

Life Cycle Energy and Greenhouse Gas Emissions for an Ethanol Production Process Based on Blue-Green Algae

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Ethanol can be produced via an intracellular photosynthetic process in cyanobacteria (blue-green algae), excreted through the cell walls, collected from closed photobioreactors as a dilute ethanol-in-water solution, and purified to fuel grade ethanol. This sequence forms the basis for a biofuel production process that is currently being examined for its commercial potential. In this paper, we calculate the life cycle energy and greenhouse gas emissions for three different system scenarios for this proposed ethanol production process, using process simulations and thermodynamic calculations. The energy required for ethanol separation increases rapidly for low initial concentrations of ethanol, and, unlike other biofuel systems, there is little waste biomass available to provide process heat and electricity to offset those energy requirements. The ethanol purification process is a major consumer of energy and a significant contributor to the carbon footprint. With a lead scenario based on a natural-gas-fueled combined heat and power system to provide process electricity and extra heat and conservative assumptions around the ethanol separation process, the net life cycle energy consumption, excluding photosynthesis, ranges from 0.55 MJ/MJ_{EtOH} down to 0.20 MJ/MJ_{EtOH}, and the net life cycle greenhouse gas emissions range from 29.8 g CO₂e/MJ_{EtOH} down to 12.3 g CO₂e/MJ_{EtOH} for initial ethanol concentrations from 0.5 wt % to 5 wt %. In comparison to gasoline, these predicted values represent 67% and 87% reductions in the carbon footprint for this ethanol fuel on a energy equivalent basis. Energy consumption and greenhouse gas emissions can be further reduced via employment of higher efficiency heat exchangers in ethanol purification and/or with use of solar thermal for some of the process heat.

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Introduction

Key challenges in the production of biofuels are to limit the competition with agriculture, to reduce other land use impacts, and to keep greenhouse gas emissions low. Biofuel produced from perennial feedstocks such as switchgrass and miscanthus can have very low greenhouse gas emissions because a significant portion of the biomass is used to generate process heat and electricity, with extra electricity produced and exported to the grid. These systems can even have negative greenhouse gas emissions if the extra electricity production is counted as displacing fossil-derived electricity (1). Perennial feedstocks can, however, affect agricultural land use, soil carbon, and ecosystems, both directly and indirectly. Managing these effects presents a significant challenge to the large-scale development of biofuels.

Biofuel can also be produced from microalgae and cyanobacteria. These require less land area than other biofuel systems, and need not use agricultural or environmentally sensitive land (2, 3). The most commonly discussed approach to algal biofuel is to grow and harvest algae, and to process the dewatered algae to yield a biodiesel fuel. The energy and greenhouse gas impacts of this type of system have been addressed previously (4–7). Here we address a different type of biofuel system, in which cyanobacteria (blue-green algae) themselves make ethanol. The cyanobacterial cultures are not harvested but are maintained for ongoing ethanol production. The key processing step involves separating the ethanol from the seawater growth medium. Such a no-harvest strategy mitigates the high energy costs and high water usage associated with the separation processes required for algae harvesting and fuel extraction (8–10). In this paper, we will explore a specific nonharvest case for ethanol production as described by Algenol Biofuels. We rely on publically available information for the basic approach (8, 10, 11), carry out engineering calculations for some of the key processes, and invoke ranges for parameters and system components that cannot otherwise be specified.

The ethanol-producing organisms are long-lived blue-green algae (genetically enhanced photoautotrophic cyanobacteria) grown in closed photobioreactors containing seawater supplemented with carbon dioxide and small amounts of nitrogen and phosphorus fertilizers. Several species of cyanobacteria, including *Chlamydomonas reinhardtii*, *Oscillatoria limosa*, *Microcystis PCC7806*, *Cyanothece PCC 7822*, *Microcystis aeruginosa PCC 7806*, *Oscillatoria sp.*, and *Spirulina platensis* produce ethanol photosynthetically; strains can be selected for ethanol-tolerance, salt-tolerance, and pH tolerance, and ethanol production can be enhanced through genetic modification (11). The ethanol is collected as a dilute ethanol–freshwater solution from the cyanobacteria–seawater culture (8) and purified to fuel grade. Along with 18 other technologies, including cellulosic approaches, this technology has been selected by the U.S. Department of Energy for biorefinery development at the pilot plant scale (12). The concentration of ethanol in the liquid collected from the cyanobacteria system will strongly affect the amount of energy needed to concentrate the ethanol: the higher the “initial” concentration of ethanol, the less energy is needed to purify the ethanol. Here we evaluate the life cycle greenhouse gas emissions as a function of initial ethanol concentration and report the results for initial concentrations (given in weight percent) ranging from 0.5% to 5%. This choice of ranges is somewhat arbitrary but has been made based on the likelihood that 0.5% is too dilute for economical recovery and that 5% would have a high likelihood of

economical recovery, in that the separation process could employ standard column distillation.

Process Description

In the process concept (8, 10) to be modeled here, cyanobacteria will be grown in flexible-film, polyethylene-based photobioreactors containing seawater or brackish water as the culture medium. Since additional carbon dioxide is required to support efficient algal growth, the production facility will be located near a fossil-fuel power plant or industrial source of carbon dioxide. Here the calculation is based on use of industrial CO_2 , such as the byproduct CO_2 from ethylene oxide production. Carbon dioxide could be dissolved in the seawater growth medium or injected into the headspace of the photobioreactor; here we develop the calculation based on introducing CO_2 into the headspace. Nitrogen and phosphorus fertilizers will be introduced into the photobioreactors to support the initial cyanobacterial growth. At mature operation, the cyanobacteria will produce ethanol which will diffuse through the cell wall into their growth medium. There will be water and ethanol in the vapor phase inside the photobioreactors; the freshwater/ethanol mixture collected from that vapor as a condensate (8) will undergo a series of separation processes to produce 99.7% pure (fuel grade) ethanol. Algenol aims to produce about 56 000 L of ethanol per hectare per year using about 430 polyethylene photobioreactors per hectare, each with about 4500 L of culture medium containing about 0.5 g/L of cyanobacterial biomass (10). This production target is within achieved photosynthetic yields (2–4) and corresponds to 1.8% solar energy conversion efficiency for average incident sunlight energy levels in the United States (3). However, since the system is still in the development phase, we will consider herein a range of production rates to test sensitivity to the yield assumption. The photobioreactors are modeled as having a length of 50 feet and a cylindrical diameter of 4 feet, composed of polyethylene of 0.2 mm thickness. The cyanobacteria will remain in the photobioreactors producing ethanol and, unlike other algae-to-fuel processes, will not be harvested for fuel or other purposes. It is anticipated that the photobioreactors will be emptied no more than once per year to replace the seawater, growth media, and cyanobacteria.

In calculating the life cycle energy and greenhouse gas emissions, we consider the production of the cyanobacteria, including the production and disposal of the photobioreactors, mixing in the bioreactors, the disposal of the “waste” biomass, the production and transport of the nitrogen and phosphorus fertilizers, ethanol separation including vapor compression steam stripping (VCSS), vapor compression distillation (VCD) and molecular sieve, ethanol transportation and distribution, and ethanol combustion in motor vehicles. Figure 1 shows the life cycle stages of the cyanobacterial ethanol production process. For the ethanol separation process, responsible for most of the life cycle energy use and greenhouse gas emissions, process-based calculations have been developed, using Aspen Plus unit operations simulations as well as literature results. In addition, we use thermodynamics to provide a transparent characterization of energy requirements and resulting greenhouse gas emissions. Details are provided in the Supporting Information.

Ethanol Separation Process

There is no published information on the ethanol concentration levels that can be achieved in the cyanobacteria cultures, though there will be some limiting value dependent on the organism's tolerance. We have chosen 0.5%

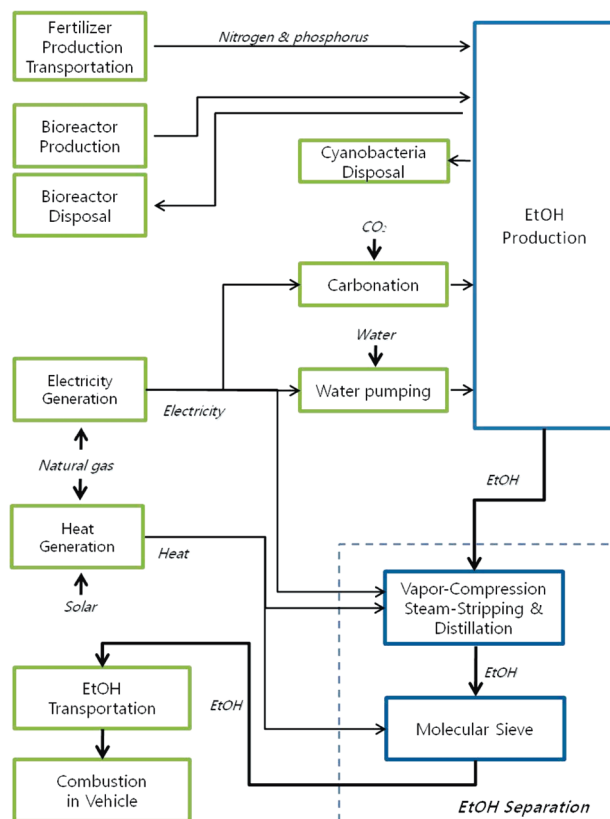
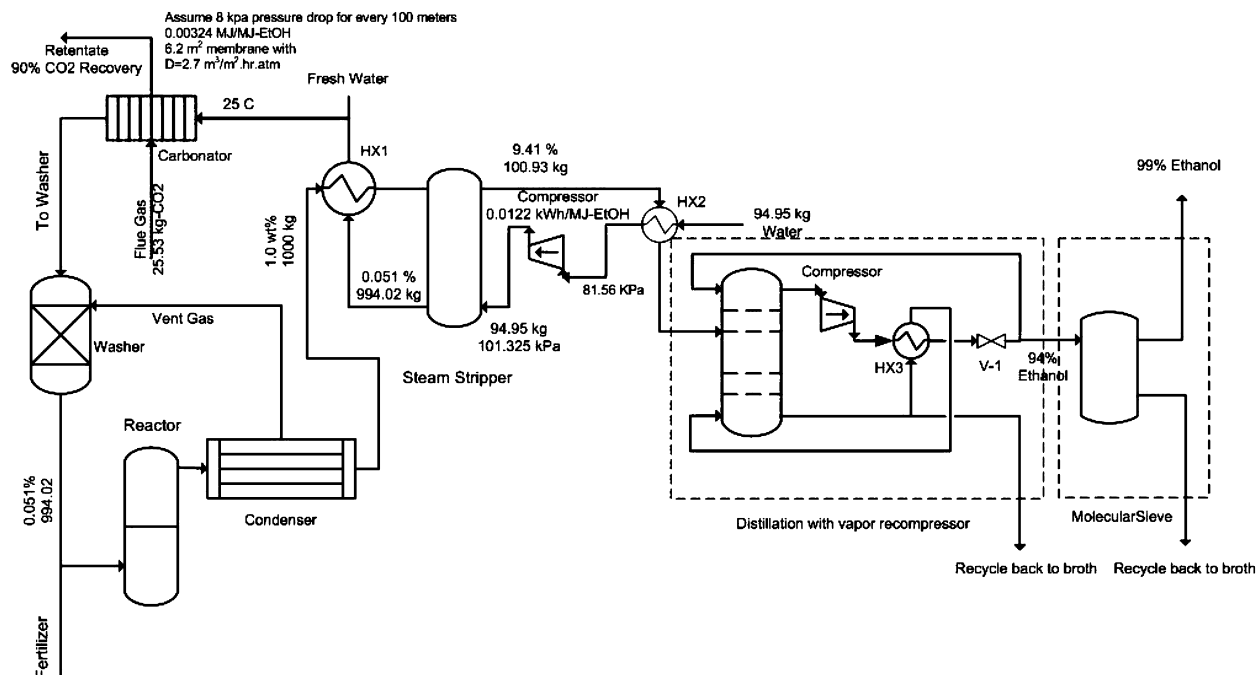


FIGURE 1. System components of cyanobacterial ethanol life cycle analysis.

to 5% as a reasonable range for this study for reasons stated earlier. Though standard column distillation could be applied to much of this range, the energy efficiency of that process falls off rapidly below 5% (13). Therefore, for the first separation stage for our concentration range, we model a unit operation based on vapor compression steam stripping (VCSS), a highly heat integrated process that offers the potential for energy efficient separation even at low ethanol concentrations (13–16). The VCSS unit will concentrate the ethanol to a value in the 5–30% range dependent on the starting value and other details of the process. To concentrate the ethanol to 94% (at or near the azeotrope), we used vapor compression distillation in our design simulations. There are a number of choices for the final stage to fuel grade ethanol (99.7%) including molecular sieves, extractive distillation, and membrane-assisted processes (13, 14). We have chosen molecular sieve dehydration for the present study. The ethanol production and separation processes are shown in Figure 2. In the baseline scenario process, heat is provided from natural gas. Ethanol production will vary with temperature and light levels (4); we develop a time-average calculation. The vaporization and compression aspects are discussed separately below using 1% concentration to explain the calculations in detail. The final sections show the results for a range of concentrations ranging from 0.5 to 5%.

Vaporization Processes. The concentration of ethanol produced by the steam-stripping column is determined by the input concentration of ethanol and the operating temperature of the column. For a 1% initial ethanol concentration, the steam-stripping column, operated at atmospheric pressure, will increase the ethanol concentration from 1% to 9.4%, and the vapor compression distillation (VCD), operated at atmospheric pressure, will raise the concentration of ethanol from 9.4% to 94% (details are provided in the Supporting Information).



The energy required for vaporization in a steam-stripping column can be estimated from the heats of evaporation of water and ethanol:

$$E_{\text{evap}} = \sum_i m_i \Delta_v H(T)_i \quad (1)$$

The process heat requirement is driven by the initial concentration of ethanol. The energy requirement for evaporation, eq 1, can be re-expressed, per unit of ethanol for a two-component, water and ethanol, system, as

$$\begin{aligned} e_{evap} &= \frac{k}{x} [x\Delta H_{EtOH} + (1-x)\Delta H_{H_2O}] \\ &= \frac{k}{x} [\Delta H_{H_2O} - x(\Delta H_{H_2O} - \Delta H_{EtOH})] \\ &\approx \frac{k}{x} \Delta H_{H_2O} \end{aligned} \quad (2)$$

Compression Processes. Steam compression is required for the stripper column and the VCD column; the compressor is electrically powered. For 1% initial concentration, process simulation (Aspen Plus) was used to derive a steam compression requirement for the steam stripper of 81.56 to 101.32 kPa, as shown in Figure 2 and described in the Supporting Information.

$$W_{\text{adiabatic}} = \frac{\gamma nRT}{\gamma - 1} \left[\left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{\gamma-1/\gamma} - 1 \right] \quad (3)$$

where R is the gas constant, T is the temperature in Kelvin, P is the pressure, and γ is the adiabatic coefficient, taken to be 1.3 (details provided in the Supporting Information). The adiabatic work required for the compression is 0.0058 kWh_e/MJ_{EiOH}. Simulation using 'Aspen Plus' yields 0.0051 kWh_e/MJ_{EiOH} for the VCSS compression and 0.0067 kWh_e/MJ_{EiOH} for the VCD compression, for a total of 0.0118 kWh_e/MJ_{EiOH}. If the electricity were produced with 38% efficiency, this would require 0.11 MJ/MJ_{EiOH}.

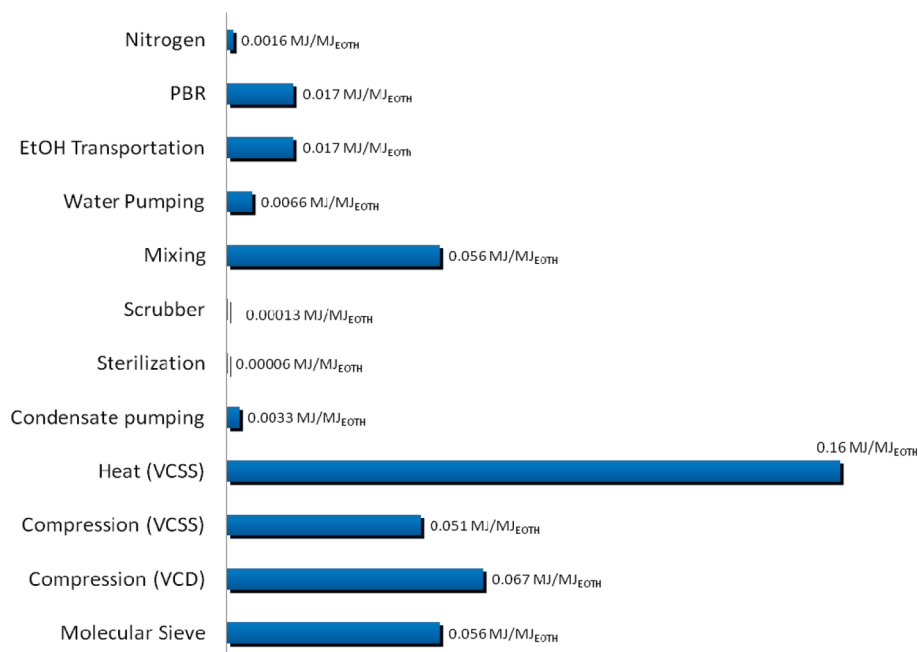


FIGURE 3. Baseline energy use for initial ethanol concentration of 1% assuming 80% heat exchange efficiency for the VCSS unit, for production of 56 000 L/ha/y.

Final Purification from the Azeotrope to Fuel Grade Ethanol. For the molecular sieves stage, the total heat requirement is estimated to be 1–2 MJ/kg_{EtOH} (19). We use 1.5 MJ/kg_{EtOH} or 0.056 MJ/MJ_{EtOH}. This value is significantly lower than for benzene extractive distillation but may be higher than that for membrane processes (13, 14).

Total Energy Required for Ethanol Purification. Ethanol purification is the largest energy consumer in this cyanobacteria-to-fuel process. For our 1% example, the energy consumption in converting the initial 1% stream to fuel grade ethanol (99.7%) is 0.28 MJ/MJ with an 80% assumption for heat exchanger efficiency and about 0.19 MJ/MJ for a 90% efficiency. The 80% result is only slightly lower than the model result for membrane-assisted vapor stripping (MAVS) of 0.33 MJ/MJ (13, 14). With a 90% efficient heat exchanger, this VCSS-based process is significantly more efficient than the MAVS process. MAVS is a better choice at 5% initial concentration: our results are 0.13 and 0.11 MJ/MJ for 80% and 90%, respectively, compared to 0.093 MJ/MJ for MAVS. For all concentrations in our range, both VCSS and MAVS are much better than conventional distillation (13, 14).

Other Processes

Mixing. We assume a mixing system for the photobioreactors that is designed in much the same way as those for raceway ponds (20) with three primary functions: uniform suspension of the cyanobacteria, uniform distribution of nutrients, and efficient transfer of gases (CO₂ mainly) between the gas and liquid interface. The system is not designed to limit the effects of photosaturation and/or photoinhibition even though more rapid mixing could increase ethanol productivity, as the energy requirements for such a system are not practical for a fuel-production process (21–23). Mixing within the photobioreactors is estimated to require 0.1 W/m² (20). For the 1% case, this corresponds to 0.056 MJ/MJ_{EtOH}.

Oxygen Removal. Removal of the oxygen will be accomplished through use of a compressor to extract the gas from the photobioreactor headspace, and a gas scrubber for oxygen removal, with an energy requirement of 0.0001 MJ/MJ_{EtOH}.

Water Consumption and Pumping. We assume that the source water is pumped from a depth of 100 m with 85%

pumping efficiency and 95% motor efficiency, requiring 0.0066 MJ/MJ_{EtOH}; water pumping requirements will scale with this depth. Pumping of the water–ethanol condensate into the separations system will require 0.004 MJ/MJ_{EtOH} under the same assumptions. Water sterilization, necessary for the initial fill of seawater and subsequent culture replacements, can be accomplished by ozonation with low energy requirements. Unlike growing algae in open ponds, we consider closed photobioreactors where water is not lost through evaporation. However, 3 mol of water are needed to produce 1 mol of ethanol, i.e., 0.926 L of water for 1 L of ethanol. This replacement water can be provided by reverse osmosis seawater desalination, which requires about 8 kWh_e per 1000 gallon of water (24). This is 9.5×10^{-5} kWh/MJ_{EtOH}.

CO₂ Source. Options for delivering CO₂ include gas delivery to the headspace of the photobioreactor, gas delivery to the culture, or CO₂-containing water delivered to the culture. Here we base our calculation on industrial CO₂ delivered to the headspace. Power plant flue gas CO₂ could also be used, although additional cleanup of flue gas may be required. CO₂ transfer from the headspace to the culture is aided by the mixing system (20), the higher delivery concentration compared to atmospheric levels, and the higher sorption of CO₂ in seawater compared to fresh water.

Nitrogen and Phosphorus Fertilizers. Emptying the photobioreactors once per year will create approximately 0.97 ton per hectare of waste biomass approximately 8% of which is nitrogen and 0.3% is phosphorus (25). Accordingly, ethanol production of 56 000 L/hectare-y corresponds to a nitrogen and phosphorus requirement of 0.065 g N/MJ_{EtOH} and 0.0024 g P/MJ_{EtOH}, respectively. If introduced all at once, the nitrogen use corresponds to three times the classic f/2 algal growth medium of Guillard (26, 27). Because this is a no-harvest process, the cyanobacteria do not need to be continuously replenished, resulting in lower nutrient requirements than those for biofuel processes involving algal harvesting (7). Greenhouse gas emissions associated with the nitrogen and phosphorus fertilizers are provided in the Supporting Information.

Bioreactor Production. The entire photobioreactor system is assumed to be replaced every five years. If the drained bioreactors are landfilled, the carbon in the plastic may be

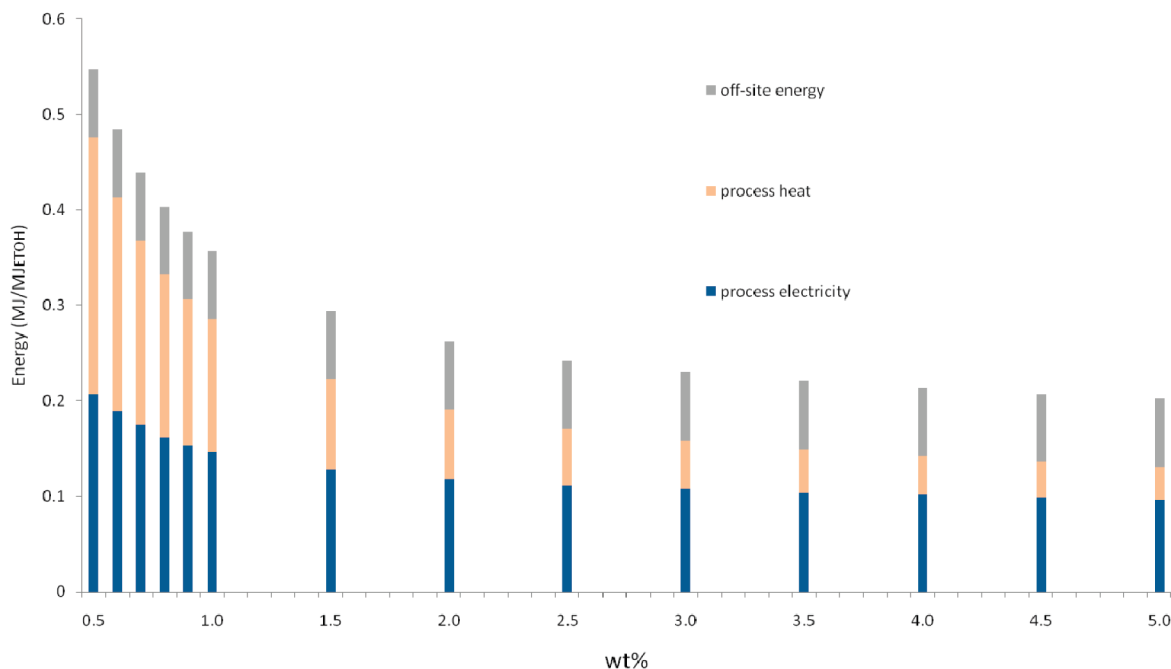


FIGURE 4. Life cycle energy use for cyanobacterial ethanol using natural-gas-fueled CHP, based on an 80% heat exchange efficiency for the VCSS unit.

sequestered, with no net greenhouse gas emission from the bioreactors themselves. If the bioreactors are recycled, greenhouse gas emissions from the displacement of virgin polyethylene will be avoided. We estimate 0.017 MJ/MJ_{EtOH} for the production energy and 1.0 g CO₂e/MJ_{EtOH} greenhouse gas emission contribution. Details are provided in the Supporting Information.

Waste Biomass Disposal. The annual disposal of cyanobacteria is assumed to be managed by deep well injection, though other options are possible. Deep well injection will sequester the cyanobacterial biomass and may result in a net greenhouse gas reduction of approximately 2% of the system CO₂ emissions. Here we attribute zero sequestration and zero net emissions to cyanobacteria disposal.

Site Preparation, Ethanol Distribution, and Ethanol Combustion. These items make relatively small contributions and are discussed in the Supporting Information.

Sensitivity to Ethanol Production Rate. The ethanol production rate could be affected by photobioreactor geometry, cyanobacteria productivity, fertilizer requirements, mixing rate and mixing effectiveness, and other factors. The life cycle elements that depend on the ethanol production rate include the bioreactor material, water, and fertilizer requirements, and the mixing and pumping energy. For the target production rate of 56 000 L/ha/y, a 50% lower or 50% higher production rate results in a total life cycle energy use that is 9% higher or 5% lower, respectively. Figure 3 summarizes the energy use for production of ethanol.

Greenhouse Gas Emissions

Greenhouse Gas Targets for Biofuels. The U.S. Energy Independence and Security Act requires that cellulosic renewable fuels have life cycle greenhouse gas emissions of less than 40% of petroleum-derived fuels (28). In addition, the act provides funding to support development of renewable fuels that have life cycle greenhouse gas emissions of less than 20% of petroleum-derived fuels, making 20% the de facto goal for biofuels. The U.S. E.P.A. uses year 2005 gasoline as its baseline for comparison, with life cycle greenhouse gas emissions of 91.3 g CO₂e/MJ_{gasoline} (29).

Greenhouse gas emissions from electricity production depend on the fuel source and technology of generation.

Full life cycle greenhouse gas emissions have been estimated to be 1.03 kg CO₂e/kWh for coal and 570 g CO₂e/kWh for natural gas (30).

Greenhouse Gas Emissions from Process Electricity Consumption. We consider two electricity sources: grid electricity and on-site combined heat and power (CHP) using gas turbines. The planned Algenol-Dow pilot plant (31), to be located in Freeport, TX, has grid electricity provided 37% from coal, 48% from natural gas, 12% from nuclear, 1.2% from wind, and 2% from other sources, implying a life cycle greenhouse gas emission of about 700 g CO₂e/kWh. Use of this electricity would result in a greenhouse gas emission of 13.5 g CO₂e/MJ_{EtOH} for on-site electricity alone in the 1% case.

Greenhouse Gas Emissions from Onsite Process Heat Consumption. Natural gas has a greenhouse gas emission of 0.050 kg CO₂e/MJ (32). If the natural gas boilers are 90% efficient, the greenhouse gas emissions per delivered MJ of natural gas are 55 g CO₂e/MJ. If all of the on-site process heat were provided by natural gas, the resulting on-site greenhouse gas emissions would be 11 g CO₂e/MJ_{EtOH} in the 1% example. Together with the 13.5 g CO₂e/MJ_{EtOH} from on-site electricity use and the 3.86 g CO₂e/MJ_{EtOH} from off-site emissions, the total for the grid-electricity system with natural gas heat is 28.3 g CO₂e/MJ_{EtOH} in the 1% example, easily meeting the renewable fuel requirement although not meeting the 20%-of-gasoline goal.

Net Energy and Greenhouse Gas Emissions from On-Site Combined Heat and Power. Gas turbines produce high-quality exhaust heat that can be used in CHP configurations to reach overall system efficiencies of 70–80% (33). With an electricity generation efficiency of 38%, production of each kWh requires input energy of 9.5 MJ. With a steam to power ratio 4 MJ/kWh, each kWh of electricity produced by natural gas will also generate 4 MJ of process heat (33). Figure 4 shows that total energy use is 0.55 MJ/MJ_{EtOH} if the initial ethanol concentration is 0.5%, is 0.36 MJ/MJ_{EtOH} if the initial ethanol concentration is 1%, and that the process electricity requirement and especially the process heat requirement decrease significantly as the initial ethanol concentration increases.

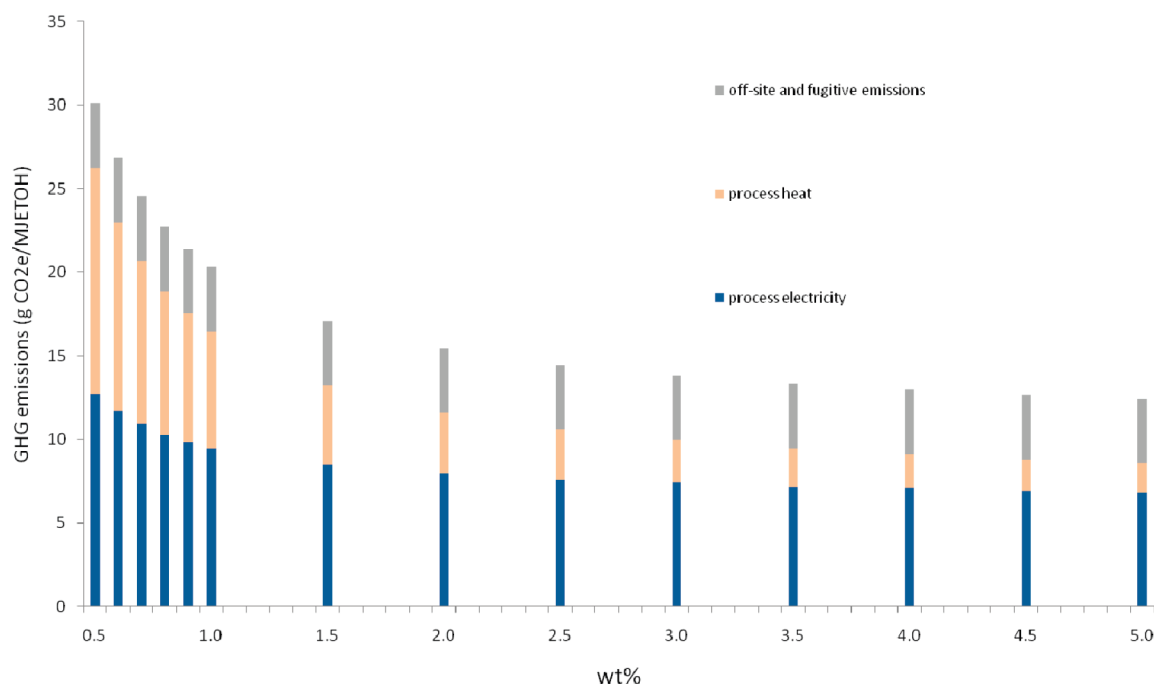


FIGURE 5. Life cycle greenhouse gas emissions for a natural-gas-fueled CHP system, based on an 80% heat exchange efficiency for the VCSS unit.

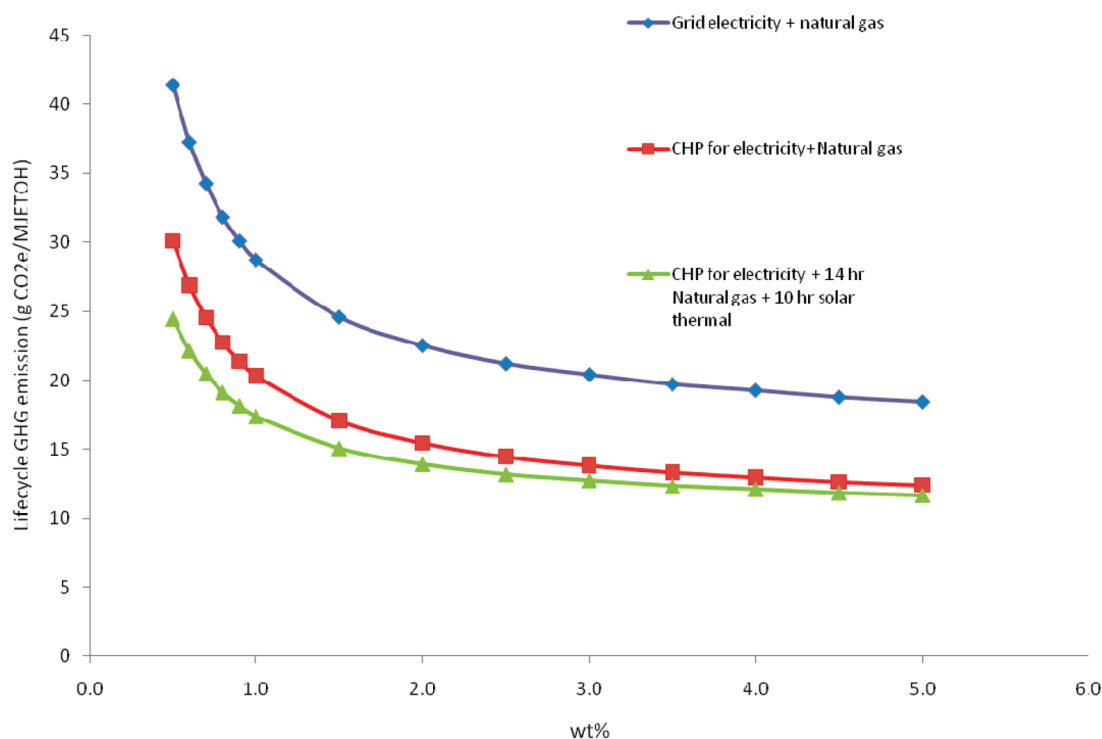


FIGURE 6. Life cycle GHG emissions with different energy supply scenarios, based on an 80% heat exchange efficiency for the VCSS unit. Values are given in Table S4, Supporting Information.

The increased energy efficiency of a CHP system can provide significant greenhouse gas savings. Figure 5 shows that life cycle greenhouse gas emissions are 29.8 g CO₂e/MJ_{EtOH} if the initial ethanol concentration is 0.5%, are 20.1 g CO₂e/MJ_{EtOH} for 1% initial concentration, and that the emissions fall to 12.3 g CO₂e/MJ_{EtOH} for an initial concentration of 5%.

To further reduce the life cycle energy use and greenhouse gas emissions, some of the process heat could be supplied by solar power. Solar power is intermittent, available for perhaps 8 h per day, and existing industrial

solar heat storage systems can extend this to up to 10 h per day (34).

Figure 6 shows the total life cycle greenhouse gas emissions for three scenarios: grid electricity with natural gas for process heat; natural gas CHP; natural gas CHP supplemented with solar heat. The figure shows that use of CHP provides a significant greenhouse gas emission benefit compared to grid-derived electricity, and that use of solar heat can provide significant additional reductions.

Sensitivity to Heat Exchange Efficiency in the First Stage of Ethanol Separation. The analysis is sensitive to the

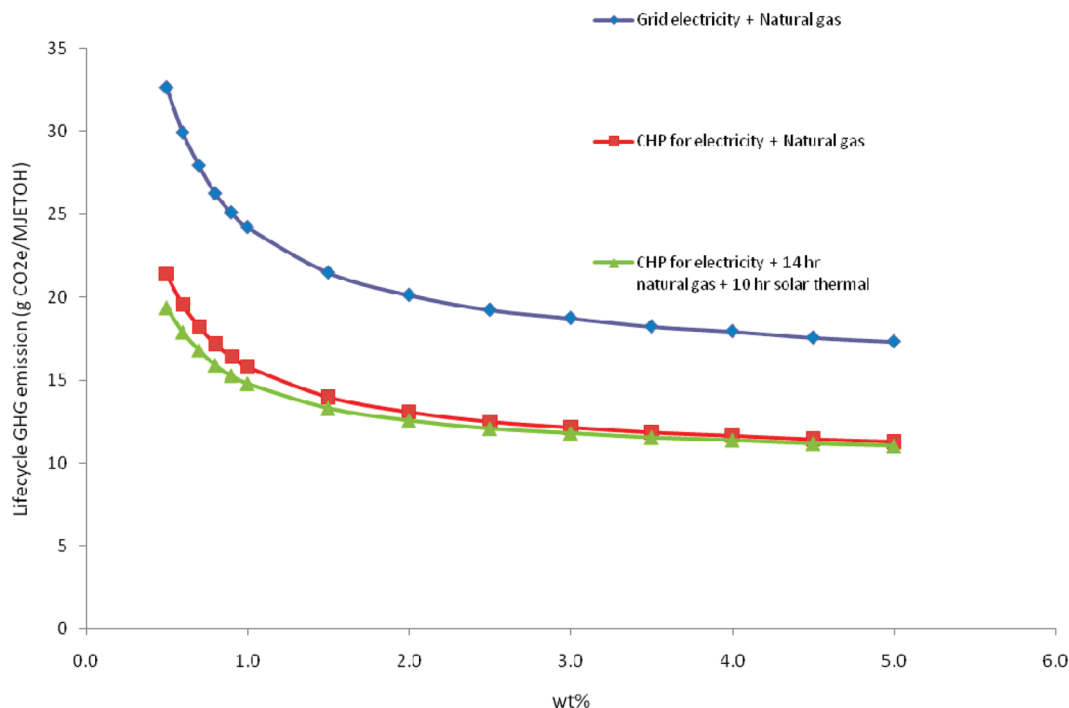


FIGURE 7. Life cycle GHG emissions with different energy supply scenarios and 90% heat exchange efficiency for the VCSS unit. Values are given in Table S5, Supporting Information.

conservative assumption of 80% heat exchange efficiency in the vapor compression steam stripping and distillation process. More efficient heat exchange may be achieved in a practical system. A 90% assumption leads to net life cycle energy consumption ranging from 0.38 down to 0.18 MJ/MJ_{EtOH} for the 0.5% to 5% initial concentration range. This compares to 0.55 to 0.20 MJ/MJ_{EtOH} for the 80% assumption. Details are provided in the Supporting Information. Figure 7 shows the life cycle greenhouse gas results for 90% heat exchange efficiency. Still higher heat exchange efficiencies are possible but would likely involve significantly higher capital investment.

Discussion

As illustrated in Figures 6 and 7, total greenhouse gas emissions from the algal ethanol process depend strongly on the initial ethanol concentration and on the energy system used to concentrate the ethanol. To meet the definition of a renewable biofuel under the U.S. Renewable Fuel Standard, the fuel must not exceed 36.5 g CO₂e/MJ_{EtOH}, which is 40% of the life cycle greenhouse gas emission of gasoline. To meet the D.O.E. target goals of 20% of the gasoline emissions, the ethanol must have a life cycle greenhouse gas emission of 18.3 g CO₂e/MJ_{EtOH} or less. Meeting the 40% requirement can be achieved under virtually all conditions and scenarios considered here. Meeting the 20% reduction target is more challenging. For an energy system consisting of moderately low-carbon grid electricity and natural gas for process heat, the initial ethanol concentration needs to be at least about 4.0–4.5% dependent on the assumed level of heat exchange efficiency in the ethanol separation process. For an energy system based on natural gas CHP, the initial ethanol concentration needs to be at least about 1.0–1.2%. For the scenario involving solar heating, the initial concentration needs to be above 0.8% assuming 80% heat exchange efficiency and above 0.55% assuming 90% heat exchange efficiency.

An advantage of cyanobacteria-produced ethanol is the potential to locate production facilities on low-value, arid, nonagricultural land, and avoid competition with agriculture.

Another advantage is the no-harvest strategy that has the potential for more energy efficient separations, lower fertilizer requirements, and lower water usage in comparison to other algal biofuel processes. We have shown that with sufficiently high initial concentrations of ethanol, fuel ethanol can be produced that has low net energy inputs and low life cycle greenhouse gas emissions.

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Supporting Information Available

Details on thermodynamics for characterization of energy requirements, tables of the life cycle energy and GHG emissions data, and additional figures are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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