Sustainability of algae derived biodiesel: a mass balance approach

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Abstract

A rigorous chemical engineering mass balance/unit operations approach is applied here to biodiesel from algae mass culture.

An equivalent of 50,000,000 gallons per year (0.006002 m^3/s) of petroleum-based Number 2 fuel oil (U.S., diesel for compression-ignition engines, about 0.1% of annual U.S. consumption) from oleaginous algae is the target. Methyl algaeate and ethyl algaeate diesel can according to this analysis conceptually be produced largely in a technologically sustainable way albeit at a lower available diesel yield. About 11 sq. miles of algae ponds would be needed with optimistic assumptions of 50 g biomass yield per day and m^2 pond area. CO_2 to foster algae growth should be supplied from a sustainable source such as a biomass-based ethanol production. Reliance on fossil-based CO_2 from power plants or fertilizer production renders algae diesel non-sustainable in the long term.

Keywords: sustainability, biofuels, diesel, algae, energy, mass balance

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1 Introduction

The highly successful mass balance/unit operations approach of chemical engineering (Walker et al., 1928; McCabe et al., 2004; Felder and Rousseau, 2000) to design, simulate, control, and optimize extremely complex material processing and conversion networks is brought to bear here to interrogate the sustainability of the example of algae diesel. The mass balance/unit operations approach has been enabled especially after the advent of modern computers to solve large numbers of simultaneous equations (Marquardt, 1996). The relation between input and output of every unit operation is mathematically described and a process is assembled out of unit operations that are interconnected by mass and energy flows including simple and nested feed-forward and feedback loops.

If this approach is expanded from traditional unit operations such as "distillation column", "heat exchanger", or "reactor" to include unit operations such as "atmosphere", "soil", "surface water" etc. one would immediately have a powerful tool to describe quantitatively and consistently (through the mandatory closure of mass balances) what material flows occur. The unit operation approach is exceptionally flexible since the complexity of individual unit operations can reach from a simple "split inflow 30/40 to two outflows" to the custom thermodynamics and hardware intricacies of a highly non-ideal multi-component distillation or a multiphase chemical reactor. Both first principles and phenomenological descriptions are easily implemented mathematically in a unit operation network, depending on available and developing knowledge. One could ask an agronomist, a soil scientist, a biologist, an engineer, or an atmospheric scientist the same question: "What are the inputs to the unit operation in question, how would you quantitatively relate them to outputs to the best of your knowledge at this time?" and one could then develop evolving quantitative unit operation models to be integrated right away in quantitative overall bio energy scenarios or any other process. The extension of the mass balance approach to non-traditional unit operations has been discussed conceptually by researchers in plant science (Davis et al., 2009).

Rigorous sustainability is here postulated if a given process (defined by a boundary), including within the boundary the energy producing aspects (solar energy excepted) does not emit or receive material streams from the outside. A conceptual example of sustainability would be a sealed (to mass flows) system containing some organisms and inorganic materials, with only solar radiation as energy input and other radiation and/or heat as energy output to maintain the energy balance, existing on average at steady state in perpetuity. The scientific principle of conservation of mass that must be observed for the planet Earth as a whole is the starting point.

In other work related to Life Cycle Assessment (LCA) of algae based diesel, Dinh et al. (2009) built on their earlier work for biodiesel production from various feedstocks and added a comparison to algae-based biodiesel using various static ad hoc weighting and prioritizing factors. Issues such as the impact of alcohol production for transesterification or the CO_2 demand of algal cultures are not discussed in detail. No mass flow analysis is shown so that a check on the consistency of the numerous assumptions and data sources is difficult.

The production of liquid transportation fuels such as diesel from lipids produced by mass culture of algae has been investigated on the bench- and pilot scale for quite some time although initially production of proteins for food was the motivation (Burlew (ed.), 1953). A maximum of 70 g biomass (dry) m^{-2} day^{-1} is mentioned in this early review of the state of the art, with scale-up estimates of 22 g biomass (dry) m^{-2} day^{-1}. Many issues, such as the harvest of algae by centrifuges vs. settling, contamination of algal cultures with undesirable competing or predatory organisms, economic design of the large-scale algae culture vessels, the basic economics of algae mass culture, and even harvesting of algae using fish are discussed in Burlew's early compilation.

Early work in Germany with a focus on lipids was motivated by a lack of fossil hydrocarbons for fuels during World War II and has been summarized (v. Witsch and Harder, 1953). The reported similarity of algae lipids (40-50wt% on dry biomass for *Chlorella*) to those of higher plants, the enhanced production of lipids under reduced nitrogen availability, and laboratory yields of 220 g biomass (dry) m^{-3} in 14 days for *Chlorella* grown in 0.03 m diameter glass tubes were reported. While it is not simple to convert this volumetric biomass yield to units of g m^{-2} day^{-1} for open ponds, one could perhaps see the 50 g m^{-2} day^{-1} in open ponds chosen for the calculations below to be not drastically different. Pilot scale mass culture of algae in enclosed reactors such as polyethylene tubes has been reported by Arthur D. Little (1953). Issues of the enclosed algal culture approach such as cleaning of reactor walls and temperature control are recognized. A growth rate of 11 g m^{-2} day^{-1} was reached over the best 10 day period with 300 sq. feet of tubing area exposed to light. Growth of *Chlorella* in four shallow non-agitated open ponds (total area 25.2 m^2) dug into the earth and lined with polymer foil was also reported (Gummert et al., 1953). Amoeba, zooflagellates, and ciliates were a serious issue.

Forty-five years after taking stock of the state of mass culture of algae in the compilation edited by Burlew a comprehensive report on an extensive effort by the U.S. to culture algae on a large scale was published (Sheehan et al., 1998a). This work was at least in the later stages geared towards producing lipids for fuels, motivated in part by the oil crisis of the 1970's.

A decade after Sheehan's report algae mass culture for fuel production is now again of great interest (for example Mouawad, J., 2009). However, there are now also concerns about the sustainability of production systems because of increasing awareness of climate change. Therefore, algae mass culture for biodiesel production is chosen here as an example for the mass balance/unit operation approach to investigate sustainability. Visually compelling and easily assimilated descriptions of bio-energy approaches through carbon mass flow diagrams are demonstrated.

It will be shown below that diesel from algae cannot be made in a rigorously sustainable fashion due to the need for nitrogen fertilizers that are at this time produced mainly from natural gas. An overall benefit for CO_2 emissions comes from the replacement of fossil-based diesel with diesel made using sunlight via algae. No CO_2 is directly sequestered by the algae diesel concept.

In summary, this work has two main goals:

1. Introduce an engineering mass balance/unit operation based approach to quantify the sustainability of bio energy processes by including non-traditional unit operations such as the atmosphere.

2. Analyze the sustainability of the mass culture of algae for biodiesel production as a quantitative example of the mass balance approach to sustainability.

2 Methods

2.1 Justifying the mass balance approach to evaluate sustainability

Earth, including the atmosphere, is thermodynamically an open system in regard to energy with solar radiation being the input, and radiation to space as output. On the other hand, Earth with the atmosphere is essentially a closed system regarding mass, and thereby for all its individual chemical elements such as carbon (Figure 1, left). Loss of volatiles from Earth is prevented by gravity, and the mass of Earth's crust alone is about 14 orders of magnitude larger than the annual mass input from space.

One can divide Earth conceptually into sub-systems that add up to the whole. The sum of all sub-systems must then still fulfill the overall requirement of a closed system with regard to total mass and the mass of each individual chemical element (shown mathematically for carbon, Figure 1, left). Change of one chemical element into another is here neglected. If a particular sub-system is not closed in regard to mass then it must rely on other (sub-) system(s) to "take care of" the mass flows that the sub-system in question receives or emits. Nonetheless, the combination of all sub-systems representing Earth must result in a closed system with respect to mass. This indisputable scientific fact forms the foundation of the mass balance/unit operation approach applied below to interrogate sustainability. This sets the approach shown here apart from the LCA method and its many variations, which lack a coherent scientific foundation.

The clear enunciation of a scientific principle as a basis for the approach to sustainability developed here is a significant advantage over using an environmental impact tool such as Life Cycle Assessment (LCA) which has no stated scientific principle and is in essence an accounting method. LCA is widely used and one may ask if this methodology is not sufficient to evaluate the sustainability of a bio-based energy approach. However, according to ISO 10440, LCA is a "compilation and evaluation of the inputs and outputs and the potential environmental impacts of a product system throughout its life cycle". Sustainability is not a focus of LCA. The issue of poor consistency of LCA is sometimes discussed, perhaps most often by non-practitioners without a stake in the established methodology (Davis et al., 2009). LCA is essentially an inventory or enumeration of *inputs and outputs* while the mass balance/unit operation approach used here is based on *specifying* process *inputs* and *calculation of* the process *outputs* through knowledge of the internal workings of networked unit operations. If, say, a particular chemical reactor was defined as a "product system" of interest for LCA (Figure 2, left) and the goal would be to analyze this product system (LCA step 1: goal and scope definition), then the collection of data on the input and output streams would be the second step of LCA (LCA step 2: inventory analysis), followed by impact assessment (assignment of weighing factors for environmental impact standardization) and accompanied by interpretation. A chemical engineering mass balance/unit operation analysis on the other hand (Figure 2, right) would specify the input streams, and calculate or at least estimate from models or experience the output streams based on knowledge of the reactor and the operating conditions. Input and output streams will by definition fulfill the mass balance while that is not necessarily so in the LCA analysis where all depends on the quality of the data. The impact of process changes can be evaluated in the mass balance/unit operation approach while the LCA will require an inventory update for any changes. It contributes to a certain degree of confusion that the LCA inventory step is called a mass balance by some practitioners (Kralisch, 2008) while it is in fact only that, an inventory. The concept of elemental mass balances (carbon for example, see below) is entirely missing from LCA. One sometimes finds that although mass balances are touted as the main subject in LCA-related publications (Eissen et al., 2008) no use is made of the power and readily available conceptual and software tools of chemical engineering mass balances. This may be partially due to the frequent absence of engineering backgrounds among LCA practitioners (a brief check of the seven co-authors of the above book chapter shows no one with an engineering background).

One could summarize that LCA has a focus on materials rather than processes, and that the quality of the datasets of inputs and outputs is absolutely crucial for LCA. Table 1 compares LCA with the mass balance approach. As an inventory method there is no scientific principle underlying LCA. The engineering mass balance/unit operation analysis is inherently consistent as far as the overall mass balance, since only inputs are specified and outputs must match inputs by definition. Models for the individual unit operations are woven into an intricate network of mass and energy flows based on knowledge of the internal workings of the unit operations while LCA takes a "black box" approach. The success of the mass balance/unit operation approach is demonstrated by successful modeling and optimization of highly complex processes such as entire refineries and all other complex physico-chemical conversion operations. Hundreds of interrelated unit operations are routinely handled using sophisticated simulation software such as ASPEN. This easily opens the door to quantitatively include unit operations such as crop land, water, atmosphere, or plants, with evolving sophistication depending on developing knowledge of the processes in these unit operations.

Discussion of a recent publication on Life Cycle Assessment (LCA) of biodiesel from microalgae may be instructive (Lardon et al., 2009). The authors state quite precisely that the potential environmental impacts are investigated via LCA. The inventory is compiled after defining the production system reaching from algae culture to the use of diesel in an engine.

Bench scale research and other extrapolations are employed since industrial operation to allow an inventory does not exist at this time. The difference of this LCA to the mass balance approach proposed here is immediately obvious in the production system schematic: no materials are actually “cycled”. The schematic does not indicate quantitative or even qualitative tracking and reconciliation of any mass flows to allow a test for (reasonable) closure of mass balances.

After a number of assumptions and extrapolations are reasonably made, the impact of streams to/from the production system is quantified based on established weighing factors. Essentially, one would assign a certain factor to, say, a kg CO_2 emitted, etc. Impact on human health, ecosystems, and resources is assigned and then normalized so all impacts are shown on the same scale to identify major contributions. While this may be called “LCA proper” the authors attempt in the discussion to expand the analysis to energy balances and this cannot succeed because a first law of thermodynamics analysis does not suffice. This type of extension of LCA away from the environmental impact is often attempted and leads to wildly different results due to the absence of a proper scientific foundation. This is perhaps demonstrated by the ongoing debates about the net energy contributions of bio-ethanol production from corn.

While LCA is concerned with the environmental impact of a given processing system, it is often used, as by Lardon et al. (2009) to prove or disprove the usefulness of a given bio-energy approach. An (often partial) first law of thermodynamics energy balance is developed along the LCA results, essentially asking the question "How many joules are used to produce one joule of the target fuel?" This can be deceiving since it only takes in account the quantity (first law of thermodynamics) but not the quality of energy. A joule of lower heating value from coal is thermodynamically and economically much less valuable than a joule as electricity. Lardon et al., for example disregard the influx of solar energy to the system and show a range from -2.6 MJ lost to +105 MJ gained per kg of algae biodiesel produced. These values may, for example, all become negative if the input of solar energy is counted. However, this does by no means invalidate all algae-based diesel concepts.

The simple mass balance approach limited for example to the critical element carbon for liquid transportation fuels shows a necessary but not sufficient condition of sustainability. However, it will allow to decide early on if a given concept has any hope of operating sustainably, and where the most serious issues reside (for example Pfromm et al., 2010). If the carbon mass balance appears promising, a complete mass balance will show environmental compatibility since for example the unit operation "atmosphere" may not be enriched or depleted over time to maintain steady state and achieve sustainability. It is acknowledged that a unit operation such as "atmosphere" is exceptionally complex and that our knowledge is in flux, but the mass balance approach is amenable to handle very high levels of complexity in an adaptable mathematical fashion.

2.2 Time scales of sustainability

It is recognized that time scales over which one averages to confirm or refute steady-state of a unit operation are vastly different for, say, a corn-to-ethanol production facility where process parameters like temperatures, fill levels of tanks, or flow rates fluctuate on a scale of days or at most months, in contrast to the "fill level" of the Ogallala Aquifer in the central Great Plains which declines over decades and where recharging does apparently not prevent the decline (Sophocleous, 2005). The aquifer may be apparently at steady state (level not measurably changing) on a scale of months while over decades it has been clearly declining. Sustainability, however, is generally meant in terms of future generations (World Commission on Environment and Development, 1984) so mass inflows and outflows for the unit operation "Ogallala Aquifer" would, for example, be taken as not balanced and the unit operation is then labeled as rigorously not sustainable.

Reliance on one non-sustainable unit operation (such as a diminishing aquifer, or coal) renders the entire process of interlaced unit operations rigorously not sustainable.

2.3 Energy

To investigate sustainability in a sub-system of planet Earth any energy transfer into the sub-system will be disallowed except for sustainable energy such as direct solar radiation (for example for plant growth), indirect solar energy (wind power, hydro power), or geothermal energy across the system boundary. Otherwise, the sub-system must be enlarged to include the energy source, for example fossil-driven power plants and their fuel reservoirs for electricity, fossil fuel fired boilers (with their fuel reservoir) for steam production, etc. It is extremely important to include all non-sustainable energy sources within the system boundaries. Otherwise, one can certainly chemically convert, for example, virtually any carbon source into virtually any desired liquid carbon-based fuel, given a sufficient quantity and quality of energy.

Quantifying sustainability would be meaningless with vast non-renewable energy resources available at will since the "behind the stage" energy production may or may not be sustainable.

2.4 Corn ethanol as a simplified qualitative example

A familiar example may be instructive. To evaluate sustainability for example of a biofuel such as corn-based ethanol one can conceive a first sub-system that comprises the land to grow corn, atmosphere and water needed, transportation and cultivation systems, the biomass-to-ethanol conversion process, and the end use of the bio-ethanol, all enclosed by a virtual system boundary (Figure 1 right, dashed line, arrows indicate major carbon mass flows, not all flows are shown for simplicity). Individual items shown for the sub-system in Figure 1 are unit operations in chemical engineering terminology. Steady-state is defined as, on average, no accumulation or depletion of mass over time within a unit operation. The mass flows (here for carbon, similarly for any other chemical element, or total mass) into and out of each individual unit operation must be balanced since otherwise the unit operation is not sustainable due to mass depletion or accumulation with time. If a unit operation "soil" for example contains a certain volume of agricultural land including the soil to some depth then the carbon flows into and out of this unit operation must balance since a net outflow will alter and perhaps degrade the land and a sustained net inflow of carbon will raise carbon concentrations steadily until agriculture will be impacted. This is qualitatively and mathematically shown in Figure 3. Usually mass flows from different information sources have to be used for complex unit operations such as "soil" which always introduces issues of consistency. However, there is a built-in check with a mass balance based analysis since the mass flows must add up to zero. This rigorous check on data consistency is absent in LCA, which also does not allow for elemental balances.

The steps of the mass balance approach for liquid transportation fuels specifically for the critical element carbon are shown as an algorithm in Figure 4.

3 Results and Discussion

The concepts outlined above will now be applied to biodiesel production from algae in open raceway ponds. The target is production of a lower heating value (LHV) equivalent to 50 million gallons of petroleum diesel per year (0.006002 m^3/s) or about 0.1% of the annual diesel demand in the U.S. The focus is to determine if this can be reached in a rigorously or at least largely sustainable manner by mass culture of algae.

A ceiling shall first be established for the maximum practical specific (per pond surface area) photosynthetic biomass and oil production of algae in an open pond. This can then be related to the maximum biofuel production of a given facility while taking in account all needs of the entire process such as thermal and electrical energy, chemicals, and water. The open pond is chosen since this has been recognized as the approach likely to show the lowest capital cost based on previous large-scale experience and development (Sheehan et al., 1998a; Ben-Amotz, 2010).

3.1 Algae diesel production assumptions

Several fundamental factors limit the specific productivity of algae biomass produced per pond area and overall time of operation: the quantum requirement for the photosynthetic process, the number of incident photons of the correct wavelength available for photosynthesis, losses through the algae's respiration processes, suboptimum temperatures, light saturation of the photosynthetic system etc. (Walker, 2009; Zhu et al., 2008). A rather optimistic sustained average productivity of 50 g of bone dry algal biomass m^{-2} open pond area day^{-1} with a total lipid content of 46.0wt% on dry biomass (Hu et al., 2008 and references cited herein; average of literature survey data on green microalgae grown under stress conditions) and a useable (for biodiesel) 80.0 wt% of target triglycerides (Hu et al., 2008 and references cited herein, estimated maximum for aging algal cells or stress conditions from several published studies) contained in the above total lipids will be assumed here. This results in 36.8wt% of the bone dry total algal biomass available as target triglycerides for diesel production. The 50 g dry algal biomass m^{-2} open pond area day^{-1} used here is assumed to include 10wt% of ash (inorganic materials such as calcium, chloride, phosphorous etc.). It may be important to point out that the unequivocal theoretical maximum (limited by the available photosynthetically useful solar radiation) is reported as about 141 g dry algal biomass m^{-2} open pond area day^{-1} for the U.S. which is somewhat different than the 354,000 l crude algae oil ha^{-1} $year^{-1}$ or about 237 g m^{-2} open pond area day^{-1} (assuming 36.8wt% oil in dry algal biomass, and a density of 0.9 kg 1^{-1} oil) given elsewhere as theoretical maximum (Weyer et al., 2010) but the assumptions for irradiation are different for these estimates. Experts in phycology rather suggest values ranging from a perhaps more realistic 11.8 to an optimistic 54.4 g dry algal biomass m^{-2} open pond area day^{-1} (Zhu et al., 2008, and references cited therein). This is more consistent with Weyer et al.'s 4.3 g m^{-2} day^{-1} reported as their high realistic large scale value (Weyer et al., 2010). The pond depth recommendations vary in the literature, but an advantageous depth is perhaps on the order of 15-30 cm (Sheehan, 1998a, Ben-Amotz, 2010).

The above specific production rate for algal biomass would have to be adjusted based at least on geographical location. The location impacts the production rate both through temperature and the available amount of useful (for algae growth) energy from the sun per day. The impact of location on insolation has been evaluated quantitatively and in detail (Walker, 2009, and references cited therein). Energy balances on bodies of water exposed to the environment and radiation from the sun are available (Keijman, 1974). The temperature swings of the surrounding air are greatly dampened even in shallow ponds of about 0.6 m depth, for example from a range of 24°C-40°C air temperature (night/day) vs. 27°C-34°C pond water temperature (Chiasson et al., 2000). The overwhelming factor for cooling to counteract heating from the surrounding air and solar radiation is evaporation of water which will have to be replaced for algae ponds. Evaporative losses through heating of open ponds pose a problem for cold climates. Losses can be several gallons of water per gallon of fuel produced. Here, a first-level sustainability evaluation based on carbon is shown. Mass balances for water can be performed but would only be needed if the carbon balance is sustainable.

The dynamic economical modeling of algae diesel production that will be reported in the future will accommodate the impact of geographical location in what-if scenarios. Here we assume an optimistic overall average biomass growth rate for an advantageous moderate climate with advantageous insolation.

3.2 Algae diesel base case

The base case is to replace 50,000,000 gallons of petroleum derived diesel (Number 2 fuel oil) per year (189,270,000 liters y^{-1}, 160,879,500 kg y^{-1}) or about 0.1% of the annual diesel consumption in the U.S. with diesel from algae oils. Biodiesel can be produced from vegetable oils or animal fats using methanol or ethanol to esterify the fatty acids from triglycerides produced by the organisms. Methanol-based biodiesel will be termed methyl soyate (from soybean oil) or methyl algaeate (from algae oil), and ethanol-based biodiesel ethyl soyate or ethyl algaeate.

Biodiesel has somewhat though not drastically different physical and chemical characteristics than petroleum-based diesel. The lower heating value (LHV) was chosen to calculate the amount of algaeate that needs to be produced to match the above petroleum-based diesel benchmark. With an LHV of 42.79 MJ kg^{-1} and a density of 850 kg m^{-3} for petroleum diesel, and an LHV of 36.95 MJ kg^{-1} (Sheehan et al., 1998b, equivalent to methyl soyate) for methyl algaeate an overall methyl algaeate production of about 186,000,000 kg y^{-1} matches the base case for petroleum diesel replacement (assuming 360 days of operation per year for the algae facility at 50 g m^{-2} of algae biomass production (dry mass including 10wt% ash) per day. Different growth rates depending on geographic location etc. will later be incorporated in the forthcoming dynamic socio-economic modeling. Using an average molecular weight of methyl algaeate of 292 g mol^{-1} based on a soybean oil-like fatty acid split of 6, 52, 25, 5, and 12 wt% of α-linolenic-, linoleic-, oleic-, stearic-, and palmitic acid, respectively; with 77wt% carbon assumed in methyl algaeate (Sheehan et al, 1998a) a first approximate mass balance for carbon is shown in Figure 5. The pond area needed is about 10 square miles in continuous algae production to replace nominally 0.1% of the annual U.S. diesel consumption.

Note that the atmosphere is included as a unit operation in Figure 5. This unit operation is here a simple pass-through with no chemical change of the form of carbon (CO_2). Since the unit operation "atmosphere" needs to be sustainable like all other unit operations (no depletion or accumulation) it is not allowed for any other unit operation to emit carbon to "atmosphere" and then assume that it will be "dumped" elsewhere in an unspecified way. The carbon (or any other element) mass balance around "atmosphere" must close (add up to zero) for sustainability.

Aquaculture in an artificial body of water such as a pond system could be compared to a very large living organism that consists of a collective of many individual organisms (algae). This "super-organism" residing in the pond system requires energy (here via sunlight), materials to build biological materials (including the target oils) here from CO_2, defense against unwanted invaders, and waste management. Sources of inorganic atoms (for example sodium, potassium), phosphorous (to build energy carrying molecules), and nitrogen (to build amino acids) are also needed since the phosphorous and nitrogen that is harvested with algae is not available in the proper biologically compatible form for direct recycling to the ponds. The carbon flows for nitrogen-containing fertilizer are indicated in Figure 5 since natural gas is the source of both energy and the reactant hydrogen to produce nitrogen-containing fertilizers. Fertilizers will emerge as a problem issue impacting sustainability (below).

Figure 5 assumes that the CO_2 needed for algae culture is obtained from a nearby coal-fired power plant or that compressed CO_2 perhaps from carbon capture at a power plant is used that is obtained via truck or railcar.

Figure 5 shows several issues for sustainability in form of unbalanced unit operations (no carbon inflow, only outflow):

- the coal reservoir for supply of CO_2 to the algae ponds after coal combustion is not sustainable
- the natural gas reservoir as energy and reactant supply for nitrogen-based fertilizer is not sustainable

It is certainly beneficial that CO_2 which would otherwise be emitted directly from the power plant is routed to biodiesel using sunlight and algae. However, the algae process provides no permanent carbon sink and all CO_2 is emitted eventually to the atmosphere when the algae diesel is combusted and through use of other algae-derived carbon streams. A carbon benefit arises from the replacement of fossil-based diesel with the solar energy based diesel from algae, not from capturing or sequestering fossil CO_2.

It is stipulated above for sustainability that no mass flows may cross the system boundary, so the methanol supply for diesel production and the byproduct glycerol need to be further investigated, the CO_2 emission to the atmosphere has to be considered, along with the unbalanced unit operations natural gas reservoir, and coal reservoir. No energy except for solar is allowed to enter the system to achieve sustainability, therefore the system will need to be enlarged (include electrical, thermal energy production) or energy will have to be provided from within the system, essentially routing some solar energy entering the system for in-system use.

3.3 Adjusted base case to approach sustainability

The following adjustments are shown in Figure 6 to approach sustainability:

- Ethanol for esterification of algae oil to ethyl algaeate is made by fermentation of the non-oil algae biomass thereby replacing methanol which is generally produced from natural gas (Cheng and Kung, 1994).
- Some ethyl algaeate is used in generator sets to supply process electricity.

- The glycerol byproduct from esterification is combusted in a boiler together with some biodiesel to raise steam for the bio-ethanol facility and other process heat requirements.
- CO_2 from the on-site ethanol facility and from the boiler is routed to the algae ponds.
- The remaining CO_2 to grow the algae is assumed to be supplied as compressed CO_2 via truck or rail from a large scale fermentation-based biofuel facility (Figure 6).

The use of ethyl algaeate instead of methyl algaeate requires small adjustments since ethyl soyate's LHV (the surrogate for ethyl algaeate) is assumed as 38.4 MJ kg^{-1} compared to methyl soyate's 36.9 MJ kg^{-1}. This was estimated using the difference reported for ethyl and methyl tallowates (Biodiesel Handling and User Guide, 2009). Therefore, slightly less mass of ethyl-based algae biodiesel is required than methyl-based algae diesel to cover the benchmark requirement.

3.3.1 Electrical energy

A best case approach will be taken. Electrical power for biodiesel production is neglected since this is mainly a chemical process, and electrical power for triglyceride recovery from concentrated algal biomass is assumed to be similarly small as for soybean oil recovery from soybeans. Estimates of the electrical energy demand to operate algae ponds and harvest algae range from 28,542 (Sheehan et al., 1998a) to 24,000 kWh ha^{-1} yr^{-1} (Ben-Amotz, 2010). Using a minimum 24,000 kWh ha^{-1} yr^{-1} with the above pond area it can be estimated that about an additional 11% of the biodiesel output to satisfy the 50,000,000 gallons of petroleum based diesel benchmark would actually be needed to supply the electrical power. The algae diesel production will therefore have to be increased by about 11% to both satisfy the target petroleum diesel replacement *and* supply all electrical energy through diesel generators (assuming 0.39 l ethyl algaeate $kWh_{(el)}^{-1}$). It is of course possible to find a more economical route than setting up diesel electric generators at the algae facility, perhaps by supplying diesel to an existing power generation facility and receiving electricity in return.

3.3.2 Thermal energy demand

About 1,107,000 MJ day^{-1} (thermal) are required for ethanol production by fermentation of algae biomass assuming the same thermal energy demand as for industrial-scale corn ethanol production with distillers dried grains as byproduct (~34,800 BTU per gallon of corn ethanol).

Steam is needed for distillation of hexane to recover hexane for re-use after extracting triglycerides from the biomass. Assuming about 2.4 MJ kg^{-1} triglycerides extracted from soybean oil (Li et al., 2006) one computes 645,000 MJ/day for the triglyceride recovery.

Combining the above thermal energy demand, an additional 5% of ethyl algaeate production compared to the target 50,000,000 gal petroleum diesel per year equivalent is required to cover the thermal energy demand assuming 77% of the LHV of ethyl algaeate is made available as steam from an ethyl algaeate fired boiler.

3.3.3 Fertilizer production

Nitrogen-containing fertilizers are produced today via the Haber-Bosch process. Natural gas is used both to supply energy and the reactant hydrogen to form ammonia with the nitrogen in air. While traditional agriculture can derive some bio-available nitrogen through certain crops like soybeans rotated on the same field with non-nitrogen fixing crops this is not possible in algae aquaculture. All needs of the "super-organism" algae in the pond system must be met by deliberate operations. At this time there is no option available to industrially produce nitrogen fertilizers using biodiesel except exotic concepts such as water splitting via electricity generated from biodiesel, and subsequent ammonia synthesis from the electro-generate hydrogen combined with nitrogen from air, again using significant amounts of bio-diesel energy for a Haber-Bosch type process. This scenario is not executed here in detail since the point of this work is to show the applicability of the mass-balance based sustainability assessment, rather than increasingly indeterminate technical what-if scenarios.

3.3.4 CO_2 source

Figure 6 indicates that CO_2 from a bio-ethanol-producing facility is used to supply the balance of CO_2 needed to produce the algae. No fossil fuel source to operate the bio-ethanol facility is shown because it is assumed that the ethanol produced will in part be used to supply the significant amount of process heat needed to operate the bio-ethanol facility. If natural gas is used to operate the bio-ethanol facility then an additional non-sustainable unit operation (the gas reservoir) would have to be added to the schematic. .

3.4 Summary of technical assessment of sustainability

The non-sustainable use of fossil fuel to produce nitrogen-based fertilizer cannot be avoided for algae aquaculture with current technology. The CO_2 demand of the algae culture can be partially covered from in-system sources (boiler, generator set, ethanol fermentation facility for esterification) with the remainder obtained from a fermentation-based biofuel facility to approach rigorous sustainability, or coal fired power plants (co-located or supply of CO_2 via truck or rail) if one accepts a higher level of non-sustainability since fossil-based CO_2 is used. While rigorous sustainability is breached when mainly fossil fuel based CO_2 is used to support the algae growth this may be a reasonable choice as long as the CO_2 emission is produced not solely for the algae process but for other reasons such as electrical power generation. The algae diesel operation does not supply a carbon sink of any kind. It only increases the benefit from the eventual CO_2 emission to the atmosphere by using sunlight to recreate a useful fuel from CO_2.

4 Conclusions

An engineering mass balance/unit operation approach is introduced to investigate the technological sustainability of algae diesel. The approach is based on the immutable principle of conservation of mass, as opposed to the Life Cycle Assessment method, which is an accounting procedure.

Algal diesel can be produced sustainably with the exception of the natural gas to produce nitrogen-based fertilizer. A pond area of about 11 square miles (28,490,000 m^2) at an optimistic growth rate of 50 g bone dry biomass m^{-2} day^{-1} might suffice to replace 0.1% of the U.S. diesel demand. A dynamic socio economical simulation will follow.

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5

Figure Captions

Figure 1: The rigorous mass balance/unit operations approach to interrogate sustainability from the global level to the system of interest.

Figure 2: A comparison of a simple application of Life Cycle Assessment (LCA) methodology vs. the chemical engineering mass balance/unit operation approach.

Figure 3: A unit operation, the carbon mass flows, and the first condition for sustainability on the unit operation level: closure of the mass balance.

Figure 4: Algorithm to apply a mass-balance based approach to interrogate sustainability of a process. The dynamic stochastic economical modeling for the example of algae diesel will be reported in a separate paper.

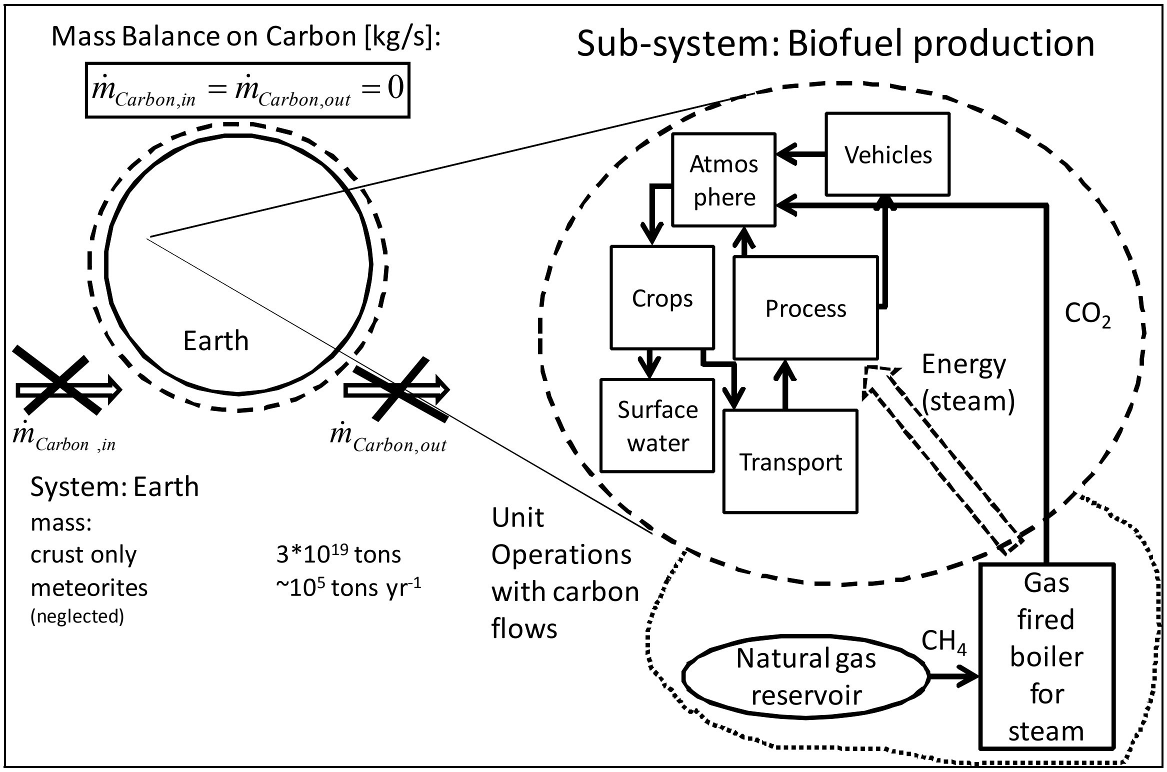
Figure 5: Carbon mass flows for methyl algaeate production enhanced by flue gas to match 50,000,000 gal y-1 petroleum diesel (based on the lower heating value, LHV) or about 0.1% of the annual diesel consumption in the U.S. All values are in 107 mol carbon day-1 unless indicated otherwise. Arrow widths are roughly proportional to carbon mass flows. Shaded unit operations involve fossil fuels.

Figure 6: Towards sustainable operation for algae diesel production using ethyl algaeate. Carbon mass flows for ethyl algaeate production to match 50,000,000 gal y-1 petroleum diesel (based on the lower heating value, LHV) or about 0.1% of the annual diesel consumption in the U.S. All values are in 107 mol carbon day-1 unless indicated otherwise. Arrow widths are roughly proportional to carbon mass flows.

Table Captions

Table 1: Qualitative comparison of Life Cycle Analysis (LCA) and the mass balance approach.

6 Figures



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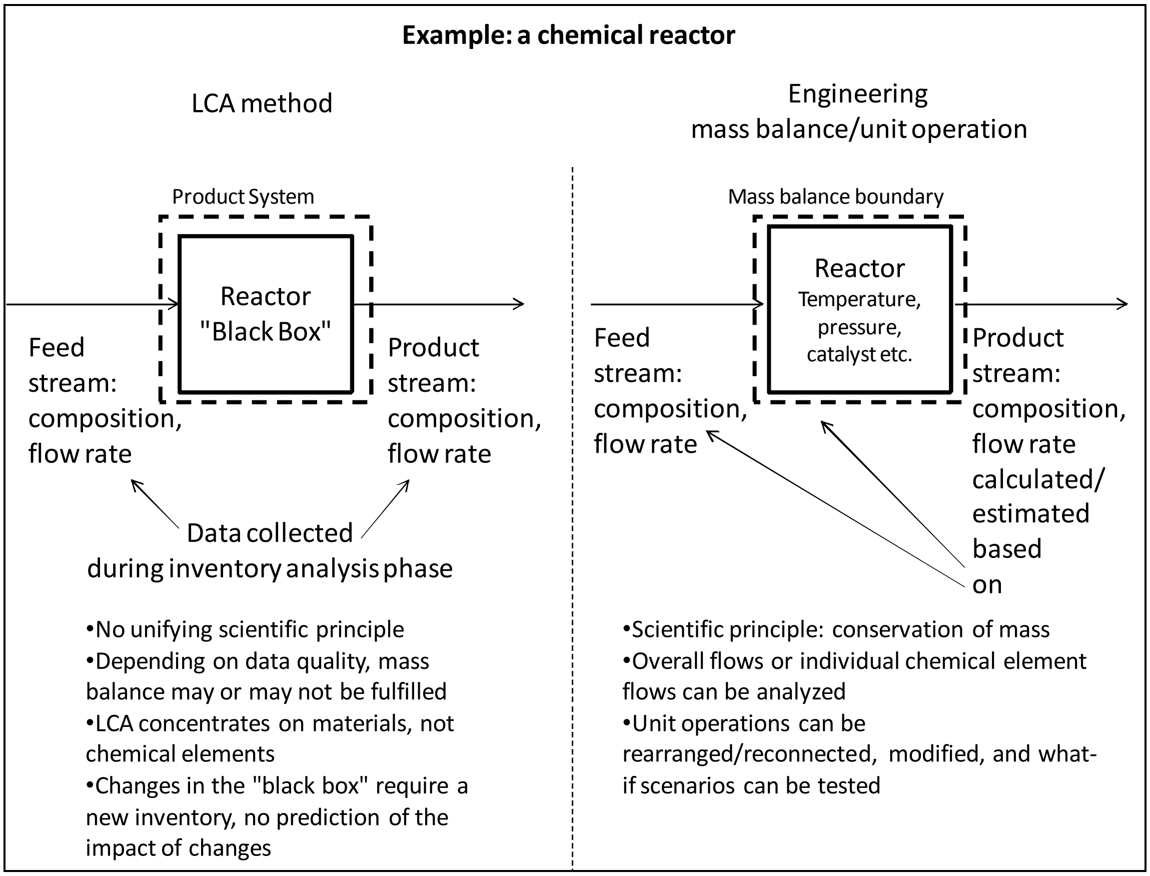
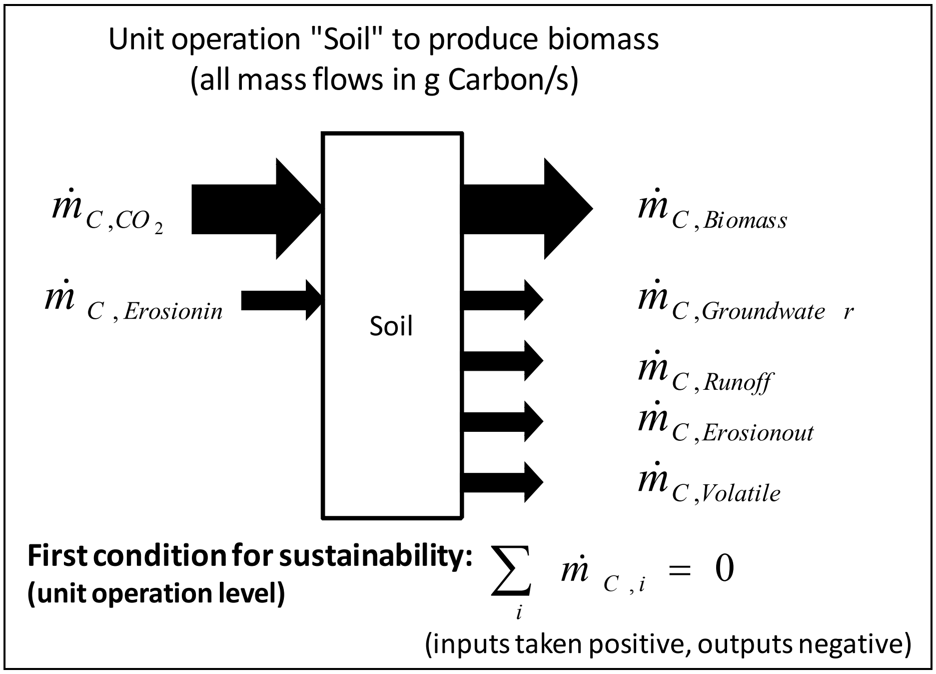


- No unifying scientific principle
- Depending on data quality, mass balance may or may not be fulfilled
- LCA concentrates on materials, not chemical elements
- Changes in the "black box" require a new inventory, no prediction of the impact of changes

- Scientific principle: conservation of mass
- Overall flows or individual chemical element flows can be analyzed
- Unit operations can be rearranged/reconnected, modified, and what-if scenarios can be tested

Figure 2: A comparison of a simple application of Life Cycle Assessment (LCA) methodology vs. the chemical engineering mass balance/unit operation approach.



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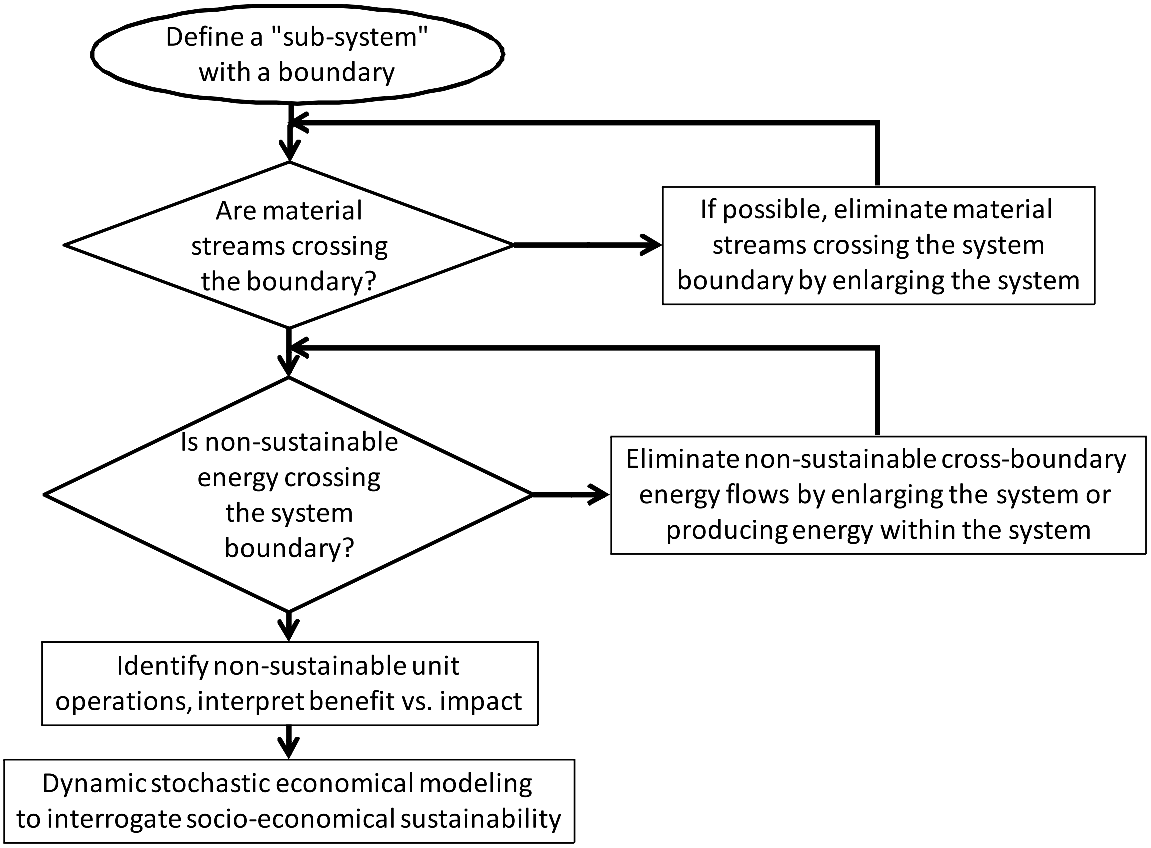

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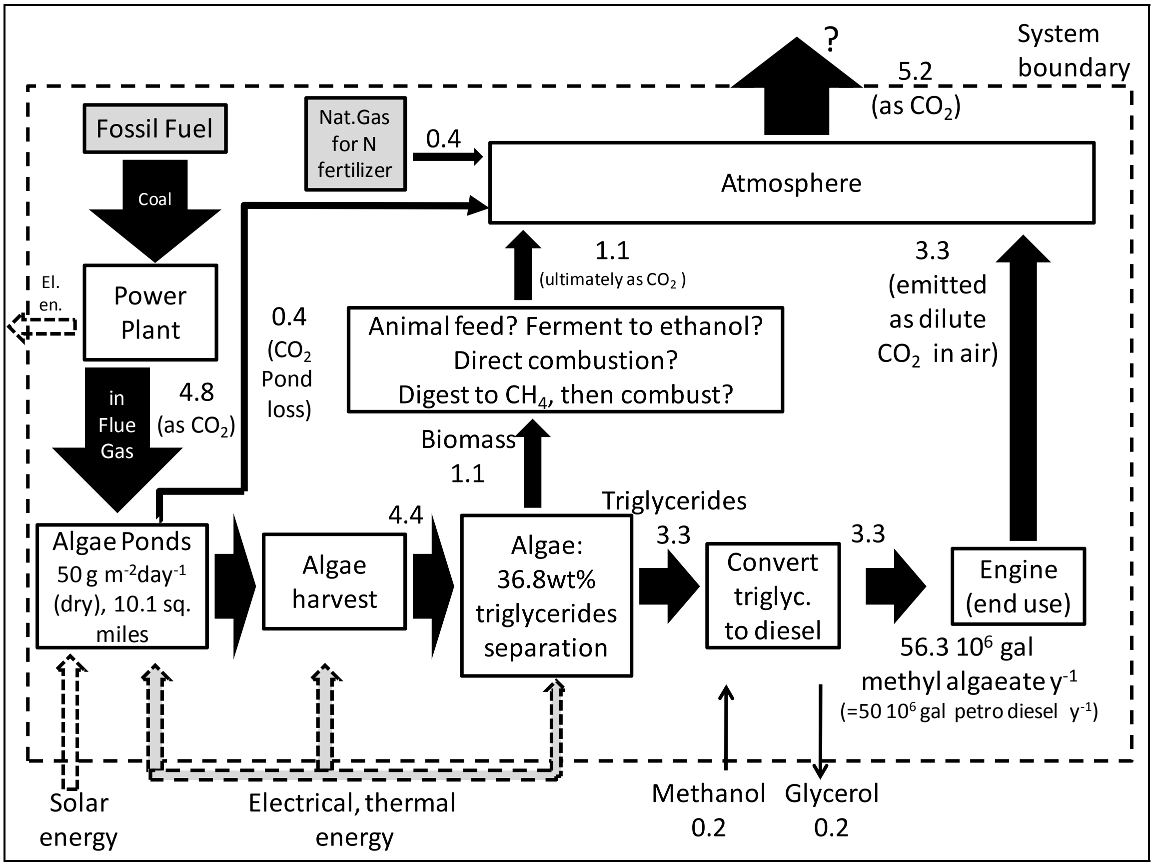

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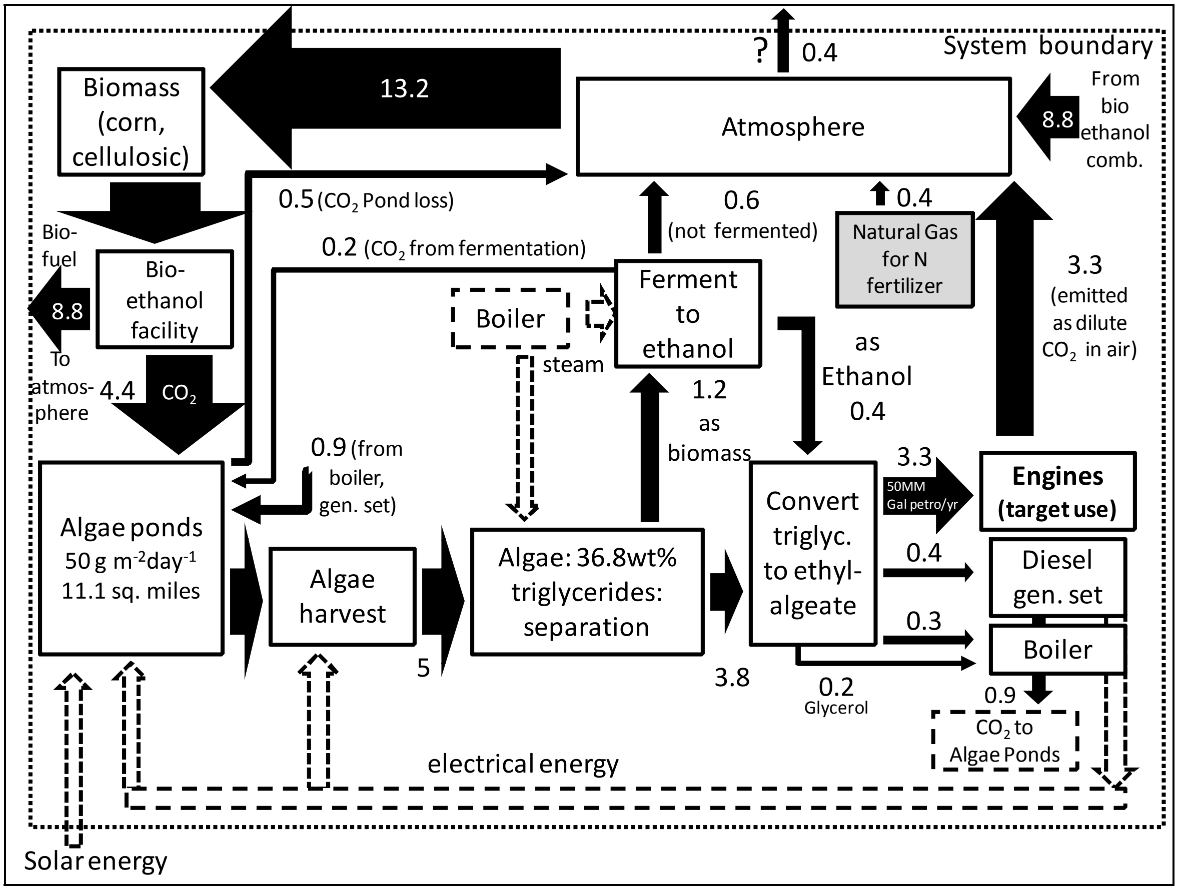

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Tables

Table 1: Qualitative comparison of Life Cycle Analysis (LCA) and the mass balance approach.

LCA	Mass balance approach
Product/material focus	Process focus
Input-Output (forward only) analysis	Recycling of outputs to inputs can be applied
No internal mechanism to check consistency of data	Conservation of mass requirement provides internal consistency check
The environment is a passive "receiver"	The environment can be completely included in form of sophisticated unit operations processing mass flows akin to complex technical processes