Sustainable Integration of Algal Biodiesel Production with Steam Electric Power Plants for Greenhouse Gas Mitigation

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ABSTRACT: Significant reductions in anthropogenic greenhouse gas (GHG) emissions, particularly of fossil carbon dioxide (CO_2), are necessary worldwide in order to prevent adverse impacts of global climate change on the socioeconomic sectors, ecological systems, and human health. In this context, this study aims to investigate the economic and environmental aspects of sustainability associated with the integration of algal biodiesel production with a steam electric power plant for microalgae biofixation of CO_2 in flue gases and then algal biomass conversion to biodiesel. This integrated



energy system is a multipurpose process that provides the CO₂ required by the microalgae cultures as well as electricity, biodiesel produced from the algal biomass, and lipid-depleted biomass which is in turn used as an auxiliary fuel in the power plant. A multiobjective optimization strategy based on genetic algorithms is proposed to yield a set of optimal solutions providing the best compromise between the profit and the environmental impact of regenerative Rankine power generation plants coupled with algae-to-biodiesel production facilities. The power plant operates continuously, but CO_2 is fed to open pond raceways only during the daytime (12 h a day) for algae growth. The rigorous IAPWS-IF97 formulation is used to calculate the thermodynamic properties of water and steam in the steam power cycle. The environmental impact is measured by the Eco-indicator 99 methodology that follows LCA principles. The optimization problem includes the selection of multiple primary energy sources for the power plant boiler, such as fossil fuels (coal, oil, and natural gas), biofuels, and biomass (switchgrass, softwood, and hardwood) in order to achieve significant reductions of CO₂ emissions. The optimal trade-off designs are obtained by implementing the ε -constraint method. The optimization method has been applied to a case study in México. The Pareto optimal solutions indicate that the current price for biodiesel of \$3.91/gal on average would make the integrated energy system under consideration profitable. In addition, the system could achieve significant environmental improvements due to life-cycle GHG reductions that result not only from biofixation of CO2 from combustion flue gases by microalgae and then algal biomass conversion and use as renewable fuels (i.e., biodiesel and lipid-depleted biomass) that substitute for fossil fuels, but also by significantly reducing the fossil fuel requirement compared to stand-alone coal-fired power plants.

KEYWORDS: GHG mitigation, Biological capture of CO₂, Microalgae biodiesel production, Steam power plants, Sustainable energy system, Multi-objective optimization, Life cycle assessment

INTRODUCTION

Worldwide electricity consumption is growing rapidly and is expected to rise significantly in the coming decades because of population growth and economic and social development, especially in developing countries. In fact, the International Energy Agency¹ estimated that the worldwide consumption of electricity will increase by 95.8% over the period of 2008– 2035; using the reference case "current policy" scenario, it is expected to increase from 16,800 TWh to 32,900 TWh (3.55% average annual growth). For meeting this growing global demand for electricity, projections from IEA² show that fossil fuels, especially coal and natural gas, will be our main source for electricity generation in fossil fuel-fired power plants at least over the next couple of decades. Because fossil fuel combustion power stations are responsible for over 65% of estimated carbon dioxide (CO₂) emissions caused by power generation systems,¹ a major challenge facing this electric power sector is how to reconcile the growing global electricity demand with the increasing urgency to reduce CO₂ emissions due to carbon dioxide being the main greenhouse gas (GHG) and, consequently, one of the most important contributors for the increase in anthropogenic climate change and global warming

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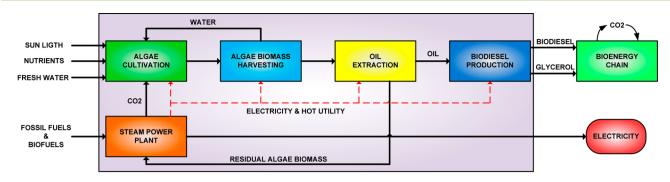


Figure 1. Schematic representation of a conceptual system for biofixation of CO₂ from steam power plants with microalgae for biofuel production.

that distorts the ecological balance and environmental sustainability.

In this context, it is clear that no single strategy will achieve over the next decades the required reduction in CO₂ emissions to stabilize GHG concentrations at 350 ppm in the atmosphere, which is the sustainable level to avoid dangerous long-term climate change.¹ Instead, it is widely accepted³ that a portfolio of social and technological options that can be used singly or in combination will be needed for achieving significant reductions in anthropogenic CO₂ emissions from various sources, ranging from industrial flue gas to exhaust emissions from personal transportation vehicles. The main components of this portfolio include changes in lifestyles to promote energy conservation and population control, improvements in the efficiency of energy conversion and demand-side use, fuel switching (i.e., switching from coal to less carbon intensive fuels such as natural gas), large-scale adoption of low- and zero-carbon renewable sources (i.e., wind, solar, and biomass), carbon capture and storage (CCS) of CO_2 emissions from fossil fuel and biomass combustion, and biological carbon mitigation.

Because fossil fuels will remain as dominant source of energy to generate electricity in the coming decades even with very strong expansion of the use of alternative energy sources,¹ in recent years, many studies have been conducted to develop innovative process designs that integrate CCS with fossil fuelburning power plants to prevent CO₂ emissions from building up in the atmosphere and to reduce the climate impact of power generation in the near-term future.⁴⁻⁹ However, CCS still resides in its precommercial phase in the context of power generation.¹⁰ In addition, before its implementation on the industrial scale, CCS is a strategy that must overcome several technological challenges such as the decrease in power plant efficiency due to high energy consumption¹¹ and the lack of a long-term safe storage method of carbon dioxide for volumes of injected CO_2 that will be larger than anything previously attempted.

A combination of biological removal of CO_2 emitted by fossil fuel-fired power plants and production of biofuels to replace fossil fuels is an alternative GHG abatement strategy consisting of two steps.^{12–15} First, autotrophic organisms and plants produce biomass in the process of CO_2 fixation through photosynthesis. Then, produced biomass can be converted into biofuels through several conversion technologies as well as some value-added chemicals.^{16–34} Therefore, biofuels from renewable biomass can be an important part of any sustainable and cost-effective strategy to avoid an increase in the atmospheric CO_2 concentration by replacing fossil fuels and thus their associated CO_2 emissions. In this context, nowadays culturing of microalgae for CO_2 biofixation is receiving considerable attention around the world because microalgae are fast-growing, unicellular, and simple multicellular photosynthetic microorganisms that have the ability to fix CO₂ while capturing solar energy with an efficiency of 10-50 times greater than that of terrestrial plants³⁵ and can double their biomass in less than 1 day for most species under favorable growing conditions.³⁶ In addition to their high growth rate, productivity, and photosynthetic efficiency, microalgae are considered an ideal raw material for production of both biofuels and valuable byproducts because they offer several advantages^{19,20} including (i) feedstock based on nonfood resources, (ii) utilization of a wide variety of water sources (fresh, brackish, saline, and wastewater), (iii) use of otherwise nonproductive non-crop lands, (iv) high capacity to capture CO₂ emissions as approximately 2 kg of CO₂ are fixed for every kg of biomass generated, and (v) higher oil yields (60 m³ ha⁻¹) than those of conventional raw materials for biodiesel such as jatropha (2 m³ ha^{-1}) and soybean (0.45 m³ ha^{-1}).

The integration of algal biofuel production (i.e., cultivation of microalgae for simultaneous biofixation of CO₂ from combustion flue gases and biofuels production) with fossil fuel-fired power plants can increase the amount of electricity produced per unit of CO₂ released. In addition, this integrated energy system could generate synergistical electricity and liquid biofuel from microalgal biomass. It should be noted that in biofuel production the CO₂ fixed by microalgae is essentially being recycled because this carbon dioxide will be released to the atmosphere when the microalgae-based biofuel is combusted. Then, it will be absorbed back by higher plants and microalgae through the photosynthesis process, and finally, in the biomass-to-energy chain, the resulting biomass can be converted again into biofuels using existing technologies, thus creating a balance between energy and carbon cycle in a more sustainable way. Under this scenario, there is no permanent CO_2 capture; however, there is a net cumulative reduction in net flows of carbon to the atmosphere when the biofuel produced from microalgae is used for the generation of work instead of some fossil fuel (displaced fossil fuel). Furthermore, after removal of the lipid component, the remaining biomass can be co-fired with fossil fuels in the power plant to reduce the total fossil fuel consumption and subsequent GHG emissions of the integrated system. Also, the power plant can supply the required thermal loads and electricity demands of the algal biofuel production subsystem. Therefore, there is a significant net benefit in terms of overall CO2 emission avoided when fossil fuel electricity generation is coupled with microalgae biofuel production. Figure 1 sums up these relevant energy and mass interactions between the components of the integrated energy system under consideration.

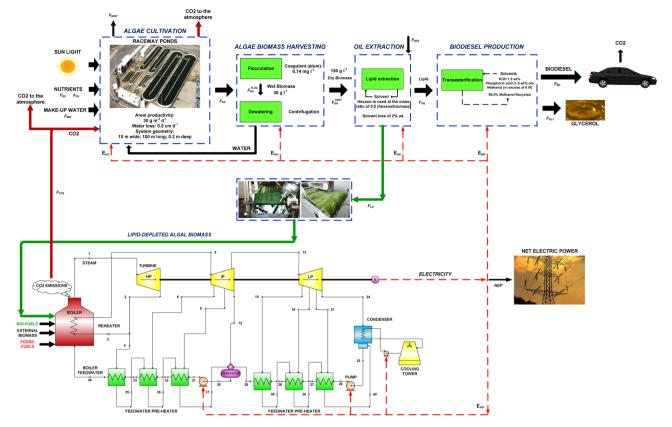


Figure 2. Integrated energy system proposed for the biological capture of CO₂ emissions from steam power plants using microalgae cultivation for biodiesel production.

Despite their aforementioned advantages, no systematic study has been undertaken to optimize these integrated energy systems involving the economic and environmental aspects of sustainability. So far, there are several studies about the life cycle assessment of stand-alone systems for biofuel production from algae feedstocks.^{37–53} Although these research works can provide insight into the economic and environmental impacts, as well as technical feasibility of different options for culture conditions, photobioreactor configurations, algae harvesting, and algal biomass processing, they fail to achieve significant improvements in both economic and environmental objectives due to assessing the microalgal biofuel production independently of the fossil fuel-fired power plant. In addition, Brune et al.⁵⁴ and Pokoo-Aikins et al.⁵⁵ have presented preliminary analyses of the conversion of CO2 from fossil fuel-fired power plant flue gas into biomass by microalgae. Although these two methods have shown that biofuel production from microalgae is both economically and environmentally sustainable, they are based on specified values for the flow rate and composition of the flue gas stream to design the microalgae biodiesel production system. Therefore, both methods optimize algaeto-biofuel systems independent of the power plants because they do not account explicitly the interactions shown in Figure 1 between the system components.

The purpose of this paper is to present a multi-objective optimization strategy for the synthesis of integrated energy systems that consist of a 400 MW fossil fuel-fired power plant with a fixed flowsheet structure and a facility for biofuel production from algae. In the proposed approach, the multi-objective optimization model by Gutiérrez-Arriaga et al.⁵⁶ for steam power plants together with the model for the algal

biofuel production are combined in a general mathematical model for the multi-objective optimization of integrated energy systems. In this way, interactions between both system components can be taken explicitly into account in the formulation of the optimization problem where the environmental impact needs to be minimized while maximizing the system's annual gross profit. Only microalgae cultivation in open ponds is investigated considering that CO_2 is delivered 12 h a day only during the daytime. The proposed procedure involves the selection of suitable primary energy sources (i.e., fossil fuels, biomass, biofuels, and solar energy) for sustainable electricity generation. The life cycle assessment (LCA) technique^{57,58} is used to quantify the overall environmental impact and GHG emissions resulting from different combinations of energy sources and operating conditions of the integrated system. This technique is based on the quantitative Eco-indicator 99 framework that expands the system boundaries to incorporate the environmental impacts associated with its life cycle stages (all processes associated with raw materials extraction and processing, energy generation, and capital manufacture), so it can generate and evaluate environmentally conscious design alternatives that are at the "global" level (expanded production system) rather than at a plant level. The thermodynamic properties for liquid water and steam are calculated rigorously using the IAPWS-IF 97 formulation.⁵⁹ Additionally, the impact of a trading price for carbon emissions (i.e., carbon tax/credit) on system profit is included in the mathematical formulation. The trade-off between economic and environmental objectives is obtained through the ε constraint method to generate the Pareto curve. An illustrative case study is presented, which consists of an advanced

regenerative-reheat steam power plant integrated with a facility for algal biodiesel production in the central part of Mexico. Results show that the integrated energy system could be profitable. Furthermore, it could contribute to enhancing sustainability because it can cultivate microalgal biomass using CO_2 emissions from thermoelectric power plants for simultaneous CO_2 biomitigation and biodiesel production.

MATERIALS AND METHODS

This section is organized as follows. We describe the system first and then state the problem of interest. The environmental impact evaluation is presented afterward. Finally, the solution procedure is described.

System Description. The schematic diagram of the hypothetical integrated energy system, summarizing the main processing operations as well as mass and energy flows, is shown in Figure 2. The system is concerned with the sustainable generation of electricity incorporating an advanced regenerative—reheat steam power plant that uses different energy sources (i.e., fossil fuels, biofuels, and biomass), along with microalgae biofixation of CO_2 in the flue gas from the power plant, conversion of algal biomass to biodiesel, and use of lipid-depleted (LD) microalgal biomass for co-firing in the power plant. The system is assumed to be located in a sunny area near Lake Cuitzeo in the central part of Mexico due to the large amounts of water and land area available to support the algal culture facility.

The advanced power plant is described in a previous work by Gutiérrez-Arriaga et al.⁵⁶ on multi-objective optimization of steam power plants. A detailed modeling of the power plant is carried out using the IAPWS-IF 97 formulation⁵⁹ for prediction of steam and water thermodynamic properties. The power plant boiler can consume fossil fuels, biofuels, external biomass, and the lipid-depleted algal biomass coming from the oil extraction plant as energy sources to generate electricity. The amount of 400 MW of electric power produced by the power plant is chosen as the baseline scenario for the system's environmental assessment.

The algal biodiesel production starts with the biomass-cultivation stage that requires culture inoculum (*Chlorella vulgaris*), water, flue gas CO_2 , sunlight, and inorganic nutrients including mainly nitrates and phosphates. The *Chlorella vulgaris* is cultivated in open ponds mixed with paddle wheels over a 12-month growing season (the number of cultivation days is 347 per year according to the climatic conditions of the cultivation facility). The biomass model considers that the production rate is 30 g/m² d,^{17,45} and microalgal lipid content is 30 wt %.⁶⁰ Also, it considers that harvest water is recycled, so to generate 1 kg biodiesel, 0.182 kg nitrogen and 0.039 kg phosphate are required.⁴⁷

The carbon dioxide in the flue gas from the adjacent power plant that continuously operates 24 h/day is delivered directly to the ponds through a system of distribution piping. CO_2 is supplied at a ratio of 1.83 tonne/tonne of algal biomass.¹⁶ It is assumed that the overall CO_2 uptake (i.e., utilization) is 70% efficient⁵⁴ and that CO_2 is delivered to the algal growth medium for a total of 12 h only during the daytime, ensuring that algal cells are exposed to a regular light–dark cycling of solar radiation in order to maintain photosynthetic activity.

Each raceway pond design is assumed to be consistent with industrial standards:⁵¹ 100 m long, 10 m wide, and 0.3 m deep. Pond water velocity is maintained at 0.25 m/s by paddle wheel mixers, and the harvest–growth–harvest cycle is assumed to be 3 days.⁵⁴ During the culture process in open ponds, water is lost mainly due to evaporation. In this study, it is assumed that the cultivation section requires a makeup water addition due to evaporation and leakages amounting to 0.5 cm/d.⁵⁴

The microalgae cultivation stage is followed by algal harvesting that consists of biomass recovery from the culture medium. Algal biomass is first recovered using a coagulation–flocculation–settling operation with the recovery yield of 97%.⁶¹ The concentration of alum coagulant is 0.74 mg/L.⁶² It is assumed that the algal biomass leaving primary harvesting has a concentration of 30 g/L.⁶¹ This concentrate is then dewatered in a secondary harvesting step using self-discharged disc-stack centrifuges with a recovery yield of 85%,^{17,62,63} wherein it is

obtained in a final concentration of 150 g/L algal biomass.⁵³ The aqueous broth-containing water-soluble nutrients from both harvesting steps are captured and returned to the cultivation process to decrease the fresh water and nutrient demands of the system, whereas the algal slurry that comes out of the centrifuge units is dried to 12 wt % moisture in a thermal dryer without biomass loss.⁵³

In the oil extraction process, *n*-hexane is used for extracting lipid molecules from microalgal biomass at a mass ratio of 0.5 (hexane/biomass). This process has a lipid recovery yield of 80% and results in solvent loss of 2 wt %.¹⁷ Solvent is recovered by distillation and reused. After the extraction of oil, the lipid-depleted biomass (residual biomass) is combusted in the power plant boiler to displace fossil fuel sources. In the final stage, every gram of triglyceride extracted is converted approximately into 1 g of biodiesel and 0.11 of glycerol via transesterification with alkali catalyst (1.5 wt % KOH) and methanol (in excess of 6 M).¹⁷ The excess unreacted methanol is recovered by distillation at an assumed efficiency of 95%, whereas the crude biodiesel is cleaned with phosphoric acid (1.5 wt % oil) and water (15 wt % oil).¹⁷

It is assumed that the electricity and thermal energy demands of the algae-to-biodiesel process is supplied by the power plant. Rickman et al.⁵² showed that algal biomass drying can be accomplished using waste heat from the power plant flue gas. Thus, it is a reasonable consideration to assume that the flue stream of the power plant provides the thermal energy required by distillation columns to dry the algal biomass using a waste heat recovery process.

The electric energy required for each stage of the algae-to-biodiesel production process is shown in Table 1. These power demands were

 Table 1. Electricity Consumption for the Stages of the Algaeto-Biodiesel Production Process⁵³

parameter (kWh/tonne algae)	value	parameter (kWh/tonne algae)	value
Cultivation		Oil Extraction	
CO ₂ transport	45	extraction	130.7
paddle wheel	200		
CO ₂ injection/pumping	28.9		
water and broth pumping	153		
Harvesting		Transesterification	
alum coagulation	167	mixing	20.4
centrifugation	26.5		

taken from Ventura et al.⁵³ Note that the power required for CO_2 transport and injection, as well as for water and broth pumping and mixing, are included in the analysis of the cultivation stage.

The resulting algae-to-biodiesel production model is presented in Appendix A.

Problem Statement. The purpose of this paper is to address the economic and environmental optimization of the system under consideration. The economic objective function is to maximize the annual gross profit (PROFIT), which is defined as the revenue from the sale of electricity and bioproducts (biodiesel and glycerol) minus the total annualized cost (TAC) plus the total subsidy (TAX CREDIT) due to the reduction of GHG emissions

PROFIT = REVENUE - TAC + TAX CREDIT(1)

The equations required to calculate the terms REVENUE and TAC of eq 1 are given in detail in Appendix B, while below, we present the TAX CREDIT calculation. It should be noted that because our main interest is in the preliminary design stage of the system, PROFIT has been selected as an appropriate economic objective to evaluate the potential system profitability and to decide if more detailed designs can be justified.

The environmental objective function is to minimize the overall environmental impact (EI99) associated with electricity and biodiesel generation in the integrated energy system using different types of primary energy sources. The environmental impact is defined by eq 7 and measured through the Eco-indicator 99 that is calculated following

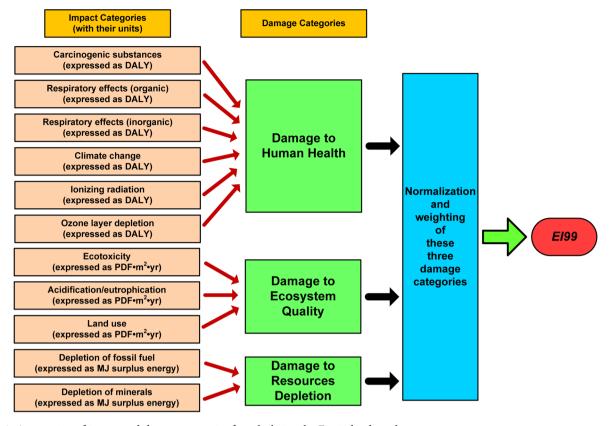


Figure 3. Aggregation of impact and damage categories for calculating the Eco-indicador value.

the LCA methodology^{57,58} as presented in the next section. It should be noted that this methodology evaluates the environmental impact not only at the plant level of the integrated system but also includes the assessment of the impacts resulting from the operations of each of its associated life cycle stages (i.e., all processes associated with raw materials extraction and processing, energy generation, and capital manufacture). Thus, this approach determines the overall environmental performance of the expanded integrated system (entire life cycle of the system), which may be useful from a decision-making standpoint.

The optimization problem of the integrated energy system is addressed through a simulation—optimization approach aiming at the maximization of the annual gross profit (PROFIT) and at the minimization of the overall environmental impact (EI99). The solution to the multi-objective problem is given by a set of Pareto optimal points that involve alternative designs, each of which represents an optimal compromise between the environmental and economic criteria.

Environmental Impact Evaluation. LCA is a systematic analytical method for environmental assessment (PRé-Consultants,⁶⁴ Guillén-Gosálbez et al.,⁶⁵ Ponce-Ortega et al.⁶⁶), normalized by the ISO^{55,56} environmental management system. The calculation of EI follows the sequential steps of (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment, and (iv) interpretation and reporting. We describe next these four steps of the LCA methodology in the context of our study.

Goal and Scope Definition. The goal of the LCA study is to determine the environmental impact of the system to aid the decisionmaking process for sustainable electricity generation in the steam power plant integrated with the algal-to-biodiesel production facility. The scope of the LCA study is to perform a cradle-to-gate analysis that accounts for the generation of primary energy sources (i.e., fossil fuels, biofuels, and biomass) and nutrients consumed by the system, as well as the impact of the construction phase of the main equipment units of the power plant and the emissions released to the atmosphere. Therefore, the system boundary in Figure 2 is expanded to include all processes from microalgal biomass production in open ponds through to the biodiesel combustion, in addition to those associated with raw material extraction and energy generation, as well as nutrients and construction materials production for main equipment units of the power plant. The environmental impact during the construction of the algae-to-biodiesel subsystem is assumed to be negligible compared to that during operation.³⁹ Also, makeup water for microalgae culture is assumed to be available at no environmental penalty. The amount of 400 MW of electric power produced by the power plant is chosen as the functional unit or basis for comparison for this study, whereas the temporal unit is 1 calendar year.

Because the production of electricity exceeds that of the biodiesel in terms of both value and total energy content, it is assumed that electricity is responsible for all of the environmental impacts of the integrated system. This assumption also reflects that the main function of the algae-to-biodiesel facility is to contribute to enhancing the sustainability of the thermoelectric power plant by using its CO_2 emissions for simultaneous CO_2 biomitigation and production of biodiesel to replace fossil diesel.

For classifying and characterizing the emission inventories of each life cycle stage, the Eco-indicator 99 proposes 11 impact categories. Each impact category is further aggregated under one of the three main categories: damage to human health (HH), damage to ecosystem quality (EQ), and damage due to resource depletion (RD). These main categories are finally translated into a single metric, the total Ecoindicator 99. In addition, life-cycle GHG emission reductions relative to fossil fuels are modeled in this study to determine the TAX CREDIT associated with the operation of the integrated system.

Inventory Analysis. In the second LCA step, mass and energy balances are performed to quantify the inputs and outputs of materials and energy associated with the operation and construction of the system for electricity and biodiesel production. In this work, the consumption rates of primary energy sources (fossil fuels, biofuels, and biomass) and the flow rates of nutrients and water are regarded as inputs, whereas emissions released to the atmosphere are outputs from the system. The amounts of material (stainless steel, carbon steel,

glass, or plastic) required for the construction of the main equipment units of the power plants are also inputs. The inventory of direct inflows and outflows of energy and mass (resources used and emissions released) must be translated into the corresponding life cycle inventory (i.e., environmental burdens) of all relevant feedstock requirements and emissions released to the environment over the whole life cycle of the system. Mathematically, the total life cycle inventory entry (i.e., emissions and feedstock requirements) of chemical b is represented by a continuous variable LCI^{tot}_b, which is expressed as a function of input streams of energy and mass as well as emissions during the operation of the integrated energy system, as shown in eq 2.

$$LCI_{b}^{tot} = \begin{bmatrix} \sum_{f} LCIE_{b}^{f}F_{f} + \sum_{bf} LCIE_{b}^{bf}F_{bf} + \sum_{bm} LCIE_{b}^{bm}F_{bm} \\ + \sum_{n} LCIE_{b}^{n}F_{n} + \sum_{emis} LCIE_{b}^{emis}F_{emis} + \sum_{u} LCIE_{b}^{u}we_{u} \end{bmatrix} \quad \forall b$$

$$(2)$$

In this equation, LCIE^b_b, LCIE^b_b, LCIE^b_b, and LCIE^b_b denote the life cycle inventory entries of chemical b per unit of fossil fuel f, biofuel bf, external biomass bm, and nutrient n, respectively. On the other hand, the parameter LCIE^b_b represents the emissions released/feedstock requirements of chemical b during the construction phase per unit of mass of equipment u, and LCIE^{emis}_b refers to the emissions of chemical b per unit of emission emis released during the operation of the system. Continuous variables F_{ib} F_{bf} and, F_{bm} are the flow rates of fossil fuel f, biofuel bf, and external biomass bm burned in the power plant boiler, respectively; F_n and F_{emis} denote the consumption of nutrient n and the total emissions released during the operation of the system. Finally, we_u represents the weight of construction material for main unit u.

It should be noted that the values of the life cycle inventory entries can be obtained either from environmental databases⁶⁷⁻⁶⁹ or by performing an *ad hoc* LCA analysis for those components that are not in the database.

Impact Assessment. As shown in Figure 3, this step involves the aggregation of the emissions released and the resources used (energy sources, nutrients, and construction materials) to quantify their potential environmental impacts, which are then reduced to a single measure of the system's environmental performance (Eco-indicator 99). First, substances from the life cycle inventory are gathered in a number of groups representing the 11 impact categories of the Eco-indicator 99 framework, as stated in eq 3.

$$IMP_{c} = \sum_{b} DF_{b}^{c}LCI_{b}^{tot} \quad \forall c$$
(3)

where IMP_c is the environmental damage caused in impact category *c*, LCI_b^{tot} is the life cycle inventory of emissions and feedstock requirements associated with chemical *b*, and DF_b^c is the damage factor associated with chemical *b* and impact category *c*.

The damage factors are given by specific environmental models that are available in the literature for each impact category.⁵⁸ As shown in the above equation, these factors are used to translate inputs and outputs from the life cycle into the environmental impacts to which they may contribute. Also note that one substance from the life cycle inventory can contribute to more than one impact category and that several substances among one group can contribute to the same environmental problem.

Figure 3 shows that the 11 impact categories are further aggregated into the following three damage categories:

(1) Human health category includes the following impacts: (i) carcinogenic effects on humans, (ii) respiratory effects on humans that are caused by organic substances, (iii) respiratory effects on humans that are caused by inorganic substances, (iv) damage to human health that is caused by climate change, (v) human health effects that are caused by ionizing radiations, and (vi) human health effects that are caused by ozone layer depletion. The human health damages are expressed as DALY, Disability Adjusted Life Years. A damage of 1

means that 1 life year of one individual is lost or one person suffers 4 years from a disability with a weight of 0.25.

(2) Ecosystem quality category includes the following impacts: (vii) damage to ecosystem quality that is caused by ecosystem toxic emissions, (viii) damage to ecosystem quality that is caused by the combined effect of acidification and eutrophication, and (ix) damage to ecosystem quality that is caused by land occupation and land conversion. The ecosystem quality damages are expressed as PDF m² year, Potentially Disappear Fraction of Species per square meter and year. A damage of 1 means all species disappear from 1 m² during 1 year or 10% of all species disappear from 1 m2 during 10 year.

(3) Resource depletion category includes the following impacts: (x) damage to ecosystem quality that is caused by the extraction of minerals, and (xi) damage to resources that is caused by extraction of fossil fuels. The damages to resources are expressed as MJ surplus energy. A damage of 1 means that due to a certain extraction of resources, further extraction of the same resources in the future will require one additional MJ of energy due to the lower resource concentration or other unfavorable characteristics of the remaining reserves.

Thus, the impact caused in each damage category is calculated as

$$DAM_{d} = \sum_{c \in IC(d)} IMP_{c} \quad \forall d$$
(4)

where IC(d) denotes the set of impact categories c that contribute to damage category d.

According to Figure 3, the damage categories are finally added and multiplied by specific normalization (NF_d) and weighting (WF_d) factors to calculate the single metric called Eco-indicator 99 (i.e., overall environmental impact)

$$EI99 = \sum_{d} NF_{d}WF_{d}DAM_{d}$$
(5)

To perform the normalization process in this study, the damage to human health is divided by a factor of 1.54×10^{-2} , the damage to ecosystem quality by 5.13×10^3 , and the damage to the resources by 8.41×10^3 . Also, the hierarchist perspective is used combined with the default weighting factors (i.e., 400-400-200 for HH, EQ, and RD, respectively).⁶⁴

The previous equation can be considered further in terms of the overall damage factor (ODF_{re}) for each resource used and emission released per unit of reference flow (i.e., fossil fuel, biofuel, biomass, nutrient, emission) or per unit of weight of equipment u, which can be calculated by the following general expression

$$ODF_{re} = \sum_{d} \sum_{c \in IC(d)} \sum_{b} NF_{d}WF_{d}DF_{b}^{c}LCIE_{b}^{re}$$
$$\forall re \in (f_{b}bf_{b}bm,n,emis,u)$$
(6)

As a result, the overall environmental impact of the integrated energy system is calculated as the sum of the overall damage factor for each resource used and emission released multiplied by its associated flow rate or weight in the case of construction material, as given below

$$EI99 = \begin{bmatrix} \sum_{f} ODF_{f}F_{f} + \sum_{bf} ODF_{bf}F_{bf} + \sum_{bm} ODF_{bm}F_{bm} \\ + \sum_{n} ODF_{n}F_{n} + \sum_{emis} ODF_{emis}F_{emis} + \sum_{u} ODF_{u}we_{u} \end{bmatrix}$$
(7)

Thus, the environmental objective consists of minimizing the overall environmental impact given by eq 7. The overall damage factors for resources used and emissions released are given in Table 2. These factors were calculated based on environmental data given by PRé Consultants Database.⁶⁴

In addition, the reduction of life-cycle GHG emissions from electricity and biodiesel production by the integrated energy system must be considered to calculate the total subsidy attained as follows

Table 2. Overall Damage Factors for Materials and FuelsConsidered

material/fuel	overall damage factor	units
steel	0.09	Eco-points/kg of steel
urea (nitrogen)	0.13	Eco-points/kg of urea
DAP (phosphate)	0.10	Eco-points/kg of phosphate
coal	24.13	Eco-points/tonne of coal
oil	157.99	Eco-points/tonne of oil
natural gas	124.52	Eco-points/tonne of natural gas
switchgrass	2.49	Eco-points/tonne of switchgrass
biogas	15.44	Eco-points/tonne of biogas
softwood	12.64	Eco-points/tonne of softwood
hardwood	11.42	Eco-points/tonne of hardwood
biodiesel	14.41	Eco-points/tonne of biodiesel

TAX CREDIT = (Total GHG emissions reduction) \times S^{GHG}

where S^{GHG} is the unit subsidy for reduction of life-cycle GHG emissions (\$/ton of GHG reduced).

The GHG contribution to global warming for each fuel takes into account CO_2 , CH_4 , and N_2O emissions that are grouped together in a single emission factor, which is estimated using the IPCC Global Warming Potential (GWP)⁷⁰ model with a time frame of 100 years. In fact, for each fuel, this GWP factor represents the total damage factor associated with all its emissions of greenhouse gases and global warming impact category. This factor is expressed in kilograms of carbon dioxide equivalent emissions per unit of fuel energy (i.e., kg CO_2 equiv/kJ). Thus, the flow rate of each primary energy source (i.e., fossil fuel, biofuel, and biomass) that can be burned in the power plant boiler is multiplied by the lower heating value and the GWP factor of the fuel to give its life-cycle GHG emissions.

To determine the amount of life-cycle GHG emissions reduction, the integrated energy system needs to be compared with the GHG emissions of a reference system for the same amount of electric power produced. The simplified schematic in Figure 4 illustrates fuel and carbon flows for the reference system without the algae biofuel production process and the integrated energy system, which includes all the processes from the microalgal production from the power plant flue gas to the biodiesel combustion. Because fuel switching from coal to biomass feedstock in the power plant boiler could be achieved without using the integrative approach proposed in this study, we only consider the GHG emissions reduction due to the displacement of fossil-derived diesel with biodiesel in the transportation sector to calculate the TAX CREDIT for the integrated energy system. Thus, this variable is given by Research Article

$$TAX CREDIT = (HV_{FD}Em_{FD}^{LCA}F_{FD} - HV_{BD}Em_{BD}^{LCA}F_{BD})S^{GHG}$$

(8)

where HV_{FD} and HV_{BD} are the heating values of fossil diesel and biodiesel, respectively; Em_{FD}^{LCA} and Em_{BD}^{LCA} are the life-cycle GHG emissions for fossil diesel and biodiesel, respectively. It should be noted that direct emissions of CO_2 removed from the power plant flue gas by microalgae are not included in previous equation because such carbon is embedded between two renewable fuels (biodiesel and residual algal biomass), and it is immediately released to the atmosphere during fuels combustion resulting in no long-term sequestration (i.e., life-cycle GHG emissions reduction).

The flow rate of the displaced fossil diesel is calculated on the basis of equivalent net energy content of fossil-derived diesel and biodiesel. Therefore, this flow rate is defined as

$$F_{FD} = \frac{HV_{BD}}{HV_{FD}}F_{BD}$$
(9)

Heating values and life-cycle GHG emissions for biodiesel and fossil-derived diesel were taken from Stephenson et al.⁴⁸ The lower calorific values of biodiesel and fossil diesel were taken to be 37.2 and 43.1 MJ/kg, while their life-cycle GHG emissions for biodiesel and fossil diesel were taken as 713 kg of CO_2 equiv/tonne of biodiesel and 3707 kg of CO_2 equiv/tonne of diesel.

Interpretation. The solution of the multi-objective problem consists of a set of optimal points (i.e., Pareto optimal set) representing alternative system designs, each achieving a unique combination of the given optimization criteria. In the last step of the LCA methodology, the Pareto solutions are analyzed to choose the best solution where significant environmental improvements can be achieved at a marginal decrease in the annual gross profit or according to the decision-maker preference and applicable environmental regulations. Also, a set of conclusions and recommendations for the system are formulated.

Solution Method. ε -Constraint Method. The main benefit of using biofuels and biomass as energy sources in the steam power plant along with microalgae removal of CO₂ from the flue stream for biodiesel production is the reduction of the overall environmental impact. However, a lower environmental impact is associated with a lower system annual gross profit. This poses a challenging multi-objective optimization problem where the overall environmental impact (EI99) needs to be minimized, while maximizing the system annual gross profit (PROFIT).

We use the ε -constraint method^{71,72} for generating the set of optimal solutions representing the trade-offs between economic and environmental criteria. The basic strategy of this technique is to transform the multi-objective optimization problem into a series of single objective optimization problems, in which one of the objectives is picked to be maximized while the other is turned into an additional

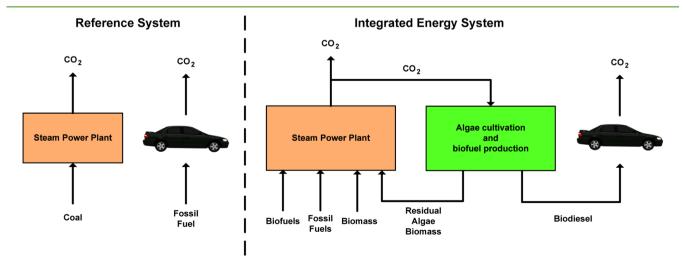


Figure 4. Schematic overview of fuel and carbon flows without and with the algae biodiesel production process.

constraint that it is forced to be lower than the epsilon parameter. Thus, the multi-objective optimization problem of interest can be mathematically formulated as follows:

Maximize

PROFIT(
$$x$$
,u, $x_{\rm D}$)

Subject to

$$EI99(x,u,x_D) \le \varepsilon$$

$$h_1(x,u,x_D) = 0$$

$$g_E(x,u,x_D) \le 0$$
(P1)

where ε is an auxiliary parameter that takes different values to obtain the entire Pareto set of solutions. The equality constraints h_1 are the system of nonlinear algebraic equations (i.e., thermodynamic property relations, mass, and energy balances, cost, and LCA constraints) that model the problem, whereas the inequality constraints g_E represent design specifications (i.e., capacity limits and upper and lower bounds on decision variables). The economic and environmental objectives are defined by eqs 1 and 7, respectively.

The problem under consideration involves a set of D optimization continuous variables called decision variables, which are denoted by the vector x_D

The vector x represents the continuous variables that are outputs from the optimization process (i.e., thermodynamic properties, mass flow rates, operating conditions, and sizes of equipment units). The continuous variables are related to the decision variables x_D by model equations. The parameters not modified during calculations are represented by the vector u.

Simulation Optimization Framework. The proposed solution method has two outer-nested loops as the one proposed by Gutiérrez-Arriaga et al.⁵⁶ In the outer loop, the method defines the ε values for the environmental impacts. In the inner loop, the single optimization problem (P1) is solved for a given value of ε . The algorithm to solve the inner loop problem combines a system simulation module with a two-level optimization methodology involving genetic algorithms (GA)⁷³ and linear programming (LP).

The steps of the coupled GA-LP algorithm for solving each singleobjective problem are as follows:

Step 1. An initial population of a specified size, $N_{\rm pop}$ number of individuals, is generated randomly. The identity of each individual (i.e., chromosome) of the population is determined by the problem decision variables, which may change within the optimization process according to previously established bounds. Therefore, there are $N_{\rm pop}$ different decision variable combinations or individuals. The set of decision variables (i.e., independent variables) for the regenerative–reheat steam power plants shown in Figure 1 includes main steam pressure/temperature, reheat steam pressure/temperature, steam extraction pressures, deaerator pressure, and condenser pressure.

Step 2. In each generation, the fitness function of each individual is evaluated by simulation and individuals are sorted based on this criterion.

In this paper, the fitness function corresponds to the economic objective function (annual gross profit), and the aim is to maximize its value. The simulation module provides the conditions of the power plant components (i.e., dependent variables) for each individual: boiler and steam conditions (temperature, pressure, flow rate, pressure drop), reheater conditions (outlet temperature, and pressure drop), steam turbines (inlet conditions and outlet conditions of temperature, pressure, enthalpy, flow rate), extraction conditions (temperature, pressure, enthalpy, flow rate), condenser (area as well as inlet and outlet conditions of temperature, pressure, enthalpy, flow rate), feedwater heaters (area, condensate inlet, condensate outlet, extraction steam inlet, drain conditions of temperature, pressure, enthalpy, flow rate), and pumps (pump power, inlet pressure, outlet pressure, flow rate). Also, for each individual, the simulation module provides the heat added in the boiler, emission flows, equipment cost as a function of size, and other information to calculate the economic objective function that corresponds to the fitness function.

The detailed description of the problem to obtain the minimum energy cost is as follows:

For each individual, the heat required by the boiler can be provided by multiple energy sources including fossil fuels, biofuels, and biomass. Therefore, there are several feasible combinations of energy sources rather than a single one to meet the energy demands of the boiler. But only one of them allows the steam power plant to operate at the minimum annual cost of energy for a given value of the environmental impact (i.e., parameter ε of the constraint method). The problem of optimal combination of energy sources can be formulated as a linear programming problem for each individual as follows:

Objective function

minimize
$$Z = \sum_{f \in F(nc)} C_f F_f + \sum_{bf} C_{bf} F_{bf} + \sum_{bm} C_{bm} F_{bm} + C_{LD} F_{LD}$$
(10)

Subject to

$$\begin{bmatrix} \sum_{f} ODF_{f}F_{f} + \sum_{bf} ODF_{bf}F_{bf} + \sum_{bm} ODF_{bm}F_{bm} \\ + \sum_{n} ODF_{n}F_{n} + ODF_{BD}F_{BD} + \sum_{u} ODF_{u}we_{u} \end{bmatrix} = EI99$$
(7)

$$\sum_{f \in F(nc)} \eta_{f} H V_{f} F_{f} + \sum_{bf} \eta_{bf} H V_{bf} F_{bf} + \sum_{bm} \eta_{bm} H V_{bm} F_{bm} + \eta_{LD} H V_{LD} F_{LD}$$

= QH (11)

$$\sum_{f \in F(nc)} \operatorname{Em}_{f}^{\operatorname{Comb}} F_{f} + \sum_{bf} \operatorname{Em}_{bf}^{\operatorname{Comb}} F_{bf} + \sum_{bm} \operatorname{Em}_{bm}^{\operatorname{Comb}} F_{bm} + \operatorname{Em}_{LD}^{\operatorname{Comb}} F_{LD}$$

$$= F_{CO} \qquad (12)$$

$$F_{\rm LD} = \sigma_{\rm Algae} F_{\rm CO_2} \tag{A7}$$

$$F_{\rm N2} = (0.0689)F_{\rm CO_2} \tag{A12}$$

$$F_{\rm PH} = (0.001475)F_{\rm CO_2}$$
 (A13)

 $F_{\rm f} \ge 0 {\rm f} \in F({\rm nc}), F_{\rm bf} \ge 0 {\rm bf} \in {\rm BF}, F_{\rm bm} \ge 0 {\rm bm} \in {\rm BM}, F_{\rm n} \ge 0 {\rm n} \in N$

 $F_{LD} \geq 0, F_{CO_2} \geq 0$

where Z is the annual cost of the energy sources; $HV_{\dot{\nu}} HV_{b\dot{\nu}} HV_{bm\nu}$ and HV_{LD} are the heating values of fossil fuel f, biofuel bf, biofuel bm, and lipid-depleted algal biomass, respectively. Em_f^{comb} , Em_{bf}^{comb} , Em_{bm}^{comb} and Em_{LD}^{comb} are direct CO_2 emission factors from combustion in the power plant for fossil fuel f, biofuel bf, biomass bm, and lipid-depleted algal biomass, respectively. F(nc) denotes the set of fossil fuels that contribute to GHG emissions reduction (natural gas and oil) in comparison to coal.

In constraint 7, EI99 is the environmental impact limit previously fixed by the constraint method (parameter ε). Constraint 11, which represents the energy balance over the boiler, shows that the energy flow provided by the energy sources serves to satisfy the boiler heat load QH. $\eta_{\theta} \eta_{b\theta} \eta_{bm}$, and η_{LD} are the boiler efficiency for fossil fuel f, biofuel bf, biomass bm, and lipid-depleted algal biomass, respectively. $C_{\theta} C_{b\theta} C_{bm}$, and C_{LD} are the unit costs for fossil fuel f, biofuel bf, biomass bm. and lipid-depleted algal biomass, respectively. Constraint 12 gives the total flow rate of CO₂ from the combustion of the fossil fuels, biofuels, external biomass, and algal biomass in the power plant boiler. Finally, constraints A7, A12, and A13 are presented in detail in Appendix A.

Table 3 presents the unit costs, heating values, and direct CO_2 emissions for the fuels associated with the problem. Direct emissions were obtained from the SENER-CONUEE report.⁷⁴ As shown in this table, the unit cost of the lipid-depleted algal biomass is very small, so this always will be part of any optimal solution

Thus, the LP problem calculates the optimal types and amounts of primary energy sources required by the boiler for each individual at each generation (i.e., iteration) of the optimization process. For each Table 3. Unit Costs, Heating Values, and Direct Emissions Factors for Fuels Considered

fuels	unit costs (\$/tonne)	heating values (MJ/tonne)	direct emissions (g CO ₂ /MJ)
coal	97.1	35,000	94.60
oil	740	45,200	72.79
natural gas	855.2	54,000	56.10
switchgrass	45	4480	100.44
biogas	444	52,000	54.42
softwood	51.67	20,400	111.76
hardwood	53.31	18,400	111.95
algal biomass	0.01	28,000	21.43

individual, the LP model takes into account mass and energy interactions between the power plant and the algae-to-biodiesel production subsystem.

After solving the LP problem, the capital costs for the main units of the system are calculated using cost relations given in Appendix B which are based on correlations reported in literature^{75,76} as well as cost data reported by Ventura et al.⁵³ Additionally, the total operating costs are evaluated following equations presented in Appendix A and Appendix B.

Step 3. The individuals with the greater values of fitness function (i.e., fittest individuals) are selected as parents to generate a new set of individuals (i.e., a new set of decision variables).

In this work, the selection approach was the *Roulette Wheel* approach, which is based on the selection of the parents through simulation in a roulette, where the area for selection is proportional to the fitness function. The parents selected are used to generate the new population. For this purpose, reproductions of genetic operators, such as elite count (the two best individuals without change go to the next

generation), crossover (two individuals randomly selected are combined to yield a new individual), and mutation (a random change is done in the search variables of a given individual to yield a new individual) are applied to this selected group. In this way, a new population with same number of individuals as the previous one is generated.

Step 4. The individuals of the new population are again evaluated based on the fitness function. The algorithm can continue evolving the population in this manner indefinitely. However, the calculation process continues until the stopping criterion is satisfied (if the number of generations is greater than a fixed number). When the convergence criterion is reached, the algorithm stops, and the best solution is the one of the current generation with the highest profit. Note that this approach satisfies the environmental constraint previously fixed by the ε -constraint method.

A MATLAB model was developed and used in our analysis for performing material and energy balances of the integrated energy system to determine the raw material and energy inputs, as well as for solving the optimization problem using GA. For the present study, we used a population size of 120 chromosomes and an elite count of two individuals. The crossover fraction was taken as 0.8 and the number of maximum generations was selected as 2000. We run the model on a Pentium 4 (1.7 GHz Due-core) processor.

OPTIMIZATION RESULTS AND DISCUSSION

The solution of the multi-objective problem provides the Pareto curves (i.e., set of solutions representing the best possible trade-offs between the economic and environmental objectives) shown in Figure 5 for both cases, without and with a subsidy for reduction of GHG emissions. These results were obtained based on the following performance data for the power plant units: efficiency for the pumps of 70%, isentropic

RACEWAY PONDS - STEAM POWER PLANT 400MW

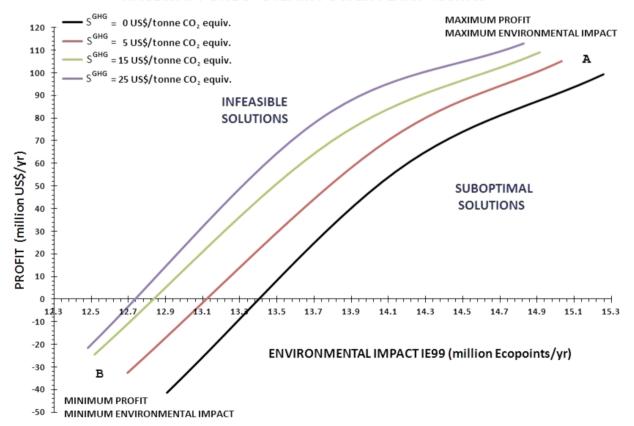


Figure 5. Pareto curves for the integrated energy system without and with different unit subsidies for reduction of GHG emissions.

efficiency for the turbine of 90%, degree of subcooling in the condenser of 5 °C, and terminal temperature difference of 5 °C. The unit selling prices of electricity, biodiesel and glycerol were taken as 0.14/kWh, 3.91/gal, and 0.91/tonne, taken as 0.14/kWh, the noted that the unit selling price of biodiesel was obtained from the U.S. Department of Energy (DOE).

Points A and B in Figure 5 represent the optimal design solutions with maximum gross profit and minimum environmental impact, respectively. As shown in this figure, a reduction in the Eco-indicator 99 can only be achieved at the expense of a decrease in the annual gross profit (i.e., increase in the total annual cost); thus, there is a clear trade-off between both criteria. Table 4 shows that the Eco-indicator 99 for a subsidy of

Table 4. Points A and B of the Pareto Curve for a S^{GHG} of $5/tonne CO_2$ equiv

	raceway ponds		
solution	PROFIT (million US\$/yr)	EI99 (million Eco-points/yr)	
point A	105.17	15.03	
point B	-32.70	12.70	

\$5/tonne of CO₂ equiv was reduced from 15.03×10^6 Ecopoints/yr to 12.7×10^6 Eco-points/yr along the Pareto curve. Also, Figure 5 shows that reducing the environmental impact below about 13.45×10^6 Eco-points/yr requires huge total annual costs that in turn lead to negative annual gross profits. Furthermore, the larger value of the unit subsidy for reduction of GHG emissions, the more profit will be made. Overall, the calculated PROFIT is promising for both cases.

In the Pareto set of the problem, each point corresponds to a different system design in terms of operating conditions and selection of energy sources. As shown in Table 5 for a subsidy of 5/tonne of CO_2 equiv, extreme solutions use lipid-depleted algal biomass as an energy source in the power plant boiler but differ in the type of the other fuels of the energy mix: the maximum annual gross profit solution (point A) uses coal, whereas the minimum *EI99* solution (point B) uses switchgrass. These are the main differences between both solutions.

Notice in Table 6 that the income from the sale of biodiesel is greater at point B (i.e., 90.74×10^6 \$/yr) than at point A (i.e.,

raceway ponds		
point A (US\$/yr)	point B (US\$/yr)	
86,861,278	90,735,921	
676,459	706,634	
402,112,545	400,653,236	
489,650,282	492,095,791	
841,015	878,530	
48,648,582	174,059,477	
5,524,929	5,771,381	
1,717,006	1,793,597	
585,721	611,849	
126	132	
4,227,830	4,416,422	
4,464,589	4,663,742	
369,952	386,454	
710,275	741,959	
66,249,014	192,445,017	
319,072,398	333,227,579	
385,321,413	525,672,597	
105,169,885	-32,698,273	
	point A (US\$/yr) 86,861,278 676,459 402,112,545 489,650,282 841,015 48,648,582 5,524,929 1,717,006 585,721 126 4,227,830 4,464,589 369,952 710,275 66,249,014 319,072,398 385,321,413	

Table 6. Economic Results for Points A and B for a S^{GHG} of

 $5/tonne CO_2$ equiv

 85.86×10^6 \$/yr). This is due to fact that the amount of CO₂ generated in the power plant and delivered to the algae biorefinery is greater at point B than at point A; as a result, the algal biomass available to be converted into biodiesel is greater at point B with respect to point A. Also note from Tables 4–6 that the energy sources selected for the labeled solutions represent the most important contributions to the annual gross profit and the overall environmental impact. In the optimal solution A, only coal is selected as the external fuel in the boiler, so it is the option with the highest environmental impact but is also the most economical. On the other hand, point B uses switchgrass instead of coal, reducing simultaneously the Eco-indicator 99 and the associated annual gross profit.

Very recently, Gong and You⁷⁹ addressed the optimal design and synthesis of algal biorefinery processes for biological carbon sequestration. Their optimization results indicate that the algal biorefinery earns 12.23/t CO₂ sequestrated for algal cultivation in open pond raceways when the annual

Table 5. Flow Rates	of Materials and Fu	els at Points A a	ind B for a S ^{GHG}	of $5/tonne CO_2$ equiv

	raceway ponds			
	point A		point B	
material/fuel	Q (MJ/yr)	flow rate (tonne/yr)	Q (MJ/yr)	flow rate (tonne/yr)
coal	1.75×10^{10}	501,015	_	_
switchgrass	-	_	2.35×10^{10}	3.86×10^{6}
biogas	-	_	_	-
softwood	-	_	_	-
hardwood	_	_	_	_
algal biomass (F_{AC})	_	341,850	_	357,099
residual biomass (F_{LD})	5.99×10^{9}	214,210	6.26×10^{9}	223,765
CO_2 generated (F_{CO_2})	-	1.78×10^{6}	_	-
steam at the outlet of the boiler	_	7.36×10^{6}	_	7.44×10^{6}
consumption of urea	-	12,277	_	12,825
consumption of DAP	_	2641	_	2759
makeup water	_	5.85×10^{7}	_	6.11×10^{7}
biodiesel produced	_	67,645	_	70,662
glycerol produced	_	7440	_	7772

sequestrated quantity balances the emissions of a 2400 MW coal-fired power plant and the feed gas is delivered to the biorefinery only during the day. Thus, these results and the results obtained in the present work reveal that the integrated energy system could be a profitable strategy for mitigation of GHG emissions from power plants.

CONCLUSIONS

This paper presents an optimization approach for the integration of advanced steam power plants with algae-tobiodiesel processes with economic and environmental concerns. The proposed approach is based on the combination of a simulation model of the system with GA and the ε -constraint method for solving the multi-objective optimization problem. The economic objective function considers the maximization of the annual gross profit, whereas the environmental objective function consists in the minimization of Eco-indicator 99 (overall environmental impact) that is evaluated following LCA methodology. The optimization problem includes the selection of primary energy sources (fossil fuels, biofuels, and external biomass) using an LP model for each individual at each generation of the GA optimization.

The capabilities of the proposed approach are illustrated through a case study, which involves the integration of an advanced regenerative Rankine power plant with a microalgae-to-biodiesel production process. This bioprocess is based on open pond raceways for algal cultivation that receive feed gas $(CO_2 \text{ from the power plant})$ only during the daytime (12 h a day).

The solution of the multi-objective problem provides a set of optimal solutions (i.e., Pareto optimal set) that represent the best possible trade-offs between the economic and environmental objectives. Results show that the biological capture of CO₂ using microalgae cultivation for biodiesel production could be a profitable strategy for mitigation of GHG emissions from power plants. This is because the integrated energy system reduces CO₂ emissions from power plants using microalgae cultivation for biological mitigation of CO₂ and at the same time produces renewable fuels (i.e., biodiesel and lipid-depleted biomass that is combusted in the power plant) from the algal biomass that displace fossil fuel sources (diesel and coal). Furthermore, by incorporating a subsidy due to GHG reductions in the problem formulation, the annual gross profit is positive in a large portion of the corresponding Pareto curve.

APPENDIX A. ALGAE-TO-BIODIESEL PRODUCTION MODEL

This appendix presents a linear set of algebraic equations describing the algae-to-biodiesel production process in terms of the mass and energy flows shown in Figure 2.

The algal biomass (F_{AC}) produced in the cultivation stage is given by

$$F_{\rm AC} = \frac{\alpha_{\rm AC}^{\rm CO_2} \tau_{\rm DT} F_{\rm CO_2}}{\delta_{\rm CO_2}} = \frac{(0.7)(0.5)}{1.83} F_{\rm CO_2}$$
(A1)

where $\alpha_{AC}^{CO_2}$ is the efficiency of CO₂ transfer into the algal growth medium, δ_{CO_2} is the CO₂ demand in kg-CO₂/kgbiomass, τ_{DT} is the fraction of the whole-day hours that CO₂ from the power plant (feed gas) is delivered to the cultivation stage, and F_{CO_2} is the flow rate of CO₂ generated by the power plant boiler.

In this study, the feed gas delivery is restricted only during the day, so $\tau_{\rm DT} = 0.5$. In addition, the parameter $\delta_{\rm CO_2}$ is set to 1.83 because for 100 tonnes of microalgae produced, 183 tonnes of CO₂ are consumed on average.¹⁶ Thus, removal of CO₂ from flue gases of power plants by microalgae and then conversion of algal biomass to biofuels to replace fossil fuels can yield an important reduction in GHG emissions to the atmosphere.

The mass balance equations for algal biomass in both harvesting steps are expressed as follows

$$F_{\rm AH}^{\rm FLOC} = \alpha_{\rm AH}^{\rm FLOC} F_{\rm AC} = (0.97) F_{\rm AC}$$
(A2)

$$F_{\rm AH}^{\rm CENT} = \alpha_{\rm AH}^{\rm CENT} F_{\rm AH}^{\rm FLOC} = (0.85) F_{\rm AH}^{\rm FLOC}$$
(A3)

where α_{AH}^{FLOC} and α_{AH}^{CENT} are the recovery fractions of algal biomass in primary and secondary harvesting, respectively; α_{AH}^{FLOC} and α_{AH}^{CENT} represent the algal biomass flow rates leaving the flocculation and centrifugation operations, respectively.

In the oil extraction stage, the amount of trigly cerides recovered ($F_{\rm OIL}$) from algal biomass is

$$F_{\text{OIL}} = \alpha_{\text{OIL}} w_{\text{OIL}} F_{\text{AH}}^{\text{CENT}} = (0.8)(0.3) F_{\text{AH}}^{\text{CENT}}$$
(A4)

where α_{OIL} is the recovery fraction of oil using *n*-hexane as solvent and w_{OIL} is the lipid content in algal biomass (wt % of dry biomass).

The fresh consumption of hexane for oil extraction is given by

$$F_{\text{HEX}} = (0.5)(0.02)F_{\text{AH}}^{\text{CENT}} = 0.0016F_{\text{CO}_2}$$
 (A5)

The lipid-depleted algal biomass or residual biomass (F_{LD}) generated by the extraction operation is given by

$$F_{\rm LD} = (1 - \alpha_{\rm OIL} w_{\rm OIL}) F_{\rm AH}^{\rm CENT} = [1 - (0.8)(0.3)] F_{\rm AH}^{\rm CENT}$$
(A6)

Combining eqs A1, A2, A3, and A5, we get

 $F_{\rm LD} = \sigma_{\rm Algae} F_{\rm CO_2} \tag{A7}$

with

$$\sigma_{\text{Algae}} = \frac{(\alpha_{\text{AC}}^{\text{CO}_2})(\tau_{\text{DT}})(\alpha_{\text{AH}}^{\text{FLOC}})(\alpha_{\text{AH}}^{\text{CENT}})(1 - \alpha_{\text{OIL}}w_{\text{OIL}})}{\delta_{\text{CO}_2}}$$
$$= 0.1198 \tag{A8}$$

The biodiesel (F_{BD}) and glycerol (F_{GLY}) produced in the final stage of the system are given by

$$F_{\rm BD} = F_{\rm OIL} \tag{A9}$$

$$F_{\rm GLY} = (0.11)F_{\rm OIL} \tag{A10}$$

Equations A1, A2, A3, and A9 give a simple expression for biodiesel produced in terms of the variable F_{CO} ,

$$F_{\rm BD} = \frac{(\alpha_{\rm AC}^{\rm CO_2})(\tau_{\rm DT})(\alpha_{\rm AH}^{\rm FLOC})(\alpha_{\rm AH}^{\rm CENT})(\alpha_{\rm OIL}w_{\rm OIL})}{\delta_{\rm CO_2}}F_{\rm CO_2}$$

= 0.03785F_{\rm CO_2} (A11)

The nitrogen and phosphate requirements for microalgae cultivation can be determined from the following equations

$$F_{\rm N_2} = (0.182)F_{\rm BD} = (0.00689)F_{\rm CO_2}$$
 (A12)

$$F_{\rm PH} = (0.039)F_{\rm BD} = (0.001475)F_{\rm CO_2}$$
 (A13)

The water losses due to evaporation and leakages (F_{WLOP} in tonne/yr) can be expressed as

$$F_{\rm WLOP} = 1 \times 10^6 \frac{(h_{\rm WEV} + h_{\rm WL})}{\gamma_{\rm AB}} F_{\rm AC} = 31.8761 F_{\rm CO_2}$$
(A14)

where $h_{\rm WEV}$ is the daily evaporation depth (m/d), $h_{\rm WL}$ is the daily water loss due to leakages (m/d), and $\gamma_{\rm AB}$ is the algal culture productivity (g/m² d). In eq A14, 1 × 10⁶ is the conversion factor between g and tonne. In this study, the total daily water loss ($h_{\rm WEV} + h_{\rm WL}$) is 0.005 m/d,⁵⁴ providing a daily water loss volume of 0.005 m³ per m².

After the secondary harvesting step, all the water presents in the outlet stream $(F_{\rm WLC})$ that is directed to the dryer is also lost. This water loss is calculated as follows

$$F_{\rm WLC} = \left(\frac{\rho_{\rm SOL}^{\rm CENT}}{C_{\rm ABS}^{\rm CENT}} - 1\right) F_{\rm AH}^{\rm CENT}$$
(A15)

where $\rho_{\rm SOL}^{\rm CENT}$ is the density of the biomass slurry leaving secondary step, and $C_{\rm ABS}^{\rm CENT}$ is the concentration of algal biomass in that stream. This equation can be rearranged to another useful form

$$F_{\rm WLC} = \left(\frac{\rho_{\rm SOL}^{\rm CENT}}{C_{\rm ABS}^{\rm CENT}} - 1\right) \frac{(\alpha_{\rm AC}^{\rm CO_2})(\tau_{\rm DT})(\alpha_{\rm AH}^{\rm FLOC})(\alpha_{\rm AH}^{\rm CENT})}{\delta_{\rm CO_2}} F_{\rm CO_2}$$
$$= 0.8936 F_{\rm CO_2} \tag{A16}$$

To obtain this equation, we let $C_{ABS}^{CENT} = 150 \text{ g/L},^{53}$ and we assume that $\rho_{SOL}^{CENT} = 1000 \text{ g/L}.$

Thus, the amount of makeup water that must be added to the algae-to-biodiesel process to compensate for the loss of water can be expressed as

$$F_{\rm MW} = W_{\rm WLOP}\rho_{\rm W} + F_{\rm WLC} = 0.9565\rho_{\rm W}F_{\rm CO_2} + 0.8936F_{\rm CO_2}$$
(A17)

where $\rho_{\rm w}$ is the density of liquid water.

The annual net electric power for the integrated energy system is given as the difference between the electric power generated by the power plant and that consumed by the algaeto-biodiesel subsystem

$$NEP = 400 \text{ MW} - E_{AC} - E_{AH} - E_{OE} - E_{BP} - E_{PP}$$
(A18)

where E_{AC} , E_{AH} , E_{OE} , E_{BP} , and E_{PP} are the annual power requirements for microalgae cultivation, algal biomass harvesting, oil extraction from algal biomass, biodiesel production, and pumping of feedwater in the power plant, respectively (Figure 2). The energy consumptions for the stages of the algae-tobiodiesel system were calculated using the data shown in Table 1.⁵³

APPENDIX B. CALCULATION OF THE REVENUE AND TAC TERMS

This Appendix provides in detail the equations required to calculate the terms REVENUE and TAC of eq 1. The term REVENUE is given by summing the total annual revenues

obtained from selling the products (electricity, biodiesel, and glycerol)

$$REVENUE = C_{EP}NEP + C_{BD}F_{BD} + C_{GLY}F_{GLY}$$
(B1)

where C_{EP} , C_{BD} , and C_{GLY} are the unit selling prices of electricity, biodiesel ,and glycerol, respectively; NEP is the annual net electric power generated per year.

The total annualized cost (TAC) is the summation of the annual capital (FC) and operating (OC) costs.

$$TAC = FC + OC \tag{B2}$$

The annual capital cost (FC) is expressed as the sum of the capital cost of each main equipment unit of the system (CAP_u) multiplied by the capital recovery factor (K_F) , as shown by

$$FC = K_F \sum_{u=1}^{NU} CAP_u$$
(B3)

where NU is the number of main equipment units in the system (e.g., boiler, turbines, condenser, pumps, open ponds, or photobioreactors, centrifuges, tanks, etc.). For the present study, the factor $K_{\rm F}$ was taken as 0.3/yr.

The operating cost (OC) accounts for the cost of external energy sources used in the power plant boiler as well as the nutrients and water consumed by the algal biodiesel production system.

$$OC = H_{Y} \begin{bmatrix} \sum_{b} C_{f}F_{f} + \sum_{bf} C_{bf}F_{bf} + \sum_{bm} C_{bm}F_{bm} \\ + \sum_{n} C_{n}F_{n} + C_{mw}F_{mw} + C_{hex}F_{hex} \end{bmatrix}$$
(B4)

where $C_{tr} C_{btr} C_{bm}$, C_{nr} , C_{wr} , and C_{hex} are the unit costs for fossil fuel f, biofuel bf, biomass bm, nutrient n, makeup water mw, and hexane hex, respectively. Note that all flow rates in this equation are provided by the system simulator and optimization process.

In this study, the unit costs of urea, phosphate, and hexane were taken⁵³ as \$ 450/tonne, \$650/tonne, and \$1500/tonne, respectively. It was assumed that the unit cost of makeup water was \$0.01/tonne because the microalgae cultivation facility would be located near the Cuitzeo lake where water is available at very low cost.

The capital costs for the main units of the power plant are determined using the following correlations. The coefficients for the costs functions were obtained from different reports.^{75,76}

Capital Cost for the Turbine

The investment cost for the turbine is calculated as follows

$$CAP_{TURB} = 2237W_{ST}^{0.41}$$
(B5)

where $W_{\rm ST}$ is the power generated by the turbine in kW.

Capital Cost for the Condenser

The capital cost for the condenser is given by

$$CAP_{COND} = 43Q_{I}^{0.68}$$
(B6)

where $Q_{\rm L}$ is the heat removed from the condenser in kW.

Capital Cost for Centrifugal Pumps

The capital cost for centrifugal pumps is calculated as follows

$$CAP_{PUMP} = (475.3 + 34.95P_{w} - 0.0301P_{w}^{2})f_{pw}$$
(B7)

where $P_{\rm w}$ is the pumping power in kW and $f_{\rm pw}$ is equal to 1 for pressures until 1.03 MPa.

Capital Cost for Feedwater Heaters

The cost for feedwater heaters is calculated as follows

$$CAP_{HEATER} = (30800 + (1644A_{heater}^{0.81}))K_{f}$$
(B8)

(B9)

where A_{heater} is the area of the feedwater heater.

The cost for the deaerator is calculated as follows

 $CAP_{DEAEATOR} = 904F_{B}^{0.62}$

where $F_{\rm B}$ is the flow rate in tonne/h.

The capital costs for main units of the algae-to-biodiesel process were calculated using the cost data reported by Ventura et al.53

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Notes

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NOMENCLATURE

Indexes

- bf = biofuel
- bm = biomass
- f = fossil fuel
- n = nutrient

NU = number of units in the system

u = main equipment unit

Parameters

 $C_{\rm BD}$ = unit price for biodiesel produced, \$/tonne $C_{\rm bf}$ = unit cost for biofuel, \$/tonne $C_{\rm bm}$ = unit cost for external biomass, \$/tonne C_e = unit price for electricity, \$/MW $C_{\rm f}$ = unit cost for fossil fuel, \$/tonne C_{GLY} = unit price for glycerol produced, \$/tonne C_{hex} = unit cost for hexane, \$/tonne $C_{\rm n}$ = unit cost for nutrient, \$/tonne C_{mw} = unit cost for makeup water, \$/tonne DF_b^c = damage factor associated with chemical b and impact category c Em_{bf}^{Comb} = direct CO₂ emissions for biofuel, kg CO₂/kg Em_{bm}^{Comb} = direct CO_2 emissions for external biomass, kg CO_2/kg Em_f^{Comb} = direct CO_2 emissions for fossil fuel, kg CO_2/kg $Em_{BD}^{LCA} =$ life-cycle GHG emissions for biodiesel, tonne of CO₂ equiv/tonne Em_{FD}^{LCA} = life-cycle GHG emissions for fossil diesel, tonne of CO₂ equiv/tonne IC(d) = set of impact categories c that contribute to damage category d HV_{BD} = heating value for biodiesel, MJ/tonne HV_{bf} = heating value for biofuel, MJ/tonne HV_{bm} = heating value for external biomass, MJ/tonne HV_f = heating value for fossil fuel , MJ/tonne HV_{FD} = heating value for diesel, MJ/tonne $K_{\rm F}$ = factor used to annualize the capital costs

 $LCIE_{b}^{bf}$ = life cycle inventory of chemical b per unit of biofuel $LCIE_{b}^{bm}$ = life cycle inventory of chemical b per unit of biomass

- $LCIE_{b}^{emis}$ = life cycle inventory of chemical b per unit of emission
- $LCIE_{b}^{f}$ = life cycle inventory of chemical b per unit of fossil fuel
- $LCIE_{h}^{n}$ = life cycle inventory of chemical b per unit of nutrient
- $LCIE_{b}^{u}$ = life cycle inventory of chemical b per unit of mass equipment

 NF_{d} = normalization factor for damage category d

 ODF_{bf} = overall damage factor for biofuel, Eco-points/tonne ODF_{bm} = overall damage factor for external biomass, Ecopoints/tonne

 ODF_f = overall damage factor for fossil fuel, Eco-points/ tonne

 ODF_n = overall damage factor for nutrient, Eco-points/ tonne

 ODF_u = overall damage factor for material construction material of unit, Eco-points/tonne

 S^{GHG} = unit subsidy for reduction of GHG emissions, \$/tonne

 WF_d = weighting factor for damage category d

 w_{OIL} = lipid content in algal biomass (wt % of dry biomass) ε = parameter of the ε -constraint method

 $\eta_{\rm bf}$ = boiler efficiency for biofuel

 $\eta_{\rm bm}$ = boiler efficiency for biomass

 $\eta_{f_{cO_2}} =$ boiler efficiency for fossil fuel $\alpha_{AC}^{CO_2} =$ utilization efficiency of CO₂

 $\alpha_{AC}^{CO_2}$ = utilization efficiency of CO₂ α_{AH}^{CENT} = recovery fraction of algal biomass in secondary harvesting (centrifugation)

 α_{AH}^{FLOC} = recovery fraction of algal biomass in primary harvesting (flocculation)

 α_{OIL} = recovery fraction of lipid in the oil extraction stage

 $\delta_{CO_2} = CO_2$ demand in kg-CO₂/kg-biomass

 $\tau_{\rm DT}$ = fraction of the whole-day hours that feed gas is delivered to the cultivation stage

Variables

 CAP_{μ} = capital cost of each main equipment unit, \$

 DAM_d = overall damage for category d

 $E_{\rm AC}$ = power requirement for microalgae cultivation, MW/yr

 $E_{\rm AH}$ = power requirement for algal biomass harvesting, MW/ vr

 $E_{\rm BP}$ = power requirement for biodiesel production stage, MW/yr

 $E_{\rm PP}$ = power requirement for pumping of feedwater in the power plant, MW/yr

 E_{OE} = power requirement for oil extraction stage, MW/yr

EI99 = Eco-indicator 99 (overall environmental impact), Eco-points/yr

FC = annual capital cost of the system, /yr

 F_{AC} = flow rate of algal biomass produced in the cultivation stage, tonne/yr

 F_{AH}^{CENT} = flow rate of algal biomass leaving secondary harvesting (centrifugation), tonne/yr

 F_{AH}^{FLOC} = flow rate of algal biomass leaving primary harvesting (flocculation), tonne/yr

 $F_{\rm BD}$ = flow rate of biodiesel produced, tonne/yr

 $F_{\rm FD}$ = flow rate of displaced fossil diesel, tonne/yr

 $F_{\rm bf}$ = flow rate of biofuel, tonne/yr

 $F_{\rm bm}$ = flow rate of biomass, tonne/yr

 F_{CO_2} = flow rate of CO₂ generated in the power plant boiler, tonne/yr

 $F_{\rm GLY}$ = flow rate of glycerol produced, tonne/yr

 $F_{\rm f}$ = flow rate of fossil fuel, tonne/yr

 F_{hex} = flow rate (consumption) of hexane, tonne/yr

 $F_{\rm LD}$ = flow rate of lipid-depleted algal biomass, tonne/yr

 $F_{\rm n}$ = flow rate (consumption) of nutrient, tonne/yr

 F_{N_2} = flow rate (consumption) of nitrogen, tonne/yr

 F_{OIL} = flow rate of lipid recovered from algal biomass, tonne/ yr

 $F_{\rm PH}$ = flow rate (consumption) of phosphate, tonne/yr

 $F_{\rm MW}$ = flow rate (consumption) of makeup water, tonne/yr $F_{\rm emis}$ = flow rate of emission released by the system, tonne/yr

 IMP_c = environmental damage caused in impact category *c* LCI_b^{tot} = total life cycle inventory of chemical b

 $\ensuremath{\mathsf{NEP}}\xspace$ = net electric power for the integrated energy system, $\ensuremath{\mathsf{MW}}\xspace/\ensuremath{\mathsf{yr}}\xspace$

OC = operating cost of the system,\$/yr

PROFIT = annual gross profit, \$/yr

QH = heat duty of the boiler, MJ/yr

REVENUE = revenue from the sale of electricity and bioproducts, \$/yr

TAC = total annualized cost, \$/yr

TAX CREDIT = total subsidy due to the reduction of GHG emissions, \$/yr

REFERENCES

(1) World Energy Outlook; International Energy Agency (IEA): Paris, 2010; pp 1-530.

(2) CO_2 Emissions from Fuel Combustion: 1971–2006; International Energy Agency (IEA): Paris, 2008; pp 1–530, .

(3) Pacala, S.; Socolow, R. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* **2004**, 305, 968–972.

(4) Rao, A. B.; Rubin, E. S. A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control. *Environ. Sci. Technol.* **2002**, *36*, 4467–4475.

(5) Rubin, E. S.; Chen, C.; Rao, A. B. Cost and performance of fossil fuel power plants with CO_2 capture and storage. *Energy Policy* **2007**, 35, 4444–4454.

(6) Sheppard, M. C.; Socolow, R. H. Sustaining fossil fuel use in a carbon constrained world by rapid commercialization of carbon capture and sequestration. *AIChE J.* **2007**, *53*, 3022–3028.

(7) Stauffer, P. H.; Keating, G. N.; Middleton, R. S.; Viswanathan, H. S.; Berchtold, K. A.; Singh, R. P.; Pawar, R. J.; Mancino, A. Greening coal: Breakthroughs and challenges in carbon capture and storage. *Environ. Sci. Technol.* **2011**, *45*, 8597–8604.

(8) Rubin, E. S.; Zhai, H. The cost of carbon capture and storage for natural gas combined cycle power plants. *Environ. Sci. Technol.* **2012**, 46, 3076–3084.

(9) Wang, L.; Yang, Y.; Shen, W.; Kong, X.; Li, P.; Yu, J.; Rodrigues, A. E. CO_2 capture from flue gas in an existing coal-fired power plant by two successive pilot-scale VPSA units. *Ind. Eng. Chem. Res.* **2013**, *52*, 7947–7955.

(10) Hetland, J. Broaching CCS into society. Timeline considerations for deployment CO_2 capture and storage linked with the challenge of capacity building. *Int. J. Greenhouse Gas Control* **2012**, *9*, 172–183.

(11) Jenni, K. E.; Baker, E. D.; Nemet, G. F. Expert elicitations of energy penalties for carbon capture technologies. *Int. J. Greenhouse Gas Control* **2013**, *12*, 136–145.

(12) Farrelly, D. J.; Everard, C. D.; Fagan, C. C.; McDonell, K. P. Carbon sequestration and the role of biological carbon mitigation: A review. *Renewable Sustainable Energy Rev.* **2013**, *21*, 712–727.

(13) Lam, M. K.; Lee, K. T.; Mohamed, A. R. Current status and challenges on microalgae-based carbon capture. *Int. J. Greenhouse Gas Control* **2012**, *10*, 456–469.

(14) Pires, J. C. M.; Alvim-Ferraz, M. C. M.; Martins, F. G.; Simoes, M. Carbon dioxide capture from flue gases using microalgae: Engineering aspects and biorefinery concepts. *Renewable Sustainable Energy Rev.* **2012**, *16*, 3043–3053.

(15) Wang, B.; Li, Y.; Wu, N.; Lan, C. Q. CO₂ bio-mitigation using microalgae. *Appl. Microbiol. Biotechnol.* **2008**, *79*, 707–718.

(16) Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* 2007, 25, 294–306.

(17) Darzins, A.; Pienkos, P.; Edye, L. Current Status and Potential for Algal Biofuels Production: A Report to IEA Bioenegy Task 39; Report T39-T2; National Renewable Energy Laboratory (NREL): Golden, CO, 2010.

(18) Harun, R.; Singh, M.; Forde, G. M.; Danquah, M. K. Bioprocess engineering of microalgae to produce a variety of consumer products. *Renewable Sustainable Energy Rev.* **2010**, 1037–1047.

(19) Santibañez-Aguilar, J. E.; González-Campos, J. B.; Ponce-Ortega, J. M.; Serna-González, M.; El-Halwagi, M. M. Optimal planning of a biomass conversión system considering economic and environmental aspects. *Ind. Eng. Chem. Res.* **2011**, *50*, 8558–8570.

(20) Ng, R. T. L.; Tay, D. H. S.; Ng, D. K. S. Simultaneous process synthesis, heat and power integration in a sustainable integrated biorefinery. *Energy Fuels.* **2012**, *26*, 7316–7330.

(21) Akgul, O.; Shah, N.; Papageorgiou, L. G. An optimization framework for a hybrid first/second generation bioethanol supply chain. *Comput. Chem. Eng.* **2012**, *42*, 101–114.

(22) Kelloway, A.; Daoutidis, P. Process synthesis of biorefineries: Optimization of biomass conversion to fuels and chemicals. *Ind. Eng. Chem. Res.* **2013**, *53*, 5261–5273.

(23) Murillo-Alvarado, E.; Ponce-Ortega, J. M.; Serna-González, M.; Castro-Montoya, A. J.; El-Halwagi, M. M. Optimization of pathways for biorefineries involving the selection of feedstocks, products and processing steps. *Ind. Eng. Chem. Res.* **2013**, *52*, 5177–5190.

(24) Ng, R. T. L.; Hassim, M. H.; Ng, D. K. S. Process synthesis and optimization of a sustainable integrated biorefinery via fuzzy optimization. *AIChE J.* **2013**, *59*, 4212–4227.

(25) Rizwan, M.; Lee, J. H.; Gani, R. Optimal processing pathway for the production of biodiesel from microalgal biomass: A superstructure based approach. *Comput. Chem. Eng.* **2013**, *58*, 305–314.

(26) Shabani, N.; Akhtari, S.; Sowlati, T. Value chain optimization of forest biomass for bioenergy production: A review. *Renewable Sustainable Energy Rev.* **2013**, *23*, 299–311.

(27) Santibañez-Aguilar, J. E.; Ponce-Ortega, J. M.; González-Campos, J. B.; Serna-González, M.; El-Halwagi, M. M. Synthesis of distributed biorefining networks for the value-added processing of water hyacinth. *ACS Sustainable Chem. Eng.* **2013**, *1*, 284–305.

(28) Santibañez-Aguilar, J. E.; González-Campos, J. B.; Ponce-Ortega, J. M.; Serna-González, M.; El-Halwagi, M. M. Optimal planning and site selection for distributed multiproduct biorefineries involving economic, environmental and social objectives. *J. Cleaner Prod.* **2014**, *65*, 270–294.

(29) Yuan, Z.; Chen, B.; Gani, R. Applications of process synthesis: Moving from conventional chemical processes towards biorefinery processes. *Comput. Chem. Eng.* **2013**, *49*, 217–229.

(30) Gebreslassie, B. H.; Waymire, R.; You, F. Sustainable design and synthesis of algae-based biorefinery for simultaneous hydrocarbon biofuel production and carbon sequestration. *AIChE J.* **2013**, *59*, 1599–1621.

(31) Wang, B.; Gebreslassie, B. H.; You, F. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Comput. Chem. Eng.* **2013**, *52*, 55–76.

(32) Gebreslassie, B. H.; Slivinsky, M.; Wang, B.; You, F. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. *Comput. Chem. Eng.* **2013**, *50*, 71–91.

(33) You, F.; Wang, B. Life cycle optimization of biomass-to-liquids supply chains with distributed-centralized processing networks. *Ind. Eng. Chem. Res.* **2011**, *50*, 10102–10127.

(34) Yue, D.; Kim, M. A.; You, F. Design of sustainable product systems and supply chains with life cycle optimization based on functional unit: General modeling framework, mixed-integer nonlinear programming algorithms and case study on hydrocarbon biofuels. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1003–1014.

(35) Li, Y.; Horsman, M.; Wu, N.; Lan, C. Q.; Dubois-Calero, N. Biofuels from microalgae. *Biotechnol. Prog.* **2008**, *24*, 815–820.

(36) Tredici, M. R. Photobiology of microalgae mass cultures: Understanding the tools for the next green revolution. *Biofuels* **2010**, *1*, 143–162.

(37) Brentner, L. B.; Eckelman, M. J.; Zimmerman, J. B. Combinatorial life cycle assessment to inform process design of industrial production of algal biodiesel. *Environ. Sci. Technol.* **2011**, *45*, 7060–7067.

(38) Clarens, A. F.; Nassau, H.; Resurreccion, E. P.; White, M. A.; Colosi, L. M. Environmental impacts of algae-derived biodiesel and bioelectricity for transportation. *Environ. Sci. Technol.* **2011**, *45*, 7554–7560.

(39) Clarens, A. F.; Resurreccion, E. P.; White, M. A.; Colosi, L. M. Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environ. Sci. Technol.* **2010**, *44*, 1813–1819.

(40) Jorquera, O.; Kiperstok, A.; Sales, E. A.; Embiruçu, M.; Ghirardi, M. L. Comparative energy life-cycle analyses of microalgal biomass production in open ponds and photobioreactors. *Bioresour. Technol.* **2010**, *101*, 1406–1413.

(41) Murphy, C. F.; Allen, D. T. Energy-water nexus for mass cultivation of algae. *Environ. Sci. Technol.* 2011, 45, 5861–5868.

(42) Shirvani, T.; Yan, X.; Inderwildi, O. R.; Edwards, P. P.; King, D. A. Life cycle energy and greenhouse gas analysis for algae-derived biodiesel. *Energy Environ. Sci.* **2011**, *4*, 3773–3778.

(43) Soratana, K.; Landis, A. E. Evaluating industrial symbiosis and algae cultivation from a life cycle perspective. *Bioresour. Technol.* **2011**, *102*, 6892–6901.

(44) Vasudevan, V.; Stratton, R. W.; Pearlson, M. N.; Jersey, G. R.; Beyene, A. G.; Weissman, J. C.; Rubino, M.; Hileman, J. I. Environmental performance of algal biofuel technology options. *Environ. Sci. Technol.* **2012**, *46*, 2451–2459.

(45) Campbell, P. K.; Beer, T.; Batten, D. Life cycle assessment of biodiesel production from microalgae in ponds. *Bioresour. Technol.* **2011**, *102*, 50–56.

(46) Xu, L.; Brilman, D. W. F.; Withag, J. A. M.; Brem, G.; Kersten, S. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresour. Technol.* 2011, 102, 5113–5122.

(47) Yang, J.; Xu, M.; Zhang, X. Z.; Hu, Q. A.; Sommerfeld, M.; Chen, Y. S. Life-cycle analysis on biodiesel production from microalgae: water footprint and nutrients balance. *Bioresour. Technol.* **2011**, *102*, 159–165.

(48) Stephenson, A. L.; Kazami, E.; Dennis, J. S.; Howe, C. J.; Scott, S. A.; Smith, A. G. Life-cycle assessment of potential algal biodiesel production in the United Kingdom: A comparison of raceways and airlift tubural bioreactors. *Energy Fuels.* **2010**, *24*, 4062–4077.

(49) Batan, L.; Quinn, J.; Willson, B.; Bradley, T. Net energy and greenhouse gas emission evaluation of biodiesel derived from microalgae. *Environ. Sci. Technol.* **2010**, *44*, 7975–7980.

(50) Khoo, H. H.; Sharratt, P. N.; Das, P.; Balasubramanian, R. K.; Naraharisetti, P. K.; Shaik, S. Life cycle energy and CO₂ analysis of microalgae-to-biodiesel: Preliminary results and comparisons. *Bioresour. Technol.* **2011**, *102*, 5800–5807.

(51) Lardon, L.; Hélias, A.; Sialve, B.; Steyer, J. P.; Bernard, O. Lifecycle assessment of biodiesel production from microalgae. *Environ. Sci. Technol.* **2009**, *43*, 6475–6481.

(52) Rickman, M.; Pellegrino, J.; Hock, J.; Shaw, S.; Freeman, B. Lifecycle and techno-economic analysis of utility-connected algae systems. *Algal Res.* **2013**, *2*, 59–65.

(53) Ventura, J.-R. S.; Yang, B.; Lee, Y.-W.; Lee, K.; Jahng, D. Life cycle analyses of CO_2 , energy and cost for four different routes of microalgal bionergy conversión. *Bioresour. Technol.* **2013**, *137*, 302–310.

(54) Brune, D. E.; Lundquist, T. J.; Benemann, J. R. Microalgal biomass for geenhouse gas reductions: Potential for replacement of fossil fuels and animal feeds. *J. Environ. Eng.* **2009**, *135*, 1136–1144.

(55) Pokoo-Aikins, G.; Nadim, A.; El-Halwagi, M. M.; Mahalec, V. Design and analysis of biodiesel production from algae grown through carbon sequestration. *Clean Technol. Environ. Policy* **2010**, *12*, 239–254.

(56) Gutiérrez-Arriaga, C. G.; Serna-González, M.; Ponce-Ortega, J. M.; El-Halwagi, M. M. Multi-objective optimization of steam power plants for sustainable generation of electricity. *Clean Technol. Environ. Policy* **2013**, *15*, 551–566.

(57) ISO 14040:2006. Environmental Management – Life Cycle Assessment – Principles and Framework; International Standards Organization (ISO): Geneva, Switzerland, 2006.

(58) ISO 14044:2006. Environmental Management – Life Cycle Assessment – Requirements and Guidelines; International Standards Organization (ISO): Geneva, Switzerland, 2006.

(59) Wagner, W.; Cooper, J. R.; Dittmann, A.; Kijima, J.; Krestzschmar, H. J.; Kruse, A.; Mares, R.; Oguchi, K.; Sato, H.; Stocker, I. The IAPWS industrial formulation 1997 for the thermodynamic properties of water and steam. *J. Eng. Gas Turbines Power* **2000**, *122*, 150–182.

(60) Benemann, J. R.; Oswald, W. J. System and Economic Analysis of Microalgae Ponds for Conversion of CO_2 to Biomass; Quarterly Technical Progress Report; Pittsburgh Energy Technology Center, U.S. Department of Energy, : Pittsburgh, PA; 1996; Grant No. DEFG22-93PC93204.

(61) Benemann, J. R.; Tillet, D. M. *Effect of Fluctuating Environments* on the Selection of High Yielding Microalgae; Final Report, Subcontract XK-4-04136-06; Solar Energy Institute: Golden, CO, 1987.

(62) Molina Grima, E.; Belarbi, E.-H.; Acién Fernández, F. G.; Medina, A. R.; Chisti, Y. Recovery of microalgal biomass and metabolite: process options and economics. *Biotechnol. Adv.* **2003**, *20*, 491–515.

(63) Heasman, D. J.; O'Connor, W.; Sushanes, T.; Foulkes, L. Development of extended shelf-life microalgae concentrate diets harvested by centrifugation for bivalve molluscs: A summary. *Aquacult. Res.* **2000**, *31*, 637–659.

(64) The Eco-Indicator 99 – A Damage Oriented Method for Life Cycle Impact Assessment: Methodology Report and Manual for Designers; PRé Consultants: Amersfoort, The Netherlands, 2001.

(65) Guillén-Gosálbez, G.; Caballero, J. A.; Esteller, L. J. Application of life cycle assessment to the structural optimization of process flowsheets. *Ind. Eng. Chem. Res.* **2008**, *47*, 777–789.

(66) Ponce-Ortega, J. M.; Mosqueda-Jiménez, F. W.; Serna-González, M.; Jiménez-Gutiérrez, A.; El-Halwagi, M. M. A property-based approach to the synthesis of material conservation networks with economic and environmental objectives. *AIChE J.* **2011**, *57*, 2369–2387.

(67) TEAM and DEAM, 1998. Ecobalance UK, The Ecobilan Group, Arundel, U.K. www.ecobalance.com/uk tam.php.

(68) *SimaPro 6 LCA Software*, 1998; PRé-Consultants: Amersfoort, The Netherlands. www.pre.nl/simapro/default.htm.

(69) Swiss Center for Life Cycle Inventories. http://www.ecoinvent. ch/.

(70) IPCC. Climate Change 2007: The Physical Science Basis; Cambridge University Press: Cambridge, U.K., 2007.

(71) Haimes, Y. Y.; Lasdon, L. S.; Wismer, D. A. On a bicriterion formulation of the problems of integrated system identification and system optimization. *IEEE Trans. Syst., Man, Cybernetics* **1971**, *1*, 269–297.

(72) Diwekar, U. M. Introduction to Applied Optimization; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003.

(73) Goldberg, D. E. Genetic Algorithms in Search, Optimization, And Machine Learning; Addison-Wesley: Reading, MA, 1989.

(74) SENER-CONUEE. Methodologies for Quantifying Greenhouse Gases Emissions and Energetic Consumptions Avoided by the Sustainable Use of Energy; Mexican Ministry of Energy: Mexico City, Mexico, 2009.

(75) Bruno, J. C.; Fernandez, F.; Castells, F.; Grossmann, I. E. A rigorous MINLP model for the optimal synthesis and operation of utility plants. *Chem. Eng. Res. Des.* **1998**, *76*, 246–258.

(76) Peters, M. S.; Timmerhaus, K. D.; West, R. E. *Plant Design and Economics for Chemical Engineers*; McGraw-Hill Science/Engineering/ Math: Berkshire, U.K., 2003.

(77) *Electric Tariffs in Mexico*; No. 31; Centre for Social and Public Opinion Studies (CESOP): Mexico City, Mexico, 2013.

(78) Fuel Prices. Alternative Fuels Data Center, U.S. Department of Energy. http://www.afdc.energy.gov/fuels/prices.html.

(79) Gong, J.; You, F. Optimal design and synthesis of algal biorefinery processes for biological carbon sequestration and utilization with zero direct greenhouse emissions. *Ind. Eng. Chem.* Res. 2014, 53, 1563–1579.