

CO₂ BALANCE FOR
BIODIESEL PRODUCTION FROM MICROALGAE

A THESIS SUBMITTED TO
THE GLOBAL ENVIRONMENTAL SCIENCE
UNDERGRADUATE DIVISION IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

GLOBAL ENVIRONMENTAL SCIENCE

JULY 2009

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I certify that I have read this thesis and that, in my opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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ACKNOWLEDGMENTS

I would like to thank Dr. Michael J. Cooney for working with me and guiding me throughout this project. I want to also thank my parents for giving me the financial and emotional support to make my university education possible. Finally I want to thank Dr. Jane Schoonmaker for advising me throughout my time at the University.

ABSTRACT

As global climate change due to increased atmospheric CO₂ becomes a greater concern, alternative energy sources such as biodiesel derived from microalgae are being explored as a way to reduce CO₂ outputs. I investigated the extent to which microalgal biodiesel production is a carbon neutral process. The total carbon and CO₂ input to the system was compared against the total carbon and CO₂ emitted during the production process. Although biodiesel production was found to be carbon neutral, excluding carbon release from energy use, it was found to emit more CO₂ than is consumed and therefore is not CO₂ neutral. While microalgal biodiesel provides several advantages over petroleum based fuels, the production of microalgal biodiesel is not a CO₂ neutral process.

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LIST OF EQUATIONS

Equation

1. (fuel) + (oxygen) = (carbon dioxide) + (water)
2. (surface area) / (width) = (length)
3. (width) x (length) x (depth) = (volume)
4. (dilution rate) x (pond volume) = (flow rate out)
5. (biomass productivity) x (pond surface area) = (biomass productivity rate)
6. (biomass productivity rate) / (flow rate out) = (biomass concentration)
7. (biomass productivity rate) x (biomass C concentration) = (C input)
8. (C input) x ((molecular weight C) / (molecular weight CO₂)) = (CO₂ input)
9. (10L) x ((.001) x (biomass productivity rate)) = (hexane in)
10. (0.837g C)/(g Hexane) x ((150L) x ((654.8g Hexane)/(L))) = (82230.7g C)
11. (biomass productivity rate) x (65%) = (delipifide biomass)
12. (g delipifide biomass) x (30.25%) = (g C)
13. (total g C per day) / (12) = (mol C per day)
14. (mol C per day) x (44) = (g CO₂ per day)
15. (biomass productivity rate) x (percent lipids) = (gdw/day lipid)
16. (gdw/day lipid) x (percent C by weight) = (g C per day)
17. ((g C per day) / (12)) x (44) = (g CO₂ per day)
18. (g triglyceride in) / (molar weight triglyceride) = (mol triglyceride)
19. (molar mass) x (moles present) = (mass present)
20. (mass of C in 1 mole) / (molar mass compound) = (percent C by weight)

21. (percent C by weight) x (mass compound present) = (mass C present)
22. (C present in compound) / (% C by weight in CO₂) = (CO₂ released)
23. (biomass in) + (biomass in) x (100 - final solid %) = (permeate in)
24. (kwhr/m³ permeate) x (permeate processed) x (BTU/kwhr) = (energy)
25. (permeate processed) x (m³/gram) x (gallons/m³) = (gallons permeate)
26. (permeate) / (gallons/centri.) x (kwhr/centri.) x (BTU/kwhr) = (energy)
27. (permeate from centrifuge) - (biomass) = (water to be dried)
28. (kg water) x (specific heat) x (change in temperature) = (energy in J)
29. (kg water) x (heat of vaporization) x (1000) = (energy in J)
30. (kg hexane) x (specific heat) x (change in temperature) = (energy in kJ)
31. (kg hexane) x (heat of vaporization) = (energy in kJ)
32. (mass of product (g)) x (heat of combustion (cal/g)) x (BTU/cal) = (energy)
33. (energy needed in kwhr/day) x (lb CO₂/kwhr) x (g/lb) = (g CO₂ released)

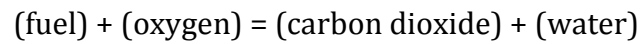
Chapter 1: Introduction

Section 1.1: The CO₂ Problem

Global climate change is a serious international problem. An increase in global temperatures will lead to a rise in sea level, changes in precipitation and weather patterns, increased spread of disease, reduction in the arctic and Antarctic ice sheets and a possible increase in dramatic weather events (IPCC, 2007). From pre-industrial times to 2005, global CO₂ concentrations increased from 280ppm to 379ppm (IPCC, 2007) and are estimated to increase to 500ppm by the end of the century if trends continue (Ahrens, 2007). By 2050 the atmospheric CO₂ emission levels are predicted to have increased on average by 15GtC globally according to a mean and median of 40 IPCC Special Report on Emissions Scenarios, or SPES (IPCC, 2000). This is predicted to correlate to between a 0.6 and 4.0 degree Celsius increase in global temperature (IPCC, 2007).

CO₂ accounts for about 26% of the greenhouse effect (Ahrens, 2007) and its levels have been rising quickly. As one of the primary greenhouse gasses associated with global warming, CO₂ levels will have dramatic effects on the planet's climate. Therefore the level of CO₂ emitted to the atmosphere needs to be reduced dramatically.

56.6% of the CO₂ emitted to the atmosphere is derived from the burning of fossil fuels (IPCC, 2007). During fossil fuel combustion the fuel is converted to CO₂ and H₂O via equation 1:



Globally 3.12Gt of carbon per year were emitted from fossil fuel use in 2000. This number is expected to increase to 4.47Gt carbon per year by 2020 (Huntley and Redalje, 2004). Of those amounts, 1.6Gt and 2.65Gt carbon per year, respectively, are associated specifically with fossil fuel use in transportation (Huntley and Redalje, 2004). This correlates to 51% of carbon released from fossil fuel use in 2000 being due to transportation. This percent is expected to rise to 59% by 2020.

Options for reducing atmospheric CO₂ have been investigated for some time now. There are two basic processes, CO₂ sequestration and reduction of CO₂ emissions. One option that has been looked at to reduce CO₂ emissions from fuel use in the transportation sector is the transition from fossil fuels to biofuels.

Section 1.2: Why Biodiesel?

Biofuel is fuel derived from biomass or organic material. Because biomass is a renewable resource, meaning that it is not irreversibly consumed, biofuel is considered to be a renewable source of energy. Finite amounts of fossil fuels exist

leading to the inevitability that they will eventually run out. Biofuel on the other hand can be created from continued growth of biomass.

Biofuel can be created using a variety of crops. Most commonly sugars, starches and cellulosic crops have been used to produce bioethanol (Rutz and Janssen, 2007).

Pure plant oil and biodiesel are two other less common biofuel sources converted from triglycerides derived from crops with high oil contents (Rutz and Janssen, 2007).

Biodiesel has been promoted by many as a renewable fuel source that not only provides energy, but also sequesters CO₂ from the atmosphere. It is true that production of biodiesel takes in CO₂ in order to grow the plants that will be turned into fuel. That fuel however is burned and the carbon in it is converted back to CO₂ which is once again released (Rutz and Janssen, 2007). In this way biodiesel is, at best, carbon neutral in its combustion. Sequestration requires that the carbon be buried rather than burned.

What this analysis will examine is the degree to which biodiesel production from microalgae is truly a carbon neutral process. Both carbon and CO₂ will be traced through the biodiesel production process. The end results of total inputs and outputs will then be compared to determine the level to which biodiesel production is a carbon neutral process.

For the analysis microalgae was the chosen crop to look at. The growth rate and oil yields of microalgae are potentially higher than other biofuel crops potentially making it the most effective renewable fuel source. Within 24 hours many microalgae can double their biomass and often times the doubling can occur in 3.5 hours (Chisti, 2007). With an average oil content of 20-50% and sometimes exceeding 80% dry biomass weight (Chisti, 2007), microalgae can be very efficient oil producers. Microalgae could potentially produce up to 6,000 gallons of oil per acre per year compared to only 43 gallons per acre per year for soybeans (Waltz, 2009). The next highest potential yield after algae is palm oil, however that only estimates 641 gallons per acre per year (Waltz, 2009), nearly one-tenth the yield for microalgae.

A box model of the microalgal biodiesel production process was used to separate calculations by stage. The process model can be seen in Figure 1.

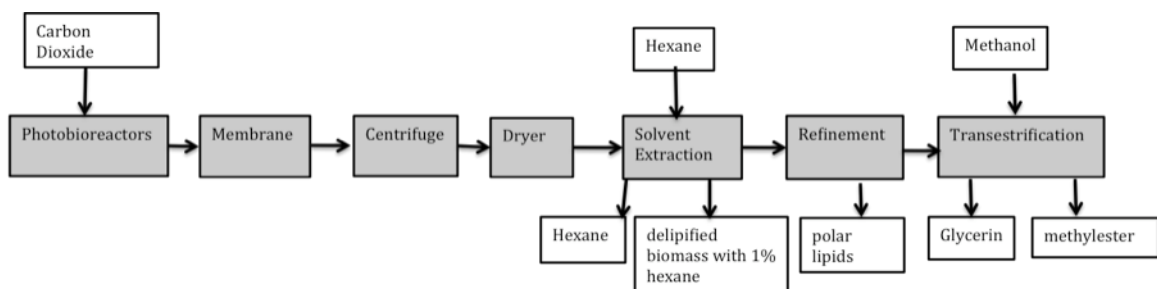


Figure 1, Box Model of the Biodiesel Production Process

The grey boxes indicate steps that the microalgae must go through to be converted to biodiesel. The white boxes indicate inputs and outputs required at each step. The

carbon and CO₂ associated with each of the white boxes will be traced in this analysis. Also energy, not shown in the box model, will be taken into account, as it will be shown to influence the CO₂ balance of the process.

Chapter 2: Carbon and Carbon Dioxide Tracking

Section 2.1: Setting and finding initial factors

The biomass productivity was set to 30 gdw per m² day. This is a realistic estimate as shown in other studies (Cooney, 2009). The dilution rate, or rate at which permeate is taken from the photobioreactors, was set at 1/3 of the material per day, or 0.33 per day. The pond size was set next. Because the final results will be a ratio, the specific pond size is not significant in the results that will be gained. The pond surface area was therefore set to 50,000m². The width was set to 8m. The depth was set to 0.2m as that is as deep as light will realistically be able to penetrate the algal mass (Benemann and Oswald, 1996).

From the pond surface area, width and depth, the length was able to be calculated by equation 2.

$$(\text{surface area}) / (\text{width}) = (\text{length})$$

The length of the ponds was found to be 6250m. The pond volume was calculated by equation 3.

$$(\text{width}) \times (\text{length}) \times (\text{depth}) = (\text{volume})$$

The volume was found to be 10,000m³. Using the dilution rate and the pond volume the flow rate out of the ponds was calculated in equation 4.

$$(\text{dilution rate}) \times (\text{pond volume}) = (\text{flow rate out})$$

The flow rate out of the ponds was calculated to be 3,300m³ per day. The biomass productivity was calculated next by equation 5.

$$(\text{biomass productivity}) \times (\text{pond surface area}) = (\text{biomass productivity rate})$$

The biomass productivity rate was found to be 1,500,000gdw per day. Using the biomass productivity rate and the flow rate out, the biomass concentration was found in equation 6.

$$(\text{biomass productivity rate}) / (\text{flow rate out}) = (\text{biomass concentration})$$

The biomass concentration was found to be 454.5gdw per m³. This is within a reasonable biomass concentration (Cooney and Nagle, 2009) therefore the numbers set were likely appropriate to this experiment.

A summary of numbers set and calculated can be seen in table 1.

biomass productivity (gdw/m ² *day)	30
pond surface area (m ²)	50,000
biomass productivity rate (gdw/day)	1500000
dilution rate (1/day)	0.33
pond width (m)	8
pond depth (m)	0.2
pond length (m)	6250
pond volume (m ³)	10000
flow rate out (m ³ /day)	3300
biomass concentration (gdw/m ³)	454.5454545

Table 1, Initial Factors Set and Calculated

Section 2.2: Finding Initial CO₂ input

To find the initial CO₂ input into the photobioreactors certain assumptions were made. First it was assumed that all carbon coming out of the photobioreactors as biomass had originally entered the photobioreactors as carbon dioxide. Next it was assumed that the biomass leaving was 50% carbon (Smith, Heath, and Jenkins, 2003). From this the carbon inputs were found in equation 7.

$$(\text{biomass productivity rate}) \times (\text{biomass C concentration}) = (\text{C input})$$

The carbon input was found to be 750,000g C per day. Using the molecular weight of C (12) and CO₂ (44), the CO₂ input was calculated in equation 8.

$$(\text{C input}) \times ((\text{molecular weight C}) / (\text{molecular weight CO}_2)) = (\text{CO}_2 \text{ input})$$

This gave an initial CO₂ input of 2,750,000g CO₂ per day. A summary of these results is found in table 2.

Biomass C content (%)	0.5
Carbon input (gC/day)	750000
CO ₂ Molecular Weight	44
C in CO ₂	12
CO ₂ input (gCO ₂ /day)	2750000

Table 2, Initial CO₂ input

Section 2.3: Solvent Extraction

The biomass extracted from the photobioreactor is passed through the dewatering stages to the solvent extraction stage. In a perfect system there is no carbon loss in those intermittent dewatering stages therefore the carbon can be traced beginning with the solvent extraction and refinement stages. During solvent extraction the lipids are separated from the delipified biomass. 65% of the carbon goes to delipified biomass. The remaining carbon goes to the refinement stage where 25%, the neutral lipids, goes on to become biodiesel and 10%, the polar lipids, is removed (Benemann and Oswald, 1996).

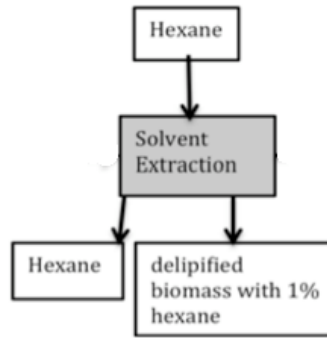


Figure 2, Solvent Extraction Block Diagram

During the solvent extraction phase the lipids are separated from the delipified biomass. Hexane is used as the separating agent. For every kg of biomass entering the solvent extraction stage, 10 liters of hexane are used. Equation 9 shows the amount of hexane being input into the system.

$$(10L) \times ((.001) \times (\text{biomass productivity rate})) = (\text{hexane in})$$

The hexane needed to separate 1,500,000gdw biomass per day was found to be 15,000L of hexane. Of the hexane entering the system about 99% is removed after extraction. The remaining 1% is expelled with the delipified biomass (Cooney, 2009). This results in 14,850L of hexane being removed and 150L going into the delipified biomass.

Hexane is 83.7% carbon by weight. The carbon in the hexane that is being added to the delipified biomass can be calculated by equation 10.

$$(0.837\text{g C})/(\text{g Hexane}) \times ((150\text{L}) \times ((654.8\text{g Hexane})/(\text{L}))) = (82230.7\text{g C})$$

The carbon in the 1% of the remaining hexane can be considered part of the carbon in the delipified biomass output at this stage.

Because 65% of the incoming biomass goes to the delipified biomass the grams dry weight per day of biomass can be found via equation 11.

$$(\text{biomass productivity rate}) \times (65\%) = (\text{delipified biomass})$$

From that 975,000g per day of delipified biomass is obtained. This delipified biomass is found to be 30.25% carbon by weight. Therefore the carbon being output as delipified biomass can be calculated in equation 12.

$$(\text{g delipified biomass}) \times (30.25\%) = (\text{g C})$$

295,082.847 grams carbon per day were obtained. This value can be added to the carbon value for the 1% of the hexane that remains with the delipified biomass. The total carbon output in the solvent extraction stage is found to be 377,313.544 grams carbon per day.

For this analysis it was assumed that the output delipified biomass would be burned. This allows the energy from burning the biomass to be recycled back into

the system which will be discussed later. The assumption that complete combustion would occur was also made. Because the release of CO₂ as a green house gas was the primary focus of this study, using incomplete combustion would have released other greenhouse gases besides CO₂, such as nitrogen oxides and carbon monoxide (ISCID). With this assumption the CO₂ released during the burning of the delipified biomass can be calculated in equations 13 and 14.

$$(\text{total g C per day}) / (12 \text{ g/mol}) = (\text{mol C per day})$$

$$(\text{mol C per day}) \times (44 \text{ g CO}_2/\text{mol}) = (\text{g CO}_2 \text{ per day})$$

1,383,483 g CO₂ per day was found.

Section 2.4: Refinement

During refinement the polar lipids are separated from the neutral lipids. The neutral lipids will go on to the next step of transestrification where they will be converted to biodiesel. The polar lipids will be output at the refinement stage. They can then be put to a number of uses, but for the same reasons as with the delipified biomass, they will be burned for energy in this analysis.

We know that the total biomass is 25% neutral lipids and 10% polar lipids.

Therefore the amount of neutral and polar lipids can be calculated in equation 15.

$$(\text{biomass productivity rate}) \times (\text{percent lipids}) = (\text{gdw/day lipid})$$

375,000gdw per day neutral lipids and 150,000gdw per day polar lipids are found. The neutral lipids in the form of triglyceride are 87.59% by weight carbon as calculated from the chemical formula for triglyceride. The polar lipids are 84.3% by weight carbon (Andersson, Selstam and Hagstrom, 1993). From these percentages the amount of carbon going to the polar and neutral lipids can be calculated by equation 16.

$$(\text{gdw/day lipid}) \times (\text{percent C by weight}) = (\text{g C per day})$$

This gives 328,467.153g C per day and 126,450g C per day for neutral and polar lipids respectively. The neutral lipids will be discussed in the next section. The polar lipids will be burned for energy in the analysis. Assuming again complete combustion, the CO₂ released is calculated by equation 17.

$$((\text{g C per day}) / (12 \text{ gC})) \times (44 \text{ gCO}_2) = (\text{g CO}_2 \text{ per day})$$

From the burning of the polar lipids 463,650g CO₂ per day are released.

Section 2.5: Transestrification

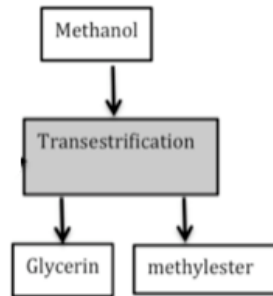


Figure 3, Transesterification Block Diagram

During transesterification, the incoming neutral lipids in the form of triglyceride are reacted with methanol and converted to methyl ester, or biodiesel, and glycerin. The chemical formula for transesterification is shown in figure 4.

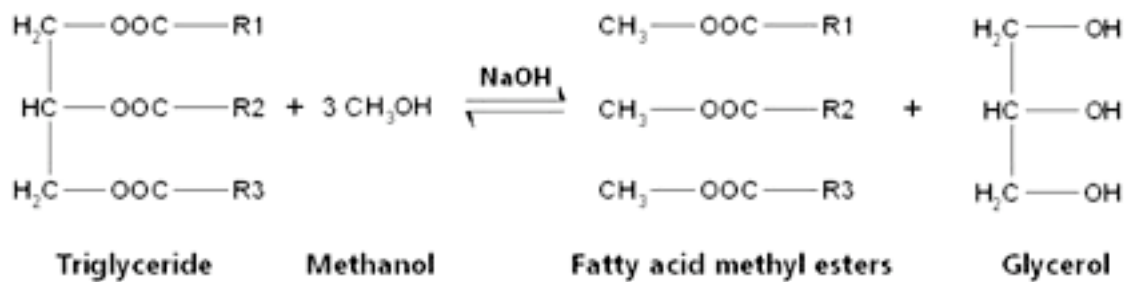


Figure 4, Chemical formula for transesterification

To calculate the total inputs and outputs, the molar ratios of the triglyceride, methanol, glycerin and methyl ester were compared. For every one mole of tryglyceride, three moles of methanol are needed and they produce three moles of methyl ester and one mole of glycerin. Because the mass of triglyceride entering the system has already been calculated, the moles of triglyceride can be found by equation 18.

$$(\text{g triglyceride in}) / (\text{molar weight triglyceride}) = (\text{mol triglyceride})$$

From the chemical formula the molar weight of triglyceride is found to be 822 grams per mole. This gives a value of 456.20438 mol triglyceride coming into the transesterification system. Table 3 shows the ratios, molar weights, and moles of each substance involved in the transesterification process.

	Ratio to Triglyceride	Molar Mass (g/mol)	Moles Present
Triglyceride	1	822	456.20438
Methanol	3	32	1368.61314
Methyl ester	3	274	1368.61314
Glycerin	1	87	456.20438

Table 3, Ratios of substances in the transesterification process

From the information in table 3 the mass of methanol, methyl ester and glycerin can be calculated in equation 19.

$$(\text{molar mass}) \times (\text{moles present}) = (\text{mass present})$$

To find the carbon in each compound the percent carbon by weight was calculated by equation 20.

$$(\text{mass of C in 1 mole}) / (\text{molar mass compound}) = (\text{percent C by weight})$$

The mass of carbon was then calculated by equation 21.

$$(\text{percent C by weight}) \times (\text{mass compound present}) = (\text{mass C present})$$

The results of the above equations are shown in table 4.

	Mass Present (g/day)	% C by Weight	C Present (gC/day)
Triglyceride	375,000	87.59	328,467.153
Methanol	43,795.6204	37.5	16,423.3577
Methyl ester	375,000	87.59	328,467.153
Glycerin	39689.781	41.38	16,423.3577

Table 4, Carbon balance from transestrification

For this analysis it was assumed that the methyl ester and the glycerin produced in the transestrification process will be combusted for energy. The methyl ester will be combusted as biodiesel when used as a fossil fuel substitute. The glycerin could have many uses, however burning it for energy will allow that energy to be recycled in the system to run other processes, therefore combustion was chosen for the analysis. As earlier, complete combustion was assumed due to the fact that even

incomplete combustion results in the release of other green house gases in addition to CO₂. The amount of CO₂ associated with the combustion of methyl ester and glycerin is calculated in equation 22.

$$(\text{C present in compound}) / (\% \text{ C by weight in CO}_2) = (\text{CO}_2 \text{ released})$$

The CO₂ released was calculated to be 1,204,379.56g CO₂/day and 60218.9781g CO₂/day for methyl ester and glycerin respectively.

Section 2.6: Summary of Carbon and CO₂ to this point

Figure 1 again shows all of the inputs and outputs for biodiesel production calculated in this analysis. Stages of production are shown in grey boxes and inputs and outputs are shown in white boxes.

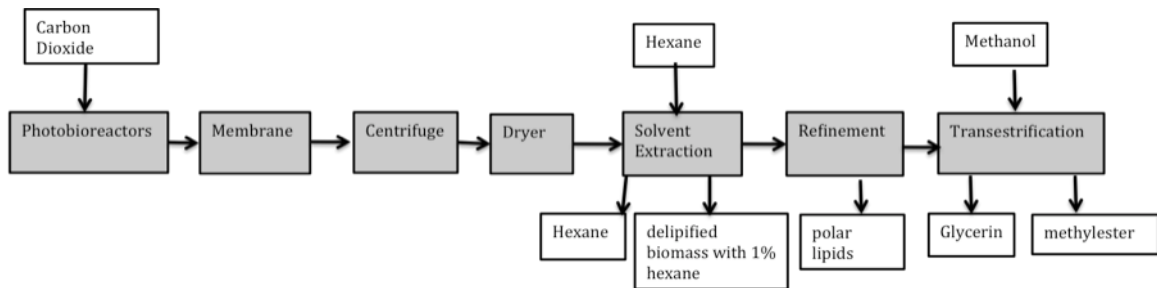


Figure 1, Box Model of Biodiesel Production Process

A summary of the carbon and CO₂ being consumed and emitted in each stage is found in table 5. The first three rows, Initial CO₂ input, hexane in and methanol,

represent carbon and/or CO₂ being input to the system. The following rows represent carbon and CO₂ output from the system.

	Carbon (gC/day)	Carbon Dioxide (gCO₂/day)
Initial CO ₂ input	750,000	2,750,000
Hexane in	8,223,069.77	n/a
Methanol	16,423.3577	n/a
Hexane out	8,140,839.07	n/a
Delipidified Biomass	377,313.544	1,383,483
Polar Lipids	126,450	463,650
Glycerin	16,423.3577	60,218.9781
Methyl ester	328,467.153	1,204,379.56
Total Input	8,989,493.13	2,750,000
Total Output	8,989,493.13	3,111,731.536
Output - Input	0	361,731.536

Table 5, carbon and CO₂ Summary

From the table it is seen that the carbon being input to the system is equal to that being emitted. This indicates that all carbon was accounted for throughout the analysis. The CO₂ however is not balanced. This is because compounds such as the methanol and hexane entered the system not as carbon dioxide. After being processed however, the carbon in those two compounds was converted to CO₂. This resulted in the emission of CO₂ that was not originally input into the system as CO₂, thus the creation of new greenhouse gases.

Chapter 3: Energy

It was important for the CO₂ balance analysis to also consider energy through the system. All energy must come from somewhere therefore a process like biodiesel production must get its energy from somewhere too. Because of the size of biodiesel production plants and the needed sunlight for photosynthesis it is most likely that the energy used will be produced from a fossil fuel burning power plant. This means that burning of fossil fuels and thus the release of CO₂ will be associated with the energy used. There are in the United States on average of 1.341 pounds of CO₂ released for every kilowatt-hour of energy produced (US DOE, 2000). From that number the CO₂ released due to energy use in biodiesel production can be calculated if the energy needed is known.

An analysis of energy needed was done for four steps in the biodiesel production process, three of them part of the dewatering stage. The steps analyzed were the membrane, centrifuge, dryer and solvent extraction. There is energy associated with all of the other steps, however that energy was not calculated in the analysis. The four chosen represent a large amount of the electrical energy needed. After examination of the energy relations for the dewatering processes and the solvent extraction, it became clear that further examination was not necessary to derive the results received. It should be noted however that if the energy calculations had been done for all stages of the production process, the result would have been an even higher amount of CO₂ being released.

Section 3.1: Membrane

The membrane stage is the first dewatering phase that the newly harvested microalgae encounter. It is estimated that 1% of the permeate leaving the membrane system will be solid biomass and the other 99% will be water (Cooney, 2009). Because the amount of biomass coming into the membrane from the photobioreactors is known to be 1,500,000gdw/day, the total permeate being processed can be calculated by equation 23.

$$(\text{biomass in}) + (\text{biomass in}) \times (100 - \text{final solid \%}) = (\text{permeate in})$$

The permeate entering the system is therefore 150,000,000 grams per day. There are 1,000,000 grams of water for every cubic meter of water giving a result of 150 cubic meters of permeate per day. The membrane process requires 0.5 kwhr per cubic meter of permeate being processed (Cooney, 2009). There are 3412.14148 BTU per kwhr. Using equation 24 the total energy in BTU needed for the membrane stage can be calculated.

$$(\text{kwhr/m}^3 \text{ permeate}) \times (\text{permeate processed}) \times (\text{BTU/kwhr}) = (\text{energy})$$

The result is 255,910.611 BTU per day required for the membrane unit.

Section 3.2: Centrifuge

The centrifuge takes the permeate from the membrane that is 1% solids and dewateres it further to be 20% solids (Benemann and Oswald, 1996). The permeate being processed by the centrifuge can be calculated similarly to that for the membrane in equation 23. From that a permeate quantity of 121,500,000 grams per day is found. The centrifuge can process 375 gallons of permeate each time it is run and requires 112 kwhr energy per centrifuge (Cooney, 2009). The permeate can be converted from grams per day to gallons per day by equation 25.

$$(\text{permeate processed}) \times (\text{m}^3/\text{gram}) \times (\text{gallons}/\text{m}^3) = (\text{gallons permeate})$$

32,096.9044 gallons of permeate per day are found to be processed. The energy associated with this quantity can be found by equation 26.

$$(\text{permeate}) / (\text{gallons}/\text{centri.}) \times (\text{kwhr}/\text{centri.}) \times (\text{BTU}/\text{kwhr}) = (\text{energy})$$

The total energy needed for the centrifuge is found to be 32709728.1 BTU per day.

Section 3.3: Dryer

The dryer is the final dewatering stage. During this step the remaining water is dried leaving only the solid biomass to be processed. The permeate is dried through evaporation of the water. Therefore the amount of water needing to be evaporated must be calculated. Equation 27 shows how this is done.

$$(\text{permeate from centrifuge}) - (\text{biomass}) = (\text{water to be evaporated})$$

It is found that 120,000,000 grams water per day need to be evaporated. This is 120,000 kilograms per day. The energy required to evaporate the water can be broken into 2 steps. First the energy needed to raise the water to the boiling point and second the energy needed to convert the water from liquid to gas. Some constants are needed for this calculation and are shown in table 6.

Specific Heat (J/kg°C)	4,186
Starting Temperature (°C)	25
Boiling Point (°C)	100
Heat of Vaporization (kJ/kg)	2,257

Table 6, Water evaporation constants

The energy needed to raise the water to its boiling point is calculated in equation 28.

$$(\text{kg water}) \times (\text{specific heat}) \times (\text{change in temperature}) = (\text{energy in J})$$

The energy to evaporate the water is calculated in equation 29.

$$(\text{kg water}) \times (\text{heat of vaporization}) \times (1000) = (\text{energy in J})$$

The total energy required to dry the water is found to be 3.08514×10^{11} Joules per day or 292,414,837.9 BTU per day.

Section 3.4: Solvent Extraction

The main energy requirement for the solvent extraction phase is that required to evaporate the hexane after separation has occurred. The energy calculation here is very similar to the energy calculation for the dryer stage. It has already been found that 14,850 L hexane need to be evaporated. Hexane has a density of 654.8 grams per liter therefore 9,723,780 g or 9,723.78 kg of hexane must be evaporated. The same constants are needed for this calculation as were for the dryer calculations. They can be found in table 7.

Specific Heat (kJ/kg°C)	2.26
Starting Temperature (°C)	25
Boiling Point (°C)	69
Heat of Vaporization (kJ/kg)	365

Table 7, Hexane evaporation constants

The energy needed to raise the hexane to its boiling point is calculated in equation 30.

$$(\text{kg hexane}) \times (\text{specific heat}) \times (\text{change in temperature}) = (\text{energy in kJ})$$

The energy to evaporate the hexane is calculated in equation 31.

$$(\text{kg hexane}) \times (\text{heat of vaporization}) = (\text{energy in kJ})$$

The total energy required to evaporate the hexane is found to be 4,516,112.383 kilojoules per day or 4,280,448.442 BTU per day.

Section 3.5: Energy Cycled Back to the System

As was mentioned earlier, some energy can be cycled back through the system. The energy received from burning the delipified biomass, polar lipids and glycerin can be used to heat the water in the dryer stage. The energy provided by burning the three byproducts can be calculated using the heat of combustion for each. Equation 32 shows the energy calculations.

$$(\text{mass of product (g)}) \times (\text{heat of combustion (cal/g)}) \times (\text{BTU/cal}) = (\text{energy})$$

Table 8 shows the heat of combustion for each substance and the energy received from burning it.

	Heat of Combustion (cal/g)	Energy (BTU/day)
Glycerin	3489	549,156.183
Delipified Biomass	4169.45525	16,121,302.9
Polar Lipids	9006.02335	5,357,232.97
Total		22,027,692.1

Table 8, Heat of combustion and energy produced in byproduct burning

The 22,027,692.1 BTU per day of energy received from the burning of biodiesel production byproducts can be recycled back to the dryer stage. Because it was found that the dryer will require 292,414,837.9 BTU per day the energy recycled can be subtracted from this amount leaving 270,387,146 BTU per day needed for drying the water.

It should be noted that in reality much of the energy available will be lost in transport and it is likely that 50% or less will truly be available for use. In this analysis however it has been assumed that no energy will be lost during transport. This is a best-case scenario therefore realistically results would not provide as much energy to be recycled.

Section 3.6: Energy Summary and CO₂ Relation

The total energy required and provided by each stage in the biodiesel production process is listed in table 9.

Energy for Membrane	255,910.611
Energy for Centrifuge	32,709,728.1
Energy for Dryer	292,414,837.9
Energy Cycled Back to System	22,027,692.1
Net Energy for Dryer (required-recycled)	270,387,146
Energy for Solvent Extraction	4,280,448.442
Total Net Energy	307,633,233

Table 9, Total energy required in biodiesel production in BTU/day

It is estimated that in the US for every kwhr of energy produced, 1.341 lbs of CO₂ are released (US DOE, 2000). The energy calculated for the production of biodiesel was 307,633,233 BTU per day or 90,158.40485 kwhr per day. There are 453.59237 grams in a pound. With these factors the grams of CO₂ released from the energy used can be calculated in equation 33.

$$(\text{energy needed in kwhr/day}) \times (\text{lb CO}_2/\text{kwhr}) \times (\text{g/lb}) = (\text{g CO}_2 \text{ released})$$

From that equation 54,840,415.64 grams CO₂ per day are found to be released due to the energy requirement of the dewatering and solvent extraction of biodiesel production.

Chapter 4: Results

Section 4.1: Carbon and CO₂ Inputs Versus Outputs

Table 10 shows a summary of all carbon and CO₂ inputs and outputs calculated in this analysis. All numeric values are in grams of carbon or CO₂ per day.

Stage of Production	Form Taken by Carbon/CO₂	Carbon In	CO₂ In	Carbon Out	CO₂ Out
Photobioreactors	CO ₂ gas	750,000	2,750,000		
Solvent Extraction	Hexane	8,223,069.77		8,140,839.07	
Solvent Extraction	Delipified Biomass with 1% Hexane			377,313.544	1,383,483
Refinement	Polar Lipids			126,450	463,650
Transestrification	Methanol	16,423.3577			
Transestrification	Glycerin			16,423.3577	60,218.9781
Transestrification	Methyl ester			328,467.153	1,204,379.56
Dewatering and Solvent Extraction	CO ₂ release from Energy Use				54,840,415.6
TOTALS		8,989,493.13	2,750,000	8,989,493.13	57,952,147.2

Table 10, Summary of all carbon and CO₂ inputs and outputs

Section 4.2: Neutrality

From the results it is apparent that microalgal biodiesel production is carbon neutral, however it is not carbon dioxide neutral. 55,202,147.17 more grams per day of CO₂ are being released than that which are consumed by the process. This is mainly due to two factors. The first is the energy consumption of biodiesel production. The vast majority of the CO₂ released was due to CO₂ associated with energy use. However, even if energy related CO₂ is removed from the analysis, CO₂ release is 3,111,731.536 g CO₂ per day. This is 361,731.536 grams per day more than is being put into the system. This imbalance is due to the fact that carbon sources in the form of hexane and methanol are being added to the system. The carbon from these two sources is being converted to CO₂ in the burning of products from the solvent extraction and transesterification stages. In that way carbon that was originally not contributing to greenhouse gas emissions is converted to carbon in the form of greenhouse gases.

Chapter 5: Conclusion

Although microalgal biodiesel has been shown to not be CO₂ neutral, that does not necessarily mean that it is not a beneficial product. After all, fossil fuels are certainly not CO₂ neutral either. By comparing biodiesel to other fuel types we can get a better idea of whether or not it is a positive transition from fossil fuel use. Table 11 shows an equivalency chart between different fuel types, showing gallons needed to produce the same amount of energy.

Fuel Type	Equivalency (US gallons)
Gasoline	1
Diesel	0.88
Biodiesel	0.96
Ethanol	1.5

Table 11, Comparison of energy content of fuel types

Of these fuel types diesel contains the most energy per unit volume and ethanol contains the least energy per unit volume. It requires more of either of the renewable fuels in order to achieve the same energy as diesel. By looking at the CO₂ release associated with each fuel type we can get a better idea of which fuel will really be better in reducing greenhouse gases. We know from the previous calculations that, not including energy use, biodiesel emits a net quantity of 3,111,731.536 g CO₂ per day to produce 375,000 g per day biodiesel. With a density

of 0.88 kg per L (Rutz and Janssen, 2007) this gives 426.1 liters, or 112.6 gallons of biodiesel. This is equivalent to 27,635.3 g CO₂ per gallon of biodiesel produced and used.

To determine the benefits of biodiesel, future research could compare the CO₂ released per unit energy of biodiesel to the equivalent CO₂ release for equivalent energy levels of fossil diesel, gasoline and ethanol.

In summary, biodiesel, like all other fuel sources, is not a perfect solution. The production of biodiesel continues to emit greenhouse gases which will contribute to global warming. The only surefire solution to eliminate transportation related CO₂ emissions with current technology would be to not burn fuels at all. This could be accomplished by simply walking and bicycling more often, rather than driving fuel consuming vehicles.

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