i
fcf Fixed cost factor
fp_i Feedstock price for feedstock i
ftc_i Fixed transportation cost for transporting feedstock i
$lcap_j$ Lower bound on capacity for technology j
mna_i Minimum availability of compound/material i
mxa_i Maximum availability of compound/material i
$pcee_j$ CO_2-eq emissions associated with processing through technology j
py_{ij} Productive yield of compound/material i in technology j
$refc_j$ Reference capacity of technology j
$refcc_j$ Reference capital cost of technology j
$refoc_j$ Reference operating cost of technology j
sf_j Capital cost scaling factor for technology j
sp_i Selling price for material/compound i
$tref_i$ Emissions associated with transporting feedstock i
$ucap_j$ Upper bound on capacity for technology j
ue_j Unit electricity requirement for technology j
vcf Variable cost factor
vtc_i Variable transportation cost for transporting feedstock i

Continuous Variables

CC_j Capital Cost of technology j
$Cost$ Variable to account for all costs incurred in the processing pathway
GHG Emissions variable for use with the ε-constraint method
IC Input CO_2-eq from biomass
OBJ_{NACR} NACR objective
OBJ_{uc} Unit cost objective
P_i Purchase quantity of biomass feedstock i
S_i Quantity produced/sold of bioproduct or biofuel i
X_j Capacity of technology j

Binary Variables

BD_j Binary decision variable to choose whether to use technology j in the processing pathway. It is 1 if technology j is chosen in the pathway and 0 otherwise

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