

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 ($0.006002 \text{ m}^3/\text{s}$) 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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27 **1 Introduction**

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

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

53 Rigorous sustainability is here postulated if a given process (defined by a boundary), including
54 within the boundary the energy producing aspects (solar energy excepted) does not emit or
55 receive material streams from the outside. A conceptual example of sustainability would be a
56 sealed (to mass flows) system containing some organisms and inorganic materials, with only

57 solar radiation as energy input and other radiation and/or heat as energy output to maintain the
58 energy balance, existing on average at steady state in perpetuity. The scientific principle of
59 conservation of mass that must be observed for the planet Earth as a whole is the starting point.

60 In other work related to Life Cycle Assessment (LCA) of algae based diesel, Dinh et al. (2009)
61 built on their earlier work for biodiesel production from various feedstocks and added a
62 comparison to algae-based biodiesel using various static ad hoc weighting and prioritizing
63 factors. Issues such as the impact of alcohol production for transesterification or the CO₂
64 demand of algal cultures are not discussed in detail. No mass flow analysis is shown so that a
65 check on the consistency of the numerous assumptions and data sources is difficult.

66 The production of liquid transportation fuels such as diesel from lipids produced by mass
67 culture of algae has been investigated on the bench- and pilot scale for quite some time although
68 initially production of proteins for food was the motivation (Burlew (ed.), 1953). A maximum of
69 70 g biomass (dry) m⁻² day⁻¹ is mentioned in this early review of the state of the art, with scale-up
70 estimates of 22 g biomass (dry) m⁻² day⁻¹. Many issues, such as the harvest of algae by
71 centrifuges vs. settling, contamination of algal cultures with undesirable competing or predatory
72 organisms, economic design of the large-scale algae culture vessels, the basic economics of algae
73 mass culture, and even harvesting of algae using fish are discussed in Burlew's early
74 compilation.

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

87 ponds (total area 25.2 m²) dug into the earth and lined with polymer foil was also reported
88 (Gummert et al., 1953). Amoeba, zooflagellates, and ciliates were a serious issue.

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

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

100 It will be shown below that diesel from algae cannot be made in a rigorously sustainable
101 fashion due to the need for nitrogen fertilizers that are at this time produced mainly from natural
102 gas. An overall benefit for CO₂ emissions comes from the replacement of fossil-based diesel
103 with diesel made using sunlight via algae. No CO₂ is directly sequestered by the algae diesel
104 concept.

105 In summary, this work has two main goals:

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

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

111 **2 Methods**

112 **2.1 *Justifying the mass balance approach to evaluate sustainability***

113 Earth, including the atmosphere, is thermodynamically an open system in regard to energy
114 with solar radiation being the input, and radiation to space as output. On the other hand, Earth
115 with the atmosphere is essentially a closed system regarding mass, and thereby for all its

116 individual chemical elements such as carbon (Figure 1, left). Loss of volatiles from Earth is
117 prevented by gravity, and the mass of Earth's crust alone is about 14 orders of magnitude larger
118 than the annual mass input from space.

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

129 The clear enunciation of a scientific principle as a basis for the approach to sustainability
130 developed here is a significant advantage over using an environmental impact tool such as Life
131 Cycle Assessment (LCA) which has no stated scientific principle and is in essence an accounting
132 method. LCA is widely used and one may ask if this methodology is not sufficient to evaluate
133 the sustainability of a bio-based energy approach. However, according to ISO 10440, LCA is a
134 "compilation and evaluation of the inputs and outputs and the potential environmental impacts of
135 a product system throughout its life cycle". Sustainability is not a focus of LCA. The issue of
136 poor consistency of LCA is sometimes discussed, perhaps most often by non-practitioners
137 without a stake in the established methodology (Davis et al., 2009). LCA is essentially an
138 inventory or enumeration of *inputs and outputs* while the mass balance/unit operation approach
139 used here is based on *specifying process inputs and calculation of the process outputs* through
140 knowledge of the internal workings of networked unit operations. If, say, a particular chemical
141 reactor was defined as a "product system" of interest for LCA (Figure 2, left) and the goal would
142 be to analyze this product system (LCA step 1: goal and scope definition), then the collection of
143 data on the input and output streams would be the second step of LCA (LCA step 2: inventory
144 analysis), followed by impact assessment (assignment of weighing factors for environmental
145 impact standardization) and accompanied by interpretation. A chemical engineering mass
146 balance/unit operation analysis on the other hand (Figure 2, right) would specify the input

147 streams, and calculate or at least estimate from models or experience the output streams based on
148 knowledge of the reactor and the operating conditions. Input and output streams will by
149 definition fulfill the mass balance while that is not necessarily so in the LCA analysis where all
150 depends on the quality of the data. The impact of process changes can be evaluated in the mass
151 balance/unit operation approach while the LCA will require an inventory update for any changes.
152 It contributes to a certain degree of confusion that the LCA inventory step is called a mass
153 balance by some practitioners (Kralisch, 2008) while it is in fact only that, an inventory. The
154 concept of elemental mass balances (carbon for example, see below) is entirely missing from
155 LCA. One sometimes finds that although mass balances are touted as the main subject in LCA-
156 related publications (Eissen et al., 2008) no use is made of the power and readily available
157 conceptual and software tools of chemical engineering mass balances. This may be partially due
158 to the frequent absence of engineering backgrounds among LCA practitioners (a brief check of
159 the seven co-authors of the above book chapter shows no one with an engineering background).

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

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

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

183 After a number of assumptions and extrapolations are reasonably made, the impact of streams
184 to/from the production system is quantified based on established weighing factors. Essentially,
185 one would assign a certain factor to, say, a kg CO₂ emitted, etc. Impact on human health,
186 ecosystems, and resources is assigned and then normalized so all impacts are shown on the same
187 scale to identify major contributions. While this may be called “LCA proper” the authors
188 attempt in the discussion to expand the analysis to energy balances and this cannot succeed
189 because a first law of thermodynamics analysis does not suffice. This type of extension of LCA
190 away from the environmental impact is often attempted and leads to wildly different results due
191 to the absence of a proper scientific foundation. This is perhaps demonstrated by the ongoing
192 debates about the net energy contributions of bio-ethanol production from corn.

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

204 The simple mass balance approach limited for example to the critical element carbon for liquid
205 transportation fuels shows a necessary but not sufficient condition of sustainability. However, it
206 will allow to decide early on if a given concept has any hope of operating sustainably, and where
207 the most serious issues reside (for example Pfromm et al., 2010). If the carbon mass balance

208 appears promising, a complete mass balance will show environmental compatibility since for
209 example the unit operation "atmosphere" may not be enriched or depleted over time to maintain
210 steady state and achieve sustainability. It is acknowledged that a unit operation such as
211 "atmosphere" is exceptionally complex and that our knowledge is in flux, but the mass balance
212 approach is amenable to handle very high levels of complexity in an adaptable mathematical
213 fashion.

214 **2.2 *Time scales of sustainability***

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

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

228 **2.3 *Energy***

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

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

240 **2.4 *Corn ethanol as a simplified qualitative example***

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

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

262 **3 Results and Discussion**

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

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

274 **3.1 Algae diesel production assumptions**

275 Several fundamental factors limit the specific productivity of algae biomass produced per pond
276 area and overall time of operation: the quantum requirement for the photosynthetic process, the
277 number of incident photons of the correct wavelength available for photosynthesis, losses
278 through the algae's respiration processes, suboptimum temperatures, light saturation of the
279 photosynthetic system etc. (Walker, 2009; Zhu et al., 2008). A rather optimistic sustained
280 average productivity of 50 g of bone dry algal biomass m^{-2} open pond area day^{-1} with a total lipid
281 content of 46.0wt% on dry biomass (Hu et al., 2008 and references cited herein; average of
282 literature survey data on green microalgae grown under stress conditions) and a useable (for
283 biodiesel) 80.0 wt% of target triglycerides (Hu et al., 2008 and references cited herein, estimated
284 maximum for aging algal cells or stress conditions from several published studies) contained in
285 the above total lipids will be assumed here. This results in 36.8wt% of the bone dry total algal
286 biomass available as target triglycerides for diesel production. The 50 g dry algal biomass m^{-2}
287 open pond area day^{-1} used here is assumed to include 10wt% of ash (inorganic materials such as
288 calcium, chloride, phosphorous etc.). It may be important to point out that the unequivocal
289 theoretical maximum (limited by the available photosynthetically useful solar radiation) is
290 reported as about 141 g dry algal biomass m^{-2} open pond area day^{-1} for the U.S. which is
291 somewhat different than the 354,000 l crude algae oil ha^{-1} year $^{-1}$ or about 237 g m^{-2} open pond
292 area day^{-1} (assuming 36.8wt% oil in dry algal biomass, and a density of 0.9 kg l^{-1} oil) given
293 elsewhere as theoretical maximum (Weyer et al., 2010) but the assumptions for irradiation are
294 different for these estimates. Experts in phycology rather suggest values ranging from a perhaps
295 more realistic 11.8 to an optimistic 54.4 g dry algal biomass m^{-2} open pond area day^{-1} (Zhu et al.,
296 2008, and references cited therein). This is more consistent with Weyer et al.'s 4.3 g m^{-2} day^{-1}
297 reported as their high realistic large scale value (Weyer et al., 2010). The pond depth

298 recommendations vary in the literature, but an advantageous depth is perhaps on the order of 15-
299 30 cm (Sheehan, 1998a, Ben-Amotz, 2010).

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

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

318 **3.2 Algae diesel base case**

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

326 Biodiesel has somewhat though not drastically different physical and chemical characteristics
327 than petroleum-based diesel. The lower heating value (LHV) was chosen to calculate the

328 amount of algaeate that needs to be produced to match the above petroleum-based diesel
329 benchmark. With an LHV of 42.79 MJ kg⁻¹ and a density of 850 kg m⁻³ for petroleum diesel, and
330 an LHV of 36.95 MJ kg⁻¹ (Sheehan et al., 1998b, equivalent to methyl soyate) for methyl
331 algaeate an overall methyl algaeate production of about 186,000,000 kg y⁻¹ matches the base case
332 for petroleum diesel replacement (assuming 360 days of operation per year for the algae facility
333 at 50 g m⁻² of algae biomass production (dry mass including 10wt% ash) per day. Different
334 growth rates depending on geographic location etc. will later be incorporated in the forthcoming
335 dynamic socio-economic modeling. Using an average molecular weight of methyl algaeate of
336 292 g mol⁻¹ based on a soybean oil-like fatty acid split of 6, 52, 25, 5, and 12 wt% of α -linolenic-
337 , linoleic-, oleic-, stearic-, and palmitic acid, respectively; with 77wt% carbon assumed in methyl
338 algaeate (Sheehan et al, 1998a) a first approximate mass balance for carbon is shown in Figure 5.
339 The pond area needed is about 10 square miles in continuous algae production to replace
340 nominally 0.1% of the annual U.S. diesel consumption.

341 Note that the atmosphere is included as a unit operation in Figure 5. This unit operation is
342 here a simple pass-through with no chemical change of the form of carbon (CO₂). Since the unit
343 operation "atmosphere" needs to be sustainable like all other unit operations (no depletion or
344 accumulation) it is not allowed for any other unit operation to emit carbon to "atmosphere" and
345 then assume that it will be "dumped" elsewhere in an unspecified way. The carbon (or any other
346 element) mass balance around "atmosphere" must close (add up to zero) for sustainability.

347 Aquaculture in an artificial body of water such as a pond system could be compared to a very
348 large living organism that consists of a collective of many individual organisms (algae). This
349 "super-organism" residing in the pond system requires energy (here via sunlight), materials to
350 build biological materials (including the target oils) here from CO₂, defense against unwanted
351 invaders, and waste management. Sources of inorganic atoms (for example sodium, potassium),
352 phosphorous (to build energy carrying molecules), and nitrogen (to build amino acids) are also
353 needed since the phosphorous and nitrogen that is harvested with algae is not available in the
354 proper biologically compatible form for direct recycling to the ponds. The carbon flows for
355 nitrogen-containing fertilizer are indicated in Figure 5 since natural gas is the source of both
356 energy and the reactant hydrogen to produce nitrogen-containing fertilizers. Fertilizers will
357 emerge as a problem issue impacting sustainability (below).

358 Figure 5 assumes that the CO₂ needed for algae culture is obtained from a nearby coal-fired
359 power plant or that compressed CO₂ perhaps from carbon capture at a power plant is used that is
360 obtained via truck or railcar.

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

- 363 • the coal reservoir for supply of CO₂ to the algae ponds after coal combustion is not
364 sustainable
- 365 • the natural gas reservoir as energy and reactant supply for nitrogen-based fertilizer is not
366 sustainable

367 It is certainly beneficial that CO₂ which would otherwise be emitted directly from the power
368 plant is routed to biodiesel using sunlight and algae. However, the algae process provides no
369 permanent carbon sink and all CO₂ is emitted eventually to the atmosphere when the algae diesel
370 is combusted and through use of other algae-derived carbon streams. A carbon benefit arises
371 from the replacement of fossil-based diesel with the solar energy based diesel from algae, not
372 from capturing or sequestering fossil CO₂.

373 It is stipulated above for sustainability that no mass flows may cross the system boundary, so
374 the methanol supply for diesel production and the byproduct glycerol need to be further
375 investigated, the CO₂ emission to the atmosphere has to be considered, along with the
376 unbalanced unit operations natural gas reservoir, and coal reservoir. No energy except for solar
377 is allowed to enter the system to achieve sustainability, therefore the system will need to be
378 enlarged (include electrical, thermal energy production) or energy will have to be provided from
379 within the system, essentially routing some solar energy entering the system for in-system use.

380 ***3.3 Adjusted base case to approach sustainability***

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

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

- 386 • The glycerol byproduct from esterification is combusted in a boiler together with some
387 biodiesel to raise steam for the bio-ethanol facility and other process heat requirements.
- 388 • CO₂ from the on-site ethanol facility and from the boiler is routed to the algae ponds.
- 389 • The remaining CO₂ to grow the algae is assumed to be supplied as compressed CO₂ via
390 truck or rail from a large scale fermentation-based biofuel facility (Figure 6).

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

397 3.3.1 Electrical energy

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

411 3.3.2 Thermal energy demand

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

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

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

422 3.3.3 Fertilizer production

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

435 3.3.4 CO₂ source

436 Figure 6 indicates that CO₂ from a bio-ethanol-producing facility is used to supply the balance
437 of CO₂ needed to produce the algae. No fossil fuel source to operate the bio-ethanol facility is
438 shown because it is assumed that the ethanol produced will in part be used to supply the
439 significant amount of process heat needed to operate the bio-ethanol facility. If natural gas is
440 used to operate the bio-ethanol facility then an additional non-sustainable unit operation (the gas
441 reservoir) would have to be added to the schematic. .

442 **3.4 Summary of technical assessment of sustainability**

443 The non-sustainable use of fossil fuel to produce nitrogen-based fertilizer cannot be avoided
444 for algae aquaculture with current technology. The CO₂ demand of the algae culture can be

445 partially covered from in-system sources (boiler, generator set, ethanol fermentation facility for
446 esterification) with the remainder obtained from a fermentation-based biofuel facility to
447 approach rigorous sustainability, or coal fired power plants (co-located or supply of CO₂ via
448 truck or rail) if one accepts a higher level of non-sustainability since fossil-based CO₂ is used.
449 While rigorous sustainability is breached when mainly fossil fuel based CO₂ is used to support
450 the algae growth this may be a reasonable choice as long as the CO₂ emission is produced not
451 solely for the algae process but for other reasons such as electrical power generation. The algae
452 diesel operation does not supply a carbon sink of any kind. It only increases the benefit from the
453 eventual CO₂ emission to the atmosphere by using sunlight to recreate a useful fuel from CO₂.

454 **4 Conclusions**

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

459 Algal diesel can be produced sustainably with the exception of the natural gas to produce
460 nitrogen-based fertilizer. A pond area of about 11 square miles (28,490,000 m²) at an optimistic
461 growth rate of 50 g bone dry biomass m⁻² day⁻¹ might suffice to replace 0.1% of the U.S. diesel
462 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 algaete 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 algaete. Carbon mass flows for ethyl algaete 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

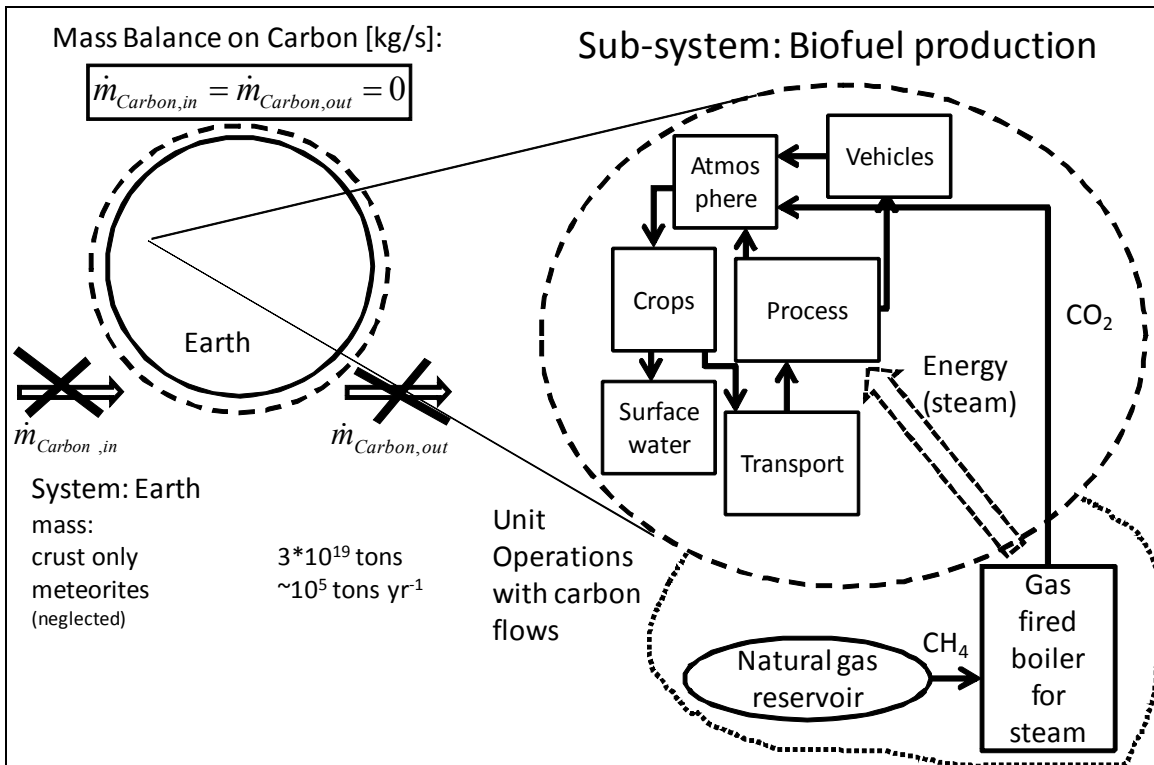


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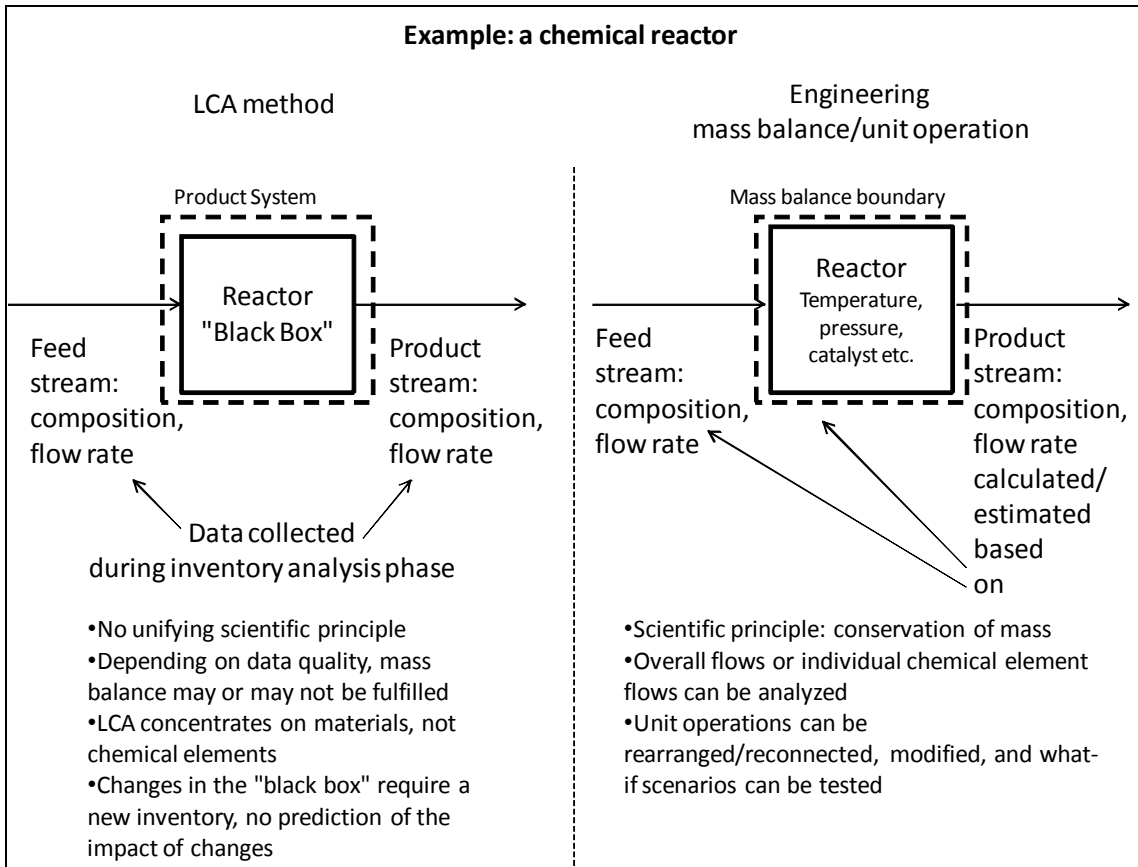


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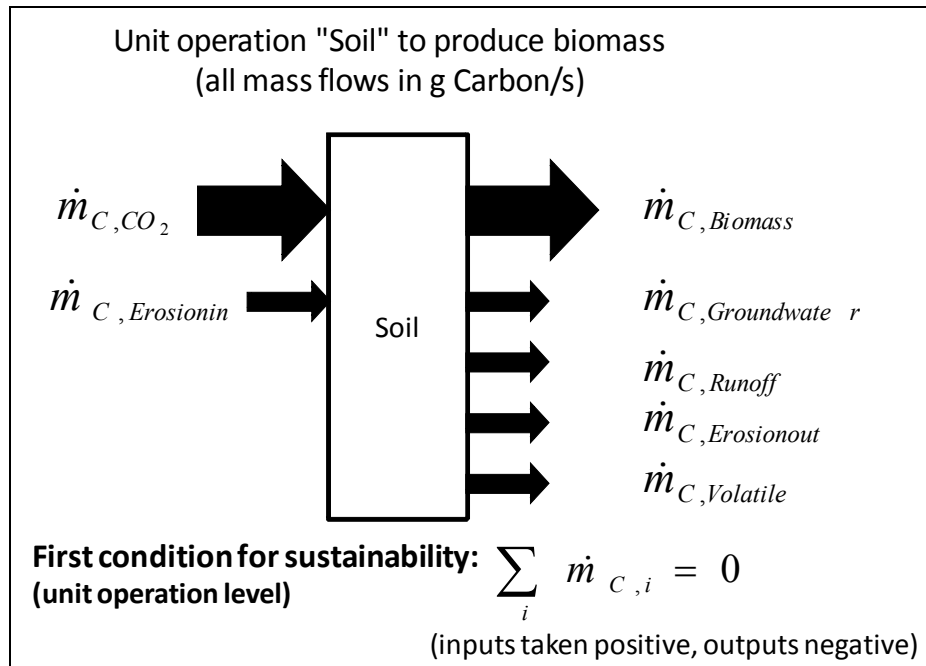


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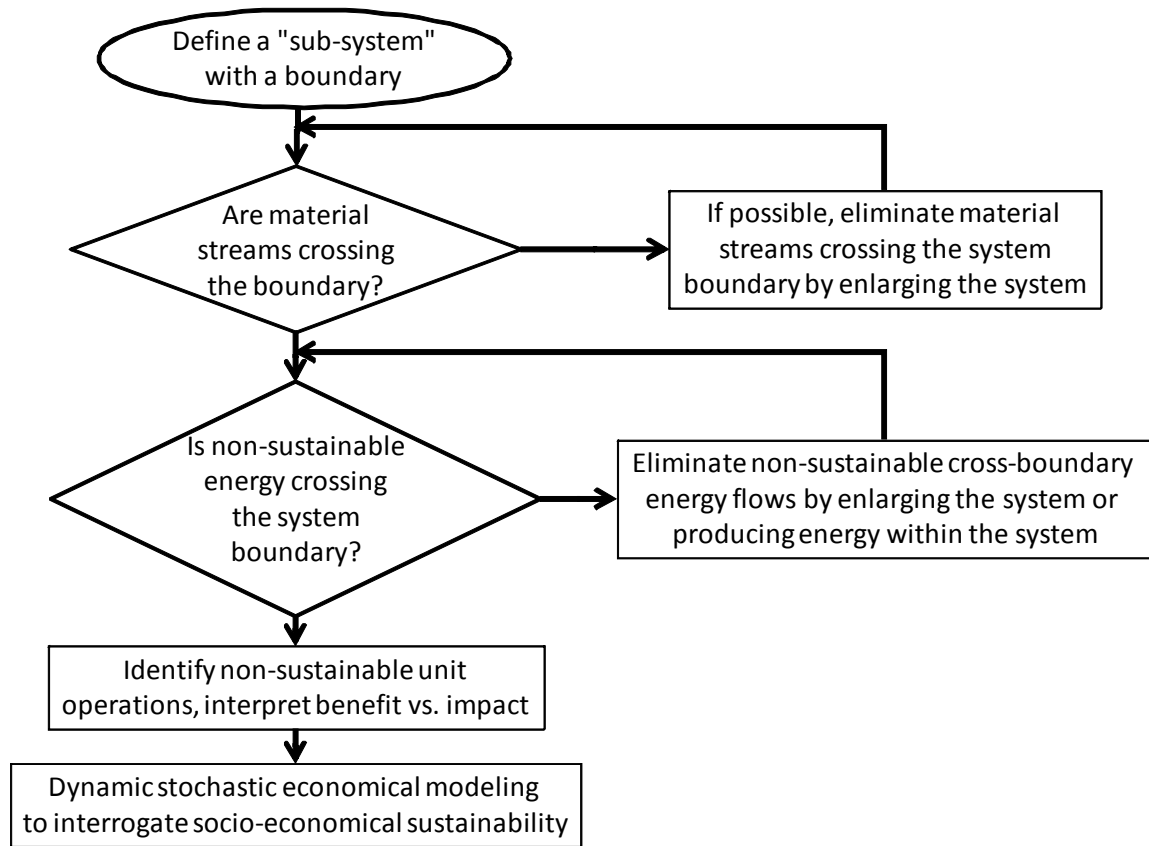


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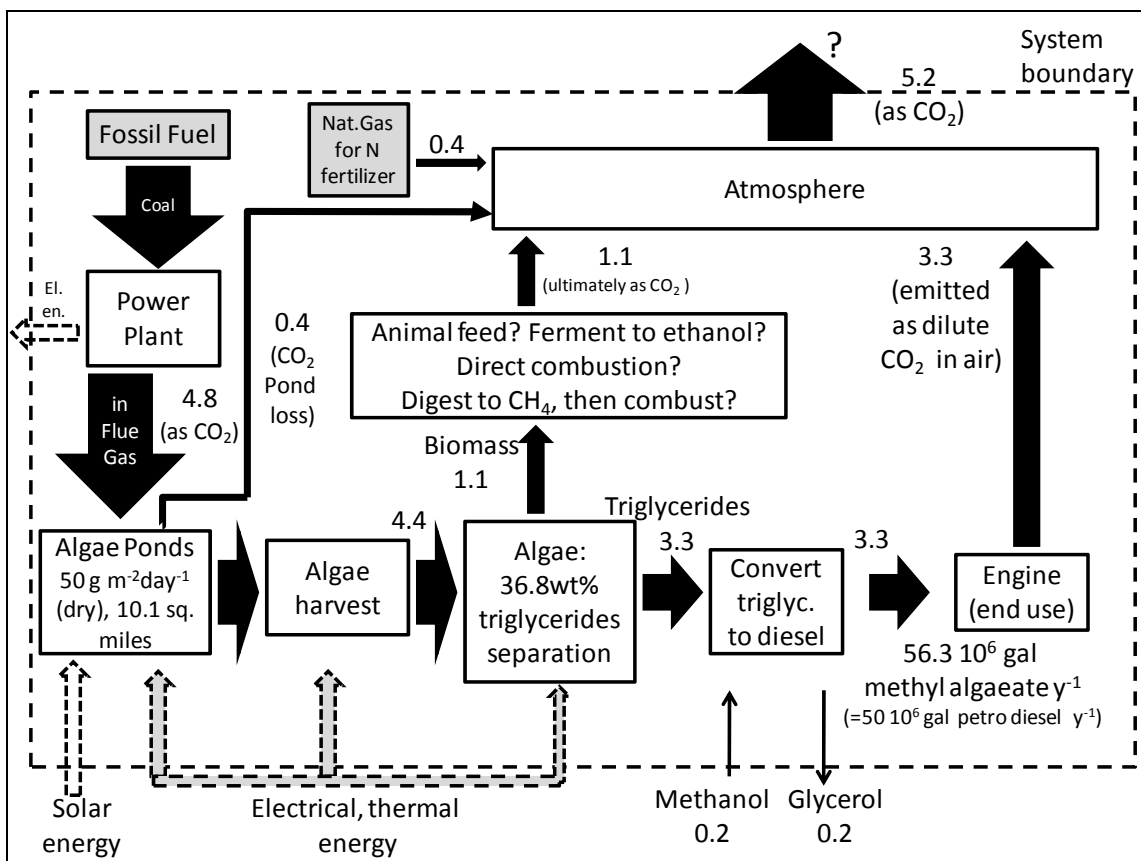


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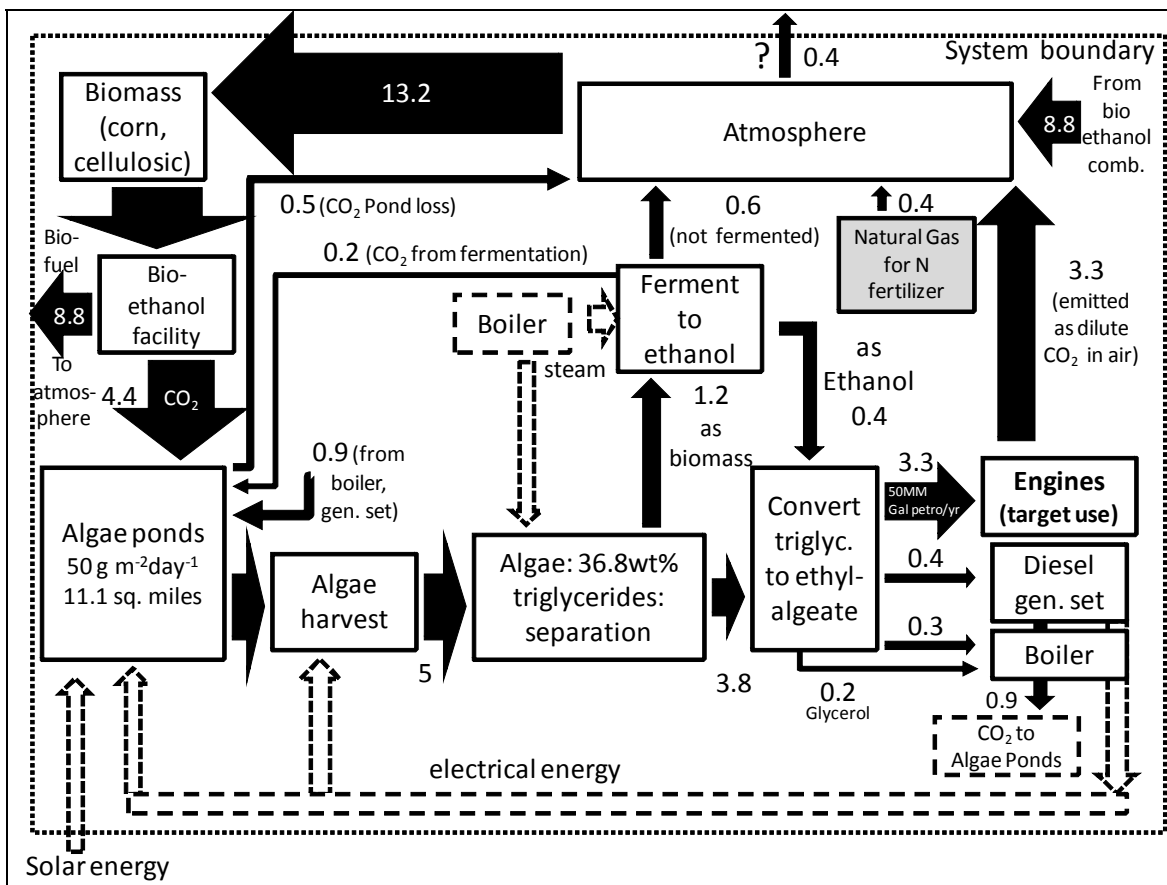


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Tables

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