AN ABSTRACT OF THE THESIS OF

Bryan Kirby for the degree of Master of Science in Chemical Engineering presented on August 15, 2014

Title: Life Cycle Assessment of Algal Biofuels

Abstract approved:____

Christine Kelly

This thesis consists of three studies to better understand the environmental sustainability potential for algal-based biofuels. Initially, a comparison of recent life cycle assessments (LCA) of theoretical full-scale algal biofuel facilities was developed. These studies include varying boundaries and scope, functional units, and technology maturity assumptions. The comparison converted results from the published studies into comparable metrics, to show uniform functional units, for comparison. Some of the major parameters that drive differences in environmental impact predictions include pond vs. photobioreactor, water and nutrient recycle, algae growth rate and lipid content.

Next, a (LCA) was performed to evaluate the environmental impacts associated with the production of glucosamine and lipids in a full scale algal biorefinery. Six environmental impact categories were investigated including global warming potential (GWP), energy returned on invested (EROI), fresh water eutrophication, marine eutrophication, water depletion, and particulate matter formation. To develop the process inventory associated with the facility, a spreadsheet-based techno-economic analysis was modified, and reformatted into a Matlab-based model to improve the user-interface. A thorough breakdown of impacts for each section of the

process and sensitivity analysis for each impact category was developed. The analysis indicated that the dominating contributor for emissions was the construction of the photobioreactor (PBR) systems. Alternative reactor materials, design and construction are proposed to improve sustainability.

Finally, a study was initiated to improve understanding of anaerobic digestion of algal biomass wastes. For this study, algal bioreactors were constructed and *C. vulgaris* was cultivated in order to supply collaborators with algae biomass for anaerobic digestion studies.

Life Cycle Assessment of Algal Biofuels

By

Bryan L. Kirby

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Approved:

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Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Bryan L. Kirby, Author

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CONTRIBUTION OF AUTHORS

Dr. Christine Kelly helped review and guide me through the research to complete the manuscripts within this thesis.

Xuwen Xiang (graduate student, Kelly lab, CBEE, OSU, Corvallis, OR) developed a techno-economic assessment model for an algal glucosamine biorefinery with lipid co-production. This model was first developed in Excel and was later converted by Xuwen and myself into Matlab. I developed the user interface and charts/graphs, while Xuwen developed the equations and variables sections. This model was used for inventory inputs for the life cycle assessment preformed in section 2. All other work described in the thesis was performed by me.

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LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
CH_4	Methane
CO_2	Carbon Dioxide
CO_2eq	Carbon Dioxide Equivalent
D	Dry Lipid Extraction
EIA	Energy Information Administration
EPA	Environmental Protection Agency
EROI	Energy Returned on Invested
e.g.	Example
g	Gram
gal	Gallon
GHG	Green House Gas
ha	Hectare
H_2O	Water
kg	Kilogram
km	Kilometer
L	Liter
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
MJ	Mega Joule
m	Meter
N	Nitrogen
N_2O	Nitrous Oxide
PBR	Photobioreactor
R	Recycle
RWP	Race Way Pond
SF_6	Sulfur Hexafluoride

SSU	Source Separated Urine
SW	Sea Water
TEA	Techno-Economic Analysis
UK	United Kingdom
W	Wet Lipid Extraction
wt%	Weight Percent
WW	Wastewater

1. Introduction:

Petroleum based fuels are recognized as an unsustainable resource due to the depletion of oil deposits and the environmental impacts associated with their extraction, manufacturing and use. One possible solution to this problem is the production of renewable fuels derived from algal feedstock. Algal derived biofuels are known as 3rd generation biofuels. Unlike 1st and 2nd generation biofuels, third generation biofuels do not require sugars from food crops or highly lignocellulosic biomass. Third generation biofuels derived from algae provide numerous advantages including high lipid yields, utilization of non-arable land, and low water consumption (depending on production technology) (Farell, et al., 2010).

Certain algae strains can possess the ability to produce an assortment of byproducts depending on the species and growth conditions. The diatomic salt water species *Cyclotella sp.* has been shown to produce extracellular chitin, which can be converted into glucosamine. Glucosamine was first synthesized by Georg Ledderhose in 1876 (Ledderhose, 1876) and since its discovery has become one of the most commonly used non-vitamin, non-mineral, natural products used by adults for health reasons (Barnes, 2008). This thesis describes the environmental impacts associated with the creation of lipid derived biofuels and the production of glucosamine from algal biomass.

Life Cycle Assessment (LCA) can be used to quantify the environmental sustainability of algal biofuels. LCA is a tool that predicts the environmental impacts associated with the manufacture of a product. In this study, LCA was used to show the environmental sustainability of the production of glucosamine and lipids using diatomic algae. Several LCA's have been performed on the production of lipids in hypothetical large-scale algal biorefineries; however, these assessments show that further work is needed in the field to achieve environmental and economic sustainability.

It is hypothesized that a LCA for glucosamine with lipid co-production in a diatomic algal biorefinery can provide information to evaluate sustainability claims and guide further research and development to realize those claims. To evaluate this hypothesis, a literature review of recent algal biofuel LCAs was conducted. This review (Chapter 2) condensed the available assessments into a comparable format with equivalent functional units in order to better understand the current state of the technology. After conducting a literature review, a techno-economic analysis (TEA) was developed (See appendix A) in collaboration with Xuwen Xiang (graduate student, Kelly lab, CBEE, OSU, Corvallis, OR). Xuwen developed the model in Excel and later we converted the model into Matlab. I developed the user interface and charting, while Xuwen developed the equations and variables. Using the predictions from the TEA, I performed an LCA to examine the sustainability of the glucosamine/lipid biorefinery. An assortment of lab-scale data and literature-based data was accumulated and applied to a LCA model.

The life cycle assessment identified a potential improvement to the biorefinery process. It was hypothesized that the addition of anaerobic digestion for biogas production and nutrient recycle would be beneficial to an algal biorefinery. Section 4 depicts the constructed a photobioreactor for the production of *C. vulgaris,* in order to study the potential of anaerobic digestion.

2. Critical Review Paper

2.1 Abstract

The use of microalgae for lipid production has been under investigation for almost a half century. Publications in this subject have grown exponentially over the last 10 years. In addition to high productivity and lipid content algal biofuels take advantage other desired traits including the ability to use non-arable land, sequester CO_2 and purify wastewater streams. Despite the theoretical benefits, the economic feasibility and the commercial future of algal biofuels is difficult to predict. However it is evident algal biofuels have the potential for lower environmental impacts than petroleum fuels. LCA has been used to predict the impacts of the production and use of algal biofuels. This paper is focused on comparing some of the most recent (2009-2013) algal biofuel LCA's and determining reasons to explain the discrepancies between studies. Selling price, CO_2eq emissions, water use, productivity, and energy returns on energy invested are compared.

2.2 Introduction

Over the last six decades the use of high energy density fuels has become an integral part of the US standard of living. Fuel sources are being consumed at an accelerated rate to produce energy for our growing population (EIA, 2013). With non-renewable supplies becoming scarce and a growing concern of the environmental impacts accompanied with the use of fossil fuels, renewable fuel sources are investigated. In addition many countries with high population densities are at the cusp of industrialization, which will put a further strain on the world's fuel supplies. Thus, renewable energy technologies such as biomass, geothermal, hydro, and solar have been developed and are beginning to be implemented (EIA, 2013). However, the utilization of algal biofuels could still fill high energy density and drop in fuel gaps, in renewable fuels.

Renewable fuels from biomass can generally be classified into three main categories, first, second and third generation biofuels (Farell, et al., 2010). First generation biofuels utilize food crops (e.g. corn, soybean) to produce renewable fuels. Using a food source as the sole production energy may not be sustainable with current food demands and is certainly not sustainable with future food demands (Solomon, 2010). The use of a food crop as a fuel source also introduces ethical debates. Second generation biofuels utilize non-food resources (e.g. corn stover, switch grass, wood chips) for their high content of cellulose, which is converted to sugars and then fermented to fuels. The main drawback of cellulosic fuel production is the energy required to separate cellulose from the high fiber structures (Solomon, 2010). The emphasis of this review will be on third generation of biofuels, which utilize algae to produce lipids that can be upgraded to fuel. Biodiesel has the potential to have lower greenhouse emissions, be less toxic and more biodegradable than petroleum diesel (Demirbas, 2009). The production of algal biofuels can be achieved using non-arable land, wastewater, and can have higher areal productivities than land-based crops (Farell, et al., 2010).

Microalgae have unique characteristics that can be exploited for the production of biofuels. Similar to plants, microalgae use sunlight in the production of oil; however microalgae can do this with higher productivity. Lipid production in microalgae greatly exceeds oil production from crops such as soybean, corn oil, palm oil, etc. (Chisti, 2007). Chisti's review indicates that algae can achieve an oil content of 30 wt% (a conservative value compared to recent literature values). With high lipid content, surface productivities from microalgae can reach 58,700 L/ha, which is almost ten times greater than that of oil palm at 5,950 L/ha, and orders of magnitude larger than corn at 172 L/ha. High aerial productivity provides greater solar utilization and less land requirement, which is a key attraction to algal biofuels. Recent literature values have reported lipid content well above 30 wt% including values as high as 66.1%, 55.2% and 44% (Hsieh and Wu, 2009; Xu et al., 2006; and Widjaja et al., 2009, respectivly). Algal growth sequesters CO_2 from the atmosphere or a flue stream providing a green approach to fuel production (Chisti, 2007). With these theoretical advantages, algal-based biofuels have become a popular focus for renewable fuels technology research and development.

To better define where research and development efforts can be focused, Life Cycle Assessment (LCA) in combination with Techno-Economic Analyses (TEA) have been applied to the production of biofuels from algae. A LCA as defined by the US Environmental Protection Agency (EPA) is a “cradle-to-grave” approach to evaluate the gathering of raw materials and energy and the associated environmental impacts in the product life cycle (Guinee and Heijungs, 2005). This review will facilitate the use and comparison of 11 LCAs published between 2001 and 2013 by comparing impacts in the same units, and by identifying reasons for discrepancies. TEA and LCA results are categorized into water consumption, productivity, greenhouse gas (GHG) emissions, net energy return on energy investment (EROI), and selling price. Table 1 compiles the 11 studies and for which of the categories they provided results.

Table 1. Summary of publication used and for which category they contributed results.

Study	Lipid Content (%)	Algal Culture	Productivity	CO_2 Emissions	Water Use	EROI	Selling Price
Davis et al. (2014)		*Chlorella*	X	X			
Passell et al. (2013)	24-50	*Nannochloris sp.* and *Nannochloropsis sp.*	X	X	X	X	
Zaimes and Khanna (2013)	20	*C. vulgaris*	X	X		X	
Davis et al. (2012)	25	No specified strain	X	X			X
Brentner et al. (2011)	25	*Scenedesmus dimorphus*	X		X		
Davis et al. (2011)	25	No specified strain	X		X		X
Shirvani et al. (2011)	30	*C. vulgaris*	X	X		X	
Yang et al. (2011)	40-56.6	*C. vulgaris*	X		X		
Clarens et al. (2010)		No specified strain		X	X	X	
Jorquera et al. (2010)	29.60	*Nannochloropsis sp.*	X			X	
Stephenson et al. (2010)	40	*C. vulgaris*	X	X		X	
Lardon et al., 2009	17.5-38.5	*C. vulgaris*	X			X	

2.3 Assumptions and Methodology

Due to a lack of standardization a wide array of units can be found in current life cycle assessments of algal biofuels. Because of the varying units it is necessary to compile current data and transform the predictions into comparable units for further analysis. To perform a unit conversion the following assumptions where made, algal biodiesel was assumed to have a density of 0.88 kg/L and the energy density of algal biodiesel was assumed to be 40 MJ/kg (Vijayaraghavan and Hemanathan, 2009). These units were used to calculate the data presented in figures 1-6.

2.4 Productivity

Due to the relatively high capital costs associated with the synthesis of algal biofuel productivity is considered one of the most important parameters. Productivity from current literature varies from 13.2 to 48 g/m^2/day for raceway pond (RWP) cultivation systems and from 0.27 to 1.9 g/L/day for photobioreactor (PBR) cultivation systems (Figures 1-2). The reasons for discrepancies in these values can be associated to the assumptions regarding the growth conditions, different technologies used throughout the process, and varying data base information. For example, Davis et al. (2012) considered weather conditions, seasonal variance and site location to produce an array of seasonal and site productivities ranging from 17.6 g/m^2/day to 2.8 g/m^2/day for RWP systems. Average estimated productivity was 16.5 g/m^2/day for summer conditions and prime growing sites; however, during winter a productivity average of 6.2g/m^2/day was projected. These values are consistent with the 10-20 g/m^2/day values from Ferrell et al. (2010), a regularly cited experimental study. Volumetric productivities assumed by Jorquera et al. (2011) for RWP, Flat-Panel PBR, and Tubular PBR where taken from Richmond and Cheng-Wu (2001), Cheng-Wu et al. (2001), and Chini Zittelli et al. (1999), respectively. These values will be shown to drastically affect the LCA outputs shown in figures 3-6.

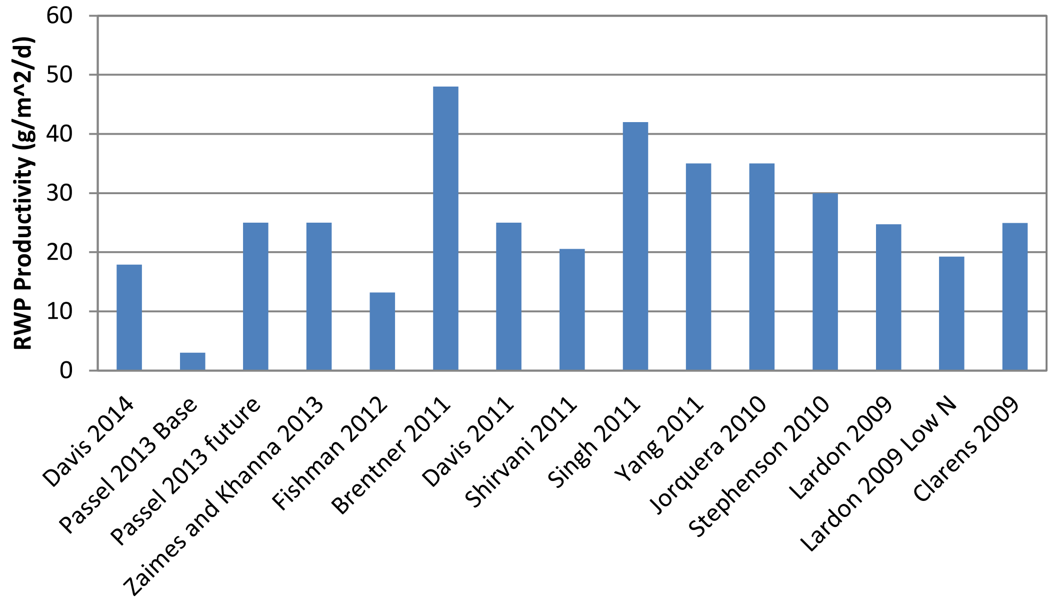

Figure 1. Summary of assumed algal productivity in race way pond (RWP) cultivation for recent LCAs of algal biofuels. Each of the studies focuses on different aspects of the process (e.g. change in cultivation location), which leads to different productivities.

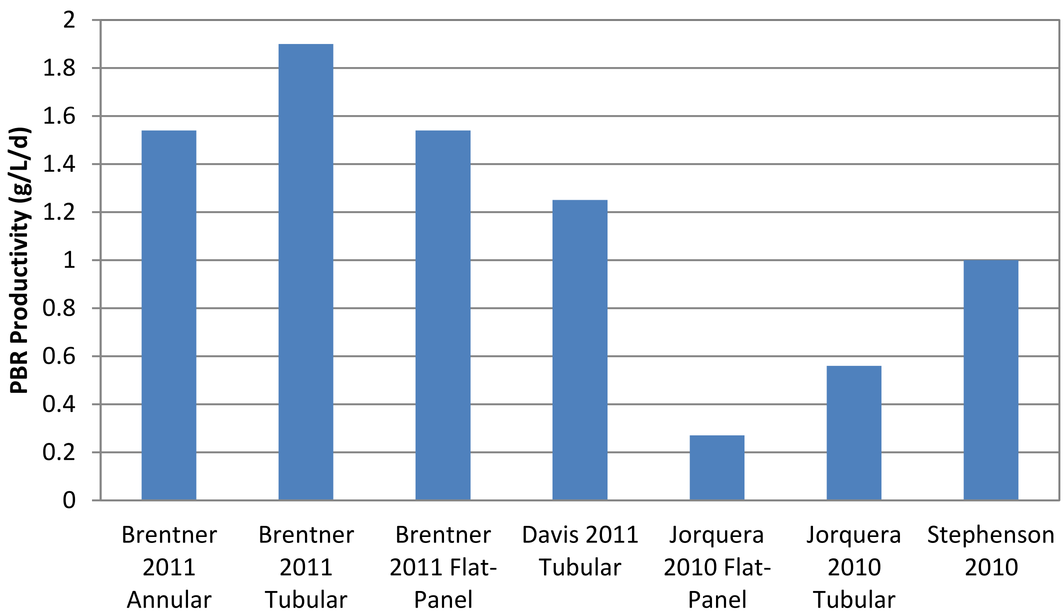

Figure 2. Summary of assumed algal productivity in photobioreactor (PBR) cultivation for recent LCAs of algal biofuels. Each of the studies focus on different aspects of the process (e.g. using wastewater sources), which leads to variable assumptions for productivities. There are fewer bioreactor analyses because of the projected high cost of bioreactors for large scale production.

2.5 Water and Nutrient Usage

One of the environmental concerns with algal biofuels is the potentially high water demand. Many studies have investigated approaches to reduce water demand, including using wastewater, brackish or sea water, and water recycling (Clarens et al., 2009). Algal cultivation processes utilize nitrogen and phosphorous from multiple sources, such as wastewater or sea water, because of this nutrient and water usage/recycle are dependent upon each other. Nutrient recycling is critical to realize the environmental benefits of algal biofuels. Phosphorus in particular is a mined nonrenewable resource that many studies suggest is relatively scarce. Recent predictions suggest a future increase in phosphorus demand with current global reserves depleting in 50-100 years (Cordell et al., 2009).

There is a wide range of water use prediction for RWPs from 3.8-13,500 (L H_2O/L biodiesel)(Figure 1). The high value of 13,500 L H_2O/L biodiesel from Clarens et al. (2010) is due to the assumption of high evaporation rates in the arid locations studied and the lack of water recycling. Stephenson et al. (2010) assumes that only 3.68 L H_2O/L biodiesel of water will be used. This prediction is low for two reasons, (1) an assumption that due to the relatively cold weather in the UK the evaporation rates will be negligible when high rain fall levels are considered, and (2) the study includes only water used in the cultivation process and excludes water use in extraction, harvesting and conversion processes. Clarens et al. (2010) and Yang et al. (2011) compared replacing freshwater with wastewater or source separated urine (SSU), and the studies predicted water use to drop by 89% and 90% respectively.

With freshwater supplies per capita diminishing rapidly in industrializing nations (Gleick, 2008), the need for a green fuel source not highly dependent on water is a necessity. Predictions of water consumption in PBR's vary from 323 to 2,230 (L H_2O/L biodiesel). These values are lower than those of their RWP counterparts because the enclosed units do not allow for evaporation. In these cases water use is accounted for in the harvesting, extraction and conversion processes, while cultivation is less water intensive. The variance in water used in a PBR facility between Brentner et al. (2011) and Davis et al. (2011) can be attributed to a variety of assumptions used in the studies. Brentner et al. (2011) predicted a water use of 221 L H_2O/L lipids; however during extraction and lipid to fuel upgrading the process increased to 2229 (L H_2O/L biodiesel).

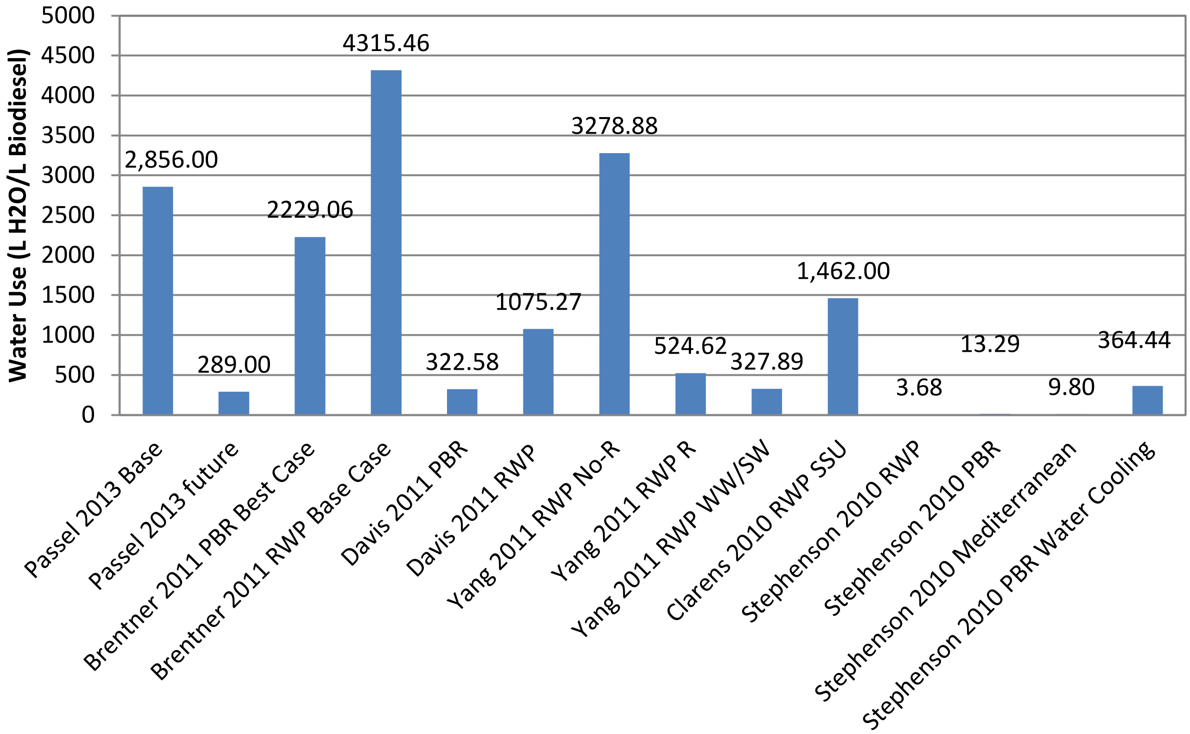

Figure 3. Summary of predicted water use for the production of algal biofuels in recent LCAs. Abbreviations: R-Recycle, WW-Waster Water, SW-Sea Water, RWP-Race Way Pond, PBR-Photobioreactor, SSU-Source-separated urine.

2.6 CO_2 Emissions

Increase in atmospheric carbon dioxide is linked with potentially dramatic global climate change. Carbon dioxide equivalent (CO_2eq) is a quantitative measurement to relate all relevant emissions to a standard of atmospheric alteration effects. Many LCAs determine the total CO_2 equivalent emissions incurred in the production of fuel. The global warming potential (GWP) of N_2O, CH_4, and SF_6 is commonly communicated in the amount of CO_2 that may cause the same amount of heat trapping. Variations in CO_2eq predictions between LCA’s can be difficult to interpret due to the varying system boundaries defined by the model. The variations in data presented in (Figure 4) can be associated to the assumptions and boundary conditions assumed in the initial studies.

CO_2 equivalent emission predictions range from 20-352 g CO_2eq/MJ biodiesel (Figure 4). PBR-based facilities tend to perform at a higher environmental impact level than RWP-based facilities due to the energy and material requirements to construct PBRs. In the LCA proposed by

Stephenson et al. (2010) the CO_2 emissions predicted for the case using a PBR system were found to be much higher than previous assessments in the field, the authors' credit this to the energy required to manufacture PBR tubes and the power required to circulate the media within the system.

Shirvani et al. (2011) presented predictions ranging from 20 to 300 g CO_2eq/MJ biodiesel. The differences in predicted emissions occur due to the use of waste products for the production of energy in the system. In Clarens et al. (2010) analysis, conventional activated sludge from waste water was used, which provided a 39% reduction in carbon emissions compared to their base case.

A goal of the Davis et al. (2012) study was to show sensitivity and variations in LCA outputs due to seasonal weather patterns. This report indicated that with low solar irradiance occurring during the winter the GHG emissions were over 20% greater than the case of a winter excluded production cycle. One of the least carbon intensive processes shown in Figure 4 (Clarens et al., 2010) did not include energy demand for the extraction of lipids or the conversion of algal oil to biodiesel. Results from the Passel et al. (2013) base case were excluded from Figure 4 due to a low productivity rate of 3 g/m^2/day. Passel et al. (2013) predicted emissions to the atmosphere to be 2880 g CO_2eq/MJ biodiesel. Stephenson et al. (2010) assumed that with the high levels of rain fall in the UK there is no need for an external water source; this assumption along with relatively high productivity rates resulted in low emission predictions due to the reduced capital equipment and material. Passel et al. (2013) predicted the production of 1 MJ of biomass energy at -34.6 g CO_2eq in Phoenix, AZ while utilizing direct injection combustion, chamber filter press, and waste heat for drying. However the authors acknowledged high technological uncertainties with the future case proposed. For these reasons it is important to further standardize LCA system boundaries to have a more comprehensive comparison between reports.

Compared to petrol-diesel and gasoline, the use of biodiesel as transportation fuel has been shown to increase particulate matter formation, nitrous oxide, and nitrogen oxides (NOx) emissions. However, biodiesel still offers a significant reduction in GHG emissions when compared to fossil fuels (Nanaki et al., 2012). For petrol-diesel, the GHG emission of the entire well-to-wheel vary between 82 and 99 g CO2eq/MJ fuel which includes 6-24 g CO2eq/MJ for well-to-tank and 73-75 g CO2eq/MJ for tank-to-wheel (Eriksson and Ahlgren, 2013), where biodiesel has CO_2 equivalent emission predictions range from -34.6-352 g CO_2eq/MJ shown in Figure 4.

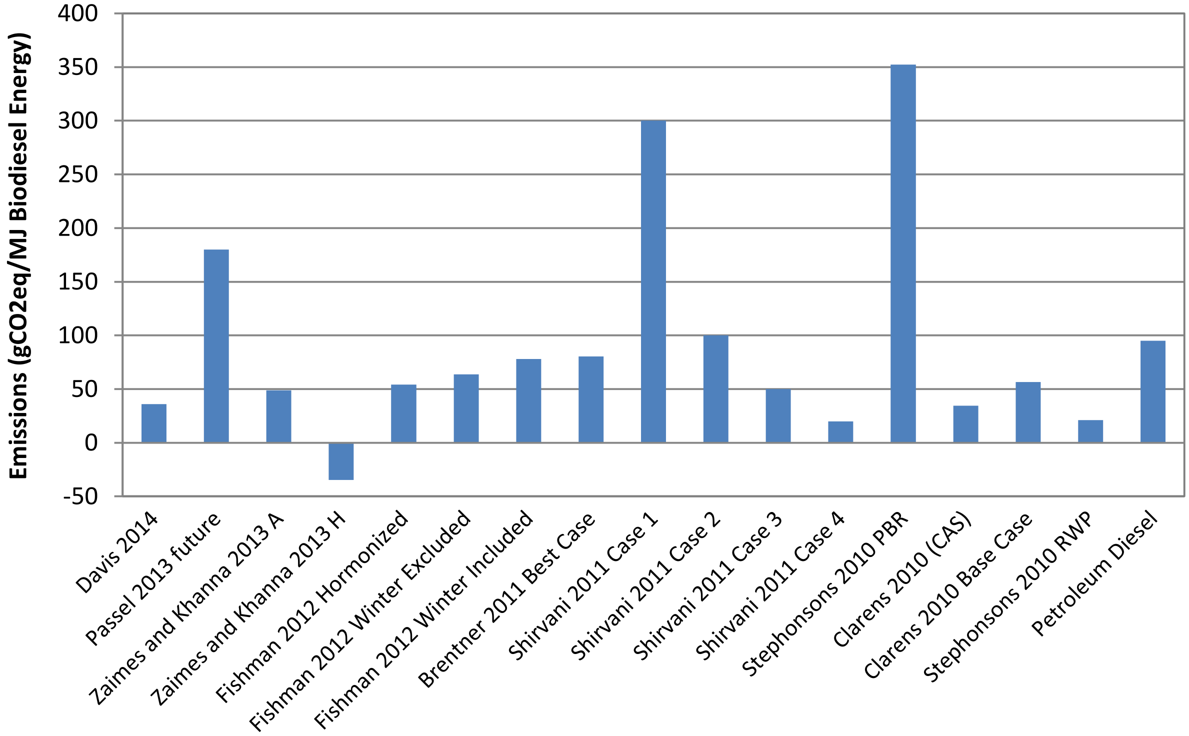

Figure 4. Summary of CO_2 Emissions predictions for current LCA's for the production of algal biofuels. Shirvani et al. (2011) cases 1-4 estimated with a carbon intensity grid of 160 g CO_{2eq}/MJ. Zaimes and Khanna (2013) predictions for Phoenix, AZ cases a and h. Petroleum diesel data taken from Davis et al. (2014). Davis et al. (2014) data for a 5 BGY Annual

2.7 Energy Returned on Energy Invested

Energy returned on energy invested (EROI) is an economic tool used to determine the energy available from a system versus the energy required by the system.

$$Energy\ Returned\ On\ Invested(EROI) = \frac{Usable\ Aquired\ Energy}{Energy\ Expended}$$

An EROI value greater than one implies that energy is being created in the sense that it takes less nonrenewable energy to produce renewable energy, the absorbed solar energy during photosynthesis is not taken into account in this energy balance. Figure 5 indicates a collection of predicted EROI's collected from recent studies.

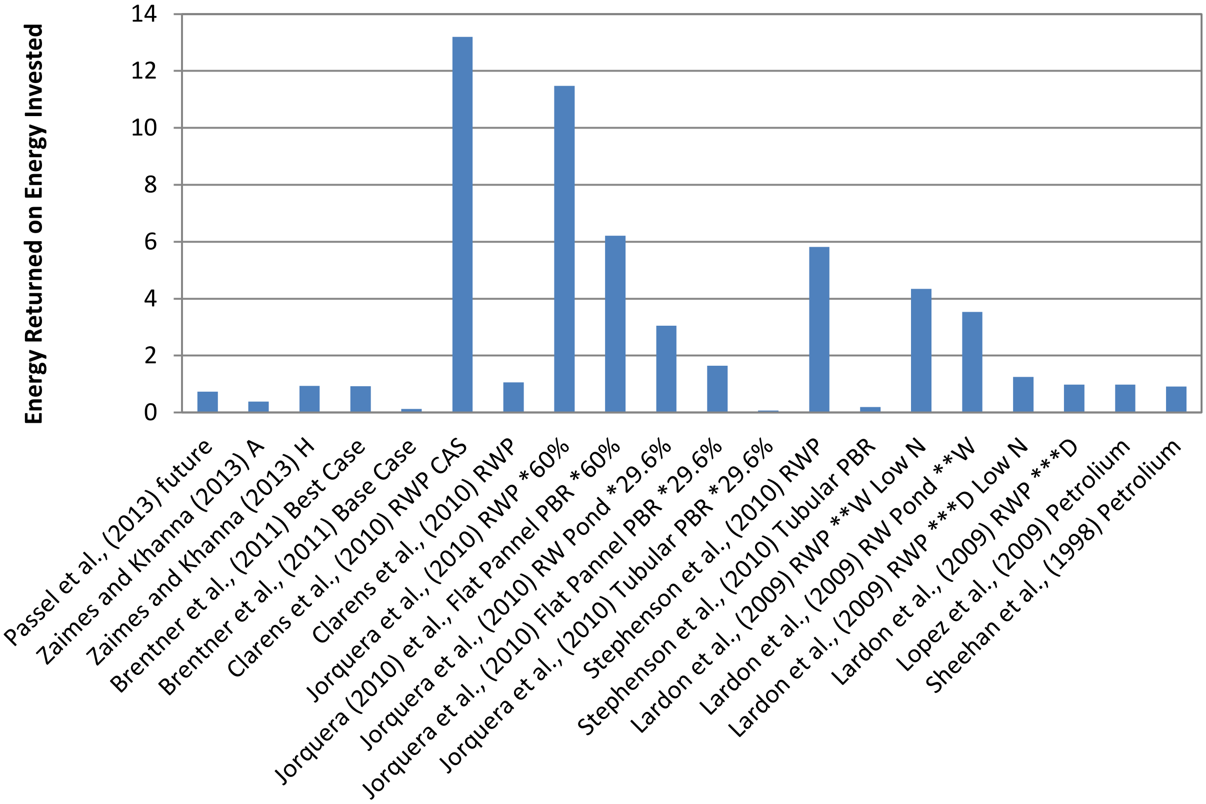

Figure 5. Summary of the EROI for the production of algal biofuels in recent LCA's. Abbreviations: * - wt. % lipids, **W - wet lipid extraction, ***D - dry lipid extraction and N - nitrogen. Zaimes and Khanna' (2013) predictions for Phoenix, AZ cases a and h.

The wide range of predicted EROI's is due to differences in the boundary conditions and assumptions in the studies. When these differences are accounted for, a comparisons between the predicted EROIs can be made, which develops an understanding of energy impacts associated with different applications, assumptions and technologies. The highest EROIs in Figure 5 are Clarens et al. (2010) and Jorquera et al. (2010). However, Clarens et al. (2010) did not include extraction of lipids and biodiesel conversion into their assessment, and Jorquera et al. (2010) also chose their system boundaries to exclude these two processes, these assumptions will artificially lower prediction. However, even with the limited information and different boundary conditions; higher lipid concentration and the use of wastewater can be shown to increase EROI. The goal of the Lardon et al. (2009) analysis was to predict the difference in wet versus dry lipid extraction and nitrogen deprivation versus regular growth conditions. These predictions show an increased EROI with nitrogen deprivation and wet lipid extraction. The energy difference between dry and wet lipid extraction was found to play a larger role than the difference between low nitrogen and normal growth parameters. Using these predictions we can begin to understand the places in which further research can be allocated in order to further reduce the energy demands of this process.

In comparison to petroleum diesel, biodiesel shows promising results. One MJ of petroleum diesel requires an input of 1.09 to 1.2 MJ of fossil energy (Sheehan et al., 1998; Lopez et al., 2009). Biodiesel has shown an EROI of 0.1-13.2 depending on the utilization of biomass and the technology assumed (Figure 5). With the possibility of higher EROI's, biodiesel could prove to be a more sustainable approach to achieving high energy density hydrocarbons.

2.8 Selling Price analysis

Few published such as the Davis et al. (2014) study include TEA modeling coupled with LCA to project costs of fuel production. These assessments shown in Figure 6 provide the predicted cost of algal biodiesel, which is the major driving force for the implementation of a sustainable process.

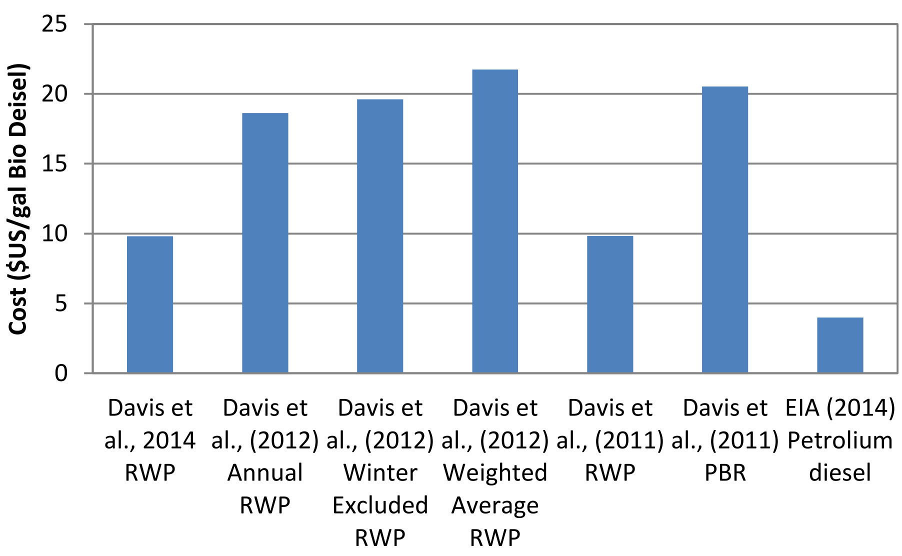

Figure 6 Projected selling prices for algal biodiesel from PBR and RWP cultivation scenarios.

In the Davis et al. (2012) study, a conservative growth rate and lipid content resulted in the high selling price. The low productivities rates assumed resulted in the high selling prices of \$21.73/gal biodiesel and \$19.60/gal algal oil projected. This report assumed the utilization of RWPs for algal growth. These prices more than double the \$9.84 selling price predicted by Davis et al. (2011) when utilizing RWPs. This discrepancy is associated with the addition of plastic liners to the algal ponds in the Davis et al. (2012) study and a lower productivity. The addition of a plastic liner to the 5 billion gallon scenario predicted by Davis et al. (2012) showed an increase in biodiesel price of \$5.50/gal. Davis et al. (2011) also predicts the increased selling price associated with the production of algal biodiesel in a PBR compared to a RWP. In a RWP production scenario, the ponds accounts for 15.4% of the biofuel selling price but 82.7% of the selling price for reactors in PBR-based facilities. With prices as high as \$21.73/gal, the economic viability of current technology is not competitive and further research will be needed to decrease these prices to competitive market values.

In order for algal biodiesel to reach economic sustainability, a target market price will have to be reached at levels that are competitive with petroleum counterparts. However, if the environmental impacts prove beneficial, subsidies using tax dollars by be justifiable. In the US during March 2014, the average price of on-highway petro-diesel was \$4.00 per gallon including taxes (12%), distribution and marketing (16%), crude oil (60%) and refining (12%)((EIA), 2014). If taxes, distribution and marketing are not included, the average price of petro-diesel in May 2014 would be \$2.88/gal with 83% from crude oil and 17% from refining. However, the cost estimations of large-scale algal biofuel are \$10-25/gal. At these levels, the economic sustainability of producing biofuel from algae is not competitive with petroleum fuel (Sun et al., 2011; Davis et al., 2012).

2.9 Sensitivity

Several authors examined the sensitivity of their environmental impact predictions to specific input variables. Davis et al. (2011) shows that by altering the lipid weight percent from 25% to 60% and increasing the productivity from 25 to 60 g/m^2/day in a RWP, selling price could drop to under \$4/gal.

For PBRs, not only do the lipid content and the productivity play a large role but the materials used to build the PBR can also drastically change the prices. PBR material and construction costs can change the selling price of algal biodiesel from $8/gal to $25/gal, when assumptions from Tapie and Bernard (1988) and Alabi et al. (2009) were both used in the Davis et al. (2011) study. In the Davis et al. (2011) assessment, it is predicted with a lipid content approaching 50% and productivities of roughly 50 g/m^2/day, the selling price of biodiesel could become competitive with fossil fuels.

Zaimes and Khanna (2013) predicted that if growth rates are dropped to 5 g/m^2/day and with a lipid content of 5 wt%, emissions could increase to 70 g CO_2eq/MJ biomass. However, under the low impact scenario predicted by Zaimes and Khanna (2013), emissions could approach 0 g CO_2eq/MJ biomass, assuming growth rates of 35 g/m^2/day and 50 wt % lipid content. If growth rates and lipid content begin to approach these theoretical maxima the implementation of algal derived biodiesel may be economically and environmentally sustainable.

2.10 Conclusion

Lipid production from algae is a promising technology for the production of renewable fuels. With the Renewable Fuel Standards 2 (EIA, 2013) federal mandate of 36 billion gallons of renewable biofuels by 2022, and a cap on current corn ethanol production, other sources of biofuels need to emerge in order to fulfill our national goal. At its current state, algal biodiesel is still economically impractical and further research and improvements are needed. Comprehensive LCA’s and TEA’s will help to define specific aspects of the production of biofuels to target which could provide dramatic improvements in environmental impacts and economic feasibility. High capital costs and low productivity are the two most limiting factors to the production of algal biofuels. Other factors that could help provide economic relief are the utilization of co-products and an improvement in lipid extraction techniques.

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3. Life Cycle Assessment of Glucosamine Production from Diatomic Algae with Lipid Co-production

By: Bryan Kirby, Xuwen Xiang, and Christine Kelly

3.1 Abstract

Algal biofuels have been studied as a potential sustainable fuel source for over a half century. Key tools in assessing the economic and environmental sustainability of this process are techno- economic analysis (TEA) and life cycle assessment (LCA). Recently many LCA's have been published that indicate producing biodiesel from algal lipids is environmentally unsustainable with current technology. Studies have shown Cyclotella sp., a marine diatom, has the ability to produce chitin fibrils and lipids while under targeted growth conditions. LCA and TEA can determine if a multi-product biorefinery, with glucosamine as a high value product, and lipid for fuel as a low value product, may be an economic and environmentally sustainable process to advance the adoption of algal biofuels. In this study, a glucosamine biorefinery with lipid co-product is considered.

3.2 Introduction

Diatomic microalgae are a potential feedstock for the production of high energy density hydrocarbons and an array of co-products. With the potential for lower environmental impacts and higher sustainability than conventional fuels, algal biofuels could be a part of the sustainable energy solution (Farell et al., 2010). In addition to the production of lipids, algae also have the ability to produce various co-products (e.g., feedstock, chitin, and biogas) that can offset the economic and environmental burdens associated with the production of biofuels (Herth & Schnepf, 1982). Lipid production in algae has been shown to exceed oil production of current feedstocks corn oil, palm oil, and soybean (Chisti, 2007).

The potential for a large scale algal biorefinery has recently been under investigation (Davis et al., 2014). Multiple products from an algal biorefinery may help provide economic sustainability (Pyle et al., 2008). Generally, fuels are a high volume product, whereas chemical, nutraceutical or other products from algae have much lower market volumes but higher market values. Market sustainability of all products is critical to economic feasibility (Davis et al., 2011); therefore, the scale of the facility was based on the potential sales of glucosamine, a much smaller scale than one based on the fuel market. The biorefinery proposed in this assessment has an annual production of 551 tons of glucosamine and 1570 tons of lipids.

The ability of algae to produce energy dense lipids has been a research focus since it was first purposed in 1942 (Witsch et al., 1942), However the production and use of co-products is a relatively new field of study. As an example, recent studies have shown how glycerol, a byproduct of lipid upgrading, can be utilized to produce docosahexaenoic acid (DHA), a drug with potential Alzheimer and cancer treatment characteristics (Pyle et al., 2008). The market volume of DHA is low however; undiscovered co-products could possess higher market volumes. Although multiple commercial algal cultivation and harvesting facilities exist (e.g. Seambiotic and Cyanotech), most synthesize high-value products (e.g. cosmetics, food supplements, and pharmaceuticals). Life cycle assessment (LCA) data for these commercial algal production sites is difficult to obtain due to proprietary information protection, which causes the need for multiple assumptions used in this assessment. In this assessment glucosamine is considered the primary product of the biorefinery due to its high economic value, and lipids, which can be upgraded into biofuels, will be considered a co-product.

Glucosamine was first synthesized by Georg Ledderhose in 1876 by the hydrolysis of chitin with hydrochloric acid (Ledderhose, 1876). Glucosamine is an amino sugar that when linked forms a polymer chain known as chitin $(C8H13O5N)_n$. Since its discovery the glucosamine nutraceutical market has escalated and as of 2007 is one the most commonly used non-vitamin, non-mineral, natural products used by adults for health reasons (Barnes et al., 2008). By 2017 the global glucosamine market is expected to reach 46.6 thousand metric tons (Global Industry Analysis, 2011). The hypothetical facility proposed here would supply 1.07% of the glucosamine market.

3.3 Goal and scope of the study

The goal of the current study was to conduct a cradle to gate (cultivation to product) LCA using a combination of published experimental data. The functional unit (also known as the reference unit) is defined as 1 kg of ≥99% purity glucosamine to meet FDA drug standards.

Further investigation is needed to show how purity will affect the process and marketing of a glucosamine product. The scope of this analysis includes the processes and materials that are required for the cultivation of micro algae, the isolation of chitin and lipids and the hydrolysis of chitin to glucosamine. Lipids are assumed to be sold at current market value and the CO_2 sequestered in the cultivation of the algae is counted as a reduction in carbon emissions, as commonly done in published LCAs for biofuels (Passell et al., 2013). Current market value of algal lipids was assumed to be 3 US$/gal (Dufreche et al., 2012), 80% of current U.S. diesel prices of 3.892$/gal (EIA, 2014). A conservative base-case was developed to examine the economic and environmental impacts of the production of glucosamine using currently available technologies. A sensitivity analysis was developed on the base-case to identify key parameters for environmental impacts. An aggressive-case was developed to predict how reasonable improvements in the existing technology would impact economic and environmental sustainability.

3.3.1 Data sources

Growth rate and cell density for Cyclotella sp., a marine diatom was extrapolated from low concentration growth rates from Ozkan et al., (2014). Energy requirements and nutrient use for harvesting through product isolation were taken from Xiang et al., (2014). Material inventory data was obtained from SimaPro 7.2 Professional database and Fawer, Concannon, & Rieber (1999). Material inventory data includes all nutrients, water, and materials in the life cycle inventory (Table 4). SimaPro libraries and databases are a compilation of published and peer reviewed life cycle inventory studies that cannot be altered in SimaPro.

3.3.2 Impact assessment methodologies

Eight impact categories were considered in this assessment (Table 2). These impact assessments are considered midpoint indicators, a midpoint indicator is measurable emission produced. Global warming potential (GWP) is based on studies by the International Panel on Climate Change (IPCC 2007 GWP 20a). This method reports data as kg CO_2-eq, which is calculated by normalizing the impacts of multiple greenhouse gasses (e.g. SO_x, NO_x) to that of CO_2. Energy returned on invested (EROI) is assessed using total energy created (energy density of lipid production) divided by the cumulative energy demand (CED). This assessment does not consider lipid upgrade energy requirements, due to the current high level of understanding of this process. Particulate matter formation measures the human health impacts of fine particles that form in the atmosphere when gaseous pollutants such as SO2 and NOx react (Environmental Protection Agency, 2012). ReCiPe Midpoint was used to calculate kg PM10-eq, a normalized particulate matter formation indicator, water depletion, freshwater eutrophication, and marine eutrophication. NOx and SOx results provide the total emissions of nitrogen oxides and sulfur oxides.

The methodologies for calculating each impact category are according to global standards. CED is based on the method published by ecoinvent version 1.01 and expanded by PRé consultants of SimaPro (Cumulative Energy Demand, 2014). IPCC 2007 is a methodology that has been updated from previous versions, and was developed by the International Panel of Climate Change. IPCC 2007 20a lists the climate change factors according to IPCC for a 20 year timeframe (IPCC, 2007). ReCiPe originated from the collaboration of 50 LCA experts following the Society of Environmental Toxicology and Chemistry (SETAC) conferences. It was jointly concluded that a common framework was needed in which midpoint and endpoint indicators could be used (Goedkoop et al., 2009).

Table 2. Impact categories estimated for the glucosamine algal biorefinery

Impact category	Unit of measure
EROI (Energy returned on invested)	MJ/MJ
GWP (Global warming potential)	kg CO_2-equivalents
NO_x (Nitrogen oxides)	kg NO_x
PM (Particulate matter) formation	kg PM10-eq
SO_x (Sulfur oxides)	kg SO_x
Water depletion	m^3
Freshwater eutrophication	kg P eq
Marine eutrophication	kg N eq

3.3.3 System boundaries

The boundaries of the biorefinery system include algae cultivation, harvesting, dewatering, lipid extraction, and extraction and hydrolysis of chitin (Figure 7). Table 5 depicts the production with unit processes at each stage. Transportation of materials, nutrients and chemicals was assumed to be 161 km (100 miles) similar to assumptions used in Ferell et al. (2010). Materials and energy related with construction of infrastructure have low impact on the

LCA output values and thus were excluded from this study to match current LCAs (e.g., Passel et al., 2013 and Campbell et al., 2011).

3.3.4 System description

A conservative base-case scenario and a future aggressive one were examined for the commercial production of glucosamine. In both cases, an airlift photobioreactor is used for algal cultivation. Similar to other LCA studies (e.g. Passell et al., 2013), CO2 flue gas sequestered during cultivation is counted as a reduction in carbon emissions. Photobioreactors are assumed to use poly(methyl methacrylate) (PMMA) tubes; however, in SimaPro the bioreactor materials are modeled as PMMA extruded sheets with identical mass that would be required for the tubes. Chitin extraction and hydrolysis data is modeled from a hypothesized dual centrifugation process depicted in Figure 7. The aggressive-case is modeled using hypothetical extrapolation of data used in the base-case to demonstrate feasible technological strides in this process. Table 3 displays these key process parameters derived from lab scale experiments by Chotyakul et al., (2014, Manuscript in review). The base-case inputs are taken from Xiang et al., (2014). The aggressive-case inputs are hypothesized goals extrapolated from data by Ozkan et al., (2014).

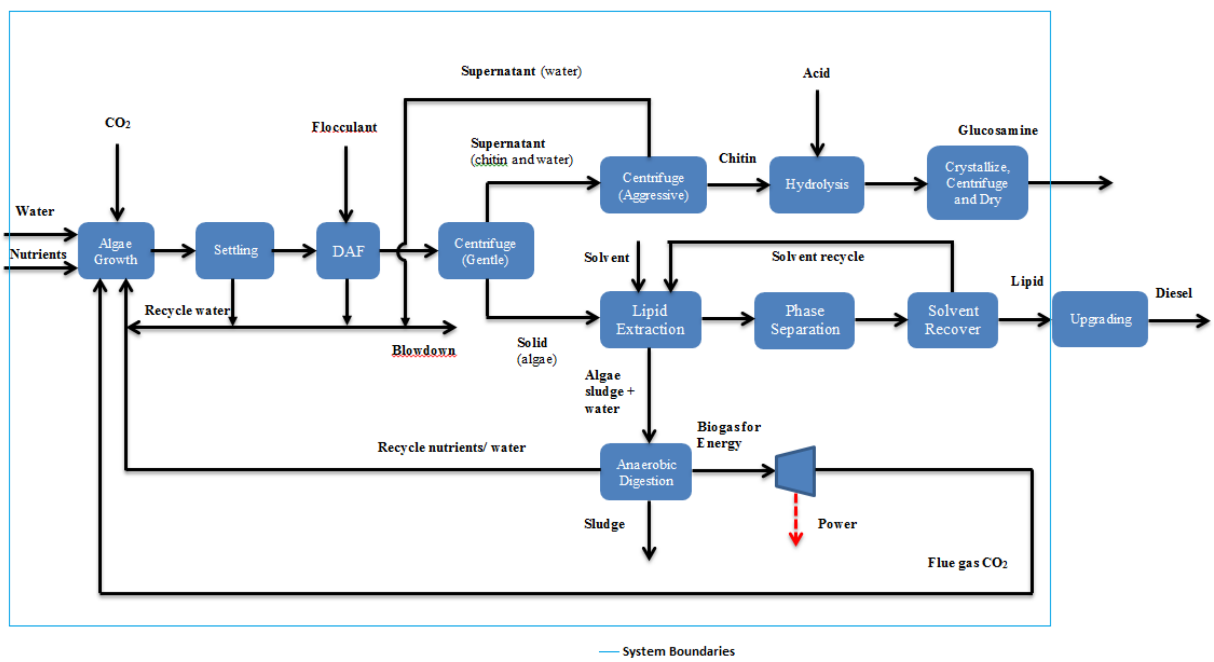

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Figure 7. Process flow diagram of purposed glucosamine biorefinery with lipid co-product. The thin blue line represents the boundary of the LCA

Table 3. Key process characteristics for the base- and aggressive-case

Input	Base Case	Aggressive Case
Lipid yield (dry wt.%)	30	35
Chitin yield (dry wt.%)	25	30
Productivity (g/L-day)	0.5	1.0
Operating days/yr	330	330
Scale (ton glucosamine/yr)	551	551
Lipid isolation (%)	80	95
Chitin extent of hydrolysis (%)	50	75
Chitin isolation (%)	80	90
Glucosamine produced (ton)	551	551
Lipids produced (ton)	1507	905.7

3.4 Life cycle inventory

A base-case LCA was developed to assess the environmental sustainability of a full scale biorefinery with glucosamine as a byproduct. The assumptions and inventory are detailed below in Table 4.

Table 4. Life cycle inventory of the base-case biorefinery (adapted from Xiang, 2014)

Life Cycle Inventory Base-Case			
Known Inputs to the technosphere (electrical/heat)	**Quantity**	**Units**	**Comments**
DAF (Dissolved air flocculation)	7.31E5	kWh	
Centrifuge	3.17E5	kWh	
Liquid-liquid extraction	1.05E6	kWh	
Stripping column	3.02E5	kWh	
Anaerobic digestion	4.85E5	kWh	
Combined heat and power	-2.25E6	kWh	
Transportation of nutrient	4.95E4	tkm	
Transportation of materials	1.02E6	tkm	
Known Inputs to the technosphere (materials/fuels)			
Extruded PMMA (Poly(methyl methacrylate))	6.79E4	ton	Extruded as sheets
Hexane, at plant	5.7	ton	
Diammonium phosphate, as P_2O_5	1.37E2	ton	
Ammonia	1.71E2	ton	
Sodium meta silicate	1.10E3	ton	
Known inputs from technosphere (resources)			
Salt/Ocean water	5.44E8	m^3	
Emissions to air			
Carbon dioxide	-7.95E3	ton	Sequestered
Carbon dioxide	3.97E1	ton	Non-sequestered
Emissions to water			
Ammonia, as N	1.71	ton	Waste after recycle
Phosphate	1.37	ton	Waste after recycle
Silicon	1.10E1	ton	Waste after recycle
Hexane	1.13E-2	ton	Waste after recycle
Products			
Glucosamine	551	ton	
Lipids	1091	ton	

3.4.1 Coproduct Allocation

The allocation of impacts with respect to product (glucosamine) and co-product (lipid) is a key decision in LCA. In this scenario allocation of co-product was determined on a weight sliding economic basis (Equations 1). Equation 1 is applied to the base-case in equations 2-3. The percent allocation determines what percentage of an impact belongs to a product.

$$\frac{(ton\ produced\ \times market\ value\ of\ product)}{(ton\ produced\ \times market\ value\ of\ product) + (ton\ co\ product\ produced\ \times market\ value\ of\ co\ product)} \times 100 \qquad (1)$$

$$\frac{\left(551\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{20\ \$US}{1\ kg}\right)}{\left(\left(551\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{20\ \$US}{1\ kg}\right) + \left(1570\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{0.88\ L}{1kg} \times \frac{0.2642\ gal}{1\ L} \times \frac{3\ \$US}{1\ gal}\right)\right)} \times 100 = 90.07\ \% \qquad (2)$$

$$\frac{\left(1570\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{0.88\ L}{1kg} \times \frac{0.2642\ gal}{1\ L} \times \frac{3\ \$US}{1\ gal}\right)}{\left(\left(551\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{20\ \$US}{1\ kg}\right) + \left(1570\ ton\ \times \frac{907.185\ kg}{1\ ton} \times \frac{0.88\ L}{1kg} \times \frac{0.2642\ gal}{1\ L} \times \frac{3\ \$US}{1\ gal}\right)\right)} \times 100 = 9.03\ \% \qquad (3)$$

3.5 Results and Discussion

The base-case key parameters inputs include 30% lipids, 25% chitin, and a productivity of 0.5 g/L-day. Table 3 indicates additional base-case parameters. GWP, NO_x and SO_x were calculated using IPCC 2007 GWP 20a in SimaPro 7. PM10 eq, water depletion, freshwater eutrophication and marine eutrophication were calculated using ReCiPe Midpoint (I) World ReCiPe I in SimaPro 7. Results for the base- and aggressive-cases can be seen in Table 5.

EROI (Equation 4) was only calculated on lipid co-product due to the projected use of the product as a fuel source.

$$EROI = \frac{1kg\ Lipid * \frac{40\ MJ}{1\ kg}}{Cumulative\ Energy\ Demand} \qquad (4)$$

Table 5. Potential environmental impacts for the base- and aggressive–case commercial glucosamine biorefinery

Life Cycle Assessment Results (Functional unit 1 kg glucosamine and associated mass of algal lipid co-product)					
Impact Category	Base Case Lipids	Base Case Glucosamine	Aggressive Case Lipids	Aggressive Case Glucosamine	Units
EROI (Energy returned on invested)	3.2E-01	N/A	9.7E-01	N/A	MJ/MJ
GWP (Global Warming Potential)	1.0E+01	2.9E+02	3.2E+00	7.0E+01	kg CO_2-equivalents
NO_x (Nitrogen Oxides)	1.4E+01	4.0E+02	4.7E+00	1.0E+02	kg NO_x
PM (Particulate Matter) formation	1.0E-02	2.9E-01	3.4E-03	7.6E-02	kg PM10-eq
SO_x (Sulfur Oxides)	5.5E+00	1.6E+02	4.9E+00	1.1E+02	mg SO_x
Water Depletion	2.0E-02	5.8E-01	7.1E-03	1.6E-02	m^3
Freshwater Eutrophication	1.3E-03	3.7E-02	7.3E-04	1.6E-02	kg P eq
Marine Eutrophication	6.5E-03	1.9E-01	3.3E-03	7.4E-02	kg N eq

If algal lipids are assumed to have an energy density of 40MJ/kg, the global warming potential for the base-case is 250.75 g CO2/MJ, which is slightly above reported values of Davis et al. (2014), and Passell et al. (2013) with predictions of 50 and 180, respectively. However these reports are for RWP growth productions. When our results are compared to PBR setups in the Brentner et al., (2011) and Stephenson et al., (2010) assessments, predictions of 80.5 and 352, respectively our results are in range. Fluctuations resulting in a large range are due to assessment assumptions and differences in technologies.

The aggressive-case shown above has a GWP of 79 g CO2/MJ which is well within RWP predictions. As seen from Table 6, the process breakdown for GWP, it is clear that PBR material is still the dominate pollutant in this production process, accounting for over 100% of the total output after accounting for credits (sequestered CO2 and CHP). Even with large volumes of photobioreactors, the environmental impacts of a large scale biorefinery with glucosamine as a co-product are competitive with large scale RWP bio refineries that do not produce high valued co-products. However, if this setup is further scaled up over saturation of the glucosamine market could occur. When compared to the base case and the aggressive case in Table 5 values determined in this study are competitive (values in table 5 exclude lipid upgrading and biofuel burning). Predictions by Passell et al. (2013) show a future case with large scale extrapolations with GWP, WD, NER, NOx, SOx, and kg PM10 for 1kg of burned algal biodiesel to be 7.2, 0.324, 0.729, 0.092, 0.0112, and 0.006, respectively. This is important when comparing this work with a study that includes biofuel use.

Tables 6-13 depict the process breakdown for each impact. The production itself consists of all waste streams including nitrogen, phosphorus, silicon, hexane, biomass and the CO2 sequestered and released from the cultivation process. The emissions released during this process are dominated solely by the polymer production and extrusion of the PMMA tubes. For each indicator, the assessment was performed with the PMMA tubes excluded to better determine ways to improve the system. GWP of the process, without considering PBR production, has a net negative CO2 eq. However, the high electrical demand of liquid-liquid extraction is a potential research focus to help lower carbon and NOx emissions. SOx emissions are largely dominated by material and nutrient delivery and production. Introducing better nutrient recycle through sources similar to anaerobic digestion would help lower fresh nutrient demand, by increasing nutrient recycle and introducing energy recovery. Fresh and marine water eutrophication is dominated by process waste streams including unused biomass, nitrogen and phosphorus, which would also benefit from nutrient recycle.

A potential improvement in biomass and nitrogen waste streams may be achieved through recycle and anaerobic digestion. This process investigated a marine water diatom (*Cyclotella sp.*) and thus the depletion of fresh water is dominated by production of nutrients and not cultivation of algae. However it is unclear if photobioreactor cooling with freshwater will be necessary and if so this could introduce large volumes of water depletion. Particulate matter formation can be accredited to nutrient production and high energy requirements in liquid-liquid extraction processes. These predictions can indicate research areas in which we could provide the greatest improvement in a biorefinery.

Table 6. Process Breakdown for GWP of base case for 1kg lipid

Process Breakdown for GWP			
Process / Material	kg CO_2 eq	Percent of Total	*Percent of total without PBR
**Production	-4.59E-01	-4.59	147.17
Sodium Meta Silicate	6.41E-02	0.64	-20.55
Ammonia E	3.10E-02	0.31	-9.94
Diammonium Phosphate	1.59E-02	0.16	-5.10
Hexane	4.00E-03	0.04	-1.28
PMMA (PBR Tubes)	1.03E+01	103.10	N/A
DAF	4.21E-02	0.42	-13.50
Centrifuge	1.52E-02	0.15	-4.87
Stripping Column	1.83E-02	0.18	-5.87
Liquid-Liquid Extraction	7.30E-02	0.73	-23.41
Anaerobic Digestion	3.35E-02	0.34	-10.74
Combined Heat and Power	-1.56E-01	-1.56	50.02
Nutrient Transportation	2.79E-04	0.00	-0.09
Material Transportation	5.74E-03	0.06	-1.84

*Percent of total without PBR has a net negative CO_2 emissions, thus a larger percent is beneficial

** Production includes all waste streams (nitrogen, silicon, biomass, hexane, and phosphorus) and sequestered CO_2

Table 7. Process Breakdown for NO_x of base case for 1kg lipid

Process Breakdown for NO_x			
Process / Material	kg NO_x eq	Percent of Total	Percent of total without PBR
Production	0.00E+00	0.00	0.00
Sodium Meta Silicate	3.37E-02	0.24	18.04
Ammonia E	2.43E-02	0.17	13.03
Diammonium Phosphate	4.42E-02	0.32	23.68
Hexane	8.98E-04	0.01	0.48
PMMA (PBR Tubes)	1.39E+01	98.67	N/A
DAF	7.35E-02	0.52	39.37
Centrifuge	2.66E-02	0.19	14.22
Stripping Column	3.19E-02	0.23	17.11
Liquid-Liquid Extraction	1.27E-01	0.91	68.24
Anaerobic Digestion	5.85E-02	0.42	31.34
Combined Heat and Power	-2.72E-01	-1.94	-145.46
Nutrient Transportation	1.73E-03	0.01	0.92
Material Transportation	3.55E-02	0.25	19.03

Table 8. Process Breakdown for SO_x of base case for 1kg lipid

Process Breakdown for SO_x			
Process / Material	mg SO_x eq	Percent of Total	Percent of total without PBR
Production	0.00E+00	0.00	0.00
Sodium Meta Silicate	3.11E-01	5.61	5.61
Ammonia E	0.00E+00	0.00	0.00
Diammonium Phosphate	0.00E+00	0.00	0.00
Hexane	0.00E+00	0.00	0.00
PMMA (PBR Tubes)	0.00E+00	0.00	N/A
DAF	0.00E+00	0.00	0.00
Centrifuge	0.00E+00	0.00	0.00
Stripping Column	0.00E+00	0.00	0.00
Liquid-Liquid Extraction	0.00E+00	0.00	0.00
Anaerobic Digestion	0.00E+00	0.00	0.00
Combined Heat and Power	0.00E+00	0.00	0.00
Nutrient Transportation	2.42E-01	4.37	4.37
Material Transportation	4.98E+00	90.01	90.01

Table 9. Process Breakdown for EROI of base case for 1kg lipid

Process Breakdown for EROI			
Process / Material	EROI	Percent of Total	Percent of total without PBR
Production	0.00E+00	0.00	0.00
Sodium Meta Silicate	2.31E-01	0.19	18.83
Ammonia E	4.25E-01	0.34	34.73
Diammonium Phosphate	1.80E-01	0.14	14.70
Hexane	2.33E-02	0.02	1.91
PMMA (PBR Tubes)	1.23E+02	99.02	N/A
DAF	4.56E-01	0.37	37.24
Centrifuge	1.65E-01	0.13	13.45
Stripping Column	1.98E-01	0.16	16.18
Liquid-Liquid Extraction	7.90E-01	0.63	64.55
Anaerobic Digestion	3.63E-01	0.29	29.64
Combined Heat and Power	-1.68E+00	-1.35	-137.60
Nutrient Transportation	3.60E-03	0.00	0.29
Material Transportation	7.41E-02	0.06	6.05

Table 10. Process Breakdown for freshwater eutrophication of base case for 1kg lipid

Process Breakdown for Freshwater Eutrophication			
Process / Material	kg P eq	Percent of Total	Percent of total without PBR
Production	7.69E-04	60.45	80.27
Sodium Meta Silicate	6.60E-06	0.52	0.69
Ammonia E	2.32E-09	0.00	0.00
Diammonium Phosphate	1.70E-04	13.37	17.75
Hexane	8.89E-08	0.01	0.01
PMMA (PBR Tubes)	3.14E-04	24.69	N/A
DAF	1.94E-05	1.53	2.03
Centrifuge	7.02E-06	0.55	0.73
Stripping Column	8.44E-06	0.66	0.88
Liquid-Liquid Extraction	3.37E-05	2.65	3.51
Anaerobic Digestion	1.55E-05	1.22	1.61
Combined Heat and Power	-7.18E-05	-5.64	-7.49
Nutrient Transportation	0.00E+00	0.00	0.00
Material Transportation	0.00E+00	0.00	0.00

Table 11 Process Breakdown for marine eutrophication of base case for 1kg lipid

Process Breakdown for Marine Eutrophication			
Process / Material	kg N eq	Percent of Total	Percent of total without PBR
Production	4.40E-03	67.37	99.61
Sodium Meta Silicate	2.90E-06	0.04	0.07
Ammonia E	5.01E-06	0.08	0.11
Diammonium Phosphate	3.17E-06	0.05	0.07
Hexane	6.06E-08	0.00	0.00
PMMA (PBR Tubes)	2.11E-03	32.36	N/A
DAF	7.40E-06	0.11	0.17
Centrifuge	2.67E-06	0.04	0.06
Stripping Column	3.22E-06	0.05	0.07
Liquid-Liquid Extraction	1.28E-05	0.20	0.29
Anaerobic Digestion	5.89E-06	0.09	0.13
Combined Heat and Power	-2.73E-05	-0.42	-0.62
Nutrient Transportation	7.17E-08	0.00	0.00
Material Transportation	1.48E-06	0.02	0.03

Table 12. Process Breakdown for particulate matter formation of base case for 1kg lipid

Process Breakdown for PM10 eq			
Process / Material	kg PM10 eq	Percent of Total	Percent of total without PBR
Production	0.00E+00	0.00	0.00
Sodium Meta Silicate	3.04E-05	0.30	15.88
Ammonia E	1.25E-05	0.12	6.55
Diammonium Phosphate	9.87E-05	0.96	51.55
Hexane	7.41E-07	0.01	0.39
PMMA (PBR Tubes)	1.01E-02	98.13	N/A
DAF	6.14E-05	0.60	32.03
Centrifuge	2.22E-05	0.22	11.57
Stripping Column	2.67E-05	0.26	13.91
Liquid-Liquid Extraction	1.06E-04	1.04	55.51
Anaerobic Digestion	4.88E-05	0.48	25.49
Combined Heat and Power	-2.27E-04	-2.21	-118.32
Nutrient Transportation	4.84E-07	0.00	0.25
Material Transportation	9.96E-06	0.10	5.20

Table 13. Process Breakdown for water depletion of base case for 1kg lipid

Process Breakdown for Water Depletion			
Process / Material	m^3	Percent of Total	Percent of total without PBR
Production	0.00E+00	0.00	0.00
Sodium Meta Silicate	6.64E-05	0.33	4.61
Ammonia E	0.00E+00	0.00	0.00
Diammonium Phosphate	1.30E-03	6.46	90.44
Hexane	2.22E-06	0.01	0.15
PMMA (PBR Tubes)	1.87E-02	92.86	N/A
DAF	1.10E-04	0.54	7.62
Centrifuge	3.97E-05	0.20	2.75
Stripping Column	4.77E-05	0.24	3.31
Liquid-Liquid Extraction	1.90E-04	0.94	13.20
Anaerobic Digestion	8.74E-05	0.43	6.06
Combined Heat and Power	-4.06E-04	-2.01	-28.14
Nutrient Transportation	0.00E+00	0.00	0.00
Material Transportation	0.00E+00	0.00	0.00

3.5.1 Bioreactor

The largest emissions process in a biorefinery is the construction and materials of multiple bioreactors as shown in Tables 6-13. After consultation with Marine Polymer Technologies, a company based out of Boston Massachusetts that develops algal chitin products, it is unclear if a

20 year life frame for the bioreactor tubes is a realistic expectation. Marine Polymer Technologies suggested that with continual use the bioreactor material can become opaque and result in decreased light delivery to the bioreactor. If this is found to decrease growth rates, replacement could be necessary, which would result in further emissions and costs. In past life cycle assessments, it has been suggested that the use of an open water pond would decreases emissions and costs (Farell, 2010 and Davis, 2011). However, open water ponds introduce drawbacks of their own. When using a photobioreactor, targeted nutrient control may be possible, which may not practical in a race way pond (Ozkan, 2014). Also race way ponds can be contaminated when growing a strain of algae that is a poor competitor (Farell, 2009). Growth rates have also been proven to decrease in ponds when compared to bioreactors (Davis, 2011).

If a PBR will be used in a commercial scale biorefinery, it is important to invest in the improvement of these systems in order to decrease costs and emissions. It may be possible to lower emissions by investigating the materials and its properties (Dunbar et al, 2014). PMMA is durable, but can become opaque. Depending on the material and orientation chosen it could be possible to decreases wall thickness from 0.3cm Jorquera et al. (2010). Another option is to investigate new forms of bioreactors similar to NASA’s OMEGA project which employs floating bioreactors (Dunbar et al, 2014). Floating bioreactors would require less rigid material, due to the lack of structural strength needed to keep a PBR upright on land.

3.6 Sensitivity Assessment

An analysis was performed to investigate the sensitivity of the predicted potential environmental impacts to the input parameters of cultivation residence time, algal content, lipid content, final cultivation biomass concentrations, chiton isolation efficiency and glucosamine conversion efficiency. The value each of the above base-case parameters was increased and decreased (holding all other constant) and the potential environmental impact determined (Figures 8-16). A steep slope on these sensitivity analysis figures indicates that the predicted environmental impact changed significantly with a change in the input parameter (i.e. that impact was sensitive to the input parameter).

It is clear from the sensitivity assessment that chitin content, which effect nutrient intake, energy use of downstream equipment, and photobioreactor size, have large effects on SOx (Figures 15 and 16). Final algal concentration and residence time directly affect algal productivity and therefore change the number of photobioreactor required while leaving downstream processing after centrifugation untouched. These assumptions play a large role in CO2 eq, and PM10 eq emission calculations (Figures 8 and 9). Chitin extraction and glucosamine conversion efficiencies prove to be crucial to the purposed biorefinery. Efficiencies of these two steps not only impact the number of photobioreactors needed to produce 551 ton/yr of glucosamine, but also the size of all the steps between harvesting and the final product. Because of the change of both downstream processes and number of photobioreactors, chitin isolation efficiency and glucosamine conversion efficiency play large roles in all 9 sensitivity assessments (Figures 8-16).

Lipid is considered a co-product and glucosamine is the desired product set at 551 ton/yr. Figures 8-16 show lipid content playing a minor role in the environmental impacts of this process due to low allocation of impacts to the lipid product compared to the glucosamine product. With lipid production not fixed a decrease in lipid production will not increase the need for PBR systems; therefore lipid production proves to impact EROI less than expected (Figure 10). Chitin content directly affects the number of photobioreactors, as well as downstream processes, and this is why emissions and energy returned are effected significantly with respect to chitin content.

In all 9 sensitivity assessments residence time has a linear relationship with the impact category. This is due to a linear increase in bioreactors with a longer residence time. Because residence time only increases the number of photobioreactors and does not increase any downstream processes, this input should provide a liner relationship (Figures 8-16). Chitin content, chitin isolation efficiency, algal concentration and glucosamine conversion efficiency will all affect the number of photobioreactors as well as downstream processing. The effect on downstream processing and number of photobioreactors results in a non-linear relationship.

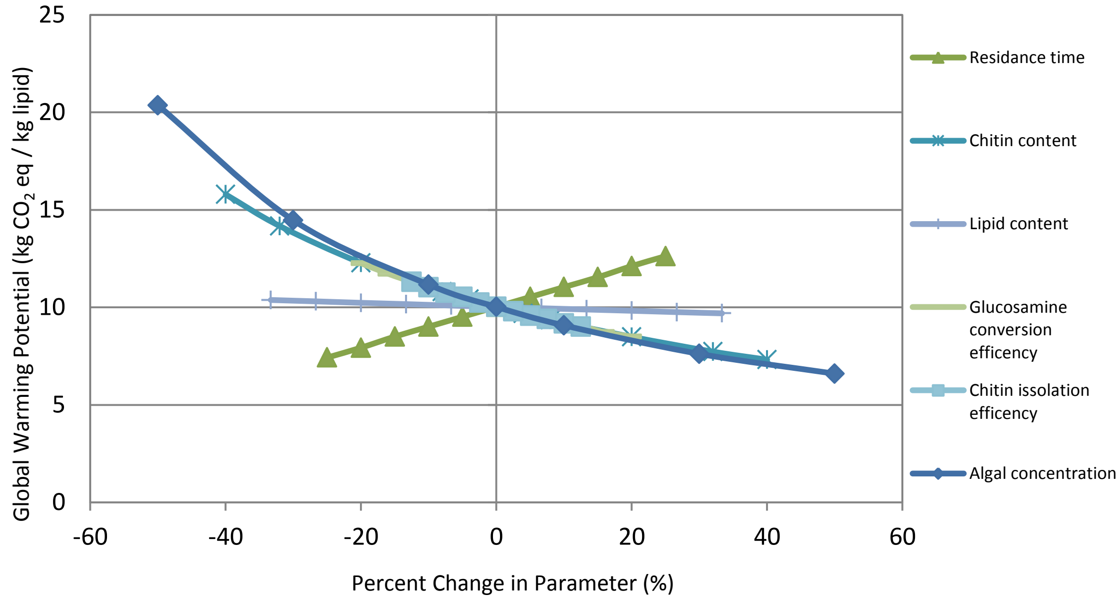

Figure 8. The effect of changes in input parameters on the global warming potential (kg CO_2-eq) for the production of 1 kg lipid.

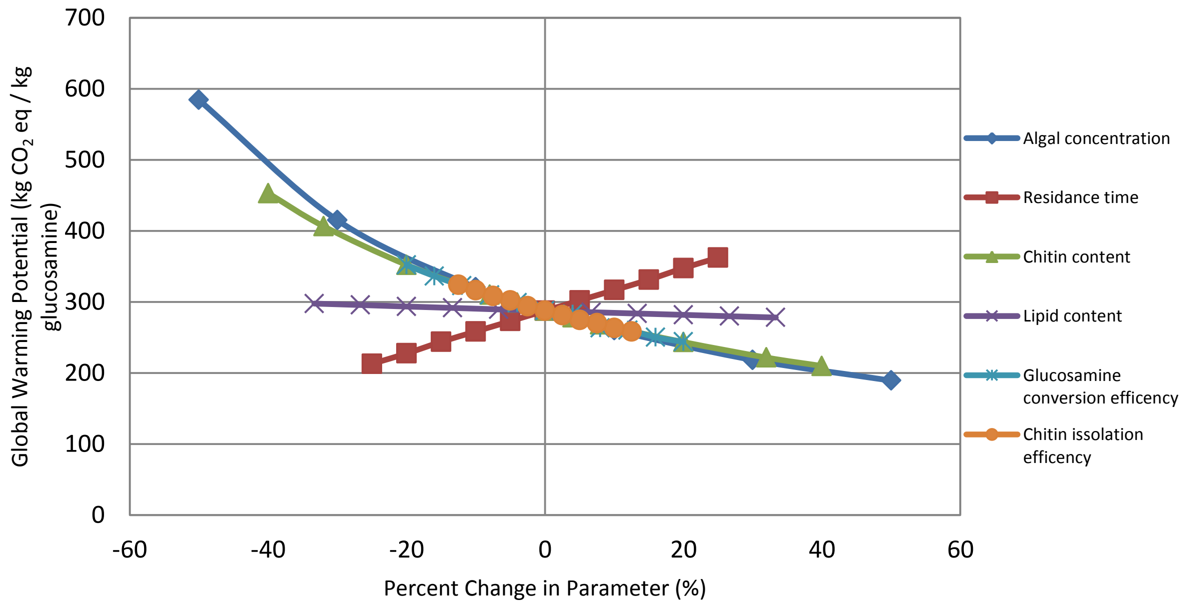

Figure 9. The effect of changes in input parameters on the global warming potential (kg CO_2-eq) for the production of 1 kg glucosamine.

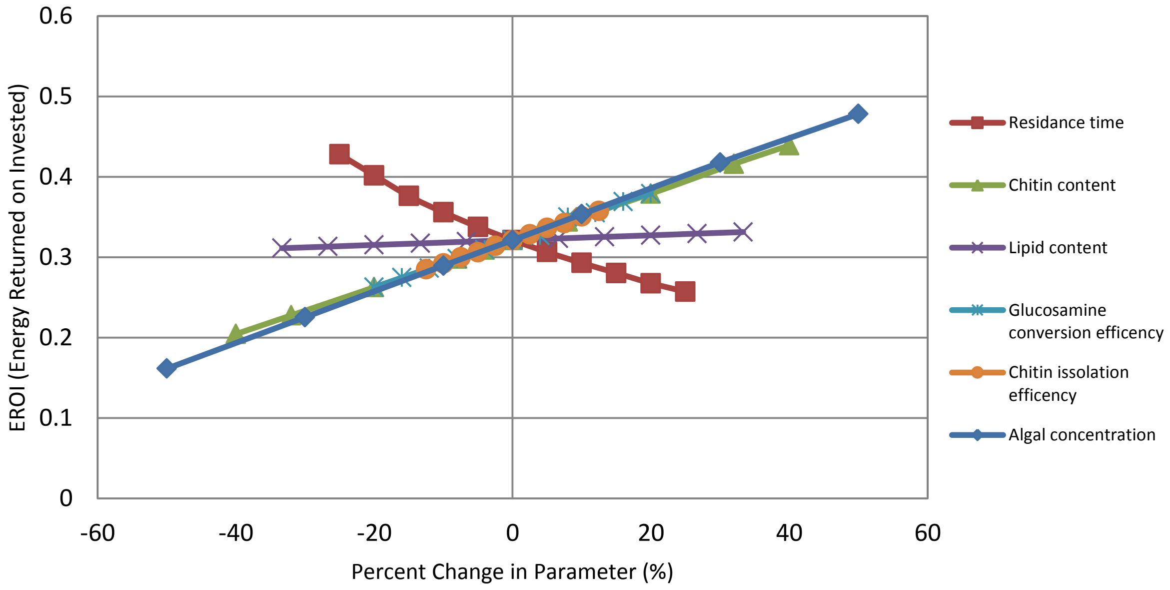

Figure 10. The effect of changes in input parameters on the energy returned on invested for the production of 1 kg lipid.

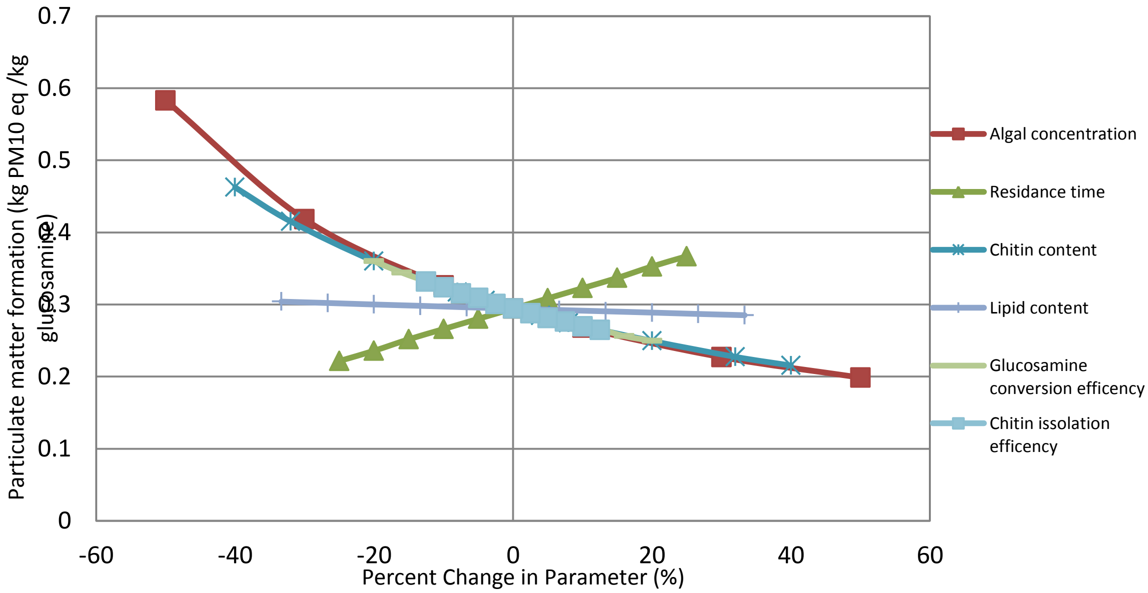

Figure 11. The effect of changes in input parameters on the global particulate matter formation (kg PM10-eq) for the production of 1 kg glucosamine.

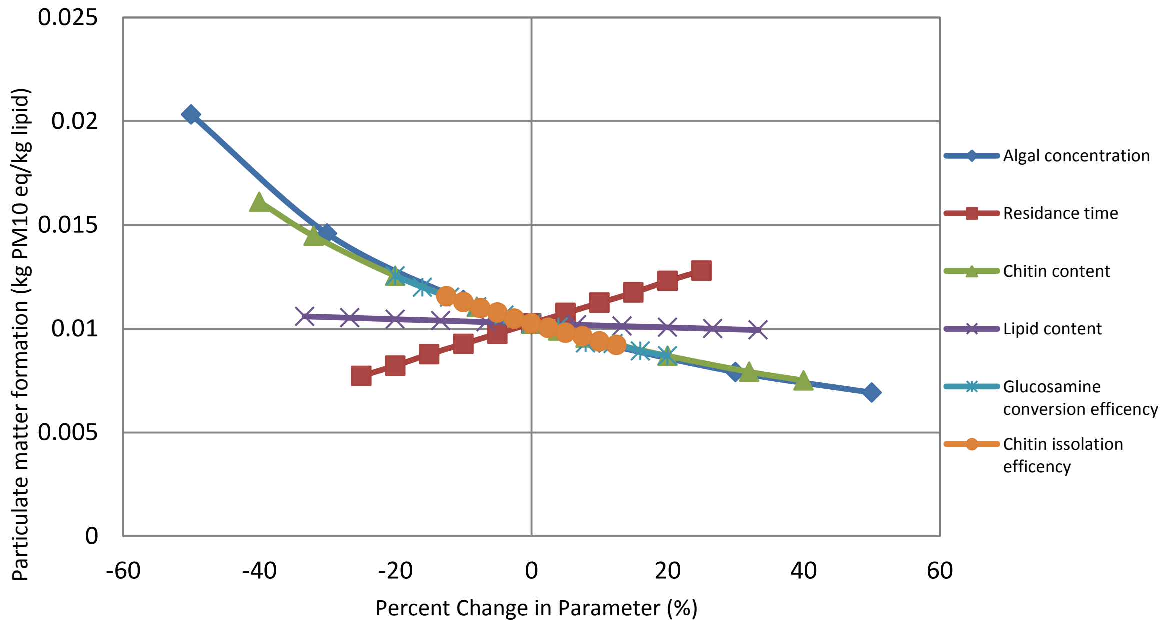

Figure 12. The effect of changes in input parameters on the global particulate matter formation (kg PM10-eq) for the production of 1 kg lipids.

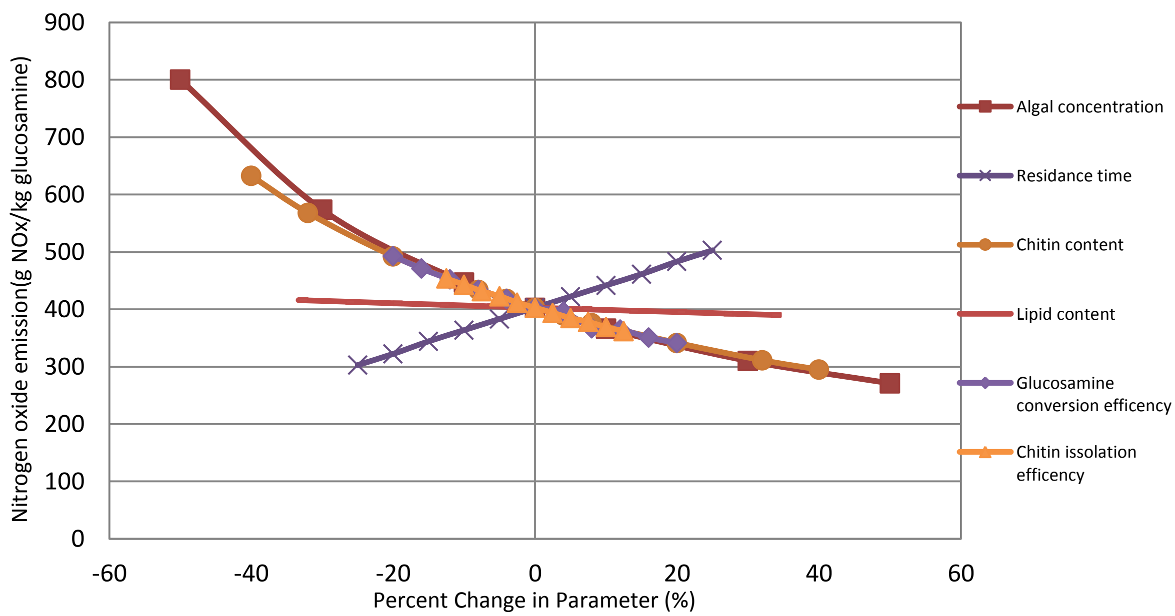

Figure 13. The effect of change in input parameters on the emission of nitrogen oxides (g NO_x) for the production of 1 kg glucosamine.

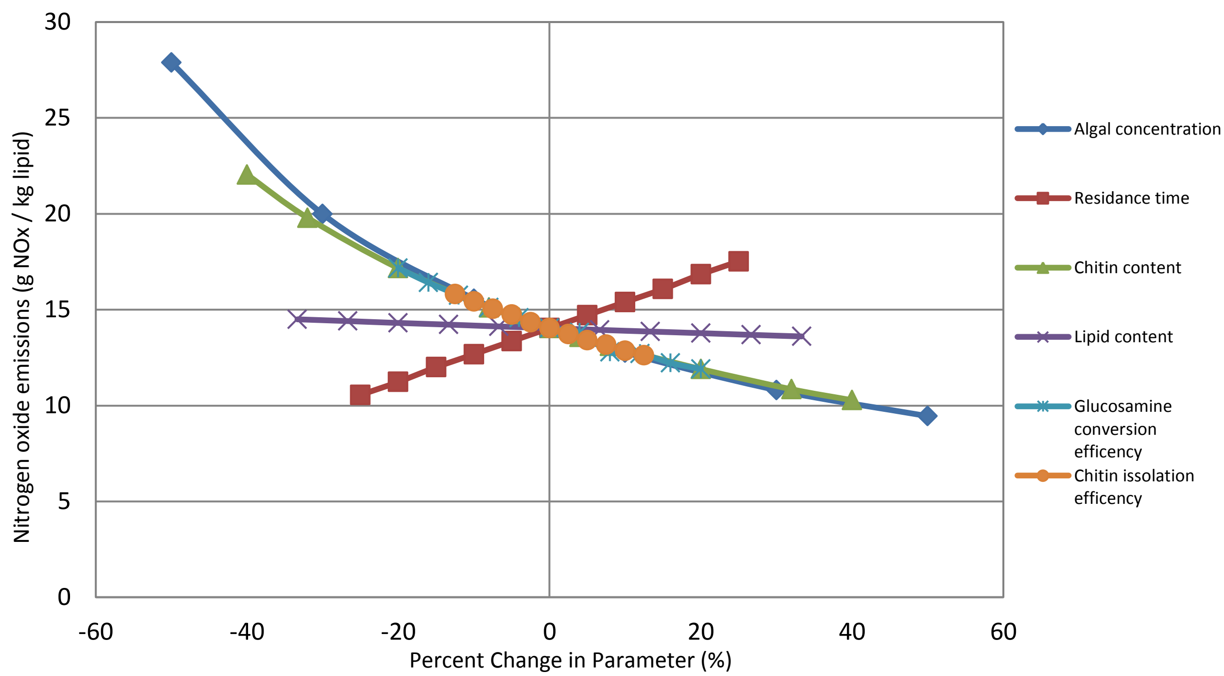

Figure 14. The effect of change in input parameters on the emission of nitrogen oxides (g NO_x) for the production of 1 kg lipids.

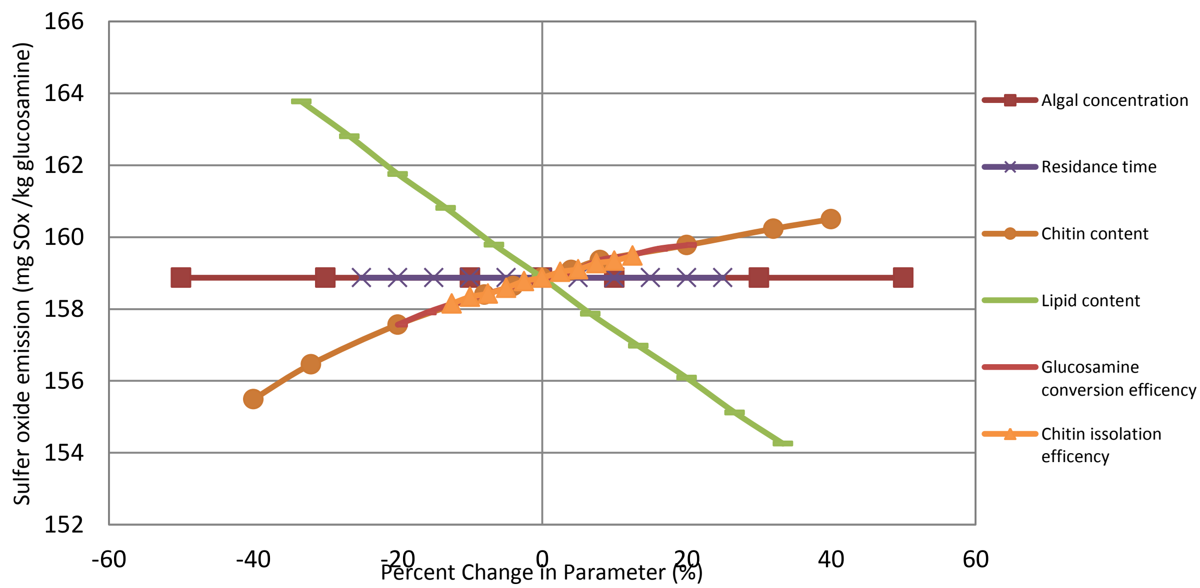

Figure 15. The effect of change in input parameters on the emission of sulfur oxides (mg SO_x) for the production of 1 kg glucosamine.

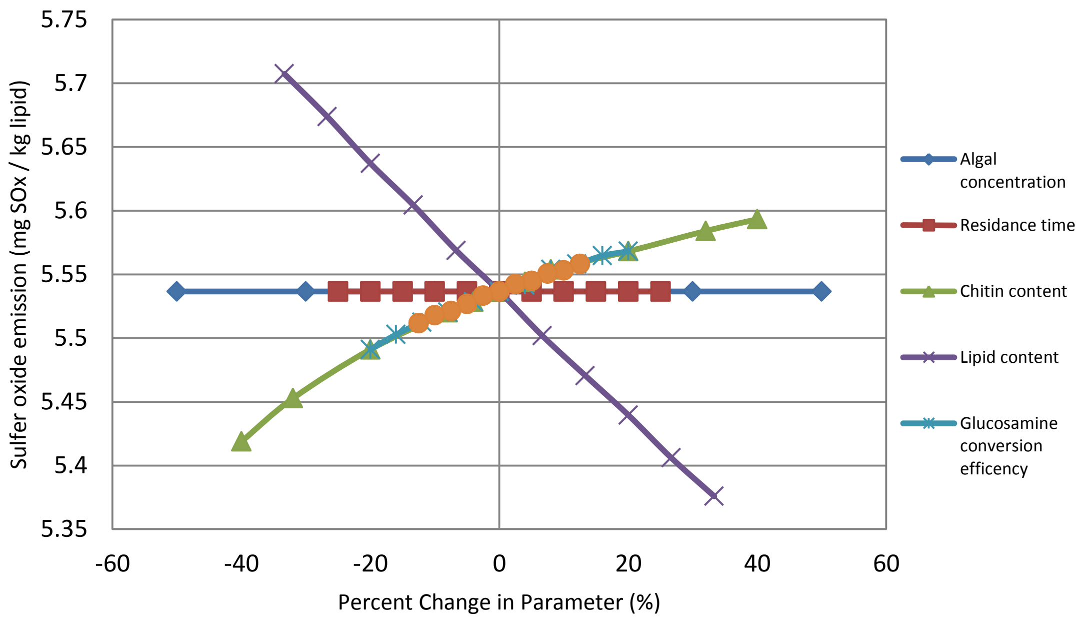

Figure 16. The effect of change in input parameters on the emission of sulfur oxides (mg SO_x) for the production of 1 kg lipids.

3.7 Conclusion

To be considered environmentally sustainable alternatives to fossil fuels, algal biorefineries should emit less GHG than the fossil fuels they replace for a specific amount of fuel produced. Also, an EROI value greater than 1 will be required to begin decreasing the need for fossil fuels. With process and technology improvements, the utilization of a glucosamine biorefinery for biofuels production may approach environmentally sustainable emissions. However, the scale of biofuels market is orders of magnitude larger than the glucosamine market. Therefore this application will contribute only slightly to the biofuels market in mass, but may provide a demonstration of successful algal lipid fuel production.

The LCA results predicted in the aggressive case show a scenario utilizing PBRs, in which environmental sustainability could be achieved. The use of a PBR system has many benefits including, less contamination, higher water recycle, and targeted nutrient control. However, at its current state the use of a photobioreactor proves environmentally unsustainable. Environmental unsustainability is due to the large quantities of PMMA used to construct the PBRs. With further investigation nutrient target growth in a RWP may be possible. The utilization of a RWP system as shown by Davis et al., (2011), provides lower environmental and economic burdens in lipid production. The utilization of a RWP could push a glucosamine biorefinery into becoming a more environmental and economically sustainable process.

Algal biofuels show the potential to be part of the solution to depleting fossil fuels. However, much work is still needed to overcome the barriers that impede the implementation of an algal biorefinery. The glucosamine market is expanding at an accelerated rate (Barnes et al., 2008). Even though the utilization of an algal glucosamine biorefinery for the production of lipids will not impact the fuels market, it could impact the glucosamine market. Utilizing algae glucosamine could provide glucosamine with the benefits of being shellfish free and vegan friendly. These benefits warrant further investigation into an algal glucosamine biorefinery.

3.8 Acknowledgments

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3.9 Contributing Authors

Techno-economic analysis model used for life cycle assessment inputs was constructed by Xuwen Xiang (graduate student, Kelly lab, CBEE, OSU, Corvallis, OR).

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4. *C. vulgaris* production and lipid extraction for anaerobic digestion

4.1 Introduction

Over the last decade, research in algal derived biofuels has begun to thrive. At their current state, algal biofuels are suspected to be economically and environmentally unsustainable (Davis, 2012 and Clarens, 2010). It has been shown that between 35-74% of the accumulated energy in algae remain in the algae cake after lipid extraction (Lardon et al., 2009). It has been hypothesized that the introduction of anaerobic digestion may improvement algal biofuel sustainability by converting algal biomass debris to biogas (methane) and recycling nutrients to algal cultivation. In this aspect of the project, I grew *Chlorella vulgaris* (UTEX 2714) in a photobioreactor I constructed which was later used for an anaerobic digestion studies performed by our collaborator, Dr. Tyler Radniecki, faculty in the School of Chemical, Biological and Environmental Engineering, and his research team.

The goal of the algal anaerobic digestion study is to determine the benefits and feasibility of nutrient recycling and biogas production through anaerobic digestion. By quantifying nutrient recovery and biogas production it will be possible to attribute the benefits of an aerobic digester system to a large scale algal refinery. In this aspect of the study, I fabricated and constructed a multiple algal cultivations system. Freshwater algae was cultivated and harvested, a model lipid extraction process was performed. I then supplied algal biomass to our collaborators for anaerobic digestion experiments.

4.2 Algal Strain, Medium and Culture Conditions

C. Vulgaris (UTEX 2714) was obtained from the culture collection of algae at the University of Texas at Austin. The cells were maintained in a freshwater BG-11 medium (BG-11, 2014) containing 17.6 mM $NaNO_3$, 0.23 mM K_2HPO_4, 0.3 mM $MgSO_4 \cdot 7H_2O$, 0.24 mM $CaCl_2 \cdot 2H_2O$, 0.031 mM Citric Acid·H_2O, 0.0027 mM $Na_2EDTA \cdot 2H_2O$, 0.19mM Na_2CO_3, 0.021 mM $NH_4Fe(SO4)_2$, 0.046 mM H_3BO_3, 0.009 mM $MnCl_2 \cdot 4H_2O$, 0.00077 mM $ZnSO_4 \cdot 7H_2O$, 0.0016 mM $Na_2MoO_4 \cdot 2H_2O$, 0.0003 mM $CuSO_4 \cdot 5H_2O$, and 0.00017 mM $Co(NO_3)_2 \cdot 6H_2O$. The pH was adjusted to 7.6-8.0 after it was inserted in the photobioreactor. The cells were grown in 250 mL

Erlenmeyer flasks each containing 100 mL of autoclaved medium, and incubated at 20 ºC in an orbital shaker set to 100 rpm. Sub-culturing was done weekly to maintain consistent algal growth in the Erlenmeyer flasks and to inoculate bioreactors.

4.3 Bioreactor Design and Fabrication

Sub-cultured algae cells were used as an inoculum for the shake flasks and photobioreactors shown (Figures 17-21). In order to produce algae for the anaerobic digestion study, a photobioreactor system was designed and fabricated. The photobioreactor consists of five 1 L polycarbonate reactors (4 ft by 1.5 in). Six Philips T8 32W Plant & Aquarium florescent lights provide 150 µmol m^{-2} s^{-1} of light to each reactor. The air flow control system is designed to deliver 0.4 L air min^{-1} L^{-1} (Cole Parmer 0.0-1.0 L/min CO_2 Acrylic Flow Meter) of filtered air (Acro 50 0.2µm PTFE filter) to each reactor (Figure 18). A 500ml VWR media bottle was used to humidify the air before entering the reactors (Figure 20).

The harvesting ports consist of a 1/8 in ID x ¼ in MIP WATTS Brass Hose Barb Adapter, connected to a PP lure lock valve. The air systems were fitted with a one way valves providing air and CO_2 to the reactors and prevents back flow of algal media. Figure 20 indicates the inoculation, sampling, and overflow ports for a single reactor. Each overflow port is constructed of a 1/8 in ID x ¼ in MIP WATTS brass hose barb adapter connected to 18 in of VWR 1/8ID PVC tubing. Sampling ports consist of a 3 ft 1/8 in OD stainless-steel pipe connected to a 1-1/4-in dia. PVC sch 40 plug using a PTFE Swagelok tube fitting. A pH bracket system was constructed from a LASCO 1-1/4-ID. PVC connector a ½ in threaded PVC adaptor and Loctite epoxy. A Milwaukee MC122 pH meter was used to maintain a pH of 8 in the bioreactor medium. If the pH exceeds 8 the pH meter signals a Milwaukee MA957 electric solenoid CO_2 regulator which when open allows pure CO_2 into the reactors to lower the pH to 8.

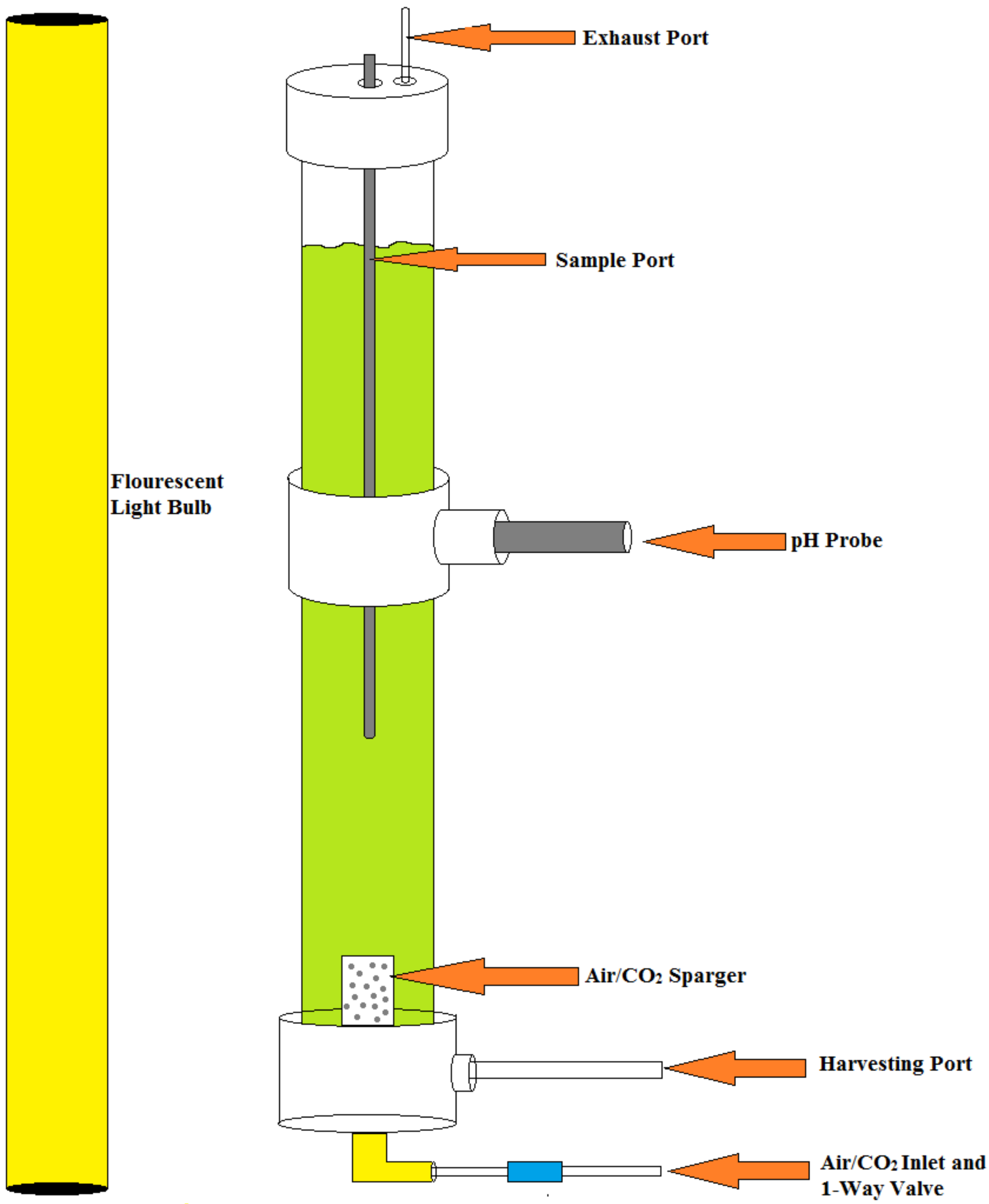

Figure 17. Schematic of a single photobioreactor tube

Figure 18. Photobioreactor tubes and air flow system

Figure 19. Photobioreactor harvesting and air inlet ports

Figure 20. Photobioreactor inoculation and sampling ports

Figure 21. Photobioreactor PH probe and bracket system

4.3 Algal Harvesting and Lipid Extraction

BG-11 media used in photobioreactors was sterile filtered. Photobioreactor growth periods consisted of a 16-8 light to dark cycle at 150 (µmol m^{-2} s^{-1}). Light intensity was measured in the center of each reactor with a LI-COR Photometer model LI-189. A 16-8 light to dark cycle was chosen to prevent photoinhibition which can damage to the photosynthetic apparatus (Chisti, 2007). To quantify the algae concentration, 10 ml of harvested bioreactor broth (algae with media) was placed in pre-weighed 57mm aluminum weighing dishes and dried in a 50 ºC oven for 12-16 hours (until constant weight was achieved), in triplicate. After the sample was fully dried, the aluminum dishes were weighed and the biomass concentration in the bioreactors at harvest was determined to be 3.04±0.1g/L, dry weight.

Photobioreactors were harvested after 7 days. The algal slurry was concentrated to ~20% w/w algae/water by centrifugation (Coulter Allegra X-12R Beckman Centrifuge) at 3000 x g for 15 minutes. The slurry was then dried in a 50 ºC oven for 12-24 hours (until a constant weight was observed). Once dried, the algal cake was crushed using a mortar and pestle, weighed using a Mettler AE200 balance, and transferred to a 250 ml borosilicate glass VWR media bottle. Hexane was added at a 50:1 w/w ratio and vigorously shaken for 2 minutes. After shaking, the media bottle was placed in an incubator at 50 ºC for 2 hours. The hexane was decanted into a 500 mL polypropylene centrifuge tube and stored for lipid analysis. A second extraction wash of 50:1 hexane to algae w/w was added to the remaining algae biomass, which was vigorously shaken for 2 min and placed back into a 50 ºC incubator for 2 hours. After 2 hours, the hexane wash was added to the previously decanted hexane. The residual hexane in the biomass was evaporated in a 50 ºC oven. The dried algae were transferred to a 50 ml VWR PP centrifuge tube and frozen at 18 ºC until required for aerobic digestion studies.

To quantify the lipid content in the algae biomass, 10 mL of the hexane-lipid solution was pipetted into each of three weighed 20 mL scintillation glass vials. These solutions were then evaporated under a steady stream of pure nitrogen in a fume hood for 15 minutes at 25 ºC. Vials where then weighed and placed back under nitrogen flow for 3 minutes, this process was repeated until a constant weight was reached for 3 consecutive readings. The remaining lipids were weighed and the lipid concentration of the algae determined from the original algae solution volume. The lipid concentration from a representative cultivation was determined to be 3.65%±0.8 w/w. A lipid concentration of 3.65% w/w is low when compared with other publications. Literature predicts lipid content for *C. vulgaris* to be between 20 and 40% w/w Zaimes and Khanna, (2013) and Stephenson et al., (2010) respectively. Due most likely to the inability to reach nitrogen deprivation with our current media.

4.4 Anaerobic Digestion Study

Preliminary anaerobic digestion studies have been performed by our collaborator, on the algae grown. Figure 22 shows cumulative biogas production verses digestion time with varying algae:wastewater treatment sludge loading ratios. Biogas formation declined at the highest algae loading. The decreased biogas formation is believed to be due to high levels of ammonium in the digester which can foul digester systems (Flicke et al., 2007).

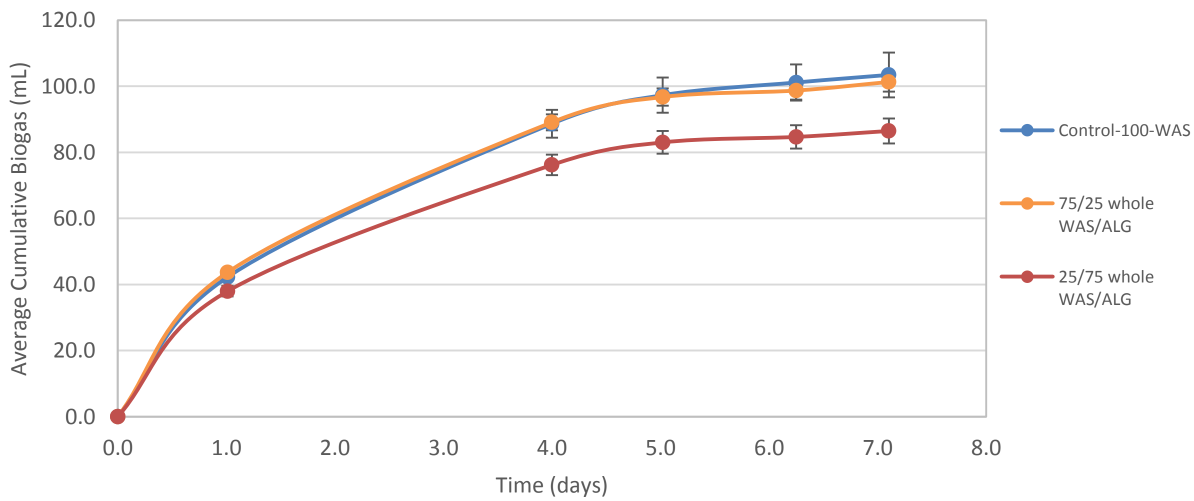

Figure 22. Cumulative biogas production (Supplied by Dr. Tyler Radniecki, faculty in the School of Chemical, Biological and Environmental Engineering, and his team.) WAS-waste water activated sludge, ALG-algae.

4.5 Conclusion

Algae were grown to a dry weight density of ~3.0g/L over a 7 day period. With algal growth rates of ~.43g/L-day our results show similar growth rates as Jorquera et al., (2011). Lipids extracted from the algal growth where much lower than expected at ~3.65% w/w. Literature values for lipid content fluctuate from 20-40% w/w (Jorquera et al., 2011) and Stephenson et al. (2010), respectivly. It is hypothesized that due to the large nitrogen source in our BG-11 media algal cells are not achieving nitrogen deprivation and therefore not accumulating larger volumes of lipids. In future work we would like to run nitrogen assays during cell growth to quantify the remaining nitrogen in the bioreactors. If nitrogen deprivation is not being achieved media can be altered to attempt to achieve it while maintaining steady growth rates.

4.6 References

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5. Conclusion

At their current state algal, derived biofuels still have boundaries that need to be addressed before implementation can be economically and environmentally sustainable. These boundaries include technological understanding, PBR and RWP material improvements, nutrient and water recycle and utilization, and co-production of a valuable substance. One of the hypothesized solutions investigated in this study was the use of a by-product (glucosamine) to help supplement costs and environmental impacts associated with the production and use of biofuels.

The results from the LCA in section 3 show that with high growth rates and large lipid and chitin content it may be possible to produce glucosamine at an environmental and economically sustainable level. With glucosamine use increasing (Barnes, 2008), the utilization of a lipid co-product could provide economic sustainability to a glucosamine biorefinery. Algal glucosamine could also fit into key niche areas including vegan-friendly and shellfish-free glucosamine (allergy purposes). The use of glucosamine to offset biofuel prices may prove ineffective. With low fuel productivity the glucosamine market could potentially become over saturated before a reasonable amount of biofuels is produced.

Although current projections suggest that algal biofuels are economically unsustainable, the potential is high. The sensitivity assessment presented in section 3.6, showed that PBR materials and construction account for a majority of the environmental impacts. With improved technologies and an increase in co-product utilization it may be possible to produce biofuels at a competitive rate. However, with low market volumes of co-products this cannot be the only solution to depleting fossil fuels.

The second technology under investigation in this study was anaerobic digestion. Anaerobic digestion has been hypothesized to have the potential to provide internal system energy trough biogas (Davis, 2011) and lower economic stresses with nutrient recycle. It is important to further investigate these technology’s to better understand their potential. In this research a photobioreactor was constructed and *C. vulgaris* was grown to 3.5 g/L. After the algae where harvested and dried, lipids where extracted with two 50:1 hexane to algae w/w washes, the remaining biomass fed to anaerobic digesters to study biogas and nutrients recycle.

In the production of algal biofuels it is important to investigate the big picture of a large scale biorefinery. The solution to environmentally sustainable fuel sources may not be a single solution but an accumulation of many technologies. In this project multiple improvements where investigated which my help provide answerers to our renewable fuels crises. None of the purposed technologies provided a single solution to algal biofuels. However, the implementation of co-product utilization and anaerobic digestion my take us one step closer to finding a solution.

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Appendix A

A.1 TEA Model and Matlab Model

A.1.1 Model Description

This algal model was developed by Xuwen Xiang and Bryan Kirby to describe a Techno-Economic Assessment of a full scale glucosamine and biorefinery.

A.1.2 Algae model

```
% Selling price of glucosamine

run Operating

lipid_income = lipid_p*ton_kg/lipid_density/gal_m3*lipid_sell;  % $/yr

for gluco_sell = linspace(0,1000,100000)
    year = 1:20;
    FCI = zeros(1,20);
    income_rest = lipid_income+gluco_p*ton_kg*gluco_sell;
    income_1 = income_rest*0.7;
    income = [income_1 linspace(income_rest,income_rest,19)];
    manufacturing = linspace(operating_cost,operating_cost,20);
    before_tax = income - manufacturing;
    depreciation = [0.1429*capital_cost 0.2449*capital_cost
0.1749*capital_cost...
        0.1249*capital_cost 0.0893*capital_cost 0.0892*capital_cost...
        0.0893*capital_cost 0.0446*capital_cost zeros(1,12)];

        cummulation_loss_gain(1) = before_tax(1)-depreciation(1);
    for n = 2:20
        cummulation_loss_gain(n) = before_tax(n)-
depreciation(n)+cummulation_loss_gain(n-1);
    end
    for m = 1:20
        if cummulation_loss_gain(m) <= 0
            cummulation_loss(m) = cummulation_loss_gain(m);
        else cummulation_loss(m) = 0;
        end
    end

    for w = 1:20
        if cummulation_loss(w)<0
            texable_income(w) = 0;
```

```
        else
            texable_income(w) = before_tax(w)-depreciation(w);
        end
    end

    income_tax = texable_income*tax_rate;
    after_tax = before_tax - income_tax;
    discount_cashflow = after_tax.*(1+ROR).^(-year);

    cummulate_cashflow(1) = discount_cashflow(1)-capital_cost;
    for z = 2:20
        cummulate_cashflow(z) = cummulate_cashflow(z-1)+discount_cashflow(z);
    end

    if cummulate_cashflow(20) >= 0
        break
    end
end

f = figure(7);
format long g
set(f,'Position',[1000 200 400 200]);
dat1 = [0,capital_cost,0,0,0,0,0,0,0,0,0,-capital_cost,-capital_cost];
dat2 =  [year',FCI',income',manufacturing',before_tax',depreciation',...
    cummulation_loss_gain',cummulation_loss',texable_income',income_tax',...
    after_tax',discount_cashflow',cummulate_cashflow'];
dat = [dat1;dat2];
columnname =   {'  Year ',   'Fixed capital ($)',   'Sales income ($)',
'Manufacturing costs ($)',...
    'Before tax cash flow ($)','Depreciation ($)','Cummul loss/gain
($)','Cummul loss ($)',...
    'Taxable income ($)', 'Income tax ($)','After tax cash flow ($)','Discnt
cash flow ($)','Cummul discnt cash flow ($)'};
t = uitable('Units','normalized','Position',...
            [0.05 0.05 0.755 0.87], 'Data', dat,...
            'ColumnName', columnname,...
            'RowName',[]);

% Explaination

fprintf('\n')
disp('           KEY ASSUMPTIONS          ')
fprintf('Siliccon Price is %0.4f $/ton\n', silicon_price)
fprintf('Algae Concetration reaches %0.4f kg/m^3\n', algae_c_growth )
fprintf('Algal retention time is %0.4f days\n', algae_retention)
fprintf('Water recycle is  %0.4f \n', medium_recycle )
fprintf('Photobioreactor tube price is %0.4f $/unit\n', tube_price)
fprintf('Chitin_content is %0.4f g/g-algae\n',chitin_content )
fprintf('lipid content is %0.4f g/g-algae\n',lipid_content )
disp('Anaerobic digestion system is for fresh water')
fprintf('\n')

disp('            OMITTED DATA          ')
disp('Cooling system for photobioreactor')
disp('CO2 delivery and air bubble system')
```

```
disp('Airlift column power consumption')
disp('Medium delivery system between processes')
disp('Hydrolysis technology and economic data')
fprintf('\n')


disp('       Product Selling Prices       ')
fprintf('Glucosimine production is %0.0f ton/yr\n', gluco_p)
fprintf('Glucosimine would be sold for %0.3f $/kg\n', gluco_sell)
fprintf('Lipid production is %0.0f ton/yr\n', lipid_p)
fprintf('Lipids would be sold for %d $/gal\n', lipid_sell)
fprintf('----------------------------------------------------\n')
```

A.1.3 Algal Menu

```
run Algal_Variable_Lab
disp('Salt water based diatomic algal biorefinery model')
disp('        By: Xuwen Xiang and Bryan Kirby')
disp('                 04/16/2014')
p=0;p1=0;p2=0;p3=0;p4=0;p5=0;p6=0;p7=0;p8=0;p9=0;
while p<10;
p = menu('Choose Variable to update','Algae Growth','Nutrient, CO2 and
Water','Photobioreactor system',...
'Downstream process','Glucosamine hydrolysis','Lipid Extraction','Anaerobic
digestion','Material cost',...
'Economics','When Done (Click Here)');
if p == 1;
    p1=0;
    while p1<7;
        p1 = menu('Choose Algae Growth Variable to update','Glucosamine
productivity','Chitin content','Lipid content','Days of operation per
year','Algae concentration','Alage retention time','Main Menu');
        if p1 ==1;
    gluco_p = input('Input new value for Glucosamine productivity (551 ton
(500 metric ton)): ');
        end
        if p1 ==2;
    chitin_content = input('Input new value for Chitin content(30%): ');
        end
        if p1 ==3;
    lipid_content = input('Input new value for Lipid content (25%): ');
        end
        if p1 ==4;
    operating_day = input('Input new value for Days of operation per year
(330 days): ');
        end
        if p1 ==5;
    algae_c_growth = input('Input new value for Algae concentration (0.5
kg/m^3): ');
        end
        if p1 ==6;
    algae_retention = input('Input new value for algae retention time (10
days): ');
        end
```

```
    end
end
if p ==2;
    p2=0;
    while p2<13;
        p2 = menu('Choose Nutrient, CO2 and Water Variable to
update','Phospherous Content / Algae','Phosphorus Content /
Nutrient','Phosphorous utilization','Nitrogen Content / Algae',...
            'Nitrogen Content / Nutrient','Nitrogen utilization','Sillicon
Content / Algae','Sillicon Content / Nutrient','Silicon utilization','Carbon
Content / Algae','Carbon Content / CO2',' CO2 utilization','Main Menu');
        if p2 ==1;
    phosph_algae = input('Input new value for phospherous content of algae
(0.01325 g/g-algae): ');
        end
        if p2 ==2;
    phosph_nutrient = input('Input new value for phospherous content of
nutrient (0.2347 g/g-DAP): ');
        end
        if p2 ==3;
    phosph_utiliz = input('Input new value for Phosphorous utilization (80%
uptake by algae growth): ');
        end
        if p2 ==4;
    nitro_algae = input('Input new value for Nitrogen content of algae
(0.0658 g/g-algae): ');
        end
        if p2 ==5;
    nitro_nutrient = input('Input new value for Nitrogen content of nutrient
(0.8235 g/g-ammonia): ');
        end
        if p2 ==6;
    nitro_utiliz = input('Input new value for Nitrogen utilization (80%
uptake by algae growth): ');
        end
        if p2 ==7;
    sillicon_algae = input('Input new value for Sillicon content of algae
(0.06 g/g-algae): ');
        end
        if p2 ==8;
    sillicon_nutrient = input('Input new value for Sillicon content of
nutrient (0.1320 g/g-Na2SiO3 5H2O): ');
        end
        if p2 ==9;
    silicon_utiliz = input('Input new value for Silicon utilization (80%
uptake by algae growth): ');
        end
        if p2 ==10;
    C_algae = input('Input new value for Carbon content of algae (0.5130 g/g-
algae): ');
        end
        if p2 ==11;
    C_CO2 = input('Input new value for Carbon content of CO2 (0.2727 g/g-
CO2): ');
        end
        if p2 ==12;
```

```
    CO2_utiliz = input('Input new value for CO2 utilization (90% uptake by
algae growth): ');
        end
    end
end
if p ==3;
    p3=0;
    while p3<5;
        p3 = menu('Choose Photobioreactor system Variable to update','Tube
diameter','Tube length','PBR life time',...
            'Tube Volume vs Land Area','Main Menu');
        if p3 ==1;
    tube_diameter = input('Input new value for Tube diameter (9 cm): ');
        end
        if p3 ==2;
    tube_length = input('Input new value for Tube length (80 m): ');
        end
        if p3 ==3;
    tube_life = input('Input new value for  PBR life time (20 years): ');
        end
        if p3 ==4;
    tube_volume_vs_land_area = input('Input new value for  Photobioreactor
area time (200 m^3/ha (393 PBRs/ha)): ');
        end
    end
end
if p ==4;
    p4=0;
    while p4<10;
        p4 = menu('Choose Downstream process Variable to update','Settler
efficiency','Settler algae content','DAF efficiency','DAF Algae content','
DAF electrical consumption','Centrifugation efficiency','Centrifugation algae
content','Centrifuge electrical consumption','Medium recycle','Main Menu');
        if p4 ==1;
    settler_eff = input('Input new value for Settler efficiency (90%): ');
        end
        if p4 ==2;
    algae_c_settler = input('Input new value for Settler algae content (10
kg/m^3): ');
        end
        if p4 ==3;
    DAF_eff = input('Input new value for DAF efficiency (90%): ');
        end
        if p4 ==4;
    algae_c_DAF = input('Input new value for DAF Algae content (100 kg/m^3):
');
        end
        if p4 ==5;
    DAF_electric = input('Input new value for DAF electrical consumption
(0.15 kWh/kg-algae): ');
        end
        if p4 ==6;
    centri_eff = input('Input new value for Centrifugation efficiency (95%):
');
        end
        if p4 ==7;
```

```
    algae_c_centri = input('Input new value for Centrifugation algae content
(200 kg/m^3): ');
        end
        if p4 ==8;
    centri_electric = input('Input new value for Centrifuge electrical
consumption per unit (40kW): ');
        end
        if p4 ==9;
    medium_recycle = input('Input new value for Medium recycle from settler,
DAF, and centrifuge (95%): ');
        end
    end
end
if p ==5;
    p5=0;
    while p5<3;
        p5 = menu('Choose Glucosamine hydrolysis Variable to update','Chitin
isolation efficiency','Glucosamine isolation efficiency','Main Menu');
        if p5 ==1;
    chitin_eff = input('Input new value for Chitin isolation efficiency
(80%): ');
        end
        if p5 ==2;
    gluco_eff = input('Input new value for Glucosamine isolation efficiency
(50%): ');
        end
    end
end
if p ==6;
     p6=0;
    while p6<10;
        p6 = menu('Choose Lipid Extraction Variable to update','Hexane to
slurry volumetric ratio','Extraction efficiency','Hexane recovery','Water
recovered from extraction','Algae recovered from extraction process',...
            'Debris recovered from extraction process','Extraction
electricity consumption','Stripping column lipid recovery','Stripping column
hexane recovery','Main Menu');
        if p6 ==1;
    hexane_vs_slurry = input('Input new value for Hexane to slurry ratio (1):
');
        end
        if p6 ==2;
    extract_lipid_eff = input('Input new value for Extraction efficiency
(95%): ');
        end
        if p6 ==3;
    extract_hexane_eff = input('Input new value for hexane recovery to
stripping column(100%): ');
        end
        if p6 ==4;
    extract_water_eff = input('Input new value for water recovered from
extraction to stripping column(0%): ');
        end
        if p6 ==5;
    extract_algae_eff = input('Input new value for algae recovered from
extraction process to stripping column(0%): ');
        end
```

```
        if p6 ==6;
    extract_debris_eff = input('Input new value for debris recovered from
extraction process (0%): ');
        end
        if p6 ==7;
    LLE_electric = input('Input new value for Extraction electricity
consumption (1.066 kWh/kg-lipid): ');
        end
        if p6 ==8;
    stripping_lipid_eff = input('Input new value for Stripping column lipid
recovery (100%): ');
        end
        if p6 ==9;
    stripping_hexane_eff = input('Input new value for Stripping column hexane
recovery ( 99.8%): ');
        end
    end
end

if p ==7;
        p7=0;
    while p7<10;
        p7 = menu('Choose Anaerobic digestion Variable to update','Anaerobic
Digester loading rate','Volatile solid to total solid ratio',...
            'Anaerobic Digester electricity consumption','Nitrogen nutrients
recovered','Phosphorous nutrients recovered','Silicon nutrients
recovered','Water recovered',...
            'CO2 recovered from Anaerobic digestion to CHP','CO2 recovered
from CHP to cultivation','Main Menu');
        if p7 ==1;
    AD_flowrate = input('Input new value for Anaerobic Digester loading rate
(6 kg-VS/m^3/d): ');
        end
        if p7 ==2;
    VS_TS = input('Input the ratio between volatile solid and total solid
(0.9):');
        end
        if p7 ==3;
    AD_electric = input('Input new value for Anaerobic Digester electricity
consumption (0.49 kWh/kg-lipid): ');
        end
        if p7 ==4;
    nitro_AD = input('Input new value for nitrogen nutrients recovered in
anaerobic Digester(75%): ');
        end
        if p7 ==5;
    phosph_AD = input('Input new value for phosphorous nutrients recovered in
anaerobic Digester (50%): ');
        end
        if p7 ==6;
    silicon_AD = input('Input new value for silicon nutrients recovered in
anaerobic Digester (50%): ');
        end
        if p7 ==7;
    water_AD = input('Input new value for water recovered in anaerobic
Digester (75%): ');
        end
```

```
        if p7 ==8;
    CO2_AD = input('Input new value for CO2 recovered from Anaerobic digester
to CHP (46.8%): ');
        end
        if p7 ==9;
    CO2_CHP = input('Input new value for CO2 recovered from CHP to algae
cultivation (85%): ');
        end
    end
end

if p ==8;
        p8=0;
    while p8<10;
        p8 = menu('Choose Variable to update for Material cost','Phosphorus
nutrient price','Nitrogen nutrient price','Silicon nutrient price','CO2
price','Water price','Hexane price','Power price','Land price','Lipid
price','Main Menu');
        if p8 ==1;
    phosph_price = input('Input new value for Phosphorous nutrient
($643/ton): ');
        end
        if p8 ==2;
    nitro_price = input('Input new value for Nitrogen price($900/ton): ');
        end
        if p8 ==3;
    silicon_price = input('Input new value for Silicon price($150/ton): ');
        end
        if p8 ==4;
    CO2_price = input('Input new value for CO2 price($40/ton): ');
        end
        if p8 ==5;
    water_price = input('Input new value for Water price($0.012/ton): ');
        end
        if p8 ==6;
    hexane_price = input('Input new value for Hexane price($4.2/gal): ');
        end
        if p8 ==7;
    land_price = input('Input new value for Land price($3800/ha): ');
        end
        if p8 ==8;
    power_price = input('Input new value for power price($0.08/kWh): ');
        end
        if p8 ==9;
    lipid_sell = input('Input new value for Lipid selling price($4/gal): ');
        end
    end
end

if p ==9;
        p9=0;
    while p9<6;
        p9 = menu('Choose Variable to update for Economics','Tube
price','Airlift column price','Fixed ratio','Tax rate','Internal rate of
return','Main Menu');
        if p9 ==1;
```

```
    tube_price = input('Input new value for  Tube Price time ($1066/Setup): 
');
        end
        if p9 ==2;
    airlift_price = input('Input new value for Airlift Price 
($100/Equipment): ');
        end
        if p9 ==3;
    fixed_ratio = input('Input new value for Fixed capital cost for the 
equipment (2.42): ');
        end
        if p9 ==4;
    tax_rate = input('Input new value for Tax rate (35%): ');
        end
        if p9 ==5;
    ROR = input('Input new value for Internal rate of return (10%): ');
        end
    end
end
end


%                ----Frame Work----
% if p ==2;
%     while p1<4;
%         p1 = menu('Choose Variable to update','','','','');
%         if p1 ==1;
%     y = input('Input new value for : ');
%         end
%         if p1 ==2;
%     y = input('Input new value for : ');
%         end
%         if p1 ==3;
%     y = input('Input new value for : ');
%         end
%     end
%     end
```

A.1.4 Algal Variables

```
% This is a file to define the original independenable variable for
% the production of glucosamine from photobioreactor algae.
clear all
close all

% Algae Growth
gluco_p = 551;                % Glucosamine productivity is 551 ton (500 
metric ton)
chitin_content = 0.3;         % Chitin content is 30% in algae
lipid_content = 0.25;         % Lipid content is 25% in algae

operating_day = 330;          % Days of operating is 330 days/yr
algae_c_growth = 0.5;         % Algae concentration is 0.5 kg/m^3 in PBR.
algae_retention = 10;         % Alage has a retention time of 10 day
```

```
% Nutrient, CO2 and water
% It is assumed that the algae has a composition of CO0.48H1.83N0.11P0.01.
%     It has a molecular weight is 23.39 g/mol. P and N fractions are
%     calculated from this composition
phosph_algae = 0.01*31/23.39;  % Phosphorus content is 0.01325 g/g-algae
phosph_nutrient = 31/132.06;   % Phosphorus content is 0.2347 g/g-DAP
phosph_utiliz = 0.8;           % Phosphorus utilization is 80% which means
80% of
                               % Phosphorus nutrient are used for algae
                               % growth

nitro_algae = 14*0.11/23.39;   % Nitrogen content is 0.0658 g/g-algae
nitro_nutrient = 14/17;        % Nitrogen content is 0.8235 g/g-ammonia
nitro_utiliz = 0.8;            % Nitrogen utilization is 80% which means 80%
of
                               % nitrogen nutrient are used for algae growth

silicon_algae = 0.06;          % Silicon content is 0.06 g/g-algae
silicon_nutrient = 28/212.14;  % Silicon content is 0.0.1320 g/g-Na2SiO3 5H2O
silicon_utiliz = 0.8;          % Silicon utilization is 80% which means 80%
of
                               % silicon nutrient are used for algae growth

C_algae = 12/23.39;            % Carbon content is 0.5130 g/g-algae
C_CO2 = 12/44;                 % Carbon content is 0.2727 g/g-CO2
CO2_utiliz = 0.9;              % CO2 utilization is 90%

% Photobioreactor system
tube_diameter = 9;             % Tube diameter is 9 cm.
tube_length = 80;              % Tube length is 80 m.
tube_volume_vs_land_area = 200;  % Photobioreactor system has 200 m^3/ha of
land
tube_volume = (tube_diameter/100)^2*tube_length*pi/4;        % One tube
volume (m^3)
tube_number_vs_land_area = tube_volume_vs_land_area/tube_volume;  % There are
393 PBR system per hectare
tube_life = 20;                % Tube life time is 20 yr.

% Downstream process
settler_eff = 0.9;             % Settler has an efficiency of 90% to harvest
algae
algae_c_settler = 10;          % Algae content is 10 kg/m^3 after settler.

DAF_eff = 0.9;                 % DAF has an efficiency of 90% to harvest
algae
algae_c_DAF = 100;             % Algae content is 100 kg/m^3 after DAF
DAF_electric = 0.15;           % DAF has an electrical consumption of 0.15
kWh/kg-algae

centri_eff = 0.95;             % Centrifugation has an efficiency of 95%
algae_c_centri = 200;          % Algae content is 200 kg/m^3 after centrifuge
centri_electric = 40;          % Centrifuge has an electrical consumption of
40kW
                               % per equipment
```

```
medium_recycle = 0.95;          % Medium recycle is 95% after downstream
process

% Glucosamine hydrolysis

chitin_eff = 0.8;               % Chitin isolation efficiency is 80%
gluco_eff = 0.5;                % Glucosamine isolation efficiency is 50% form
chitin

% Lipid Extraction
lipid_density = 920;            % Lipid density is 920 kg/m^3

hexane_vs_slurry = 1;           % Hexane to slurry volumetric ratio is 1:1
extract_lipid_eff = 0.95;       % 95% of lipid is extracted from extraction
                                % process. The rest of lipid is send to
                                % anaerobic digetion
extract_hexane_eff = 1.00;      % 100% of hexane is recovered from extraction
                                % process. The rest of lipid is send to
                                % anaerobic digetion
extract_water_eff = 0;          % 0% of water is recovered from extraction
                                % process. The rest of lipid is send to
                                % anaerobic digetion
extract_algae_eff = 0;          % 0% of algae is recovered from extraction
process
extract_debris_eff = 0;         % 0% of debris is recovered from extraction
process

LLE_electric = 1.066;           % Extraction has a electricity consumption of
                                % 1.066 kWh/kg-lipid

stripping_lipid_eff = 1.00;     % Stripping column recover 100% of lipid
stripping_hexane_eff = 0.998;   % Stripping column recover 99.8% of hexane


% Anaerobic digestion
AD_flowrate = 6;                % AD has loading rate of 6 kg-VS/m^3/d
VS_TS = 0.9;                    % Volatile solid to total solid ratio is 0.9
AD_electric = 0.49;             % AD has an electricity consumption of 0.49
kWh/kg-lipid

nitro_AD = 0.75;                % 75% of nitrogen nutrients are recovered from
AD
phosph_AD = 0.5;                % 50% of Phosphorus nutrients are recovered
from AD
silicon_AD = 0.5;               % 50% of silicon nutrients are recovered from
AD
water_AD = 0.75;                % 75% of water is recovered from AD

CO2_AD = 0.468;                 % 46.8% of CO2 is recovered from AD
CO2_CHP = 0.85;                 % 85% of CO2 can be recovered from CHP

% Material Cost
phosph_price = 643;             % Phosphorus nutrient is $643/ton
```

```
nitro_price = 900;            % Nitrogen nutrient is $900/ton
silicon_price = 150;          % Silicon nutrient is $150/ton
CO2_price = 40;               % CO2 price is $40/ton
water_price = 0.012;          % Water price is $0.012/ton

hexane_price = 4.2;           % Hexane price is $4.2/gal
land_price = 3800;            % Land price is $3800/ha
power_price = 0.08;           % Electricity price is $0.08/kWh
lipid_sell = 3;               % Lipid selling price $3/gal

% Labor cost
wage_hr = 35;                 % Direct wages and benefits per hour
hours_per_day_shift = 8;      % Working hours per operator per shift
shift_per_cultivation_day = 2; % Shift for PBR per day
operator_PBR = 0.00003;       % Operators per PBR

shift_per_equipment_day = 2;  % Shift for equipment per day
operator_settler = 0.1;       % Operators per settlers
operator_DAF = 1;             % Operators per DAF
operator_centri = 0.5;        % Operators per centrifuge
operator_LLE = 0.5;           % Operators per LLE
operator_stripping = 1;       % Operators per stripping column
operator_AD = 1;              % Operators per anaerobic digestion
operator_CHP = 1;             % Operators per CHP

% Economics
tube_price = 1000;            % One tube system is $1000
airlift_price = 100;          % Airlift price is $100 per equipment

fixed_ratio = 2.42;           % Fixed capital cost for the equipment
tax_rate = 0.35;              % Tax rate is 35%
ROR = 0.1;                    % Internal rate of return 10%
```

A.1.5 Capitol Costs

```
% Total capital cost
run Equation

land_cost;

photo_cost = tube_cost+airlift_cost;

settler_cost = 13000*0.125*land_demand;

DAF_cost = 1800000*(DAF_flowrate/15)^0.65*DAF_number;

centri_cost = 920000*(centri_flowrate/20)^0.65*centri_number;

LLE_cost = 399661*(LLE_flowrate/1.2)^0.65*LLE_number;

stripping_cost = 3600000*(stripping_flowrate/17769)^0.65*stripping_number;
```

```
hydrolysis_cost = 0;

AD_cost = 330000*(AD_volume/9987)^0.65*AD_number;

CHP_cost = (lipid_p/38389)^0.65*8000000;

equipment_cost =
settler_cost+DAF_cost+centri_cost+LLE_cost+stripping_cost+hydrolysis_cost+AD_
cost;

% Fixed capital cost
total_equipment_cost = equipment_cost*(1+fixed_ratio);

settler_cost_fixed = settler_cost*(1+fixed_ratio);
DAF_cost_fixed = DAF_cost*(1+fixed_ratio);
centri_cost_fixed = centri_cost*(1+fixed_ratio);
LLE_cost_fixed = LLE_cost*(1+fixed_ratio);
stripping_cost_fixed = stripping_cost*(1+fixed_ratio);
hydrolysis_cost_fixed = hydrolysis_cost*(1+fixed_ratio);
AD_cost_fixed = AD_cost*(1+fixed_ratio);

capital_cost = land_cost+photo_cost+total_equipment_cost+CHP_cost;

% Pie chart
% x1 = [land_cost photo_cost settler_cost_fixed DAF_cost_fixed
centri_cost_fixed...
%    LLE_cost_fixed stripping_cost_fixed hydrolysis_cost_fixed AD_cost_fixed
CHP_cost];

% figure(5)
% pie(x1)
%
legend('Land','Photobioreactor','Settler','DAF','Centrifuge','Extraction',...
%    'Stripping Column','Hydrolysis','Anaerobic
Digestion','CHP','location','best')

% Bar Graph
x1 = [land_cost photo_cost settler_cost_fixed DAF_cost_fixed
centri_cost_fixed...
    LLE_cost_fixed stripping_cost_fixed hydrolysis_cost_fixed AD_cost_fixed
CHP_cost];
x2 =
[land_cost+photo_cost+settler_cost_fixed+DAF_cost_fixed+centri_cost_fixed+LLE
_cost_fixed+stripping_cost_fixed+hydrolysis_cost_fixed+AD_cost_fixed+CHP_cost
];
x3 = x1./x2*100;
figure(1)
bar(x3)
set(gca,'XTickLabel',{'Land','Photobioreactor','Settler','DAF','Centrifuge','
Extraction','Stripping Column','Hydrolysis','Anaerobic Digestion','CHP'})
title('Capital Cost Economic Breakdown')
ylabel('%')
run xticklabel_rotate

%Figure Table
```

```
f = figure(2);
format long g
set(f,'Position',[50 500 300 150]);
dat =  {'Land', x1(1)/1000000,x3(1);...
        'Photobioreactor', x1(2)/1000000,x3(2);...
        'Settler', x1(3)/1000000,x3(3);...
        'DAF',  x1(4)/1000000,x3(4);...
        'Centrifuge', x1(5)/1000000,x3(5);...
        'Extraction', x1(6)/1000000,x3(6);...
        'Stripping Column', x1(7)/1000000,x3(7);...
        'Hydrolysis', x1(8)/1000000,x3(8);...
        'Anaerobic Digestion', x1(9)/1000000,x3(9);...
        'CHP', x1(10)/1000000,x3(10);...
        'Total', x2,x2/x2*100};
columnname =   {'      Parameter           ',   'Capital Cost (MM$)',   '  %
'};
columnformat = {'char', 'numeric', 'numeric'};
t = uitable('Units','normalized','Position',...
            [0.05 0.05 0.755 0.87], 'Data', dat,...
            'ColumnName', columnname,...
            'ColumnFormat', columnformat,...
            'RowName',[]);
```

A.1.6 Equations Used

```
run Algal_Menu

% This photobioreactor has 20 years of life time.

% Unit converstion
ha_m2 = 10000;             % 1 hactor is equal to 10000 m^2
ton_kg = 907.185;          % 1 ton is equal to 907.185 kg
gal_m3 = 0.00378541;       % 1 gal is equal to 0.00378541 m^3
life_time = 20;            % Life time of this system is 20 years

% Glucosamine hydrolysis 1
chitin_p = gluco_p/gluco_eff;                          % Chitin productivity
(ton/yr)
algae_p_harvest = chitin_p/chitin_eff/chitin_content;   % Algae productivity
after harvesting (ton/yr)

% Algae growth
algae_p = algae_c_growth/algae_retention;                               %
Algae productivity (kg/m^3/d)
algae_p_growth = algae_p_harvest/settler_eff/DAF_eff/centri_eff;        %
Algae prodivitity after algae growth (ton/yr)
land_demand =
algae_p_harvest/(algae_p/ton_kg*operating_day)/tube_volume_vs_land_area; %
Land demand (ha)
land_cost = land_demand*land_price;                                     %
Land cost $
```

```
% Photobioreactor system
photo_volume = (algae_p_harvest*ton_kg)/operating_day/algae_p;        %
Photobioreactor system total volume (m^3)
tube_volume = (tube_diameter/100)^2*tube_length*pi/4;                 % One
tube volume (m^3)
tube_number = photo_volume/tube_volume;                               % Total
number of tube
airlift_number = tube_number;                                         % One
airlift equipment is required for a tube system
airlift_cost = airlift_number*airlift_price;                          %
Airlift total cost $
tube_cost = tube_price*tube_number*ceil(life_time/tube_life);         %
Photobioreactor system total cost $

% Downstream process
settler_retention = 2;                                                %
Settler has a retention time of 2 hour
settler_diameter = 11.7;                                              %
Settler has a diamter of 11.7 m
settler_height = 4;                                                   %
Settler has a height of 4 m

settler_input_total = algae_p_growth/(algae_c_growth/1000);           %
Settler total input (ton/yr)
settler_input_algae = algae_p_growth;                                 %
Settler algae input (ton/yr)
settler_input_water = settler_input_total-settler_input_algae;        %
Settler water input (ton/yr)
settler_output_algae = settler_input_algae*settler_eff;               %
Settler algae output (ton/yr)
settler_output_total = settler_output_algae/(algae_c_settler/1000);   %
Settler total output (ton/yr)
settler_output_water = settler_output_total-settler_output_algae;     %
Settler water output (ton/yr)

settler_volume = (settler_diameter/2)^2*pi*settler_height;            %
Settler volume (m^3)
settler_number =
ceil((settler_input_total*ton_kg/operating_day/24/1000)*settler_retention/set
tler_volume); % Settler number

DAF_input_total = settler_output_total;                               % DAF
total input (ton/yr)
DAF_input_algae = settler_output_algae;                               % DAF
algae input (ton/yr)
DAF_input_water = settler_output_water;                               % DAF
water input (ton/yr)
DAF_output_algae = DAF_input_algae*DAF_eff;                           % DAF
algae output (ton/yr)
DAF_output_total = DAF_output_algae/(algae_c_DAF/1000);               % DAF
total output (ton/yr)
DAF_output_water = DAF_output_total-DAF_output_algae;                 % DAF
water output (ton/yr)

DAF_input_MGD = DAF_input_total*ton_kg/1000/operating_day/gal_m3/10^6; % DAF
input (MGD)
```

```
if DAF_input_MGD >= 15;
    DAF_flowrate = 15;
    DAF_number = ceil(DAF_input_MGD/DAF_flowrate);
else
    DAF_flowrate = DAF_input_MGD/0.8;                              % DAF
equipment flow rate (MGD)
    DAF_number = 1;                                                % DAF
equipment number
end
DAF_power = DAF_electric*(DAF_input_algae*ton_kg/operating_day/24);  % DAF
total power consumption (kW)

centri_input_total = DAF_output_total;                             %
Centrifuge total input (ton/yr)
centri_input_algae = DAF_output_algae;                             %
Centrifuge algae input (ton/yr)
centri_input_water = DAF_output_water;                             %
Centrifuge water input (ton/yr)
centri_output_algae = centri_input_algae*centri_eff;               %
Centrifuge algae output (ton/yr)
centri_output_total = centri_output_algae/(algae_c_centri/1000);   %
Centrifuge total output (ton/yr)
centri_output_water = centri_output_total - centri_output_algae;   %
Centrifuge water output (ton/yr)

centri_input_m3h = centri_input_total*ton_kg/operating_day/24/1000;  %
Centrifuge total input (m^3/h)
if centri_input_m3h >= 20;
    centri_flowrate = 20;
    centri_number = ceil(centri_input_m3h/centri_flowrate);
else
    centri_flowrate = centri_input_m3h/0.8;                        %
Centrifuge equipment flow rate (m^3/h)
    centri_number = 1;                                             %
Centrifuge number
end
centri_power = centri_electric*centri_number;                      %
Centrifuge total electric consumption (kW)

harvset_recyc_total = (settler_input_total-
centri_output_total)*medium_recycle;  % Total recycle after harvesting
process (ton/yr)
harvest_recyc_algae = (settler_input_algae-
centri_output_algae)*medium_recycle;  % Algae recycle after harvesting
process (ton/yr)
harvest_recyc_water = (settler_input_water-
centri_output_water)*medium_recycle;  % Water recycle after harvesting
process (ton/yr)

harvest_output_nitro = (algae_p_growth-
harvest_recyc_algae)/nitro_utiliz*nitro_algae/nitro_nutrient*(1-
nitro_utiliz)*centri_output_total/settler_input_total;
harvest_output_phosph = (algae_p_growth-
harvest_recyc_algae)/phosph_utiliz*phosph_algae/phosph_nutrient*(1-
phosph_utiliz)*centri_output_total/settler_input_total;
```

```
harvest_output_silicon = (algae_p_growth-
harvest_recyc_algae)/silicon_utiliz*silicon_algae/silicon_nutrient*(1-
silicon_utiliz)*centri_output_total/settler_input_total;

harvest_waste_total = (settler_input_total-centri_output_total)*(1-
medium_recycle);
harvest_waste_algae = (settler_input_algae-centri_output_algae)*(1-
medium_recycle);
harvest_waste_water = (settler_input_water-centri_output_water)*(1-
medium_recycle);

harvest_waste_nitro = (algae_p_growth-
harvest_recyc_algae)/nitro_utiliz*nitro_algae/nitro_nutrient*(1-
nitro_utiliz)*harvest_waste_total/settler_input_total;
harvest_waste_phosph = (algae_p_growth-
harvest_recyc_algae)/phosph_utiliz*phosph_algae/phosph_nutrient*(1-
phosph_utiliz)*harvest_waste_total/settler_input_total;
harvest_waste_silicon = (algae_p_growth-
harvest_recyc_algae)/silicon_utiliz*silicon_algae/silicon_nutrient*(1-
silicon_utiliz)*harvest_waste_total/settler_input_total;

% Glucosamine hydrolysis 2
hydrolysis_input_total = centri_output_total;
hydrolysis_input_algae = centri_output_algae;
hydrolysis_input_water = centri_output_water;
hydrolysis_output_total = centri_output_total-chitin_p;

nitro_chitin = 14/203;  % Nitrogen faction in chitin
nitro_consum_chitin = chitin_p*nitro_chitin/nitro_nutrient;

% Lipid extraction
lipid_p = algae_p_harvest*lipid_content*extract_lipid_eff; % lipid
productivity

extract_input_total = hydrolysis_output_total;
extract_output_lipid =
hydrolysis_input_algae*lipid_content*extract_lipid_eff;

hexane_density = 0.65;
hexane_demand =
(hexane_vs_slurry*(hydrolysis_input_algae/1)*hexane_density)*(1-(1-
extract_lipid_eff)-(extract_lipid_eff*stripping_hexane_eff));
hexane_cost = hexane_demand*hexane_price;

LLE_input_algae_m3h = hydrolysis_input_algae*ton_kg/operating_day/24/1000;
if LLE_input_algae_m3h >= 1.5
    LLE_flowrate = 1.5;
    LLE_number = ceil(LLE_input_algae_m3h/LLE_flowrate);
else
    LLE_flowrate = LLE_input_algae_m3h/0.8;
    LLE_number = 1;
end
LLE_power = LLE_electric*(extract_output_lipid*ton_kg/operating_day/24);  %
kW
```

```
stripping_input_lipid = extract_output_lipid;
stripping_input_hexane =
(hexane_vs_slurry*(hydrolysis_input_algae/1)*hexane_density)*extract_hexane_e
ff;
stripping_input_total = stripping_input_lipid+stripping_input_hexane;
stripping_input_kgh = stripping_input_total/operating_day/24*ton_kg;

stripping_flowrate = stripping_input_kgh;
stripping_number = 1;
stripping_power = stripping_input_kgh/17769*1450;  % kW

% Anaerobic Digestion
AD_input_total = hydrolysis_input_total-chitin_p-lipid_p;
AD_input_water = hydrolysis_input_water;
AD_input_sludge = hydrolysis_input_algae-chitin_p-lipid_p;
C_content_sludge = 1*12/23.39;

AD_total_volume = (AD_input_sludge*VS_TS*ton_kg/operating_day)/AD_flowrate;
if AD_total_volume >= (34/2)^2*pi*11;
    AD_diameter = 34;                % Anaerobic cylindrical tank has a
diamter of 34m
    AD_height = 11;                  % Anaerobic cylindrical tank has a
height of 11m
    AD_volume = (AD_diameter/2)^2*pi*height;
    AD_number = ceil(AD_total_volume/AD_volume);
else
    AD_volume = AD_total_volume/0.8;
    AD_number = 1;
end
AD_power = (lipid_p*ton_kg/operating_day/24)*AD_electric;

AD_N_recycle = ((algae_p_harvest*nitro_algae-
chitin_p*nitro_chitin)/nitro_nutrient+harvest_output_nitro)*nitro_AD;
AD_P_recycle =
((algae_p_harvest*phosph_algae)/phosph_nutrient+harvest_output_phosph)*phosph
_AD;
AD_Si_recycle =
((algae_p_harvest*silicon_algae)/silicon_nutrient+harvest_output_silicon)*sil
icon_AD;
AD_H2O_recycle = AD_input_water*water_AD;
CHP_CO2_recycle = AD_input_sludge*C_content_sludge/12*44*CO2_AD*CO2_CHP;

AD_N_waste = ((algae_p_harvest*nitro_algae-
chitin_p*nitro_chitin)/nitro_nutrient+harvest_output_nitro)*(1-nitro_AD);
AD_P_waste =
((algae_p_harvest*phosph_algae)/phosph_nutrient+harvest_output_phosph)*(1-
phosph_AD);
AD_Si_waste =
((algae_p_harvest*silicon_algae)/silicon_nutrient+harvest_output_silicon)*(1-
silicon_AD);
AD_H2O_waste = AD_input_water*(1-water_AD);
CHP_CO2_waste = AD_input_sludge*C_content_sludge/12*44*(1-CO2_AD)*(1-
CO2_CHP);

% Nutrient, CO2 and Water
```

```
nitro_demand1 = (algae_p_growth-
harvest_recyc_algae)/nitro_utiliz*nitro_algae/nitro_nutrient-
harvest_waste_nitro*(medium_recycle/(1-medium_recycle))-AD_N_recycle;
nitro_demand2 =
harvest_waste_nitro+harvest_waste_algae*nitro_algae/nitro_nutrient+AD_N_waste
+nitro_consum_chitin;
nitro_cost = nitro_demand1*nitro_price;

phosph_demand1 = (algae_p_growth-
harvest_recyc_algae)/phosph_utiliz*phosph_algae/phosph_nutrient-
harvest_waste_phosph*(medium_recycle/(1-medium_recycle))-AD_P_recycle;
phosph_demand2 =
harvest_waste_phosph+harvest_waste_algae*phosph_algae/phosph_nutrient+AD_P_wa
ste;
phosph_cost = phosph_demand1*phosph_price;

silicon_demand1 = (algae_p_growth-
harvest_recyc_algae)/silicon_utiliz*silicon_algae/silicon_nutrient-
harvest_waste_silicon*(medium_recycle/(1-medium_recycle))-AD_Si_recycle;
silicon_demand2 =
harvest_waste_silicon+harvest_waste_algae*silicon_algae/silicon_nutrient+AD_S
i_waste;
silicon_cost = silicon_demand1*silicon_price;

CO2_demand1 = (algae_p_growth-harvest_recyc_algae)/CO2_utiliz*C_algae/C_CO2-
CHP_CO2_recycle;
CO2_cost = CO2_demand1*CO2_price;

water_demand = harvest_waste_water+AD_H2O_waste;
water_cost = water_demand*water_price;

% Labor costs
labor_PBR =
operator_PBR*tube_number*hours_per_day_shift*shift_per_cultivation_day*wage_h
r*operating_day;
labor_settler =
operator_settler*settler_number*hours_per_day_shift*shift_per_equipment_day*w
age_hr*operating_day;
labor_DAF =
operator_DAF*DAF_number*hours_per_day_shift*shift_per_equipment_day*wage_hr*o
perating_day;
labor_centri =
operator_centri*centri_number*hours_per_day_shift*shift_per_equipment_day*wag
e_hr*operating_day;
labor_LLE =
operator_LLE*LLE_number*hours_per_day_shift*shift_per_equipment_day*wage_hr*o
perating_day;
labor_stripping =
operator_stripping*stripping_number*hours_per_day_shift*shift_per_equipment_d
ay*wage_hr*operating_day;
labor_AD =
operator_AD*AD_number*hours_per_day_shift*shift_per_equipment_day*wage_hr*ope
rating_day;
labor_CHP =
operator_CHP*1*hours_per_day_shift*shift_per_equipment_day*wage_hr*operating_
day;
```

A.1.7 Operation Costs

```
% Operating cost
run Capital

% Chemistry
CO2_cost;
nitro_cost;
phosph_cost;
silicon_cost;
hexane_cost;
water_cost;
chemistry_cost =
CO2_cost+nitro_cost+phosph_cost+silicon_cost+hexane_cost+water_cost;

% Materials Table

f = figure(3);
format long g
set(f,'Position',[50 200 300 150]);
dat =  {'CO2',CO2_demand1 , CO2_cost , CO2_cost/chemistry_cost*100 ;...
        'Nitrogen',nitro_demand1 , nitro_cost,nitro_cost/chemistry_cost*100
;...
        'Phosphorus',phosph_demand1 , phosph_cost
,phosph_cost/chemistry_cost*100 ;...
        'Silicon', silicon_demand1 ,
silicon_cost,silicon_demand1/chemistry_cost*100 ;...
        'Hexane',hexane_demand , hexane_cost,hexane_cost/chemistry_cost*100
;...
        'Water',water_demand , water_cost,water_cost/chemistry_cost*100  ;...
        'Total', 0 , chemistry_cost,chemistry_cost/chemistry_cost*100 };
columnname =   {'      Material           ',   'Demand ton/year',   '  Cost
($) ', '   %   '};
columnformat = {'char', 'numeric', 'numeric', 'numeric'};
t = uitable('Units','normalized','Position',...
            [0.05 0.05 0.755 0.87], 'Data', dat,...
            'ColumnName', columnname,...
            'ColumnFormat', columnformat,...
            'RowName',[]);

% Power
DAF_power;
centri_power;
LLE_power;
stripping_power;
hydrolysis_power = 0;
AD_power;
CHP_power = -((lipid_p/38389)*10000);
```

```
total_power =
DAF_power+centri_power+LLE_power+stripping_power+hydrolysis_power+AD_power+CH
P_power;
power_cost = total_power*operating_day*24*power_price;

% Power Table

f = figure(4);
format long g
set(f,'Position',[50 150 300 150]);
dat =  {'DAF', DAF_power
,DAF_power*24*operating_day,DAF_power*power_price*24*operating_day;...
        'Centerfuge', centri_power
,centri_power*24*operating_day,centri_power*power_price*24*operating_day;...
        'Liquid Liquid Extraction',
LLE_power,LLE_power*24*operating_day,LLE_power*power_price*24*operating_day;.
..
        'Stripping Column',stripping_power
,stripping_power*24*operating_day,stripping_power*power_price*24*operating_da
y;...
        'Hydrolysis', hydrolysis_power ,hydrolysis_power*24*operating_day
,hydrolysis_power*power_price*24*operating_day;...
        'Anirobic Digestion', AD_power,
AD_power*24*operating_day,AD_power*power_price*24*operating_day;...
        'CHP',
CHP_power,CHP_power*24*operating_day,CHP_power*power_price*24*operating_day;.
..
        'Total', total_power,total_power*24*operating_day, power_cost};
columnname =   {'      Equipment            ',  'Electricity capacity (kW)',
'Electricity demand (kWh/yr)'   '  Cost ($)   ',};
columnformat = {'char', 'numeric', 'numeric','numeric'};
t = uitable('Units','normalized','Position',...
            [0.05 0.05 0.755 0.87], 'Data', dat,...
            'ColumnName', columnname,...
            'ColumnFormat', columnformat,...
            'RowName',[]);

% Labor, maintenance and total operating
labor =
(labor_PBR+labor_settler+labor_DAF+labor_centri+labor_LLE+labor_stripping+lab
or_AD+labor_CHP)*1.6;
maintenance = capital_cost*0.02;
operating_cost = chemistry_cost+power_cost+labor+maintenance;

% Total operating
f = figure(5);
format long g
set(f,'Position',[50 100 300 150]);
dat = {'Raw Materials',chemistry_cost;
       'Power',power_cost;
       'Labor and overhead',labor;
       'Maintenance',maintenance;
       'Gross operating costs',operating_cost};
columnname =   {'      Operating Cost          ',  '  Cost ($)   '};
columnformat = {'char', 'numeric'};
t = uitable('Units','normalized','Position',...
```

```
            [0.05 0.05 0.755 0.87], 'Data', dat,...
            'ColumnName', columnname,...
            'ColumnFormat', columnformat,...
            'RowName',[]);


 % Bar Graph
x1 = [capital_cost/20 chemistry_cost power_cost labor maintenance];
x2 = [capital_cost/20+chemistry_cost+power_cost+labor+maintenance];
x3 = x1./x2*100;
figure(6)
bar(x3)
set(gca,'XTickLabel',{'Capital Cost/Life Time','Raw Material','Power','Labor
and Overhead','Maintenance'})
title('Cost Comparison')
ylabel('%')
run xticklabel_rotate
```