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Title: Techno-Economic Analysis of Algal Lipid Fuels

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A techno-economic analysis (TEA) was performed to evaluate the technology, cost, and resource use for algal biofuel production based on today's economics and technology. The basic goal of this study is to develop a model to calculate the mass and energy balances and costs to produce 10 million gal of lipid per year from microalgae. There are previous studies that estimate these parameters, but the detailed assumptions and calculations are not published. This analysis considers two algal growth pathways, e.g. open pond and photobioreactor (PBR) cultivation. This study demonstrated that large-scale PBRs costs are much more than open pond systems for the production of biofuel from algae. Lipid production costs are highly sensitive to the assumption of algae productivity and lipid content. Currently, the economics of producing biofuel from algae is not competitive with petroleum fuels. In future, several strategies can be performed for potential enhancement algal biofuel economics, includes the production of high value co-products from algae, integrating wastewater treatment, and improvement of algal biofuel technology.

Techno-Economic Analysis of Algal Lipid Fuels

by

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CONTRIBUTION OF AUTHORS

Dr. Christine Kelly reviewed and modified the manuscript and helped the author to design the study. She also helped the author analyze the economic values for the lipid price.

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LIST OF ABBREVIATION

AD	Anaerobic digestion
ANL	Argonne National Laboratory
ATM	Atmospheric pressure
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CHP	Combined heat and power
CSTRs	Continuous stirred tank reactors
DAF	Dissolved air flotation
DAG/DG	Diglyceride
DAP	Diammonium phosphate
EPA	Environmental Protection Agency
FAME	Fatty acid methyl esters
FFA	Free fatty acid
gpm	Gallon per minute
ha	Hectare
HDPE	High-density polyethylene
HRT	Hydraulic retention time
ID	Inside diameter
kWh	Kilowatt hour
LCA	Life-Cycle Analysis
LLE	Liquid-liquid extraction
MAG/MG	Monoglyceride
MEC	Major equipment cost

MGD	Million gallon per day
mM	Millimole/L solution
MM	Million
MW	Megawatts
NREL	U.S. National Renewable Energy Laboratory
PBR	Photobioreactor
PC	Polycarbonate
PE	Polyethylene
PP	Polypropylene
PPM	Parts per million
PSU	Practical Salinity Scale Unit, grams of salt per liter of solution
PUFA	Polyunsaturated fatty acid
PVC	Polyvinyl chloride
RPM	Revolutions per minute
SERI	Sustainable Europe Research Institute
TAG/TG	Triglyceride
TEA	Techno-economic analysis
TS	Total solid
TSS	Total suspended solids
UV	Ultraviolet
v/v	Volume of solute/ volume of solution
VS	Volatile solid
μM	Micromole/ L solution

ALGAE MENTIONED

Ankistrodesmus

Arthrospira

Chlamydomonas perifranulata

Chlorella phrotothecoides

Chlorella pyrenoidosa

Chlorella sp.

Chlorella vulgaris

Chlorococcum sp.

Cyanidium

Cyclotella crpytica

Dunaliella bioculata

Dunaliella salina

Dunaliella sp.

Dunaliella tertiolecta

Haematococcus

Haematococcus pluvialis

Nitzschia sp.

Isochrysis sp.

Microcystis aeruginosa

Nannochloris sp.

Nannochloropsis sp.

Phaeodactylum tricormutum

Porphyridium cruentum

Scenedesmus

Scenedesmus obliquus

Spirulina

Spirulina maxima

Spirulina platensis

Tetraselmis chuii

Tetraselmis maculata

Tetraselmis sp.

1 INTRODUCTION

Petroleum fuel is recognized as an unsustainable resource due to scarcity of known deposits. Renewable energy technologies are necessary for energy sustainability in natural resource management. One possible source of renewable fuel is biodiesel from algal feedstock. Algae are a promising biomass with high fuel yield potential that can potentially serve as a sustainable feedstock for biodiesel. The primary advantages of algae over other biomass feedstock are the ability for algae to grow very quickly and the potentially high oil content, which is readily converted to fuel.

A techno-economic analysis (TEA) is a process to analyze the technical and economic viability of a process (Sun et al., 2011). The TEA provides a quantitative framework that can be used to compare performance among different technologies and systems. Several TEAs have been performed for proposed large-scale algal biofuels systems, including Benemann et al, (1982), Welssmen and Goebel (1987) and Benemann and Oswald (1996) at SERI, and Davis et al. (2012) at the National Renewable Energy Laboratory (NREL). Some later studies were derivative of the earlier studies.

This study examines the existing published studies that analyze the technological and economic of algal biofuel production. The published information cannot itemize all the details of a TEA, and many assumptions are required. A TEA was completed based on the work published by NREL (Davis et al., 2012). Details and assumptions missing from the study were calculated and gathered from other studies. In selecting parameters for the TEA, the most realistic capabilities for the current state of technology were the primary consideration. The spreadsheet software Excel and the process simulation software Aspen Plus were used to solve the material and energy balances and cost of product calculations for a 10 million gal lipid per year facility.

This thesis consists of an algal biodiesel literature review (Chapter 2), a techno-economic analysis of a large scale biofuel facility (Chapter 3), and a brief discussion and conclusion (Chapter 4).

2 ALGAL BIOFUELS TECHNOLOGY REVIEW

2.1 Microalgae

Algae have several types of metabolism. Autotrophic growth uses CO_2 as a sole substrate, while heterotrophic growth requires organic compounds as carbon sources (e.g. sugar). Mixotrophic growth can use both substrates (Frank et al., 2011a; Mata et al., 2011). Based on morphology and size, algae also can be grouped into microalgae and macroalgae. Microalgae are generally microscopic unicellular algae (3-60 μm) and macroalgae are composed of multiple cells (John et al., 2011; Zamalloa et al., 2011). Microalgae can produce natural oil, which has become a focus of research for production of biodiesel. Photoautotrophic microalgae can grow and reproduce by using sunlight, atmospheric CO_2, water, and nitrogen and phosphorus as nutrient inputs. Microalgae have a large variety of species living in all earth ecosystems. It is estimated that more than 50,000 species exist and about 30,000 have been studied (Mata et al., 2011).

2.2 Potential of Microalgal Biodiesel

Compared to conventional crop-derived feedstock, algae are easy to cultivate, grow rapidly and do not require large amounts of arable land. Microalgae have significantly higher potential oil yield per area than terrestrial plants. Potential oil yield from certain algae have experimentally been shown to be at least 60 times higher than from soybeans and approximately 15 times more than jatropha (Chisti, 2007; Ferrell et al., 2010). Current available oil from cooking waste oils and crops is not enough to satisfy a significant fraction of the demand of biodiesel for transportation. Chisti (2007) claimed that microalgae appeared to be the only feedstock of biodiesel that had the potential to replace fossil oil.

2.3 Strain Isolation and Selection

Algae can be isolated in a variety of natural aqueous habitats, including freshwater, brackish water, marine and hyper-saline environment, and soil (Ferrell et al., 2010). High-throughput automated isolation techniques involving fluorescence-activated cell sorting can be used for large-scale sample and isolation effects (Ferrell et al., 2010).

Certain species or strains with characteristics useful for large-scale growth have been chosen as algal model systems. However, studies done by the Aquatic Species Program indicated that the algae strains that grow well in the laboratory were not always suitable for large-scale cultivation (Sheehan et al., 1998). There are a number of considerations in choosing an algae strain for lipid production, such as growth rate, cell density, tolerance to environmental variables (pH, temperature, salinity, oxygen, CO_2, and nutrient level), cellular composition of proteins, lipids, and carbohydrate, target fuel, target co-product, culture consistency, and resistance ability to predators and viruses (Ferrell et al., 2010). For example, high saline environment species may be selected to prevent contamination for microalgae cultivation in outdoor open ponds (Molina et al., 2001). Autoflocculate for algal harvesting is able to recover more water and save money because it allows algae species settle without adding of chemical flocculants (Ferrell et al., 2010). Table 2.3a presents the lipid content and lipid productivity for some most common commercial-scale algae.

Table 2.3 a: Summary of lipid content and algae productivities for common suggested commercial-scale microalgae species (Becker, 1994; Mata et al., 2010).

Microalgae Species	Culture Systems	Lipid Content (% dry weight)	Biomass Productivity ($g/m^2/d$)
Chlorella sp.	Raceways, PBR & Circular ponds	10-48	12-21
Chlorococcum sp.	Raceways	19.3	3.5-13.9
Dunaliella sp.	Extensive ponds & Raceways	17.5-67.0	-
Haematococcus	Raceways & Circular ponds	25	10.2-36.4
Nannochloris sp.	Tanks	20-56	-
Nannochloropsis sp.	--	12-53	1.9-5.3
Phaeodactylum tricormutum	--	18-57	2.4-21
Scenedesmus obliquus	--	11-55	11-30
Spirulina	Raceways	4.0-16.6	8-15
Tetraselmis sp.	--	12.6 -14.7	18

2.4 Chemical Composition and Lipid

Based on the Redfield ratio, an approximation for algal composition of C:N:P is 106:16:1. Grobbelaar (2004) suggested an average composition of microalgae is $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$, while Davis et al. (2012) assumed an algal composition of $C_{106}O_{45}H_{181}N_{15}P$ for the techno-economic analysis. However, the chemical composition of algae is not an intrinsic constant. The constituents of some algae can be modified by varying culture conditions, such as nitrogen or phosphorus depletion. Williams and Laurens (2010) reported that the algae composition is about 15-60% of algal lipid, 20-40% of protein, 3-5% nucleic acid and 10-50% carbohydrate. Carbohydrate is present in the form of starch, glucose, sugars, and other polysaccharides (Spolaore et al., 2006). Table 2.4a summarizes the gross composition of some common algae species.

Table 2.4 a: Gross composition of some common algae (Becker, 1994).

Microalgae Species	Protein (%)	Carbohydrate (%)	Lipids (%)	Nucleic Acid (%)
Chlorella pyrenoidosa	57	2	6	-
Chlorella vulgaris	51-58	12-17	14-22	4-5
Dunaliella bioculata	49	4	8	-
Dunaliella salina	57	32	6	-
Scenedesmus obliquus	50-56	10-17	12-14	3-6
Spirulina maxima	60-71	13-16	6-7	3-4.5
Spirulina platensis	46-63	8-14	4-9	2-5
Tetraselmis maculata	52	15	3	-

Depending on the algae species and growth methods, algae productivity is not a constant value. The average lipid content for microalgae varies between 1% and 70% (Becker, 1994; Mata et al., 2010). Griffiths and Harrison (2009) summarized that the average lipid content of eight algal species is 26% of dry weight. Table 2.4b summarizes the average lipid content for microalgae from four sources.

Table 2.4 b: General lipid content summarized by published literature.

Source	Lipid Content (% of Dry Weight)
Hu et al. (2008)	25.5
Griffiths and Harrison (2009)	26
Williams and Laurens (2010)	15-60
Davis et al. (2012)	25

The major parts of lipid of microalgae can be divided into non-polar lipids which includes triglyceride (TAG), diglyceride (DAG), monoglyceride (MAG), and free fatty acid (FFA), whereas polar lipids are phospholipids and glycolipids (Becker, 1994). TAG is the main potential fuel constituting up to 80% of total lipid fraction (Becker, 1994). Microalgal lipids are composed of saturated and unsaturated fatty acids with a carbon number in the range of 12-22. Both Becker (1994) and Thomas (1984) analyzed the composition of lipids and found that C16:0, C18:1, C18:2, and C18:3 are the major fatty acids for microalgal lipids. Table 2.4c demonstrates the major fatty acids for various microalgae.

Table 2.4 c: Major fatty acid for various algae species (Sheehan et al., 1998).

Strain	Nitrogen-Sufficient Cells	Nitrogen-Deficient Cells
Ankistrodesmus	16:0, 16:4, 18:1, 18:3	16:0, 18:1, 18:3
Dunaliella salina	14:0, 14:1, 16:0, 16:3, 16:4, 18:2, 18:3	16:0, 16:3, 18:1, 18:2, 18:3
Isochrysis sp.	14:0, 14:1, 16:0, 16:1, 18:1, 18:3, 18:4, 22:6	14:0, 14:1, 18:1, 18:2, 18:3, 18:4, 22:6
Nannochloris sp.	14:0, 14:1, 16:0, 16:1, 16:2, 16:3, 20:5	--
Nitzschia sp.	14:0, 14:1, 16:0, 16:1, 16:2, 18:3, 20:6	--

2.5 Algae Cultivation

The growth rate of algae is affected by many environmental factors, including light, temperature, nutrient concentration, O_2, CO_2, pH, salinity, and toxic chemicals. These factors can affect photosynthesis and productivity of the algae cell, changes in the pathway of cellular metabolism and the composition of algae cells (Hu, 2004; Mata et al., 2010). This section describes some cellular responses to the major environment factors.

2.5.1 Sunlight

Intensive outdoor production of algal biomass is limited by several factors: nutrients, CO_2, temperature and light. The first three factors are easier to maintain at optimal conditions. Therefore the growth rate is generally limited by the amount of light (Shelef et al., 1984).

One approach to evaluate the sunlight utilization for biomass growth is light utilization efficiency which based on the light saturation constant (I_s) and the intensity of incoming solar radiation (Huesemann et al., 2009; Ferrell et al., 2010). Light utilization efficiency is the fraction of light energy that is converted to chemical energy, which can be calculated by Bush equation in Appendix A.1.1 (Brennan and Owende, 2009). Borowitzka (2005) suggested that the actual light efficiency for algae culture ranges from less than 1% to 5%. Most algal groups have a light saturation constant of 50 to 200 μE m^{-2} s^{-2} (Tredici and Zittelli, 1998). For example, *Phaeodactylum tricornutum* has a light saturation constant for algae of 185 μE m^{-2} s^{-2} (Mann and Myers, 1968). However, several studies show that the outdoor light intensity is about 2000 μE m^{-2} s^{-2} which is much more than the light saturation constant (Tredici and Zittelli, 1998; Molina et al., 2000; Chisti, 2007).

The typical response of biomass growth rate to increasing light is shown in Figure 2.5.1a (Vonshak and Torzillo, 2004; Chisti, 2007). At a light-limited region, the algae growth increases with increasing irradiance. On the other hand, high light intensity can reduce the biomass growth rate which is called photoinhibition (Figure 2.5.1a). The biomass productivity depending on the light irradiance can be calculated in Appendix A 1.2.

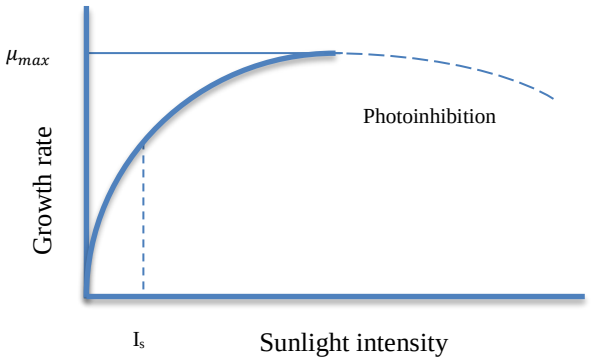


Figure 2.5.1 a: Effect of light intensity on specific growth rate of microalgae.

Light and dark photoperiods should be required for the algae growth. Algae growth can be photoinhibited at a high irradiance with continuous light, while growth on the light:dark regimen between 12:12 hours to 16:8 hours would benefit the algae growth (Price et al., 1998). Studies show that marine species are sensitive to long light-time photoperiods (Price et al., 1998).

2.5.2 Temperature

The temperature of the culture medium is an important factor in algal growth and directly impacts growth rate. In general, freshwater algal species have higher tolerance for temperature fluctuations than marine strains (Lorenz et al., 2005). Lorenz et al (2005) reported that the optimal temperature for many freshwater microalgae ranges from 15 to 20 ℃. West (2005) found that the optimal temperature ranges from 20 to 25 ℃ for both tropical and subtropical algae. Table 2.5a displays the optimal temperature level for several common algae species.

Temperature also can affect the algal cell composition. For example, Liu and Lee (2000) found that the carotenoid composition in *Chlorococcum sp.* will increase when growth temperature increased from 20 to 35 ℃. Nishida and Murata (1996) reported that decreasing temperature below the optimal level increases the content of unsaturated lipids.

For outdoor algae ponds, daily and seasonal variations in temperature affect algal growth. Low temperature in winter limits the algal growth, while tropical and subtropical climate are suitable for large-scale algae production (Borowikzka, 2005).

2.5.3 Salinity

Algae cells are generally able to live in a certain range of salt concentrations. In general, offshore seawater salinity ranges from 32 to 35 PSU (grams salt per liter liquid) and inshore water is less than 30 PSU (Harrison and Berges, 2005). Studies show that most unicellular marine algae species are tolerant to a wide range of salinity (McLachlan, 1961). At high salt concentration, the well-balanced osmotic relation between the cell and surrounding medium will be broken and force water efflux from the cells. Water loss and salinity in the cell will lead to a new state of growth (Erdumann and Hagemann, 2001). Table 2.5a displays salinity tolerance for several common algae species.

2.5.4 pH

The pH is an important factor for algae growth. It determines the solubility of carbon dioxide and ammonia in the medium and influences the metabolism of algae (Becker, 1994). For example, *Cyanidium* has a growth optimum at pH 2.0, while *Spirulina* grows well at pH between 9 and 11. The optimal pH values of several algae species are shown in Table 2.5a.

When pH values are above 9, the precipitation of trace metal (e.g. Ca^{2+} > 10 mM) leads to nutrient deficiencies and growth retardations (Becker, 1994). The ratio of NH_4:NH_3 can be 9:1 at low pH. When pH reach to 9.3, the ratio of NH_4:NH_3 will increase to 1:1 (Harrison and Berges, 2005; Sunda et al., 2005). A method for maintaining pH at a desired value in photobioreactors is to use pH controllers (Becker, 1994). Adding NaOH, HCl and CO_2 through pH controller is a method to change the pH value.

Table 2.5 a: Optimal algae cultivation for some algae species (Becker, 1994).

Microalgae Species	Natural Habitat	Salinity, Optimum (% w/v NaCl)	Salinity, Maximum (% w/v NaCl)	Temperature (℃), Optimum	pH, Optimum
Chlorella vulgaris	Freshwater	0	1%	25	6.5-7.5
Dunaliella salina	Hypersaline brines	22% (growth) 35% (caroteno-genesis)	35%	30-40	9.0
Haematococcus pluvialia	Freshwater	0	1%	18-22	7.0
Phaeodactylum tricornutum	Marine	3%	5%	18-24	8.0
Spirulina platensis	Alkaline soda lakes	0-1%	3%	30-38	9.0-10.0

2.5.5 Contamination

There are several major types of contamination in algal cultures, including bacteria, zooplankton, viruses, fungi and insects (Becker, 1994). The invasion of undesirable algae is another major problem for outdoor algal cultivation. Several strategies are helpful to prevent infections, such as periodic cleaning of the ponds or bioreactor, and creating optimal environmental conditions for

growing the desired algal species. It had been reported that the culture of *Chlorella* required frequent start-up with uncontaminated algae (Becker, 1994). The quality and quantity of algae that are affected by microbial contamination is rarely reported except those for food or feed (Becker, 1994).

2.5.6 Scale-up cultivation

Scaling-up from laboratory to commercial operations have both technical and economic difficulties. Previous studies have shown that algae strains that grow well in the laboratory are not always suitable for large-scale culturing (Sheehan et al., 1998). There are numerous considerations for outdoor scaling up of microalgae cultures, such as

- Cost of land
- Source and quality of water
- Potential contamination from competitor algae, pathogens, and predators.
- Climate conditions including the daily and annual temperature range, annual rainfall and rainfall pattern, intensity of sunlight, and degree of cloud cover (Borowitzka, 2005).

The ideal scale-up strategy for algal cultivation may include enough sunlight for algae growth, available water resources, inexpensive land, and available CO_2 from nearby industrial.

2.6 Nutrients, CO_2 and Water

Biodiesel production based on microalgae as feedstock is associated with a high demand for nutrients: phosphorus, nitrogen, silicon, sulfur, trace metal and vitamins. The major nutrient demands come from phosphorus and nitrogen. Phosphorus is especially critical for large-scale algal cultivations due to scarcity. Silicon is a nutrient that is required only for diatoms, silicoflagellates and some chrysophytes (Harrison and Berges, 2005).

Phototrophic algae can convert solar energy and nutrients to biomass using photosynthesis. The general algae growth equation can be written in the following way:

$$CO_2 + H_2O + \text{Nutrients} + \text{Sunlight} = \text{Algae} + O_2$$

2.6.1 Nutrients for algae cultivation

2.6.1.1 Nitrogen

There are three forms of nitrogen suggested in algae cultivations, including ammonia (NH_3), nitrate (NO_3^-), or urea ($CO(NH_2)_2$) (Ferrell et al., 2010). Some algae can fix nitrogen and sulfur from the air in the form of NO_x (Brennan and Owende, 2009; Ferrell et al., 2010).

The most commonly proposed nitrogen source is nitrate which has the formation of NO_3^-. In general, nitrate can be obtained from mineral sources and animal wastes. A variety of types of nitrate have been used for algae cultivation, including $NaNO_3$, KNO_3, NH_4NO_3, $Ca(NO_3)_2$, and $Ca(NO_3)_2 \cdot 4H_2O$.

NH_3 is an alternative nitrogen source that can be added for algae growth. Several ammonia species have been used as algal nutrient, including NH_4Cl, NH_4NO_3, $(NH_4)SO_4$ and anhydrous ammonia. Urea is another kind of nitrogen nutrient with the formation of $CO(NH_2)_2$. Table 2.6.1.1a summarizes the nitrogen nutrient for algal cultivation.

Table 2.6.1.1 a: Summary of nitrogen nutrient for algal cultivation (Andersen et al., 2005)

Nitrogen Nutrient Category	Formula	Concentration Range in Final Medium (µM)	Average Concentration in Final Medium (µM)
Nitrate	$NaNO_3$	500-8000	1500
	KNO_3	500-2500	1000
	$Ca(NO_3)_2$ or $Ca(NO_3)_2 \cdot 4H_2O$	250-750	500
Ammonia	NH_4Cl*	50	50
	NH_4NO_3*	275-625	450
Urea	$CO(NH_2)_2$*	50-142	100

*Combined with nitrate

Nitrate, ammonia and urea are major sources of nitrogen for algal cultivation. The economically preferred nitrogen supply is ammonia and urea which are less expensive than nitrate (Becker, 1994). In addition, nitrate is toxic at high concentration which may decrease water recycle rates (Becker, 1994). Davis et al. (2012) assumed algae growth with anhydrous ammonia or urea as nitrogen nutrients for the NREL TEA and LCA.

2.6.1.2 Phosphorus

Phosphorus can be added to cultures as phosphate (PO_4^{-3}) or Na_2 β- glycerophosphate·$5H_2O$ (Na_2PO_4-$CH(CH_2OH)$·$5H_2O$) that can also make trace metals less likely to precipitate. There are several kinds of phosphorus nutrients for algae cultivation, including KH_2PO_4, K_2HPO_4, $NaH_2PO_4·H_2O$, $Na_2HPO_4·12H_2O$, and Na_2 β- glycerophosphate·$5H_2O$. The most common laboratory P nutrients are K_2HPO_4, $NaH_2PO_4·H_2O$, and Na_2 β- glycerophosphate·$5H_2O$. Table 2.6.1.2a summarizes the commonly used phosphorus nutrients for algal cultivation. Other materials could be alternative choices for P nutrients due to their phosphate structure, including diammonium phosphate (DAP, $(NH_3)_2HPO_4$), superphosphate ($Ca(H_2PO_4)_2$), and struvite ($MgNH_4PO_4·6H_2O$).

Table 2.6.1.2 a: Summary of phosphorus nutrients for algal cultivation (Andersen et al., 2005)

Formula	Concentration Range in Final Medium (μM)	Average Concentration in Final Medium (μM)
KH_2PO_4	150-2000	500
K_2HPO_4	10-2000	50
$NaH_2PO_4·H_2O$	10-128	50
$Na_2HPO_4·12H_2O$	56-780	400
Na_2 β- glycerophosphate·$5H_2O$	10-163	40

2.6.2 Effect of Nutrients

The biomass productivity can change if key nutrients are limited. On the other hand, too much of particular nutrient may prove toxic for algae growth. Nutrient deficiency, such as nitrogen-deficiency in algae and silicon-deficiency in diatoms, can increase the lipid content (Becker, 1994). Some experimental results of nutrient effects are described in Table 2.6.2a. Studies showed that the oil production in the cell is high under nutrients limitation, which leads to an accumulation of oil. However, the total oil production may not increase because of lower algal cell growth under nutrient starvation. The total rate of oil productivity is low during nutrient deficiency (Sheehan et al., 1998).

Table 2.6.2 a: The effect of nutrient deficiency on the content of lipid and protein (Becker, 1994).

	Algae Species	N-Source	0.0003%	0.001%	0.003%	0.01%	0.03%
Total protein (% of dry weight)	*Chlorella vulgaris*	NH_4Cl	7.79	11.1	19.9	28.9	31.2
	Scenedesmus obliquus	NH_4Cl	9.36	9.43	22.0	33.2	34.4
	Chlorella vulgaris	KNO_3	12.6	6.75	14.5	30.7	31.1
	Scenedesmus obliquus	KNO_3	8.19	9.00	8.81	34.0	32.1
Total lipid (% of dry weight)	*Chlorella vulgaris*	NH_4Cl	52.8	41.8	20.2	14.1	11.8
	Scenedesmus obliquus	NH_4Cl	34.6	33.1	21.7	23.0	22.4
	Chlorella vulgaris	KNO_3	57.9	62.9	42.7	22.0	21.8
	Scenedesmus obliquus	KNO_3	45.6	44.3	50.1	26.9	29.8

Similar to the effects observed with algae growth under nitrogen starvation, phosphorus limitation can increase lipid content (mainly TAG) for some species. Results from Reitan et al. (1994) showed that phosphorus limitation will enhance the levels of C16:0 and C18:1 and decrease the amounts of 18:4n-3, 20:5n-3, and 22:6n-3. It is also believed that phosphorus limitation can reduce the phospholipid content and enhance the production of neutral lipid (mainly TAG) (Reitan et al., 1994).

2.6.3 Nutrients recycle

One option to decrease the demand of nitrogen and phosphorus for microalgae cultivation is nutrient recycling. Catalytic hydrothermal gasification of algae are catalytic wet processes that can be used to recover nutrients to the cultivation (Davis et al., 2012; Rosch et al., 2012). Anaerobic digestion processes can mineralize algal waste to methane and recover nutrient rich liquid phase to bioreactors. Davis et al. (2012) suggested that 75% of nitrogen and 50% of phosphorus can be recovered from algal waste during anaerobic digestion. Rosch et al. (2012) suggested that the nutrient recycling rates are in the range from 30% to 90% for nitrogen and 48% to 93% for phosphorus during hydrothermal gasification.

2.6.4 CO_2

Since about half of algal biomass molecular weight consists of carbon, a sufficient supply of carbon is critically important for algal culture. CO_2 is a common carbon resource that can be used for algae growth. In water, CO_2 disassociates according to the equation below:

$$CO_2 + H_2O \leftrightarrow H_2CO_2 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{-2}$$

CO_2 for photosynthesis is delivered by gas sparing into the algal cultivations system. Air or air enriched with CO_2 is used in both open ponds and photobioreactors. Open ponds can allow for greater than 90% utilization of injected CO_2 (Sheehan et al., 1998). For open ponds algae growth, the flow rate of CO_2 is 70 to 130 mM min^{-1} m^{-2} at culture temperature of 25 to 30℃. The loss of CO_2 is about 7 mM min^{-1} m^{-2} at the maximum concentration of 1.5 mM CO_2 L^{-1} (Becker, 1994). Benemann and Oswald (1996) reported that the maximum demand of about 45 g CO_2 m^{-2} day^{-1} is required for the algae productivity of 30 g m^{-2} day^{-1}.

In general, large-scale algal culture cannot be supplied by air because its low CO_2 concentration in air is insufficient to sustain optimal growth and high productivity (Becker, 1994). The flue gas emitted from coal or natural gas fired power plants contain CO_2 up to 13% (the maximum value for natural gas fired power station) (Sheehan et al., 1998; Stephenson et al., 2010). Davis et al. (2011) and Kadam (1997) listed the prices of CO_2 at $36/ton and $40/ton when sourced from power plants.

CO_2 can be supplied by bottled CO_2, pressurized pipelines, low-pressure pipelines, and supercritical pipelines (Davis et al., 2012). Bottled CO_2 are not suitable for large scale of culture, whereas pressurized and supercritical pipelines are relatively expensive even for short distance CO_2 transportation (Kadam, 1997; Zhang et al, 2006).

Low-pressure transport is the most commonly used CO_2 transportation option (Frank et al., 2011a). The site location, CO_2 source location, CO_2 demand, and pipeline economics must be considered for low-pressure CO_2 transportation (Davis et al., 2012). Davis et al. (2012) assumed four 1-mile pipelines to transport flue gas and adding a blower for each 1-mile pipeline. Benemann et al. (1982) and Benemann and Oswald (1996) estimated a low-pressure CO_2 system with 2 meter diameter and 5 km long pipeline (3 miles). The authors reported that the CO_2 cost for open pond is about $250-300/ha. However, the total delivered cost of CO_2 is about $10,000/ha which includes $6300/ha for the delivery of the flue gas CO_2 from the power plant to open ponds (3 miles) and $3650/ha for the internal distribution within the pond. Welssmen and Goebel (1987) estimated that the internal CO_2 distribution cost is about $2350/ha. When the CO_2 pipeline is shorter, the transportation cost will reduce dramatically (Benemann and Oswald, 1996).

2.6.5 Water

Water demands are enormous for large-scale of open pond algae cultivation. For example, an open pond size of 2 raceways × 0.3 m (depth) × 10 m (width) × 150 m (length) requires 900 m^3 of water to fill the raceways. If the evaporation rate is 0.003 m/d, 9 m^3 of water (1% of water in pond) will evaporate every day. To produce 1 kg biodiesel, Yang et al. (2011) suggested a requirement of about 3730 kg water for a non-recycle system or about 370 kg water for recycle system when the harvest biomass concentration is 1 g/L in open ponds. In order to decrease water demand, it is desirable to recycle most of water back to the cultivation. Full recycle is not possible in many cases because accumulated salts, chemical flocculants, etc. may impair algae growth.

Brackish and marine water is a water source for algal growth (Davis et al., 2012). Wastewater is another source of nutrients for microalgae cultivation that could reduce the operations costs of algae production. There is potential for combining municipal wastewater treatment for nutrient removal and biofuel production from algae. The use of waste water could reduce nutrient addition for nitrogen and phosphorus by approximately 55% (Yang et al., 2011). Aslan and Kapdan (2006) presented a removal efficiency of 72% for nitrogen and 28% for phosphorus when using wastewater for algae growth. However, the direct use of wastewater may introduce pathogens, predatory microorganisms, chemical compounds, or heavy metals into the process (Ferrell et al., 2010; Pittman et al., 2011).

Costs associated with water include pipelines, pumps, and general operating costs. Davis et al. (2012) assumed a pumping power of 30 m total head for water delivery from sources to open pond raceways. With 67% to 75% pump efficiency and 90% motor efficiency, the power requirement of water delivery to a PBR system is 0.3 kWh/m^3 (Davis et al., 2012).

2.7 Algae Cultivation Pathways

Two methods have been commonly used for large-scale production of microalgae, including raceway open ponds and photobioreactors.

2.7.1 Open pond

Several types of open ponds have been used for commercial-scale culturing of microalgae, including extensive ponds, tanks, circular rotating ponds, raceway ponds (Borowitzka, 2005). Very large (extensive) ponds have been used in Australia for the cultivation of *D.salina*, which can grow in high-salinity environments and then contamination can be easily controlled. The size of extensive ponds range from 1 to 5 ha with an average depth of 20 to 30 cm (Borowitzka, 2005). Tanks are always used for small-scale production of algae, such as *Nannochloropsis*. The area of tanks is generally less than 10 m^2 with depth of 50 cm or more (Borowitzka, 2005). Circular ponds have a centrally pivoted rotating agitator and are based on similar systems used in wastewater treatment. The circular ponds can be the maximum of 10,000 m^2 with depth of 30 cm (Borowitzka, 2005).

The most common open ponds are raceway ponds made of a closed loop channel (Figure 2.7.1 a). Typical area ranges from 0.5 to 1 ha (Borowitzka, 2005). Raceway ponds are built in concrete or brick and may be lined. A paddle wheel provides power for the mixing and circulation of water (Chisti, 2007). Rectifiers are built to prevent the buildup of materials in the corner of the raceway.

Figure 2.7.1 a: Schemetic open pond system for algae cutlture.

There are several limitations for open pond algal culturing, including: 1. large amounts of water are lost due to evaporation, 2. temperature is difficult to control, 3. contamination and other algae are easily introduced (Ferrell et al., 2010), 4. CO_2 efficiency is low due to diffusional limitation. Tropical and subtropical zones are the best climatic regions for commercial outdoor open pond cultivation due to high rainfall and temperature (Borowitzka, 2005).

2.7.1.1 Pond design

Open ponds are made of closed loop recirculation channels and are less expensive and easier to operate than PBR systems. There are several considerations for open ponds design, including pond size, location (climate conditions), land cost, and source and quality of water (Borowitzka, 2005).

Pond depths of 5-100 cm are used to provide sufficient sunlight for algae growth (Stephenson et al., 2010; Gong and Jiang, 2011) and the optimal depth is about 0.3 m (Chisti, 2007). The depth of open pond can be calculated by equation in Appendix A.3.2. Adequate mixing will achieve higher productivities and more stable cultures. Flow velocities of at least 20 to 30 cm/s are required to maintain turbulent flow for large ponds (Borowitzka, 2005). Stephenson et al. (2010) chose the size of first kind of open pond with 2 (number of raceway) × 0.3 m (depth) × 10 m (width) × 150 m (length) and second kind of open pond with 2 (number of raceway) × 0.3 m (depth) × 20 m (width) × 190 m (length). Benemann and Oswald (1996) recommended the pond dimension of 2 (number of raceway) × 50 m (width) × 1000 m (length) for large-scale open ponds culture.

2.7.1.2 Pond construction

Ponds can be excavated and lined with impermeable material or constructed above ground with bricks or concrete (Borowitzka, 2005). Excavated ponds are cheap to construct, but the sloping walls can lead contamination with insects, other species of algae, and predators. The choice of construction material may depend on several factors, such as salinity. For example, concrete ponds are unsuitable for saline cultures such as D. *salina* because of corrosion (Borowitzka, 2005). Stephenson et al. (2010) chose concrete hollow blocks, with a density of 650 kg/m^3 and dimension of 0.44 × 0.22 × 0.215 m for open pond wall construction. Concrete blocks are effective in terms of both cost of construction and operation (Borowitzka, 2005). Welssmen and Goebel (1987) estimated that the cost of open pond wall and structure is $8300/ha which includes walls, flow defectors, sumps, and solids removers.

The floors of ponds can be constructed with concrete or some suitable liner (Borowitzka, 2005). Lining material is a significant part of pond construction because it is in contact with the medium and determines seepage, erosion and turbidity, and also effect the chemical composition of algae medium (Becker, 1994). The liner used for outdoor open ponds should be durable, resistant to UV

light and chemicals, non-toxic, and easy to seam (Becker, 1994). UV-resistant polyvinylchloride (PVC) or white reinforced UV-resistant polyethylene (PE) sheets are the most common materials for lining open ponds. Stephenson et al. (2010) suggested that a white PVC liner of 0.75×10^{-3} m thickness and a lifetime of five years be installed at the bottom of an open pond to prevent resuspension of sediments (Borowitzka, 2005; Stephenson et al., 2010). However, it may not be recommended to use PVC liner if the algae are used for food because PVC contains lead and unreacted vinyl chloride that are harmful to humans (Borowitzka, 2005). PVC also has a short life time that may increase the cost of replacement and installation (Becker, 1994). Davis et al. (2012) suggested adding high-density polyethylene (HDPE) liner to prevent pond drainage and percolation. The liner cost is $\$0.47/ft^2$ with a typical lifetime of 20 years or more (Davis et al., 2012).

Land costs for pond construction are variable. Benemann and Oswald (1996) reported that the land cost is $100,000/ha in Hawaii and only a few hundred dollars per hectare in California's Central Valley. Based on the result from Benemann and Oswald (1996), total costs for open ponds sites are $2500/ha which includes costs for site preparation and rough leveling ($1000/ha), laser grading ($1000/ha) and percolation and erosion control ($500/ha).

2.7.1.3 Pond equipment

Figure 2.7.1a displays the general open pond geometry. The paddle wheel is an efficient device that is widely used to provide mixing and circulation. The paddle wheel sits in a depression or sump at the bottom. A minimum clearance between the blades and pond bottom is maintained to reduce backflow (Borowitzka, 2005). Large paddle wheel diameters have greater efficiency because of low backflow. However, larger paddle wheels also result in higher construction cost and greater weight (Borowitzka, 2005). In general paddle wheels can be 5 to 10 m for length and about 30 to 120 cm in diameter depending on the size of open pond. Hydraulic power can be calculate by equations in Appendix A.3.1. Benemann and Oswald (1996) suggested that paddle wheel costs are $5000/ha.

The electricity consumption by paddle wheel mixing has been analyzed in several published sources. Borowitzka (2005) gave the equation for paddle wheel power which is based on hydraulic power in open pond:

$$P = \frac{QW\Delta d}{102e}$$

Where P is the power (kW), Q is the flow rate (m^3/s), Δd is the head loss of water which can be calculate by Manning's equation in Appendix A.3.1. W is the density of water (kg/m^3), 102 is conversion factor to convert m kg s^{-1} to kW (Borowitzka, 2005).

Flow rectifiers should be used at right-angled corners to prevent the buildup of material in the corners. The rectifiers are generally constructed of steel (Borowitzka, 2005).

CO_2 is an essential substrate for algae growth. Benemann and Oswald (1996) suggested the CO_2 transfer system is a 1.5 m deep sump with a baffle and CO_2 sparger at the downflow side. The flow rate of CO_2 is 70 to 130 mM (millimole/L solution) min^{-1} m^{-2} at culture temperature of 25 to 30 ℃. The loss of CO_2 is about 7 mM min^{-1} m^{-2} at the maximum concentration of 1.5 mM CO_2 L^{-1} (Becker, 1994). The flue gas can be added in hourly intervals to the culture. Experiments have shown that CO_2 supply for 4 h per day is sufficient to maintain good algal growth (Becker, 1994). Welssmen and Goebel (1987) estimated that the total cost of the transfer of CO_2 in the sumps system is $2350/ha of open pond which includes the pH controller, control valve, CO_2 flow meter, and associated piping.

2.7.1.4 Pond algae culture

Griffiths and Harrison (2009) summarized that the average microalgae growth in open pond is 24 g m^{-2} d^{-1}. Davis et al. (2011) assumed the algae productivity is 25 g m^{-2} d^{-1} and cell concentration is 0.5 g/L for open ponds. Amer et al. (2011) suggested the algae productivity is 24 g m^{-2} d^{-1}. Stephenson et al. (2010) assumed 1 and 1.7 g/L for algae concentration and 0.3 m/s for medium flow velocity. Table 2.7.1.4a summarizes the algae productivity and concentration for open ponds from several published literature.

Table 2.7.1.4 a: Algae productivity of open pond from published literature.

Source	Algae Productivity (g m^{-2} d^{-1})	Algae Concentration (g/L)
Griffiths and Harrison (2009)	24	--
Amer et al. (2011)	24	--
Davis et al. (2012)	25	0.5
Stephenson et al. (2010)	--	1 or 1.7

2.7.2 Photobioreactor

Photobioreactors (PBRs) designs include tubular PBR, flat-plate, vertical column PBR, aquarium-like tanks, and polyethylene sleeves or containers (Chaumont, 1993; Chisti, 2007; Gong and Jiang, 2011). PBR systems have been mostly used for high-value products since they are relatively expensive to build. Compared to open ponds, PBRs have the advantages of less water consumption, lower probability of contamination, higher CO_2 efficiency, less land use, and improved control (Chisti, 2007; Davis et al, 2011; Gong and Jiang, 2011). The major drawback of using a PBR pathway is substantially greater capital costs when compare with open ponds. In addition, PBRs require periodic cleaning due to biofilm formation. A brief comparison between the open pond and PBR raceway is provided in Table 2.7.2 a.

Table 2.7.2 a: Comparison of open pond versus PBR systems (Chisti, 2007; Mata et al., 2010; Davis et al, 2011; Gong and Jiang, 2011).

	Open Pond	PBR
Capital cost	Low	High
Operating cost	Low	High
Land use	High	Low
Water use	High	Low
Downstream processing cost	Medium (dilute culture)	Low (higher density culture)
Flexibility of culture condition control (Temperature, pH)	Difficult	Easy
Contamination control	Difficult	Easy
Ease of scale-up	Good	Difficult

2.7.2.1 Tubular PBR design

Tubular PBR systems are generally made of a network of glass or plastic tubes (Figure 2.7.2a). Glass tubes have a long lifespan of 20 years. The disadvantages of using glass tube are the limitation of tube length and that they are difficult to transport. Plastic tube can be made of polypropylene (PP), polyvinylchloride (PVC) polyethylene (PE), polycarbonate (PC), and acrylic (Becker, 1994; Briassoulis et al., 2010; Posten, 2012). Polyethylene tubes have a short lifespan. Ultraviolet (UV)-stabilized acrylic tube are widely used because the material is light, flexible, strong and easy to make (Behrens, 2005). PE tubes have been used by the company AlgaeLink Inc. (2013) and glass tubes are used by the company Algomed Inc. (2013).

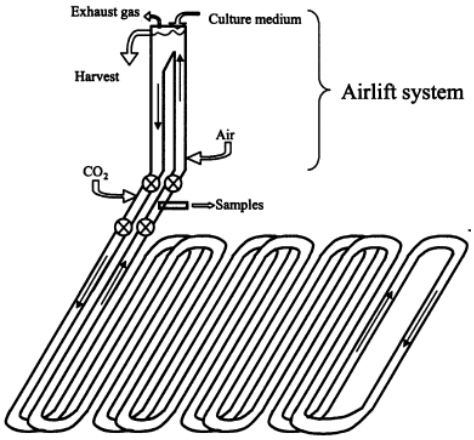


Figure 2.7.2 a: Tubular photobioreactor system (Molina et al., 2001).

The length of tubes vary which depending on the concentration of biomass, growth rate, flow rate, and light intensity (Molina et al., 2001; Chisti, 2007; Stephenson et al., 2010) (Figure 2.7.2a). The solar collector tubes are generally 0.1 m or less in diameter because the light must penetrate the tube. The studies by University of Florence suggested a tube with 4 cm in diameter and about 40 m in length. The parallel PBR system has an inclination of 10% slope and every 40 tubes are connected by manifolds at the bottom and a degasser on the top (Tredici et al., 1998). Tubes with 13 cm diameter and 4 mm thicknesses made of polymethyl methacrylate have been selected as PBR system (Becker, 1994). Davis et al. (2011) suggested a tube with 8 cm ID (inside diameter) × 80 m length. One airlift pump was used for every 80m tube section to strip the oxygen and provide hydraulic power. A tubular system with 5.3 cm × 95 m and 10 cm × 193 m is discussed in Stephenson et al. (2010). Molina et al. (2001) suggested that, for areal productivity of 35 g m^{-2} d^{-1} and volumetric productivity of 1.5 kg m^{-3} d^{-1}, the optimal PBR design is a tube of 6 cm diameter, 80 m long, and 9 cm diameter for the second tube layer with vertical distance of 3 cm between two layers.

Table 2.7.2.1 a: Tubular PBR design from published literature.

Source	Tube Diameter (cm)	Tube Length (m)
Tredici et al. (1998)	4	40
Molina et al. (2001)	6	80
	9	80
Stephenson et al. (2010)	5.3	95
	10	193
Davis et al. (2011)	8	80

Oxygen is generated during the photosynthesis process. In order to prevent damage to the cells, the maximum tolerable dissolved oxygen level cannot be larger than 400% of air saturation in algal culture. Oxygen should be removed by stripping with air in the degassing zone (Molina et al., 2001; Chisti, 2007; Stephenson et al., 2010) (Figure 3.7.2a). In large tubular PBR systems, airlift pumps have been used to strip oxygen and provide hydraulic power to mix the culture without damaging the cells. Fernandez et al. (1997) suggested a 2 m airlift column for a degassing zone, while Molina et al. (2001) recommended a 4 m tall airlift column. The linear velocity of medium in PBR ranges from 0.2 to 0.6 m/s (Becker, 1994). Molina et al. (2001) and Stephenson et al. (2010) chose the linear velocity of 0.50 and 0.35 m/s. The fluid velocity is necessary to prevent settling of the algae, but high velocities can lead to shear force that may damage the algal cells (Becker, 1994).

In the tubes, the temperature can reach 10-15 ℃ higher than the air temperature due to sunlight and metabolic heat generation. Spraying water on the surface of PBR or employing cooling towers has been used to keep cultures cool under outdoor conditions (Ferrell et al., 2010).

2.7.2.2 PBR algae culture

Griffiths and Harrison (2009) summarized that the average microalgae growth rate for PBR is 1.33 kg m^{-3} d^{-1}. Davis et al. (2011) assumed the algae productivity is 1.25 kg m^{-3} d^{-1}, the PBR cultivation volume is 200 m^3/ha and cell concentration is 4 kg/m^3. Amer et al. (2011) suggested the PBR algae productivity is 39.6 g m^{-2} d^{-1}. Two PBR biomass productivities system of 32 g m^{-2} d^{-1}, 1.9 kg m^{-3} d^{-1} and 35 g m^{-2} d^{-1}, 1.5 kg m^{-3} d^{-1} were given by Molina et al. (2001). Stephenson et al. (2010) selected 5 g/L or 8.3 g/L as the concentration of algae, while Chisti (2007) gave 4 g/L. Several equations (Appendix A.2.1) have been used to predict the annual production of algae,

such as *P. tricornutum*. The volumetric productivity of algae will decline as the tube diameter increase due to light limitation (Molina et al., 2001). The suggested algal productivities for PBR systems are demonstrated in Table 2.7.2.2a, while achievable algal concentrations are reported in Table 2.7.2.2b.

Table 2.7.2.2 a: Summaries of algae productivity for airlift PBR.

Source	Algal Strain	Algae Productivity ($g\ m^{-2}\ d^{-1}$)	Algae Productivity ($kg\ m^{-3}\ d^{-1}$)	Volume to Area Ratio (m^3/ha) *
Acien Fernandez et al. (1998)	*Porphyridium cruentum*	20	1.2	167
Rubio et al. (1999)	*Phaeodactylum tricornutum*	-	1.5	-
Molina et al. (2001)	*Phaeodactylum tricornutum*	32	1.9	168
		35	1.5	233
Griffiths and Harrison (2009)	General	-	1.33	-
Amer et al. (2011)	General	39.6	-	-
Davis et al. (2012)	General	25	1.25	200

* Volume to area ratio = algae productivity ($g\ m^{-2}\ d^{-1}$) ÷ algae productivity ($kg\ m^{-3}\ d^{-1}$) × 10.

Table 2.7.2.2 b: Summaries of algae concentration for PBR.

Source	Algae Concentration (kg/m^3)
Stephenson et al. (2010)	5
	8.3
Chisti (2007); Davis et al. (2011)	4

2.8 Downstream Processing: Harvesting and Dewatering

Most microalgal cells have a cellular size range between 3 and 60 μm (Molina et al., 2003; Uduman et al., 2010). The concentration of suspended algae is about 0.02-0.07% in open pond and 0.2-0.83% in PBR (Ferrell et al., 2010; Stephenson et al., 2010; Davis et al., 2011; Davis et al., 2012). Small size and low concentration makes microalgae difficult to harvest (Ferrell et al., 2010). Algae must be concentrated for downstream processing, which includes sedimentation,

flocculation, dissolved air flotation (DAF), filtration, and centrifugation. Energy costs climb steeply when the concentration of the slurries increases (Ferrell et al., 2010).

The criteria for selecting harvesting techniques are dependent on several variables: the species of algae, quantity and quality of production, and economic cost. For commercial-scale treatment of algal culture, sedimentation by natural gravity is recommended (Sahoo and Yarish, 2005). The harvesting process of sedimentation and flocculation, DAF, and centrifugation are recommended by Davis et al. (2012).

2.8.1 Flocculation and sedimentation

Two kinds of equipment, lamella separators and sedimentation tanks, have been used for gravity sedimentation (Shelef et al., 1984; Uduman et al., 2010). However, the reliability of gravity sedimentation is very low and flocculation is frequently used to enhance the sedimentation of algal cells (Shelef et al., 1984).

Flocculation is a process where the algae and flocculants form an aggregate and sediment. There are a variety of forms of flocculation which leads to the sedimentation. Using a chemical additive is an important method to promote flocculation, which can be divided into two groups: inorganic agents and organic agents (Shelef et al., 1984; Uduman et al., 2010). Common chemical additives include alum, lime, cellulose, salts, polyacrylamide polymers, surfactants, chitosan, and other man-made fibers (Ferrell et al., 2010). Chemical additives can reduce the cell surface charge and form precipitates by cell aggregation. Adding some salts, like ferric chloride ($FeCl_3$), ferric sulphate ($Fe_2(SO_4)_3$), and aluminum sulphate ($Al_2(SO_4)_3$) can reduce the surface charge on negative cells which lead to the coagulation of suspended cells (Molina et al., 2004). The optimal dose and pH for several kinds of flocculants are described in Table 2.8.1a.

Table 2.8.1 a: The optimal dose and pH for flocculants (Shelef et al., 1984).

Type	Flocculants	Optimal Dose (mg/l)	Optimal pH
Inorganic	Alum $Al_2(SO_4)_3 \cdot 18H_2O$	80-250	5.3-5.6
	Ferric sulfate $Fe_2(SO_4)_3$	50-90	3-9
	Lime $Mg(OH)_2$	500 -700	10.5-11.5
Organic	Purifloc	35	3.5
	Zetag 51	10	>9
	Dow 21M	10	4-7
	Dow C-31	1-5	2-4
	Chitosan	100	8.4

Flocculation techniques based on pH adjustment has been developed for algae harvest. Knuckey et al. (2006) suggested that adjusting the pH, followed by adding a typical concentration of a non-ionic polymer, can increase the final concentration by a factor of between 200 and 800-fold (800 times of original value). The efficiency of harvesting can be 80% or higher (Knuckey et al., 2006). Autoflocculation and bioflocculation are another two commercial methods for algae harvesting (Chen et al., 2009).

Flocculation and sedimentation is a superior method which can be applied for large quantities of microalgal treatment. High concentrations of algae can be collected by sedimentation in the column. Adding flocculants is an effective method to increase algal cells sedimentation for algal harvesting. For example, Stephenson et al. (2010) selected aluminium sulphate ($Al_2(SO_4)_3$) with a concentration of 0.15 kg/m^3 as flocculants for the LCA analysis. Davis et al. (2012) assumed that natural settling (autoflocculation) or trace flocculants are used for large-scale culturing. Chitosan is selected as flocculant due to its biodegradability in anaerobic digestion (Davis et al., 2012). Eletrocoagulation is an alternative flocculation method that does not involve flocculants. It is an electrochemical technology that can separate microalgae in an electric field without using flocculating agent.

Welssmen and Goebel (1987) proposed a two stage settling process with two large (16,000 m^2) settling ponds. The first pond can concentrate the algae by a factor of 20, and the second pond can be concentrated by an additional factor of 2.5. The settling pond has a dimension of 73 m in width

and 3 m in depth. This system has a long retention time including draining time and settling time. Welssmen and Goebel (1987) proposed a capital cost of $7360/ha for open pond.

Davis et al. (2011) suggested the algae culture can be concentrated to 1 vol% after settling when the concentrations of algae are 4 kg/m^3 (0.4%) for PBR and 0.5 kg/m^3 (0.05%) for open ponds. The efficiency of settling is assumed to be 90% and 5% of water is blowdown that prevents salt build up (Ferrell et al., 2010; Davis et al., 2012). Flocculation and gravity sedimentation are used to separate microalgae in water. The settling tank has a retention time of 2 hours (Davis et al., 2012).

Collet et al. (2011) selected the cone-shaped concrete settler with 1722 m^3 volume, 4 m height and a radius of 11.7 m. One settler is used for 20 open ponds (Collet et al., 2011). Davis et al. (2012) recommended simple in-ground settler tanks with plastic-lined walls and a concrete floor instead of above-ground settlers made of steel and concrete. The capital cost can be reduced by 50% as compared to original settler units (Davis et al., 2012).

2.8.2 DAF

Dissolved air flotation (DAF) is a common dewatering process applied in industrial effluent treatment. The liquid containing dissolved air is injected into the flotation tank. The dissolved air can increase the size of algae aggregates, and the air floats the algae floc to the surface (Ferrell et al., 2010; Uduman et al., 2010; Frank et al., 2011b). The top layer with a high concentration of algae is skimmed off for further processing (Ferrell et al., 2010). Several factors determine the efficiency of DAF harvesting, including the concentration, size and distributions of air bubbles, the pressure of tank, recycle rate, hydraulic retention time, and floc size (Chen et al., 2009; Uduman et al., 2010).

Algae particles can float up faster than they settle down so DAF is more effective than settling (Becker, 1994). The nominal residence time is less than 10 min in DAF. The dissolved air can be pressurized to 3 atm with an air to algae mass ratio of 0.01 (Becker, 1994). Shelef et al. (1984) and Becker (1994) reported that the algae slurry of up to 4-6% can be obtained by DAF. The solid content can increase to 6-8% by holding for 2-4 h (Becker, 1994).

In order to increase the efficiency of separation, algae separation by DAF has often been combined with flocculation (Shelef et al., 1984; Uduman et al., 2010). Studies show that using

autoflocculation by photosynthetically produced dissolved oxygen, the algae removal efficiency can be 80% to 90% (Shelef et al., 1984). Davis et al. (2012) suggested 90% of algae were recovered and algae were thickening to 10% (100 g/L) by DAF using a chitosan as flocculants when algae concentration is 1% (10 kg/m^3) before the DAF process. Sim et al. (1988) estimated the energy consumption for DAF is 0.15 kWh/dry-kg algae. Benemann and Oswald (1996) reported that a 1 MGD (million gallons per day) DAF system cost $215,000, and a 15 MGD unit would cost $1.2 million.

2.8.3 Filtration and screening

Screening utilizes a permeable medium to pass a suspension that retains the solids (Shelef et al., 1984; Uduman et al., 2010). It has specific pore sizes that allow suspension to pass. Two screening devices have been used for algae harvesting: microstrainers and vibrating screen filters (Shelef et al., 1984).

Filtration is another method that applies pressure drop in order to force fluid to flow through a porous material (Shelef et al., 1984). This process is more suitable for relatively large microalgae instead of small cells, such as *Dunaliella* (Molina et al., 2003). The parameters of several filters are summarized in Table 2.8.3a.

Table 2.8.3 a: Comparison of harvesting by filtration methods (Shelef et al., 1984; Molina et al., 2003).

Type	Machine	Operational Mode	%TSS in Concentrate	Energy Consumed (kWh/m^3)	Reliability
Pressure filter	Chamber filter	Discontinuous	22-27%	0.88	Very high
	Belt press	Continuous	18%	0.5	Low
	Suction filter	Discontinuous	16%	-	Good
	Cylindric sieve	Continuous	7.5%	0.3	Good
	Filter basket	Discontinuous	5%	0.2	Good
Vacuum filter	Non-precoat vacuum drum filter	Continuous	18%	5.9	Low
	Potato starch precoat vacuum drum filter	Continuous	37%	-	Good
	Suction filter	After precoating	8%	0.1	Satisfactory
	Belt filter	Continuous	9.5%	0.45	Good
	Filter thickener	Discontinuous	5-7%	1.6	Satisfactory

2.8.4 Centrifugation

Centrifugation has been widely used in algal harvesting. The separation efficiency depends on the characteristics of algae species, such as particle size and density. Although centrifugation is an effective method for algae harvesting, large initial capital equipment investments and operating costs must be considered before any widespread implementation (Becker, 1994; Ferrell et al., 2010; Uduman et al., 2010).

Five major types of centrifuges are used for algae harvesting, including chamber bowl centrifuge, tubular bowl centrifuges, self-cleaning disc-stack centrifuges, nozzle discharge centrifuges, and decanter centrifuges (Becker, 1994; Molina et al., 2004). Chamber centrifuges are suitable for small quantities with low solid fractions (Becker, 1994). Tubular bowls have a large acceleration factor which generally corresponds to high centrifuge efficiency. But this sort of centrifuge has a small capacity that can only be used for small scale operations (Molina et al., 2004). Self-cleaning

disc-stack centrifuges have an acceleration factor of 4000-15,000 g (Appendix A.5.2), and allow a feed biomass content of 0.2-20%. Nozzle centrifuges can concentrate the medium to achieve a concentration of 1-2%. The advantage of this device compared to disc-stack centrifuge is low cost in investment for the same capacity (Becker, 1994). The decanter bowl discharge centrifuge can generate the highest solids fraction (Becker, 1994). Three types of centrifuges for algal biomass dewatering are shown in the Table 2.8.4a.

Table 2.8.4 a: Comparison of centrifugal methods for algae harvesting (Molina et al., 2003; Frank et al., 2011b).

Machine	Operational Mode	Type of Concentration Procedure	Input TSS (total suspended solids) (%)	Output TSS (%)	Energy Consumed per m^3 (kWh/m^3)	Reliability
Self-cleaning Disc-stack centrifuge	Suspension continuous, Concentrate discontinuous	One step	0.1-1	5-12	1	Very good
Nozzle discharge centrifuge	Continuous	For final concentration	1-2	2-15	0.9	Good
Decanter Bowl Centrifuge	Continuous	For final concentration	0.5-4	10 -22	8	Good

Harvesting efficiency depends significantly on species and type of centrifuge (Heasman et al., 2001). Algae recovery efficiency is 85-97% for self-cleaning disc-stack centrifuges and 85%-95% for decanter bowl centrifuges (Frank et al., 2011b). Heasman et al. (2001) summarized that the average centrifuge efficiency is more than 95% for an industrial centrifuge with applied acceleration factor of 13000 g. The average centrifuge efficiency is about 64% for cream separator with applied acceleration factor of 6000 g, while the average centrifuge efficiency is about 45% for low speed laboratory bucket centrifuge with an applied acceleration factor of 1300 g (Appendix A.5.2).

Benemann and Oswald (1996) reported that the largest capacity centrifuge on the market in 1996 was for a feed stream of 20 m^3/h with cost of $600,000. Algae can be concentrated to 200-220 kg/m^3 with the efficiency of 95% (Stephenson et al., 2010; Davis et al., 2012). Stephenson et al.

(2010) and Davis et al. (2012) reported the similar energy consumption number of 8 and 5 kWh/m^3 of feed, respectively.

2.8.5 Drying

The algal biomass can be converted to stable storable product by drying or dehydration (Shelef et al., 1984). Drying is commonly used when the biomass is the final product (Molina et al., 2003). There are several major drying methods that have been used, including rotary dryer, spray drying, sun drying, cross-flow air drying, vacuum shelf-drying, and freeze-drying (Shelef et al., 1984; Molina et al., 2003) (Table 2.8.5a). The cost of harvesting depends on the concentration of algae, temperature and time for the process. Drying is one of most dominant costs for algae harvest and may account for 30% of the total product costs (Becker, 1994). Sun drying is an easy and low-cost possibility for drying, however it requires extra space, considerable time and suitable climate (Ferrell et al., 2010). Table 2.8.5a summarized the characteristics of drying methods.

Table 2.8.5 a: Comparison of microalgae harvesting by drying methods (Becker 1994).

Method	Characters	Cost
Drum drying or rotary drying	Fast and efficient	Cost intensive
Spray drying	Fast and efficient	Cost intensive
Vacuum shelf-drying	Gentle process	Cost intensive
Freeze-drying	Slow process	Cost intensive
Cross-flow air drying	Gentle process	Medium cost
Sun drying	Slow process, whether dependent	Very low cost

2.9 Extraction of Lipid from Algae

Existing extraction technology for algal biomass is widely applied at laboratory-scales and analytical rather than large-scale purposes for biofuel production (Ferrell et al., 2010). There are three major approaches for lipid extraction, including solvent-based extraction relying on cell disruption, using solvent to extract algal lipid without disrupting cellular functions, and extraction bypass schemes (Ferrell et al., 2010).

2.9.1 Cell disruption

Cell disruption can be necessary because the cell wall may present formidable barriers to the solvent extraction process. Disrupted cells can reduce the temperature and pressure requirement

for extracting the lipid from biomass (Ferrell et al., 2010). Based on the microalgal cell wall, different methods can be chosen to disrupt the microalgal cells. Mechanical methods include cell homogenizers, bead mills, sonication, microwaves, autoclave, and spray drying. Non-mechanical methods include freezing, organic solvents, osmotic shock and acid, base, and enzyme reactions (Mata et al., 2010). For example, high frequency sound waves by sonication can cause disruption of cells at high acoustic power (Chisti and Moo-Young, 1986; Geciova et al., 2002). Microwaves are efficient methods using the shock of high-frequency waves to shatter cells (Lee et al., 2010). Lee et al. (2010) reported that microwave is the more efficient method in comparison to bead beating, sonication, autoclave, and osmotic shock. In general, mechanical methods are more effective and popular than other methods (Chisti and Moo-Young, 1986; Geciova et al., 2002).

Homogenization is a common method to disrupt the algal cell membrane (Ferrell et al., 2010). The high-pressure Manton-Gaulin APV type homogenizer is the most widely used device for liquid shear cell disruption and it is suitable for bacteria and yeasts (Chisti and Moo-Young, 1986). Both Stephenson et al. (2010) and Frank et al. (2011a) suggested GEA Niro Soavi homogenizer with flow rates up to 5000 L/h and pressure up to 21,750 psi for algal cell disruption (GEA, 2013a). 96% homogenization efficiency was observed in one pass at 1400 bar with a 15 wt% feed and 79% efficiency in one pass at 1200 bar (GEA, 2013b). GEA NS-3037 (GEA, 2013c) has 37 kW of motor power with a flow rate range from 800 to 12000 L/h, and a pressure range from 1500 to 100 bar. Davis et al. (2012) suggested high-pressure homogenizers have an efficiency of 90% and the power demand is 2.03×10^{-4} kWh/g. Frank et al. (2011a) selected 183 kWh/tonne-algae for power demand and 90% disruption efficiency, corresponding to a 20 wt% feed algae concentration.

2.9.2 Extraction and purification process

Solvent extraction is the most common method to separate the lipid from algae. Different combinations of solvents have been proposed for the extraction of lipids. Nagle and Lemke (1990) suggested three efficient solvents for extraction, including butanol (90% efficiency), followed by hexane/isopropanol and ethanol. Lee et al. (1998) used chloroform/methanol (2:1 v/v (volume of solute/ volume of solution)) as the extraction solvent. Molina et al. (1994) reported that ethanol (96%) and hexane/ethanol (96%) with 1:2.5 v/v are effective for the extraction. Fajardo et al. (2006) used ethanol (96%) as the first step and added water and hexane as second step. The first

step resulted in 90% lipid extraction by two consecutive extractions at room temperature, 5 ml/g-biomass, for 10 h and 1.25 h respectively. The second step yielded 80% recovery of the remaining lipid by four consecutive extractions with a hexane/hydroalcoholic (water 40% v/v, ethanol 60% v/v) phase ratio of 0.2 v/v (Fajardo et al., 2006).

The optimal extraction conditions should be analyzed regarding to temperature, pressure and time of extraction. Laurenz (2008) analyzed the effect of extraction conditions to the lipid yield (Table 2.9.2a). As table 2.9.2a displays, it is apparent that the solvent mixture, temperature and pressure have influence on extraction efficiency. Lipid extraction efficiency increases with increased severity of extraction conditions (Laurenz, 2008). That is because increasing the temperature helps to reduce the viscosity and surface tension of water which can improve the mixing between the solvent and solute. Increasing the pressure also can enhance the transport of solvent contact with solute (Ferrell et al., 2010).

Table 2.9.2 a: Comparison of the lipid yield for three species of microalgae by different extraction methods and conditions (Laurenz, 2008).

Algae Species	Chloroform: Methanol (2:1) (%)			Hexane: Isopropanol (3:2) (%)
Extraction Conditions	40℃/500 psi	70℃/1500 psi	100℃/1500 psi	70℃/1500 psi
Nannochloropsis sp.	25.25 ± 0.15	29.83 ± 0.01	33.33	15.15 ± 0.51
Tetraselmis chuii	14.28 ± 0.17	-	16.93 ± 0.055	-
Nannochloris sp.	9.81 ± 0.41	-	13.08 ± 0.20	-

Although several major extraction solvent mixtures have been used to extract lipid from various microalgae, such as hexane, ethanol, butanol, isopropanol, chloroform and methanol (Nagle and Lemke, 1990; Molina et al., 1994; Lee et al., 1998; Fajardo et al., 2006), these techniques have not been vetted for large-scale biofuel production (Ferrell et al., 2010; Frank et al., 2011a). Methanol is suggested to be replaced by less volatile and toxic alcohols (e.g. isopropanol and ethanol) (Ferrell et al., 2010). Davis et al. (2012) used hexane as extraction solvent, instead of butanol, due to a lower cost and boiling point which is better for solvent stripping and recovery. Both Stephenson et al. (2010) and Frank et al. (2011a) also suggested hexane as the extraction solvent.

Stephenson et al. (2010) suggested that 99% of TAG can be recovered with volumetric flow ratio of hexane to algal slurry of 1:2. Davis et al. (2012) recommended a hexane to biomass ratio of 5:1 to ensure adequate mixing (e.g. hexane to slurry ratio is 1:1 at 20% solid) and result in a 5% of oil lose after extraction. Amer et al. (2011) reported a hexane price is $0.48/kg ($1.15-1.19/gal), while commerce website shows that the low price for hexane is about $1.7/kg ($4.2/gal) (Alibaba, 2013).

Davis et al. (2012) recommended using liquid-liquid extraction (LLE) column as the extraction equipment. The most efficient LLE can provide mechanical agitation of the liquid phase (Seider et al., 2004). In general, LLE has a height-to-diameter ratio of 1, and provides 5 minutes or less residence time depending on the properties of liquid. The rotating-disk extractor has a maximum diameter of 25 ft (7.6 m) and maximum liquid throughout of 120 ft^3 (3.4 m^3) of liquid/hr-ft^2 of column cross-sectional area (Seider et al., 2004). Therefore, the maximum liquid flow rate of LLE is 1.7 m^3/h in a single column (Appendix A.6.1). Stephenson et al. (2010) suggested the countercurrent extraction decanters made by GEA Westfalia (CA 226-29 model) can treat 1.5-2 m^3/h of slurry by 0.75-1 m^3/h of solvent. Table 2.9.2b summarizes the thermal and electricity requirement for algal oil extraction from published literature.

Table 2.9.2 b: Energy inputs for algae oil extraction using hexane as solvent.

Input per kg oil	Heat (kWh)	Electricity (kWh)	Hexane Loss (g)
Lardon et al. (2009)	1.97	0.42	15.2
Lundquist et al. (2010)	0.75-1.00	0.045-0.092	-
Stephenson et al. (2010)	0.47	0.056	3
Davis et al. (2012)	3.15	0.069	-

The solvent can be recovered by separation from the aqueous phase in a stripping column. Stephenson et al. (2010) simulated solvent recovery with HYSYS software by applying the Peng-Robinson equation for vapor-liquid equilibrium. Davis et al. (2012) analyzed the heat and electricity demand using a rigorous TEA Aspen simulation.

2.10 Conversion of Algal Extracts

After the extraction process, the lipid (mainly TAG) can be converted into biodiesel through a transesterification process. Transesterification is a multi-step reaction process, where TAGs are

reacted with methanol (or ethanol) to convert to DAG, MAG, and finally yielding fatty acid methyl esters (FAME) and glycerol (Xu et al., 2005). This reaction is described in Figure 2.10a. The general reaction conditions of lipid transesterification have the temperature between 30 and 70 ℃, typical mixing intensity, and 0.5 to 1.5 wt% of catalyst (e.g. H_2SO_4, HCl, or H_3PO_4) (Noureddini and Zhu, 1997; Vicente et al., 2005). Transesterification technology is relatively mature and has been used at commercial-scale for the conversion of vegetable oil to biodiesel (Ferrell et al., 2010).

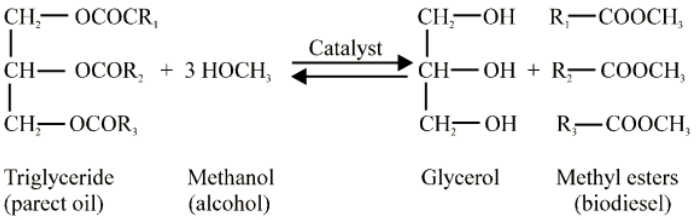


Figure 2.10 a: Transesterification of TAG

2.11 Other Biofuel Conversion Technologies

Potential biofuels produced by algae includes methane, hydrogen, alcohols, and oil (Ferrell et al., 2010). A number of pathways have been used for the production of biofuels from algae.

2.11.1 Biofuels from heterotrophic algae

Biofuels can be directly produced through heterotrophic fermentation and growth without an extraction process. Several major biofuels can be produced by algae, including hydrogen, alcohols, and alkanes (Ferrell et al., 2010).

The productions of hydrogen from algae and cyanobacteria have been studied for decades. The methods to generate hydrogen include direct biophotolysis, indirect biophotolysis, photo-fermentation, and dark-fermentation (Ferrell et al., 2010).

Some algae, such as *Chlamydomonas perifranulata* and *Chlorella vulgaris*, can synthesize starch via photosynthesis or by feeding sugar, store it in the cell, and the cells can be harvested, deconstructed and fermented to produce ethanol and other alcohol (Bush, 2006; Hon-Nami, 2006; Ferrell et al., 2010). Starch-accumulating, filament-forming or colony-forming algae are selected

for the production of alcohol. After harvesting, algae are placed in an anaerobic and dark environment to initiate decay and fermentation of carbon source to alcohol (Bush, 2006; Hon-Nami, 2006). If the alcohol can be separated directly from algal culture media, the algal biofuel process cost will drastically decrease (Ferrell et al., 2010).

Alkanes can be produced directly using algae or cyanobacteria (Schirmer et al., 2010). Rather than growing in sunlight, these algae species can grow heterotrophically by consuming sugar, such as treated lignocellulosic biomass. The algae grow in the dark and can produce more alkane than photosynthetic species. Alkanes can also be produced through catalytic hydrotreating when triglyceride is extracted from algae (Carlson et al., 2010).

2.11.2 Pyrolysis

Pyrolysis is a heating induced decomposition process to convert dried biomass into bio-oil, a carbon rich solid residue and a hydrocarbon rich gas mixture (Aresta et al., 2005). With some hydrotreating and hydrocracking, the bio-oil can be converted to standard diesel in the refinery steam (Ferrell et al., 2010). The pyrolysis product distribution, such as charcoal, bio-oil, gas or methanol, can be driven by changing the process conditions (Aresta et al., 2005).

Three pyrolysis methods have been used for pyrolysis processes, including conventional pyrolysis, fast pyrolysis and flash pyrolysis (Demirbas, 2006). Compared with other algal biofuel conversion methods, pyrolysis is extremely fast with only seconds to minutes of reaction time. For example, the flash pyrolysis takes less than 2 second to achieve when algal biomass is heated to 350 to 500 ℃ (Ferrell et al., 2010). However, there is a significant drawback in using pyrolysis because of high dehydration requirements (Ferrell et al., 2010).

Demirbas (2006) summarized that the maximum yields of oil ranges from 33.6% to 55.3% of biomass weight for seven algae samples using pyrolysis. The yield of bio-oil will increase with increased temperature. For example, with the temperature increase from 525 to 775 K, the bio-oil yield of *Chlorella phrotothecoides* rises from 5.7 to 55.3% (Demirbas, 2006).

2.11.3 Gasification

Gasification is a process for the conversion of organic biomass to pressurized gases rich in H_2, CO, CO_2, and CH_4 (Chakinala et al., 2010). The selectivity of the gas production towards H_2,

syngas (H_2 and CO), or CH_4 depend on the process conditions and catalysis usage (Chakinala et al., 2010).

During the hydrothermal gasification process, high temperature (300-350 ℃) and sufficient pressure (2300-3000 psia) must be maintained for conversion of the algae slurry (Elliott et al., 2009). Fischer-Tropsch synthesis or mixed alcohol synthesis are the two main pathway methods for the production of syngas (Ferrell et al., 2010). Haiduc et al. (2009) found that, using Ni as catalyst, the carbon gasification efficiency is 68-74% and C1- C3 are the primary hydrocarbons for hydrothermal gasification processes.

2.11.4 Liquefaction

Hydrothermal liquefaction is a technology that, at high temperature by applying pressure, wet algal biomass can be converted to liquid fuels without reducing water content (Patil et al., 2008). Compared to pyrolysis and gasification, thermochemical liquefaction has the major advantage of treating algal biomass without requiring drying (Sawayama et al., 1999). This technology harnesses the high activity of subcritical water to decompose the algal biomass into smaller molecules (Ferrell et al., 2010).

In general, liquefaction conditions are maintained at temperature between 200 and 350 ℃, pressure of 10 MPa, reaction time between 5 to 60 min, and heating value between 35 and 50 MJ/kg (Brown et al., 2010). Sodium carbonate serves as a catalyst for the process. The yield of oil generally ranges from 35 to 65% with high N (6%) and O (12%) content (Brown et al., 2010). Major constituents for liquefied oil are C17-C18 n-alkanes and polyaromatic hydrocarbons. Minowa et al. (1995) found that *Dunaliella tertiolecta* with a moisture content of 78.4% gave an oil yield (oil/organic in algal cells) of about 37% at temperature of 340 ℃ and reaction time of 60 min. Liquefaction of algae is a promising technological method, but more research is needed for commercial viability (Ferrell et al., 2010).

2.11.5 Anaerobic digestion

Anaerobic digestion is a biological process to produce methane (CH_4) biogas. Algae are suitable biomass as feedstock for methane production because of its relatively high lipid, starch and protein content (Zamalloa et al., 2011). There are several advantages to using anaerobic digestion

as a process for algae waste treatment after lipid extraction. First, algae contain large quantities of nitrogen and phosphate that are valuable nutrients and should be recovered. Anaerobic digestion can mineralize and recycle nitrogen and phosphorus as substrate of algae (Sialve et al., 2009). Second, the management of huge quantities of residual biomass must be considered after the lipid extraction process. Anaerobic digestion is a key process to convert large quantities of residual biomass into methane which can be burned in a gas turbine to produce power (Davis et al., 2012). Then carbon dioxide can be recycled to the ponds lowering the carbon footprint of the whole process.

Anaerobic digestion (AD) can be thought of as two main reactions. One reaction is liquefaction fermentation by facultative anaerobic bacteria (liquefying bacteria group) in which organic material is degraded to lower molecular weight substances and volatile fatty acids (Ishida, 1982). The other reaction is gasification fermentation by an obligatory anaerobic bacteria (gasifying bacteria group) in which fatty acids are converted into methane (Ishida, 1982). The major groups of bacteria include hydrolytic, acetogenic and methanogenic bacteria (Vergara-Fernandez et al., 2008). General AD reaction conditions are 25-40 ℃ and 6.8-7.3 pH (Ehimen et al., 2011; Sialve et al., 2011). However, anaerobic digestion has a major drawback of slow proceeding, and is conducted for 20-30 days, which may pose important cost for large-scale application (Ishida, 1982; Zamalloa et al., 2011).

Depending on the algae feedstock and the conditions of digestions, the methane concentration in the biogas ranges from 45% to 70% (Ishida, 1982). Sialve et al. (2009) summarized seven articles showing that the common methane yield is between 0.25 and 0.34 L CH_4 g VS^{-1} and the CH_4 volume concentration ranges from 62% to 76%. VS represents volatile solid which is approximately 90% of total algal solid (TS) (Collet et al., 2011). Yen and Bruce (2007) reported that the algal sludge loading rate can reach 6 kg VS m^{-3} d^{-1} for an AD system with 10 days retention time. A longer AD retention time would result in a higher CH_4 yield.

Table 2.11.5a summarizes several studies of AD performance with algae feed. Ras et al. (2011) suggested the COD/VS ratio ranges from 1.33 to 1.43 for algae. Chemical oxygen demand (COD) is a common method to measure the carbon content in water. Benemann and Oswald (1996) reported that about half of the carbon is recovered in the form of methane and the remainder carbon in the digester effluents.

Table 2.11.5 a: Summary of the parameters of anaerobic digestion for algae.

Source	Feed	Digestible Fraction	CH_4 Yield (L/g-VS)	CH_4 Concentration	CO_2 Concentration	Digestion Time (d)
Samson & Leduy (1982)	*Spirulina*	66% of VS	0.26	68-72%	28-32%	33
Collet et al. (2011)	*Chlorella*	56% of carbon	0.29	70%	30%	46
Ras et al. (2011)	*Chlorella*	33% of COD or 29% of carbon	0.15	-	-	16
		51% of COD or 49% of carbon	0.24	-	-	28

Previous research on the anaerobic digestion of microalgae have mostly used for laboratory-scale reactors, including batch reactors, continuous stirred tank reactors (CSTRs), and semi-continuous reactors. High rate reactors are rarely studied to digest microalgae (Zamalloa et al., 2011). A large cylindrical tank with a diameter of 34 m and 11 m high has been considered by Davis et al. (2012) for the AD vessel.

The digester requires thermal and electrical energy. Heat energy is necessary for operating the anaerobic digester and electric energy is required mainly for pumping (Collet et al., 2011; Zamalloa et al., 2011). Collet et al. (2011) reported the energy requirements are 0.68 $kWh_{thermal}$/kg-TS and 0.108 $kWh_{electricity}$/kg-TS. The energy demand values from Zamalloa et al. (2011) for AD reactor are 0.58 $kWh_{thermal}$/kg-TS and 0.19 $kWh_{electricity}$/kg-TS. Davis et al. (2012) summarized three articles and suggested that the total AD energy demand are 0.22 $kWh_{thermal}$/kg-TS and 0.085 $kWh_{electricity}$/kg TS. Benemann and Oswald recommended a capital cost of $3250/ha for the digestion system.

Anaerobic digestion can mineralize and recycle nitrogen and phosphorus as substrate for algae (Sialve et al., 2009). The amount of NH_3 losses in AD depends on pH, hydraulic retention time (HRT), and fermentation temperature (Rosch et al., 2012). At 35 ℃ and pH 7.1, the nitrogen mineralization efficiency is 19% for 16 day HRT and 68% for 28 day HRT (Ras et al., 2011). Both Welssmen and Goebel (1987) and Davis et al. (2012) suggested 75% of nitrogen and 50% phosphorus could be recycled from AD back to algal cultivation. Zamalloa et al. (2011) also assumed the similar nutrient recovery, that 70% of nitrogen and 50% of phosphorus are recovered

during AD process. While Rosch et al. (2012) suggested 61.3% of nitrogen and 79.2% of phosphorus are recycled.

Then the biogas is sent to the gas turbine for power generation. Davis et al. (2012) considered a combined heat and power (CHP) model which including gas compression, combustion, turbine, heat exchangers, and pressure drop. CHP is an integrated system that generates power by burning a variety of fuels. CHP systems have a number of components, including prime mover, generator, heat recovery, and electrical interconnection (EPA, 2008). Stephenson et al. (2010) assumed a 60% electrical efficiency for gas turbine. A total electrical efficiency of 25% is assumed by Davis et al. (2012). Frank et al. (2011a) estimated the electric power generation is 30 MW scale for a 4700 ha algae cultivation with algae productivity of 25 $g/m^2/d$, 25% lipids content, 25 million gallon of algal biofuels per year, and 0.30 L CH_4 g VS^{-1} yield from digester. The typical electrical efficiency is 32% at the 10-MW scale. Rigorous cost estimation of a 10-MW scale process have been conducted by the EPA (2008) (Table 2.11.5b).

Table 2.11.5 b: Cost estimation of 10-MW scale CHP (EPA, 2008).

Cost Component	Cost (Thousand $ in 2007)
Combustion turbines	6,102
Electrical equipment	652
Fuel system	188
Water treatment system	293
Heat recovery steam generators	779
SCR, CO, and CEMS	0
Building	0
Total equipment	8,015
Construction	2,568

2.12 Non-fuel Valuable Products

A large amount of non-fuel commercial products have been derived from algae and cyanobacteria. These include human and animal food and nutrients, poly-unsaturated fatty acids (mainly omega-3), anti-oxidants (mainly β-carotene), coloring substances (carotenoids & astaxanthin), fertilizers

and specialty production for cosmetics and pharmaceuticals (Ferrell et al., 2010). Common commercial products from algae are summarized in Table 2.12a.

Table 2.12 a: Microalgae species with high relevance for application (Pulz and Gross, 2004; Spolaore et al., 2006; Ferrell et al., 2010).

Algae Species	Product	Application Areas
Arthrospira	Omega-3	Nutrient, cosmetics
Chlorella	Biomass	Health food, feed
Chlorophyta	Biomass, Carotenoids, β-carotene	Health food, feed, food colorant
Dunaliella salina	Biomass, β-carotene	Health food, feed
Haematococcus pluvialis	Carotenoids, astaxanthin	Food colorant
Nanochloropsis	Biomass, Omega-3	Aquaculture, nutrient
Phaedactylum tricornutum	Omega-3	Nutrition
Spirulina	Biomass	Health food, feed

Algae can also be used as human food and animal feed. The consumption of microalgae biomass for human food is restricted to few species, mainly *Spirulina* and *Chlorella* (Pulz and Gross, 2004). During the past decades, more than 75% of annual microalgal biomass was utilized in the human health food market (Pulz and Gross, 2004). Algae are also important food sources for the larva of mollusks, echinoderms, fish, and crustaceans (Muller-Feuga, 2000). The main algae species for feed are *Chlorella*, *Spirulina*, and *Dunaliella* which are worth about $15-20 per kg dry algae (Borowitzka, 1997). In addition, animals, such as cows, horses, and pigs, can be fed by algae. The frequently used species are *Chlorella*, *Spirulina*, and *Scenedesmus* (Pulz and Gross, 2004).

Microalgae have a very promising polyunsaturated fatty acid (PUFA) market for food and feed. PUFA can be divided into omega-3, omega-6, and omega-9 which depend on the number of double bonds. Omega-3 fatty acid (e.g. DHA, RPA) and omega-6 fatty acid (e.g. GLA, AA) are potentially beneficial for human health (Spolaore et al., 2006; Ferrell et al., 2010). Microalgae also can produce anti-oxidants that are used for health food. β-carotene from *Dunaliella salina*, has already reached large-scale production (Pulz and Gross, 2004).

In addition, there are a number of other valuable products that can be obtained from microalgae. Microalgae species, such as *Arthrospira* and *Chlorella*, can produce face and skin care products

(Spolaore et al., 2006). The astaxanthins extracted from *Haematococcus* can be used as natural food colorants (Spolaore et al., 2006).

2.13 Algae Biodiesel Economic Review

Large-scale algal biofuel production is a theoretical rather than a mature commercial process. The literature parameters are derived from a mixture of small-scale algae growth experiences, wastewater treatment, lab-scale experiments, and some purely theoretical research (Frank et al., 2011a). Literature TEAs of large-scale algal biofuel process are based on similar industrial operations, pilot-scale facilities and research.

In the US during February 2013, the average price of on-highway petrodiesel was $4.11 per gallon including taxes (12%), distribution and marketing (16%), crude oil (60%) and refining (12%) (EIA, 2013). If taxes, distribution and marketing are not included, the average price of petrodiesel in February 2013 will be $2.96/gal with 83% from crude oil and 17% from refining.

Research on microalgae has been performed for more than 50 years (Chisti, 2007; Mata et al., 2010; Gong and Jiang, 2011). However, commercial implementation of microalgal biofuel is still in its infancy for feasibility and viability at large-scales. The cost of producing the microalgae is the most important factor for a comprehensive assessment of microalgal biofuel. The cost estimations of large-scale open pond algal biofuel from literature are summarized in Table 2.13a.

Table 2.13 a: Cost estimation of open pond algal biofuel from various published literature.

Source	Algae Productivity (g m^{-2} d^{-1})	Lipid Content	Biofuel Cost ($/gal)
Sun et al. (2011) NMSU	35	35%	25.2
Sun et al. (2011) Sandia	30	35%	15.7
Sun et al. (2011) California	20	unknown	16.8
Davis et al. (2012)	25	25%	9.3

3 TECHNO-ECONOMIC ANALYSIS RESULTS

There have been a few algal biofuel TEAs published in the literature. However, in each of these studies, most of the detailed calculations are not presented. A detailed TEA was completed based on the most reliable published process descriptions from NREL (Davis et al., 2011; Davis et al., 2012). Additional literature was utilized to fill in the methodological and calculation gaps in the NREL reports. The results of the TEA were validated with the NREL conclusions to ensure the TEA methodology was correct. Then a sensitivity analysis was performed on a suite of parameters that were not specified in the NREL studies, or parameters where other studies suggested different values.

3.1 Baseline Algal Biofuel Pathway Overview for TEA

The production of biodiesel from lipid is a relatively mature process and has been used for commercial-scale biodiesel production (Ferrell et al., 2010). Therefore, biodiesel conversion from lipid will not be analyzed in this scenario.

The algae production and processing pathway is based on the model created by NREL (Davis et al., 2012). As demonstrated by Figure 3.1a (Davis et al., 2012), the algae grow through the inputs of nutrients, CO_2 and water. Raceway open ponds and tubular PBRs are the most common commercial-scale algae culture systems. Most lipid extraction processes require high concentration of algae cells so dewatering processes are utilized to harvest algae. Several dewatering processes can concentrate low concentration algae into slurries, including flocculation, sedimentation, DAF, filtration, and centrifugation. Based on the TEA model developed by NREL (Davis et al., 2012), sedimentation, DAF and centrifugation are selected for algae harvesting. Some culture medium, including water and some algae, can be recycled after the dewatering process. Cell disruption is implemented before lipid extraction in order to prevent the barriers of the cell wall in the solvent extraction process. Then the extraction solvent will be recovered in a stripping column. Algae debris from extraction is sent to anaerobic digestion to produce CH_4 and generate electricity and heat by combined heat and power (CHP) systems. Nutrients and water can also be recovered back to algae cultivation from anaerobic digestion.

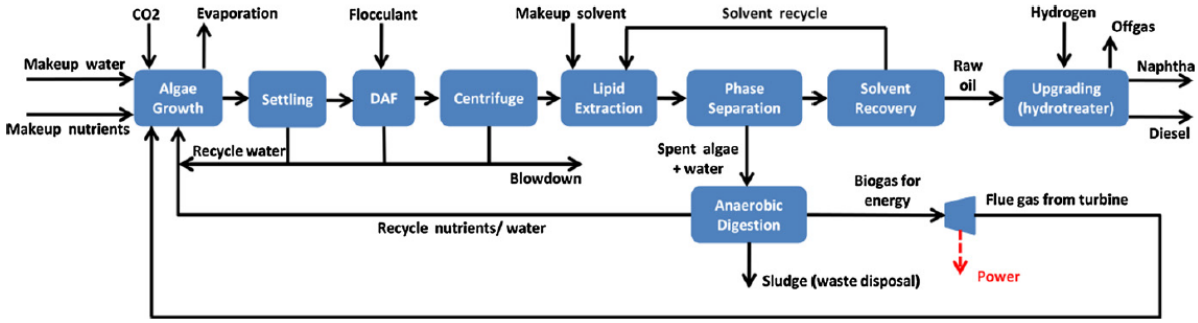


Figure 3.1 a: Baseline process for TEA analysis. (Davis et al., 2012)

3.2 Open Ponds

More than 1,000 open ponds are required to produce 10 million gallons of lipid per year. For commercial-scale algae culture, it was assumed that the open pond was excavated and lined with clay and liner. Thin concrete might be used to set the clay, but this cost is neglected in this analysis. A white reinforced UV-resistant polyethylene liner was installed on the floor and walls of the open ponds to prevent leaking. The base case will be set up with one pond containing two 20 m wide and 400 m long raceways. An eight-blade paddle wheel with dimension of 1 m diameter and 20 m width is selected to provide the mechanical power to water movement. Steel rectifiers are installed in the four corners to guide the water flow. A porous pipe diffuser system spans the raceway on the downstream side of CO_2 sumps. Construction and equipment has a life time of 20 years. The land cost is assumed to be $3800/ha based on the study of Benemann and Oswald (1996) (cost update). Table 3.2a summarizes the parameters and installation costs for open ponds. The electricity consumption of paddle wheel mixing is calculated by equation in 2.7.1.3 and summarized in Table 3.2b.

Table 3.2 a: Summary of a base-case open pond cost and total cost of 1,234 ponds.

	Material	Dimension	Size	Price ($)	Direct Cost ($)	Total Direct Cost ($MM)*
Open pond wall and floor	Clay and concrete	2 m × 20 m × 400 m	16,000 m^2	15,000/ha[2]	24,000	30
Liner	PVC (0.75×10^{-3} m) [1]	50 m × 410 m	20,500 m^2	5/m^2[3]	102,500	127
Paddle wheel	Steel	1 m × 20 m	1	8000[4]	8,000	9.9
Rectifier	¼'' Steel	44 m × 0.6 m + 88 m × 0.6 m	2.0 m^3	700/tonne	10,920	13
CO_2 injector	Pipe	-	-	4,200/ha[2]	6,720	8.3
Total cost					152,140	188

*Total direct cost is calculated by direct cost of one open pond multiplying pond number (1234).

[1] Stephenson et al. (2010).

[2] Welssmen and Goebel (1987), cost update.

[3] Benemann and Oswald (1996); Davis et al. (2011).

[4] Benemann and Oswald (1996), cost update.

The assumed algae productivity of open ponds is 25 g m^{-2} d^{-1}. Open ponds have an algae concentration of 0.5 g/L and flow velocity of 0.3 m/s. The pond depth and water evaporation is assumed to be 0.3 m and 0.003 m/d respectively. The general open pond parameters are summarized in Table 3.2b.

Table 3.2 b: TEA open pond parameters assumptions.

Parameters	Value	Source and Note
Algae productivity ($g/m^2/d$)	25	Griffiths and Harrison (2009); Amer et al. (2011); Davis et al. (2012)
Algae productivity ($kg/m^3/d$)	0.083	Calculation
Algae concentration (g/L)	0.5	Stephenson et al. (2010); Davis et al. (2012)
Land demand (acre)	4880	Calculation
Land cost ($/ha)	3800	Benemann and Oswald (1996), cost update
Land cost ($MM)	7.5	Calculation
Mean velocity (m/s)	0.3	Stephenson et al. (2010)
Pond depth (m)	0.3	Chisti (2007); Stephenson et al. (2010); Gong and Jiang, (2011)
Water evaporation (m/d)	0.003	Yang et al. (2011); Davis et al. (2012)
Pond width (m)	20	Benemann and Oswald (1996); Stephenson et al. (2010)
Pond length (m)	400	Benemann and Oswald (1996); Stephenson et al. (2010)
Hydraulic mean depth (m)	0.29	Calculation
Raceway number (for one open pond)	2	Assumption
Pond flow rate (m^3/s)	1.8	Calculation
One pond water evaporation (m^3/d)	48	Calculation
Pond number	1234	Calculation
Total water evaporation (m^3/d)	59,246	Calculation
Total water evaporation (ton/yr)	21,551,625	Calculation
One pond area (m^2)	16,000	Calculation
One pond volume (m^3)	4800	Calculation
Algae weight in open pond (ton)	3265	Calculation
Algae growth residence time (d)	6.0	Calculation
Open pond total area (m^2)	19,748,799	Calculation
Open pond total volume (m^3)	5,924,640	Calculation
Liner dimension (m × m)	50 × 410	Assumption
Pond life time (yr)	20	Stephenson et al. (2010); Davis et al. (2012)

Paddle wheel dimension (diameter (m) × width (m))	1 × 20	Borowitzka (2005)
Paddle wheel number for one pond	1	Borowitzka (2005)
Total paddle wheel number	1234	Calculation
Open pond head loss	0.084	Calculation
Paddle wheel efficiency	17%	Borowitzka (2005)
One paddle wheel power (kW)	8.7	Calculation
Total paddle wheel power (kW)	10,751	Calculation

3.3 PBR

A two-layer tubular PBR system with 6 cm (diameter) × 80 m (length) and 9 cm (diameter) × 90 m (length) are selected for algae cultivation based on the model from Molina et al. (2001) (Figure 3.3a). The tubes are made of acrylic and have a life time of 20 years. One 4 m airlift column is connected to every section of PBR tubes to strip oxygen and provide hydraulic power to mix the culture. Tubular PBRs are cooled with water sprays to maintain the cultivation temperature.

Figure 3.3 a: two-plane reactor at the Centro di Studio dei Microrganismi Autotrofi of the CNR (Florence, Italy) (Tredici, 2004)

The cost of the PBR system includes feed pumps, the main tubular PBR and U-bend connectors, airlift pump, water spray and miscellaneous items. Few literature studies have discussed the economics of PBRs. Molina et al. (2003) reported that the direct cost of one PBR system (0.8 m^3) is $3524 and the direct cost of PBR feed pump (0.04 m^3/h) is $349. Eplastics (2013) demonstrated that the 6 cm ID and 9 cm ID acrylic tubes are about $11/m and $24/m, respectively,

which result in a cost of $2800 (80 m length for pipe) for pipe in one PBR system. Basic on the assumptions of Molina et al. (2003), the total direct cost of one PBR system (0.74 m^3) is calculated to be is $3260 (Table 3.3a).

Table 3.3 a: Cost of a single PBR system and the total cost of PBRs to produce 10 MM gal biofuel per year.

	Direct cost ($/System)	Quantity	Total direct cost (MM $)
PBR	4700[1]	537,000	2520

[1] Molina et al. (2003), cost update.

The algae productivity in the PBR is assumed to be 25 g m^{-2} d^{-1}, which by volume is 1.25 kg m^{-3} d^{-1}. The PBR has an algae concentration of 4.0 g/L and fluid velocity of 0.5 m/s. The general PBR parameters are summarized in Table 3.3b.

Table 3.3 b: TEA main PBR design and operating parameters.

Parameters	First Layer of Tubular PBR	Second Layer of Tubular PBR	Source and Note
Algae productivity (g/m^2/d)	25		Griffiths and Harrison (2009); Amer et al. (2011); Davis et al. (2012)
Algae productivity (kg/m^3/d)	1.25		Acien Fernandez et al. (1998); Rubio et al. (1999); Molina et al. (2001); Davis et al. (2012)
Land demand (acre)	4880		Calculation
Algae productivity (ton/ha/yr)	91		Calculation
Lipid productivity (gal/acre/yr)	2049		Calculation
Lipid content	25%		Becker (1994); Griffiths and Harrison (2009); Mata et al., 2010; Davis et al. (2012)
Mean velocity (m/s)	0.5		Becker (1994); Molina et al. (2001); Stephenson et al. (2010)
Tube diameter (cm)	6	9	Tredici et al. (1998); Molina et al. (2001); Stephenson et al. (2010); Davis et al. (2011)
Tube length (m)	80	80	Tredici et al. (1998); Molina et al. (2001); Stephenson et al. (2010); Davis et al. (2011)

Tube nominal land area (m^2)	4.8	7.2	Calculation
PBR total nominal land area (m^2)	6,447,614		Calculation
PBR nominal area/ total land area	32.65%		Calculation
Tube volume (m^3)	0.23	0.51	Calculation
Tube volume/ nominal land area (m^3/ha)	613		Calculation
Tube volume/land area (m^3/ha)	200		Davis et al. (2011)
Tube number	537,301	537,301	Calculation
PBR total volume (m^3)	394,976		Calculation
PBR life time (yr)	20		Assumption
Reynolds number	30,000	45,000	Calculation
Water flow retention time (s)	160	160	Calculation
One tube flow rate (m^3/h)	5.1	11	Calculation
Algae concentration (kg/m^3)	4		Chisti (2007); Stephenson et al. (2010); Davis et al. (2011)
Algae weight in PBR (ton)	1742		Calculation
Algae growth residence time (d)	3.2		Calculation
Airlift pump number	1,074,602		Calculation

3.4 Nutrients, Water, and CO_2

In order to evaluate the general nutrient demand, an algae composition of $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$ is selected for this scenario (Grobbelaar, 2004). Two major nutrients, nitrogen and phosphate, will be evaluated for TEA. Additional nutrients, such as silicon, sulfur, trace metals, and vitamins, which vary depending on the specific algae strain, will not be considered during this TEA study. It is assumed that 95 % of the water is recycled during the dewatering process. Some of the nutrients and algae are included in the water recycled to the algal cultivation system.

3.4.1 Phosphorus

DAP ($(NH_3)_2HPO_4$) is selected as the basic source of phosphorus nutrient (Davis et al. 2012). It was assumed phosphorus utilization is 80% for algae growth, meaning that of the phosphorus supplied to the cultivation media, 80% is taken up by the algae and 20% remains in the water. None of the literature gives guidance for this assumption. 50% of the phosphorus contained in the algal biomass is recycled from anaerobic digestion to the biomass cultivation system. Table

3.4.1a presents the main phosphorus nutrient parameters in order to produce 10 MM gal biofuel per year. The main mass flows of phosphorus are presented in Figure 3.8.2.1a to Figure 3.8.2.6a under different conditions. The average price of DAP was about $643/ton between 2007 and 2009 (Campbell, 2009), which is similar to the price of $600-660/ton in 2013 (USDA, 2013a; USDA, 2013b).

Table 3.4.1 a: P nutrient parameters for TEA to produce 10 MM gal biofuel per year.

Parameters	Value	Source and Note
Composition of algae	$CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$	Grobbelaar (2004)
Algae molecular weight (g/mol)	23.39	Calculation
Algae required to grow (ton/yr) (*some algae recycled after harvesting)	182,287	Calculation
Gross phosphorus as P (g/dry – g algae)	0.013	Calculation
Composition of DAP	$(NH_4)_2HPO_4$	--
DAP molecular weight	132	Calculation
Gross phosphorus as DAP (g/dry – g algae)	0.056	Calculation
Gross phosphorus as DAP (ton/yr)	10,140	Calculation
DAP utilization	80%	Assumption
DAP recycle rate after AD	50%	Davis et al. (2012); Rosch et al. (2012)
DAP demand (ton/yr)	5351	Calculation
DAP price ($/ton)	643	Campbell (2009); USDA (2013a); USDA (2013b)
DAP cost ($MM/yr)	3.44	Calculation

3.4.2 Nitrogen

Nitrogen is assumed to be supplied by urea ($CO(NH_2)_2$) or anhydrous ammonia (NH_3) for TEAs. In this study, it was assumed nitrogen utilization is 80% for algae growth, meaning that of the phosphorus supplied to the cultivation media, 80% is taken up by the algae and 20% remains in the water. None of the literature gives guidance for this assumption. 75% of the nitrogen in the algal biomass is recycled to algal cultivation after anaerobic digestion. DAP ($(NH_3)_2HPO_4$) has nitrogen structure which may reduce the demand of urea or ammonia. The main mass flows of nitrogen are presented in Figure 3.8.2.1a to Figure 3.8.2.6a by different conditions.

The average price of urea was about $497/ton between 2007 and 2009 (Campbell, 2009) which is not much different to the price of $480-540 in 2013 (USDA, 2013a; USDA, 2013b). The average price of anhydrous ammonia is about $900/ton (Campbell, 2009; USDA, 2013a; USDA, 2013b). The parameters for urea and ammonia are summarized in Table 3.4.2a.

Table 3.4.2 a: N nutrient parameters for TEA.

Parameters	Value		Source and Note
Composition of algae	$CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$		Grobbelaar (2004)
Algae molecular weight (g/mol)	23.39		Calculation
Algae need to grow (ton/yr) (*some algae recycled after harvesting)	182,287		Calculation
Nitrogen nutrient	Ammonia	Urea	--
Gross nitrogen as N (g/dry – g algae)	0.066		Calculation
Gross nitrogen as ammonia or urea (ton/yr)	14,359	32,929	Calculation
Utilization	80%		Assumption
Recycle rate after AD	75%		Davis et al. (2012); Rosch et al. (2012)
N demand as format of NH_3 (ton/yr)	3987	7036	Calculation
Ammonia actual demand (ton/yr) (DAP has NH_3)	2595	5644	Calculation
Price ($/ton)	900	497	Campbell (2009); USDA (2013a); USDA (2013b)
Cost ($MM/yr)	2.34	2.81	Calculation

3.4.3 Water Demand

The assumed algae concentrations are 0.5 kg/m^3 (0.005%) for open ponds and 4 kg/m^3 (0.04%) for PBRs. It was assumed that the evaporation rate is 0.03 cm/day for open ponds and there is no evaporation for PBR. The concentration of algae is 1% in the settling tank effluent, which is thickened to 10% by dissolved air flotation and further concentrated to 20% by the centrifuge. The harvesting efficiency is 90% in settling (meaning 90% of the influent algal biomass is in the settled effluent), 90% in DAF, and 95% in centrifugation. There is a 5% water loss in the entire harvesting process which includes settling, DAF, and centrifugation. The concentrated algae (20%) are sent to the lipid extraction process and then anaerobic digestion. It is assumed that 75%

of water influent to anaerobic digestion is returned to the algal cultivation. The main mass flows of water are presented in Figure 3.8.2.1a to Figure 3.8.2.6a by different conditions.

The water price is assumed to be $0.05/1000 gal (Davis et al., 2011). Costs associated with water supply include pipelines, pumps, and general operating costs. It is assumed a pumping power of 30 m total head and 1 mile of pipeline for water delivery from sources to pathways. The pump has total efficiency of 67% from 75% pump efficiency and 90% motor efficiency. The power consumption by pump is calculated in Appendix A.4.1 and displayed in Table 3.4.3b.

Table 3.4.3 a: Water parameters for TEA for 10 MM gal biofuel per year.

Parameters	PBR Value	Open Ponds Value	Source and Note
Water recycle after dewatering process	95%		Davis et al. (2011)
Total flow rate after algae cultivation (ton/yr)	58,348,561	466,788,491	Calculation
Water flow rate after algae cultivation (ton/yr)	58,115,167	466,555,097	Calculation
Water evaporation (m/d)	0	0.003	Yang et al. (2011); Davis et al. (2012)
Water evaporation (ton/yr)	0	21,551,625	Calculation
Water demand (ton/yr) (Open pond has evaporation)	3,049,611	45,023,232	Calculation
Water demand (MM gal/yr)	731	10,790	Calculation
Water demand (m^3/h)	349	5157	Calculation
Water demand/diesel productivity	79	1173	Calculation
Water Price ($/1000 gal)	0.05	0.05	Davis et al. (2011)
Water cost ($MM/yr)	0.037	0.539	Calculation
Water pipeline length (m)	1609		Davis et al. (2012)
Water pipeline head (m)	30		Davis et al. (2012)
Water pump efficiency	67%	67%	Davis et al. (2012)
Water Pump from off-site, kW	43	629	Calculation
Water Pump from off-site, kWh/m^3	0.12	0.12	Calculation
Centrifugal pump flow rate (gpm)	1000		Assumption
Centrifugal pump flow rate (m^3/h)	227		Calculation
Pump number	2	24	Calculation

Centrifugal pumps were selected to deliver the water for open ponds and PBRs since they are the most commonly used pumps for water movement. The volumetric flow rate of centrifugal pumps ranges from 10 gpm (gallon per minute) to 5000 gpm and hydraulic head ranges from 50 ft (15.24 m) to 3200 ft (975.4 m) (Seider et al., 2004). Since a large amount of water is demanded for algal growth, a centrifugal pump with a flow rate of 1000 gpm was selected for water transportation. The general parameters and costs for pumping are calculated in Appendix A.4.1 and displayed in Table A.3.4.3b.

Table 3.4.3 b: Pump cost for water transportation to algal cultivation from off-site.

	Pump Cost ($)	Quantity	Total Direct Cost ($)
Centrifuge pump for PBR	19,000	3	57,000
Centrifuge pump for open pond	19,000	24	456,000

3.4.4 CO_2 Demand

It was assumed that the composition of algae is $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$ and the algal lipid is 100% of TAG. In order to calculate nutrient demand, all of the TAG is assumed to be triolein ($C_{57}H_{104}O_6$, C18:1). The only source of carbon in both the algae and lipids comes from CO_2. For both PBR and open pond, the utilization of CO_2 is 90% for algae growth (Sheehan et al., 1998). The water blowdown is 5% after the dewatering process to prevent salt build up. After lipid extraction, algal sludge is sent to anaerobic digestion which recycles 46.8% of the carbon to the cultivation (calculated in A.7.1 and displayed in Table 3.7.1b). The main mass flows of CO_2 are presented in Figure 3.8.2.1a to Figure 3.8.2.6a under different conditions.

Flue gas with 13% of CO_2 (the maximum value for natural gas fired power station) is selected as the carbon source. The price of CO_2 is $40/ton. The main parameters for CO_2 usage are summarized in Table 3.4.4a.

Table 3.4.4 a: CO_2 parameters for TEA to produce 10 MM gal biofuel per year.

Parameters	Value	Source and Note
TAG formula	$C_{57}H_{104}O_6$	Triolein formula
Triolein molecular weight	885.44	Calculation
Carbon concentration in triolein	77.3%	Calculation
Carbon concentration in algae	51.3%	Calculation
Gross CO_2 for lipid (ton/yr)	108,835	Calculation
Gross CO_2 (g/dry - g algae)	1.882	Calculation
Gross CO_2 for algae (ton/yr)	337,925	Calculation
CO_2 efficiency	90%	Sheehan et al. (1998)
CO_2 Demand (ton/yr)	289,907	Calculation
CO_2 Price ($/ton)	40	Kadam (1997); Davis et al. (2011)
CO_2 cost ($MM/yr)	11.6	Calculation
Anaerobic digest CO_2 recycle rate to CHP	46.8%	Calculation
CO_2 recovery from CHP	85%	Benemann and Oswald (1996)
CO_2 recycle from anaerobic digest (ton/yr)	91,132	Calculation
CO_2 emission from CHP	16,048	Calculation

It was assumed that low-pressure CO_2 is transported by pipelines. The cost of the CO_2 supply system includes the main pipe from the power plant, distribution piping, blower, and miscellaneous items (Benemann and Oswald, 1996). The cost estimations for CO_2 delivery are available in Table 3.4.4b.

Table 3.4.4 b: Cost for CO_2 delivery.

Parameters	Value	Source and Note
CO_2 pipeline length (mile)	3	Benemann et al. (1982); Benemann and Oswald (1996)
Cost of CO_2 from the power plant to open pond ($/ha)	9600	Benemann and Oswald (1996), cost update
Total cost of CO_2 off-site delivery ($MM)	19	Calculation

3.5 Downstream Processing: Harvesting and Dewatering

This scenario suggests three downstream processes for algae harvesting and dewatering, including: flocculation and sedimentation, dissolved air flotation (DAF), and centrifugation.

3.5.1 Flocculation and Sedimentation

In this scenario, chemical flocculants should be carefully controlled in order to recover water that is unaffected by accumulation of chemical. Eletrocoagulation will be used as a flocculation method which does not involve chemical flocculants. Because of this most of water can be recycled without considering chemical accumulation.

The concentration of algae is 4 kg/m^3 (0.4%) for PBR and 0.5 kg/m^3 (0.05%) for open ponds. It was assumed that the algae can be concentrated to 1% by settler with the efficiency of 90%. The settler has a retention time of 2 h with a dimension of 4 m for height and 11.7 m in diameter. The main parameters of the settler are summarized in Table 3.5.1a.

Table 3.5.1 a: Main parameters for flocculation and sedimentation.

Parameters	PBR Value	Open Pond Value	Source and Note
Settler efficiency	90%		Knuckey et al. (2006); Ferrell et al. (2010); Davis et al. (2012)
Settler input flow rate (ton/yr)	58,348,561	466,788,491	Calculation
Settler input algae flow rate (ton/yr)	233,394	233,394	Calculation
Settler input water flow rate (ton/yr)	58,115,167	466,555,097	Calculation
Settler output algae concentration (%)	1%		Davis et al. (2012)
Settler output algae concentration (kg/m^3)	10		Calculation
Settler output flow rate (ton/yr)	21,005,482	21,005,482	Calculation
Settler output algae flow rate (ton/yr)	210,055	210,055	Calculation
Settler recycle stream output (ton/yr)	37,343,079	445,783,009	Calculation
Settler recycle stream algae output (ton/yr)	23,339	23,339	Calculation
Settler retention time (h)	2		Davis et al. (2012)
Settler height (m)	4		Collet et al. (2011)
Settler diameter (m)	11.7		Collet et al. (2011)
Settler volume (m^3)	430		Calculation
Settler number	32	250	Calculation

The setting cost of a settler for open pond system is $7360/ha, which was estimated by Welssmen and Goebel (1987). In order to calculate the cost of settler for PBR system, it is assumed that the number and cost of settler is proportional to the amount of algae treatment in settling process.

Table 3.5.1 b: Cost of settler system for open ponds.

	Direct Cost ($)	Total Direct Cost ($MM)
Settler for open pond	13,000/ha[1]	26
Settler for PBR	--	3.2

[1] Welssmen and Goebel (1987), cost update.

3.5.2 DAF

The concentration of algae is 1% (10 kg/m^3) before DAF process. It is assumed that 90% of algae are recovered and algae are thickened to 10% (100 g/L) by DAF with the use of chitosan as a flocculent. DAF units that process 15 MGD (million gallons per day) are required to harvest algae (Table 3.5.2a and Table 3.5.2b). The energy consumption for DAF is assumed to be 0.15 kWh/dry-kg algae based on the result of Sim et al. (1988).

Table 3.5.2 a: Main parameter for DAF process.

Parameters	Value	Source and Note
DAF efficiency	90%	Shelef et al. (1984); Davis et al. (2012)
DAF input flow rate (m^3/h)	2406	Calculation
DAF input flow rate (MGD)	15.3	Calculation
DAF input algae flow rate (ton/yr)	210,055	Calculation
DAF output algae content	10%	Shelef et al. (1984); Becker (1994); Davis et al. (2012)
DAF output algae content (kg/m^3)	100	Calculation
DAF output flow rate (m^3/h)	217	Calculation
DAF output algae flow rate (ton/yr)	189,049	Calculation
DAF recycle stream output (ton/yr)	19,114,989	Calculation
DAF recycle stream algae output (ton/yr)	21,005	Calculation
DAF energy, kWh/kg-algae	0.15	Sim et al. (1988)
Electricity, DAF, kW	3609	Calculation

Table 3.5.2 b: Cost of DAF system.

	DAF Unit Flow Rate (MGD)	DAF Unit Cost ($MM)	Quantity	Total Direct Cost ($MM)
DAF	15[1]	1.8[1]	2	3.6

[1] Benemann and Oswald (1996), cost update.

3.5.3 Centrifugation

A high-capacity decanter bowl centrifuge was selected as a final separator for algal harvesting. The concentration of algae is 10% (100 kg/m^3) before centrifugation. It was assumed that 95% of algae are recovered and algae are thickened to 20% (200 g/L) by centrifuge. The bowl decanter centrifuge has a capacity of 20 m^3/h and an electricity consumption of 40 kW. The main parameters and costs of centrifugation are summarized in Table 3.5.3a and Table 3.5.3b.

Table 3.5.3 a: Main parameters for centrifuge.

Parameters	Value	Source and Note
Centrifugation Efficiency	95%	Heasman et al. (2001); Stephenson et al. (2010); Frank et al. (2011b); Davis et al. (2012)
Centrifugation input flow rate (ton/yr)	1,890,493	Calculation
Centrifugation input algae flow rate (ton/yr)	189,049	Calculation
Centrifugation output algae content	20%	Molina et al. (2003); Frank et al. (2011b); Davis et al. (2012)
Centrifugation output algae content (kg/m^3)	200	Calculation
Centrifugation output flow rate (ton/yr)	897,984	Calculation
Centrifugation output algae flow rate (ton/yr)	179,597	Calculation
Centrifugation recycle stream output (ton/yr)	992,509	Calculation
Centrifugation recycle stream algae output (ton/yr)	9452	Calculation
Centrifugation flow rate (m^3/h)	20	Benemann and Oswald (1996)
Centrifuge number	12	Calculation
One centrifuge power (kW)	40	Assumption (based on parameters for similar centrifuges)
Electricity, Centrifugation, kW	480	Calculation
Centrifuge energy, kWh/kg-out	2.33E-5	Calculation

Table 3.5.3 b: Cost of centrifuge system.

	Price ($)	Quantity	Direct Cost ($MM)
Centrifuge (20 m^3/h)	920,000[1]	12	11
Addition cost (e.g. storage tank, pump)	10%[1]	-	1.1

[1] Benemann and Oswald (1996), cost update.

The waste water effluent streams from settler, DAF, and centrifugation are combined in a recycle stream. It was assumed that only 5% of the total recycled water stream is blowdown to avoid salt accumulation. Meanwhile, 95% of waster effluent is recycled to the cultivation stage. This stream contains algae, DAP and ammonia. Table 3.5.3c presents the recycle parameters for harvesting process of PBR. The main mass flows are also presented in Figure 3.8.1a to Figure 3.8.6a for different conditions.

Table 3.5.3 c: Recycle parameters for harvesting process of PBR.

Parameters	Value	Source and Note
Harvesting medium recycle	95%	Davis et al. (2011)
Harvesting total recycle flow rate (ton/yr)	54,578,048	Calculation
Harvesting total algae recycle flow rate (ton/yr)	51,108	Calculation
Harvesting total DAP recycle flow rate (ton/yr)	2408	Calculation
Harvesting total ammonia recycle flow rate (ton/yr)	3410	Calculation

3.6 Extraction of Lipid from Algae

Cell disruptions are selected for lipid extraction in order to prevent the barriers of the cell wall in the solvent extraction process.

3.6.1 Cell disruption

This analysis uses a homogenizer with a flow rate of 1200 L/h and 1000 bar in one pass. The motor power is 37 kW. At an influent mass percent of 20 wt% (achieved by the harvesting process), the efficiency of the homogenizer is assumed to be 90% in single-pass, which means that 90% of algal biomass is disrupted during homogenization. Table 3.6.1a summarizes the main parameters for algae cell disruption.

Table 3.6.1 a: Main parameters for cell disruption process.

Parameters	Value	Source and Note
Homogenizer efficiency	90%	Davis et al. (2012); GEA (2013b)
Homogenizer input flow rate (m^3/h)	103	Calculation
Homogenizer input algae flow rate (kg/h)	20,572	Calculation
Homogenizer output flow rate (m^3/h)	103	Calculation
Homogenizer output algae flow rate (kg/h)	2057	Calculation
Homogenizer output lipid flow rate (kg/h)	4629	Calculation
Homogenizer output debris flow rate (kg/h)	13,886	Calculation
Homogenizer flow rate (m^3/h)	1.2	GEA (2013b)
One homogenizer power (kW)	37	GEA (2013b)
Homogenizer number	86	Calculation
Total homogenizer power (kW)	3182	Calculation
Homogenizer power demand by algae (kWh/kg)	0.15	Calculation

Table 3.6.1 b: Cost of homogenizers.

	Flow rate (m^3/h)	Price ($)	Quantity	Direct cost ($MM)
Homogenizer	1.2[1]	50,000[1]	86	4.3

[1] Dairy Engineering Company (2013). The price of homogenizer is assumed based on the price of high pressure and high flowrate homogenizer in this web.

3.6.2 Extraction and purification process

This analysis uses liquid-liquid extraction (LLE) column as the equipment for extraction. Hexane is chosen as the extraction solvent and the hexane to biomass volumetric ratio is 5:1 which means that hexane to slurry ratio is 1:1 for 20 wt% of solid. The extraction decanter has a loading rate of 1.5 m^3/h algal slurry and hexane. It provides 5 minutes residence time for separation. The cost is estimated by equation in Appendix A.6.1.3. The general cost is summarized in Table 3.6.2a.

Table 3.6.2 a: Cost of liquid-liquid extractors.

	Flow rate (m^3/h)	Price ($)	Quantity	Direct cost ($MM)
LLE	1.5[1]	400,000	7	2.8

[1]Seider et al. (2004); Stephenson et al. (2010); calculation

It was assumed that 95% of lipid is extracted in LLE column. The water and algae debris are extracted and then are sent to anaerobic digestion. Lipid and hexane are sent to the stripping column to harvest the lipid and recover and recycle the hexane. The thermal and electrical energy are 1.00 kWh/kg-lipid and 0.066 kWh/kg-lipid. Extraction operating parameters are summarized in Table 3.6.2b.

Table 3.6.2 b: Main parameters for extractor.

Parameters	Value	Source and Note
Extraction input flow rate (m^3/h)	103	Calculation
Extraction input algae flow rate (kg/h)	2057	Calculation
Extraction input lipid flow rate (kg/h)	4629	Calculation
Extraction input debris flow rate (kg/h)	13,886	Calculation
Extraction lipid recovery to stripping column	95%	Davis et al. (2012)
Extraction hexane recovery to stripping column	100%	Assumption
Extraction water recovery to stripping column	0%	Assumption
Extraction algae recovery to stripping column	0%	Assumption
Extraction debris recovery to stripping column	0%	Assumption
Hexane to slurry volumetric ratio	1:1	Stephenson et al. (2010)
Hexane input to extraction (L/h)	20,572	Calculation
LLE algal slurry flow rate (m^3/h)	1.25	Seider et al. (2004); Stephenson et al. (2010); Calculation
LLE residence time (min)	5	Seider et al. (2004)
LLE number	7	Calculation
Extraction thermal power (kWh/kg-lipid)	1.00	Lardon et al. (2009); Lundquist et al. (2010); Stephenson et al. (2010)
Extraction electricity power (kWh/kg-lipid)	0.066	Lundquist et al. (2010); Stephenson et al. (2010); Davis et al. (2012)
Extraction thermal power (kW)	4397	Calculation
Extraction electricity power (kW)	290	Calculation

The hexane is separated from the oil in the stripping column and 99.8% of hexane is recycled. The stripping column has a diameter of 1.73 m and 25 stages (Table A.6.2a). The cost and dimensions are summarized in Appendix A.6.1.3. The lipid effluent is sent to the oil refining process. The price of hexane is $4.2/gal. The stripping column parameters are summarized in table 3.6.2c.

Table 3.6.2 c: Main parameters for stripping column.

Parameters	Value	Source and Note
Stripping column input lipid flow rate (kg/h)	4397	Calculation
Stripping column input hexane flow rate (L/h)	20,572	Calculation
Stripping column lipid recovery	100%	Assumption
Stripping column hexane recovery	99.8%	Assumption
Stripping column output lipid flow rate (kg/h)	4397	Calculation
Stripping column output lipid flow rate (gal/yr)	10,000,000	Calculation
Stripping column output hexane flow rate (L/h)	41	Calculation
Stripping column output hexane flow rate (kg/h)	27	Calculation
Stripping column output lipid purity	99.4%	Calculation
Stripping column thermal power (kW)	1450	Calculated by Aspen Plus
Stripping column thermal power (kWh/kg-lipid)	0.33	Calculation
Total hexane recovery	99.8%	Calculation
Hexane demand (L/h)	41	Calculation
Hexane demand (gal/yr)	86,082	Calculation
Hexane loss per kg-lipid (g)	6.1	Calculation
Hexane price ($/gal)	4.2	Amer et al., (2011); Alibaba (2013)
Hexane cost ($MM/yr)	0.36	Calculation

3.7 Anaerobic Digestion

3.7.1 Anaerobic Digestion

It is assumed that volatile solids are 90% of the total algal solid (TS) which contains algae and debris. The large AD cylindrical tank has a dimension with diameter of 34 m and height of 11 m. The cost estimation is summarized in Table 3.7.1a. The AD reactor has a loading rate of 6 kg VS m^{-3} d^{-1} and retention time of 20 days. The methane yield in AD reactor is 0.30 L CH_4 g VS^{-1}. The product biogas has a 70 vol% of CH_4 and 30 vol% of CO_2. Then the biogas will be sent to gas turbine for power generation and 85% of the CO_2 gas is captured for the algal growth. The technical parameters for AD are summarized in the Table 3.7.1b. Digestible fraction can be calculated from equations in Appendix A.7.1.

Table 3.7.1 a: Cost estimation of AD.

	Direct cost ($)	Land demand (ha)	Total direct cost ($MM)
AD	5,000/ha[1]	1,975	9.8

[1] Benemann and Oswald (1996), cost update.

Table 3.7.1 b: Technical parameters for AD.

Parameters	Value	Source and Note
Loading rate (kg VS m^{-3} d^{-1})	6	Yen and Bruce (2007)
CH_4 yield (L/g-VS)	0.3	Sialve et al. (2009)
CH_4 concentration	70%	Samson & Leduy (1982); Collet et al. (2011)
CO_2 concentration	30%	Samson & Leduy (1982); Collet et al. (2011)
Digestion time (d)	20	Samson & Leduy (1982); Collet et al. (2011); Ras et al. (2011); Davis et al. (2012)
Digestible Fraction	46.8% of carbon	Calculation by five parameters above

In the AD process, 75% of nitrogen and 50% phosphorus that are present in the influent stream are transformed into soluble nitrogen and phosphorus and recycled to the algal cultivation. It was assumed that the thermal and electrical energy for AD reactor are 0.38 $kWh_{thermal}$/kg-TS and 0.11 $kWh_{electricity}$/kg-TS. The general parameters for AD are summarized in the Table 3.7.1c.

Table 3.7.1 c: Main parameters for AD.

Parameters	Value	Source and Note
AD input water flow rate (m^3/h)	82	Calculation
AD input algae flow rate (ton/yr)	17,960	Calculation
AD input lipid flow rate (kg/h)	231	Calculation
AD input debris flow rate (kg/h)	13,886	Calculation
AD total sludge flow rate (kg/h)	16,174	Calculation
AD total sludge flow rate (ton/yr)	141,208	Calculation
AD cylindrical tank diameter (m)	34	Davis et al. (2012)
AD cylindrical tank height (m)	11	Davis et al. (2012)
AD cylindrical tank volume (m^3)	9987	Calculation
AD loading rate (kg VS m^{-3} d^{-1})	6	Yen and Bruce (2007)
AD cylindrical tank number	6	Calculation
AD thermal power (kWh/kg-lipid)	0.38	Collet et al. (2011); Zamalloa et al. (2011); Davis et al. (2012)

AD electricity power (kWh/kg-lipid)	0.11	Collet et al. (2011); Zamalloa et al. (2011); Davis et al. (2012)
AD thermal power (kW)	6146	Calculation
AD electricity power(kW)	1779	Calculation
N recycle from anaerobic digestion	75%	Davis et al. (2012); Rosch et al. (2012)
P recycle from anaerobic digestion	50%	Davis et al. (2012); Rosch et al. (2012)
Water recycle rate from AD	75%	Assumption
Water recycle from AD (ton/yr)	538,616	Calculation
Water flow from AD (ton/yr)	179,539	Calculation
Sludge from AD (ton/yr)	66,040	Calculation
CH_4 yield (L/g-VS)	0.3	Sialve et al. (2009)
VS to TS (algae) ratio	0.9	Collet et al. (2011)
CH_4 yield (m^3/h)	4367	Calculation
Biogas CH_4 vol%	70%	Samson & Leduy (1982); Collet et al. (2011);
Biogas CO_2 vol%	30%	Samson & Leduy (1982); Collet et al. (2011);
Biogas Carbon mole (kmol/h)	279	Calculation
CO_2 recovery from CHP	85%	Benemann and Oswald (1996)
CO_2 recycle from CHP (ton/yr) *(Calculated by carbon mole)	90,939	Calculation
C recycle rate from AD	46.8%	Calculation
CO_2 recycle from AD (ton/yr) *(Calculated by CO_2 recycled rate)	91,132	Calculation
CO_2 emission from CHP (ton/yr)	16,048	Calculation

3.7.2 CHP systems

The microbial community in the AD reactor converts the carbon in algae and debris to methane. This biogas is sent to the gas turbine for power generation. It was assumed that the electric power generation is at the 10 MW scale. The economic data for the CHP system is in Table 3.7.2a (EPA, 2008).

Table 3.7.2 a: Cost of 10-MW scale CHP.

	Scale	Cost ($MM)
CHP	10-MW[1]	8.0[1]

[1] EPA (2008).

3.7.3 Extraction and anaerobic digestion process flow.

Figure 3.7.3a displays the flowsheet of main components in extraction and anaerobic digestion processes. Before lipid extraction, 90% of algae are disrupted to lipid and debris. The algae lipid content is 25 wt%.

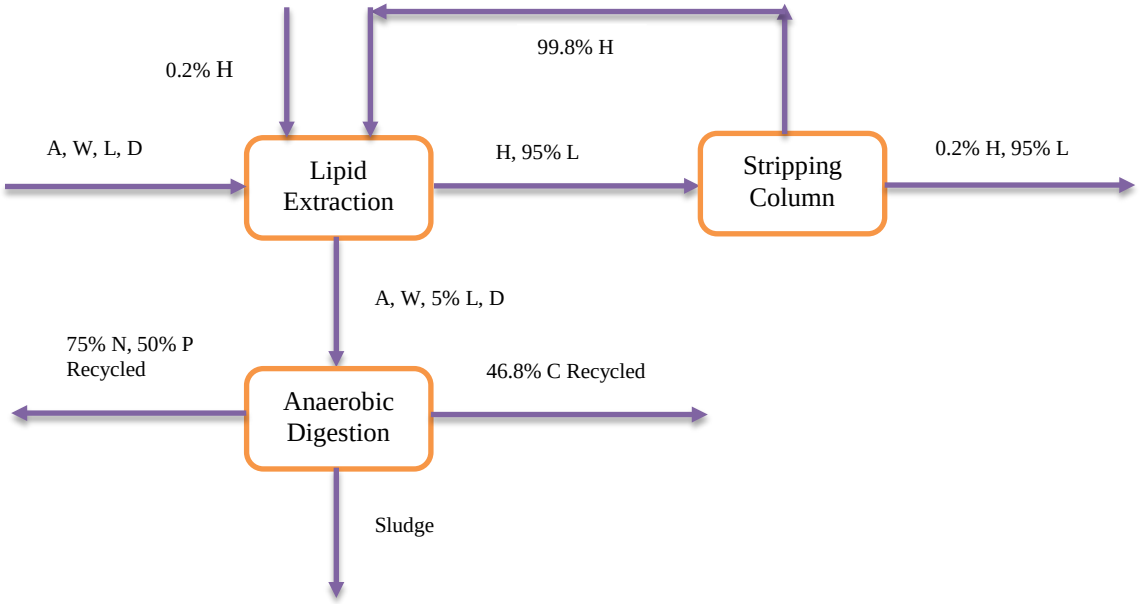


Figure 3.7.3 a: Flowsheet of main components in extraction and anaerobic digestion process

Label	A	W	L	H	D	N	P	C
Component	Algae	Water	Lipid	Hexane	Debris	Nitrogen	Phosphorus	CO_2

3.8 Baseline Algal Biofuel Model and Mass Flows

3.8.1 TEA baseline model

The lipid production is 10 million gallons per year. As demonstrated by Figure 3.1a (Davis et al., 2012), algae can be grown in both open ponds and PBRs. The algae harvesting process includes settling, DAF and centrifugation which have the efficiency of 90%, 90% and 95%, respectively. There is a 5% water loss in the entire harvesting process which includes settling, DAF, and centrifugation. The algal cells are disrupted by homogenizer, which has 90% efficiency. The lipid content is 25% on a dry weight basis and the lipids are treated as 100% TAG. In order to calculate nutrient demand, this TAG is defined as triolein ($C_{57}H_{104}O_6$, C18:1). A 5% carryover loss of oil into the water phase is assumed which results in a combined 85.5% overall extraction efficiency. This model uses hexane for lipid extraction. Finally, the hexane solvent was recycled via a stripping column. The spent algae and wastewater are sent to anaerobic digestion to provide heat and electricity for other equipment. 75% of the nitrogen and 50% of the phosphorus from the algal biomass are assumed to be recycled from anaerobic digestion to the algal cultivation system. The flue gas from the biogas turbine is also recycled to deliver CO_2 for algae growth.

Table 3.8.1a summarizes the major parameters used in determining the full-scale design of the algal biofuels facility in this scenario. All the parameters for TEA have been justified in this chapter. There are several strategies to select the parameters for TEA model. First, the most common value from literature will be used to fill in the model. These parameters include lipid content, algae productivity, tubular PBR diameters, etc. For example, the lipid content for microalgae has the similar value of 25% from several sources, such as Hu et al. (2008), and Griffiths and Harrison (2009). This value falls within the range of lipid content from other literatures. Second, an average number from different literature sources is selected as the value for some parameters, which includes AD electricity consumption, methane fraction generated from AD, AD retention time, etc. This is because only three to five articles have studied the anaerobic digestion of algae. The values from the sources are not that different. Therefore, it is reasonable to choose an average value for this TEA model. Third, in this TEA scenario, some main parameters have been selected based on NREL TEA model (Davis et al., 2011; Davis et al., 2012). NREL is a research facility which is funded by U.S. Department of Energy. The reports developed by NREL are deemed reliable and are routinely a source for other studies. The

parameters based on NREL TEA model include settler efficiency, centrifuge efficiency, biomass concentration after the dewatering process, etc. In this study, every parameter has been investigated with a literature review. For example, the efficiency of centrifugation has been summarized and analyzed in Table 2.8.4a. Other literature sources are considered to confirm that the parameters from NREL are reasonable. Fourth, some parameters are difficult to calculate and these values are directly referred from the literatures. These parameters are mostly related to economics; include the capital cost of settling system, CO_2 delivery system, open pond wall and structure, etc. Finally, there are a few of parameters that are unavailable from the literature, such as the consumption efficiency of nutrients for algae growth, and water recycle rate after anaerobic digestion. A reasonable value is assumed based on the technology related to these parameters.

Table 3.8.1 a: Summary of the major parameters presented in this workshop.

Parameters	Open Ponds Value	Tubular PBR Value	Source and Note
Lipid production (MM gal/yr)	10		Davis et al. (2012)
Lipid content	25%		Hu et al. (2008); Griffiths and Harrison (2009); Mata et al. (2010); Davis et al. (2012)
Days of operation (d/yr)	330		Davis et al. (2011); Davis et al. (2012)
Life time (yr)	20		Assumption
Land demand (acre)	4880		Calculation
Algae productivity ($g/m^2/d$)	25	25	Griffiths and Harrison (2009); Amer et al. (2011); Davis et al. (2012)
Algae productivity ($kg/m^3/d$)	0.083	1.25	Acien Fernandez et al. (1998); Rubio et al. (1999); Molina et al. (2001); Davis et al. (2012); Calculation
Algae concentration (kg/m^3)	0.5	4	Becker (1994); Molina et al. (2001); Stephenson et al. (2010); Davis et al. (2012)
Pond area (m^2)	16,000	--	Calculation
Pond number	1234	--	Calculation

Tube diameter (cm)	--	6 and 9	Tredici et al. (1998); Molina et al. (2001); Stephenson et al. (2010); Davis et al. (2011)
Tube length (m)	--	80	Tredici et al. (1998); Molina et al. (2001); Stephenson et al. (2010); Davis et al. (2011)
Total tube number	--	1,070,000	Calculation
Settler efficiency	90%		Ferrell et al. (2010); Davis et al. (2012)
DAF efficiency	90%		Shelef et al. (1984); Davis et al. (2012)
Centrifugation Efficiency	95%		Heasman et al. (2001); Stephenson et al. (2010); Frank et al. (2011b); Davis et al. (2012)
Water recovery after dewatering process	95%		Davis et al. (2011)
Homogenizer efficiency	90%		Davis et al. (2012); GEA (2013b)
Extraction efficiency	95%		Davis et al. (2011); Davis et al. (2012)
N recycle from AD	75%		Davis et al. (2012); Rosch et al. (2012)
P recycle from AD	50%		Davis et al. (2012); Rosch et al. (2012)
CO_2 recycle from AD and CHP	40% (46.8% × 85%)		Calculation

3.8.2 Algae Process Flow Diagram

Table 3.8.2a presents the main parameters of algae production analyzed by TEA. The mass balances for algae biomass (whole cells to debris), carbon, water, phosphorus and nitrogen are indicted on the flow sheets in Figure 3.8.2.1a to Figure 3.8.2.6a. Cases examined include the following:

- Open Pond-DAP-Ammonia (Figure 3.8.2.1a)
- Open Pond-DAP-Urea (Figure 3.8.2.2a)
- Open Pond-Struvite-Ammonia (Figure 3.8.2.3a)
- PBR-DAP-Ammonia (Figure 3.8.2.4a)

- PBR-DAP-Urea (Figure 3.8.2.5a)
- PBR-Struvite-Ammonia (Figure 3.8.2.6a)

Table 3.8.2 a: Main parameters about algae productivity for each step.

Parameters	Open Pond Value	PBR Value	Source and Note
Algae productivity (kg/yr)	162,927,588		Calculation
Algae productivity (ton/yr)	179,597		Calculation
Algae need to grow (kg/yr) (*some algae recycled after harvesting)	165,367,797		Calculation
Algae need to grow (ton/yr) (*some algae recycled after harvesting)	182,287		Calculation
Water demand (ton/yr) (Open pond has evaporation)	45,023,232	3,049,611	Calculation
CO_2 Demand (ton/yr)	289,907		Calculation
DAP demand (ton/yr)	5351		Calculation
N demand as format of NH_3 (ton/yr)	3987		Calculation
Ammonia actual demand (ton/yr) (DAP has N nutrient)	2595		Calculation
Algae production before settling (kg/yr)	211,731,759		Calculation
Algae production before settling (ton/yr)	233,394		Calculation
Settler output algae flow rate (ton/yr)	210,055		Calculation
DAF output algae flow rate (ton/yr)	189,049		Calculation
Centrifuge output algae flow rate (ton/yr)	179,597		Calculation

3.8.2.1 Open Pond-DAP-Ammonia

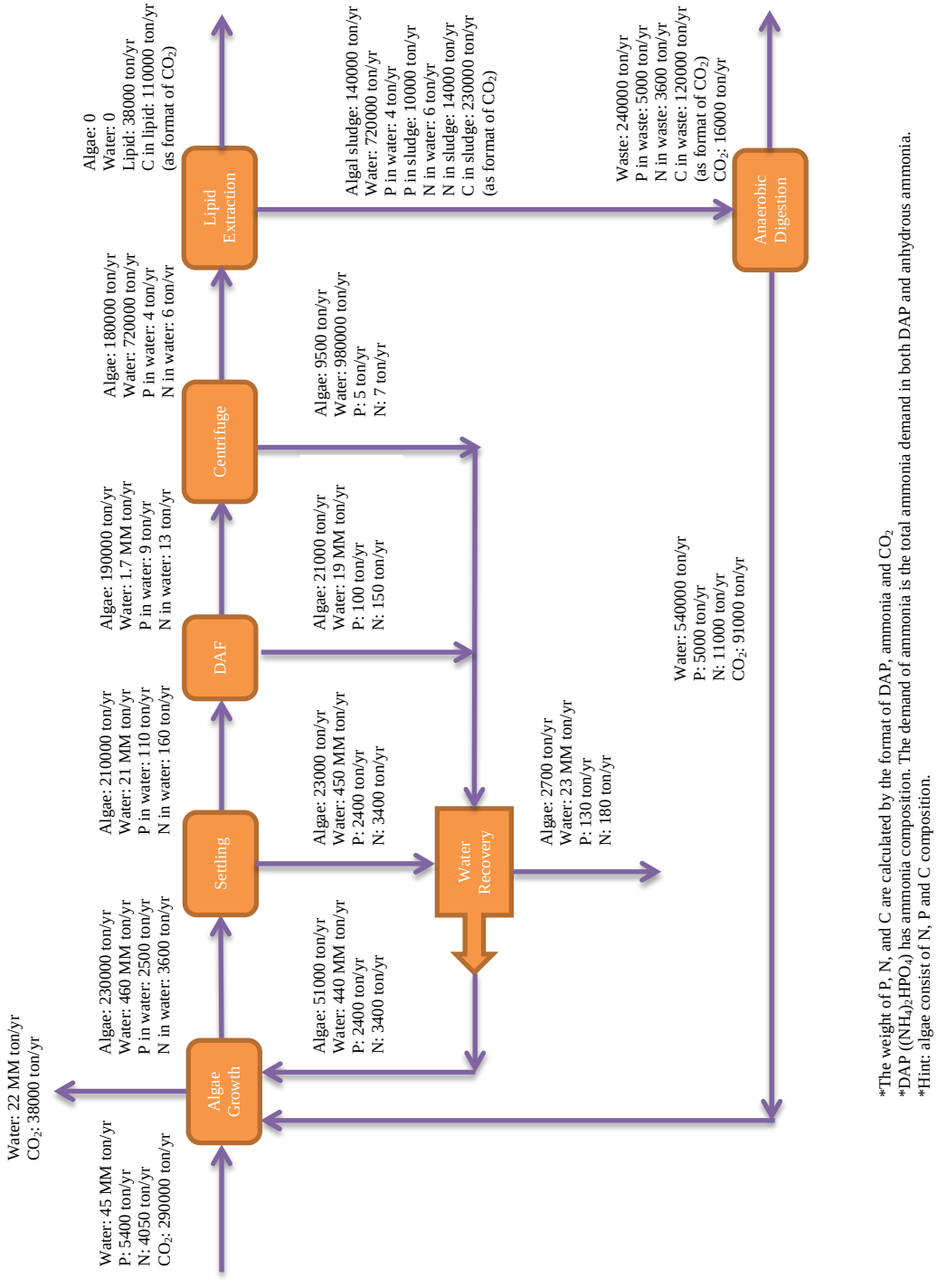
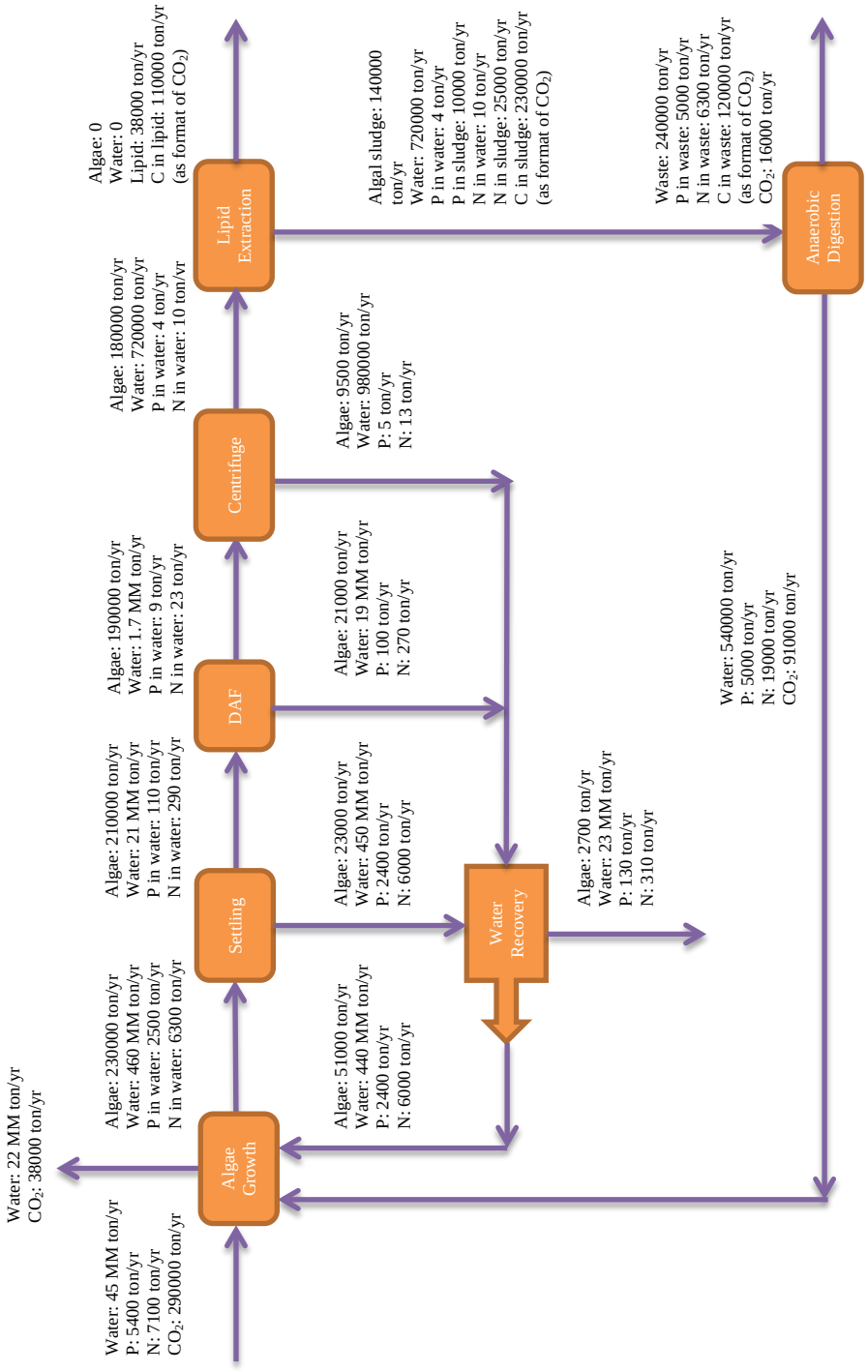


Figure 3.8.2.1 a: The main mass flows of algal lipid system by open pond cultivation. DAP and ammonia are nutrients for algae growth.

3.8.2.2 Open Pond-DAP-Urea



*The weight of P, N, and C are calculated by the format of DAP, urea and CO_2
*DAP ($(NH_4)_2HPO_4$) has N composition. The demand of N is the total N demand in both DAP and urea.
*Hint: algae consist of N, P and C composition.

Figure 3.8.2.2 a: The main mass flows of algal lipid system by open pond cultivation. DAP and urea are nutrients for algae growth.

3.8.2.3 Open Pond-Struvite-Ammonia

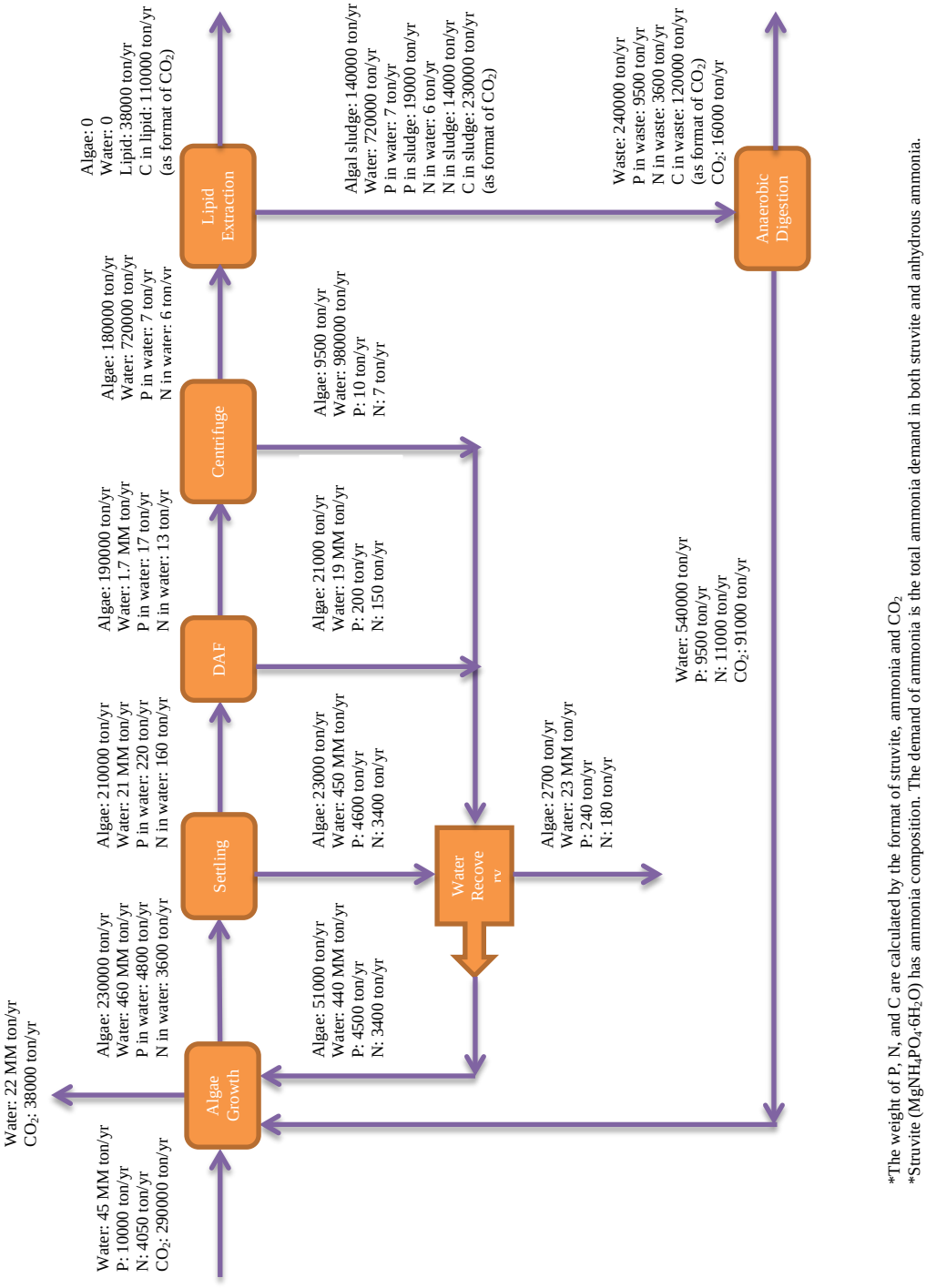
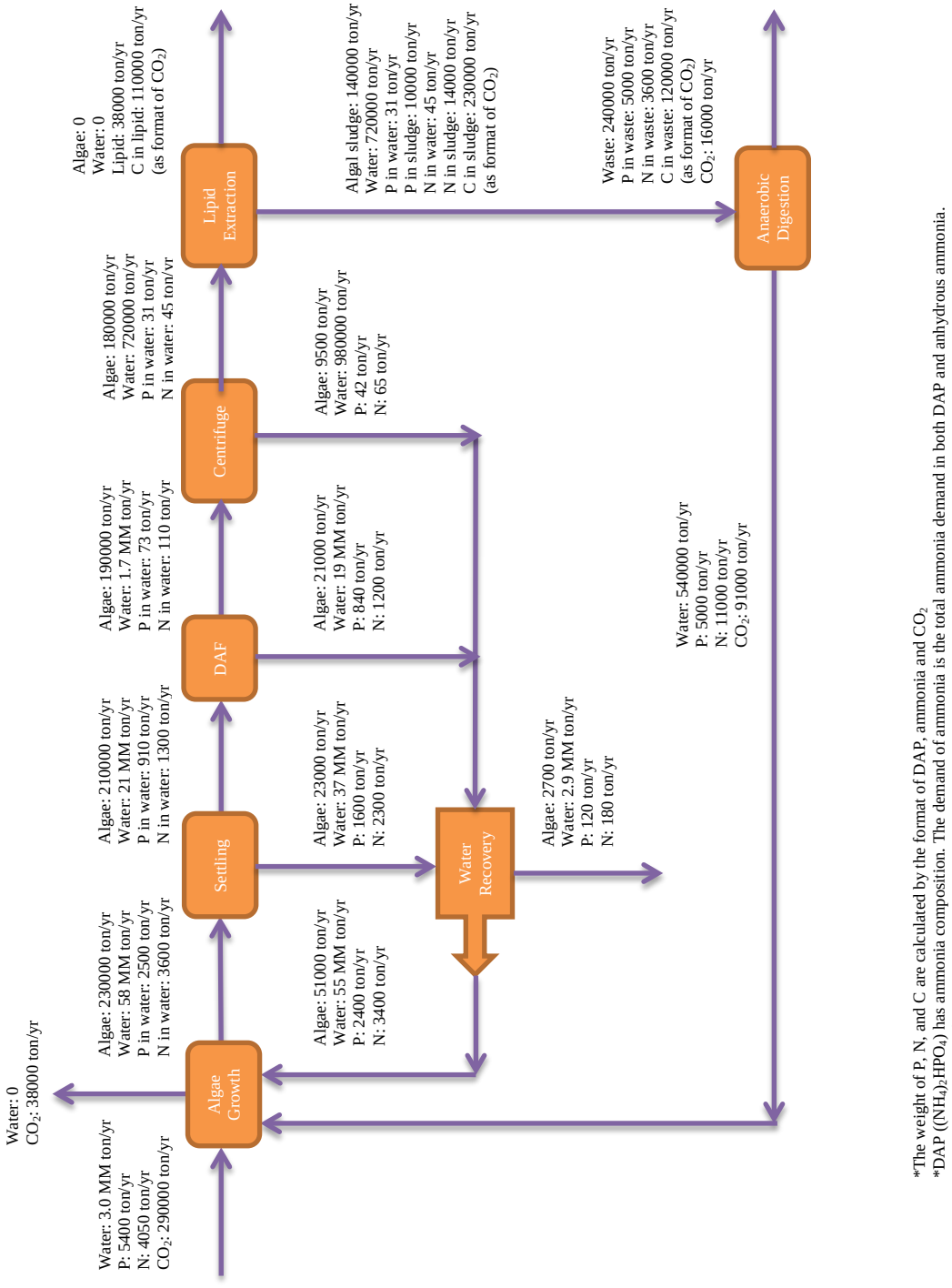


Figure 3.8.2.3 a: The main mass flows of algal lipid system by open pond cultivation. Struvite and ammonia are nutrients for algae growth.

3.8.2.4 PBR-DAP-Ammonia



*The weight of P, N, and C are calculated by the format of DAP, ammonia and CO_2
*DAP ($(NH_4)_2HPO_4$) has ammonia composition. The demand of ammonia is the total ammonia demand in both DAP and anhydrous ammonia.
*Hint: algae consist of N, P and C composition.

Figure 3.8.2.4 a: The main mass flows of algal lipid system by PBR cultivation. DAP and ammonia are nutrients for algae growth.

3.8.2.5 PBR-DAP-Urea

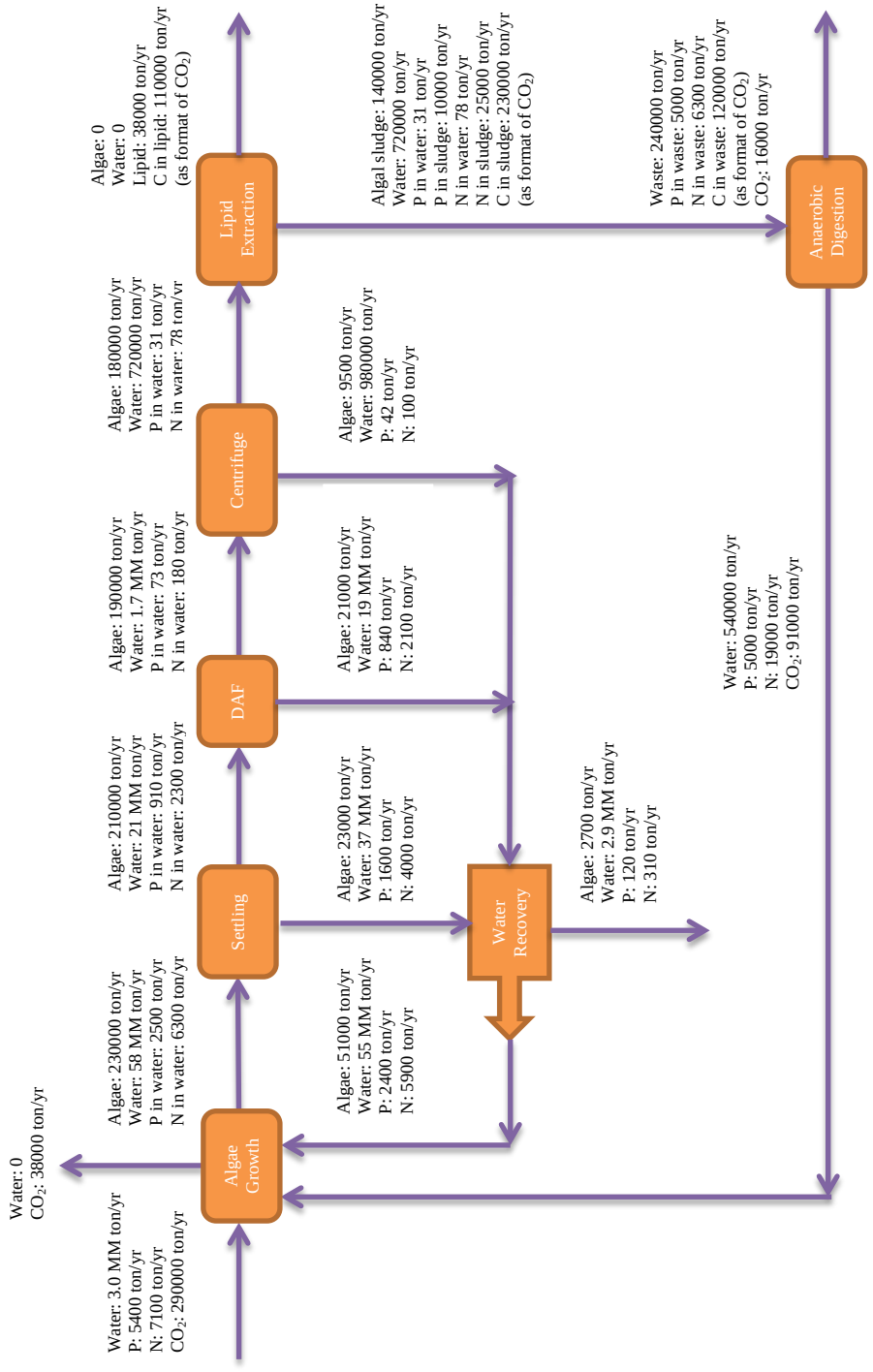


Figure 3.8.2.5 a: The main mass flows of algal lipid system by PBR cultivation. DAP and urea are nutrients for algae growth.

3.8.2.6 PBR-Struvite-Ammonia

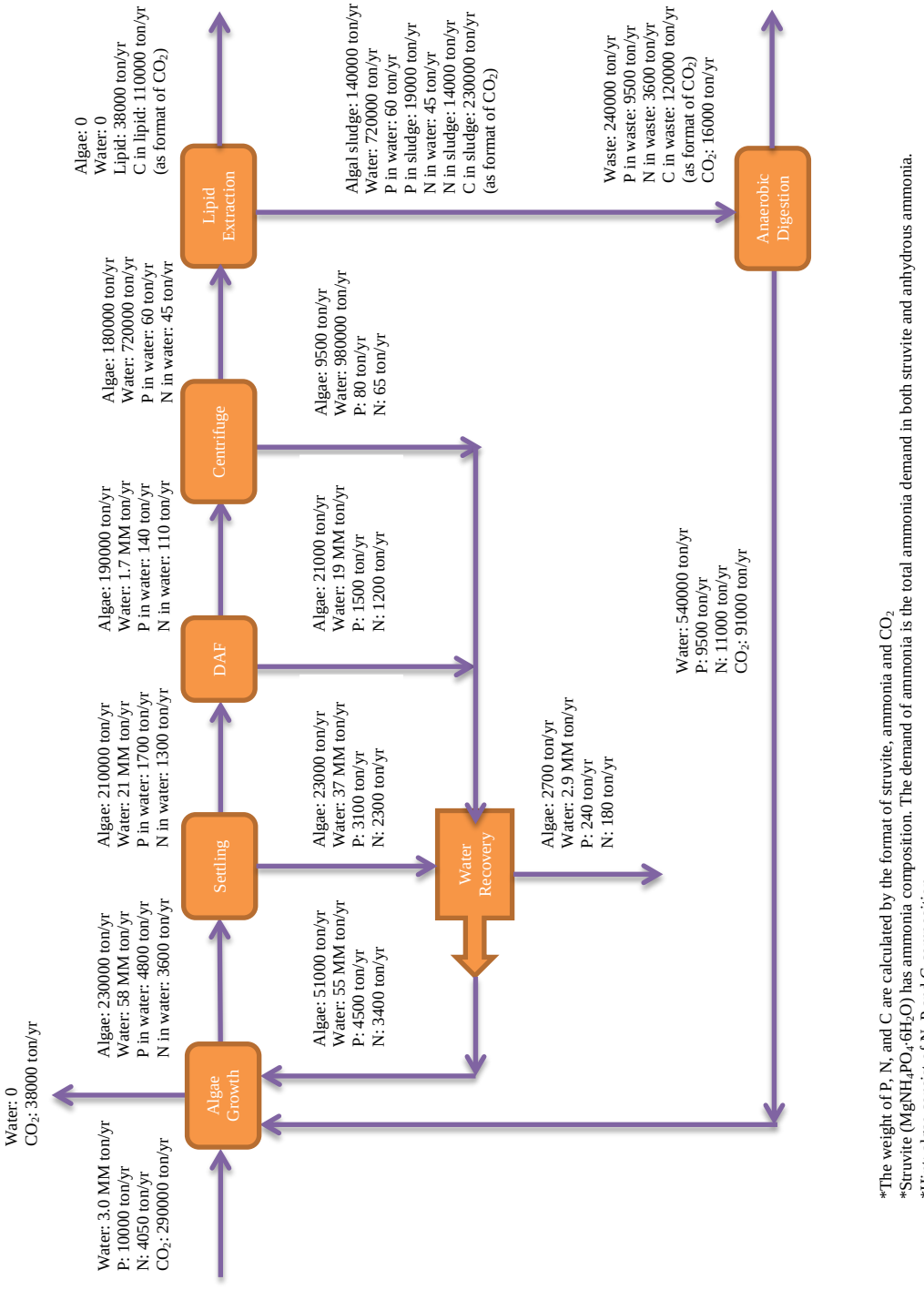


Figure 3.8.2.6 a: The main mass flows of algal lipid system by PBR cultivation. Struvite and ammonia are nutrients for algae growth.

3.8.2.7 Nutrients, water, and CO_2 demand to generate 1 kg lipid

The baseline study target of lipid productivity is 10 MM gal/yr which is equal to 38,389 ton/yr. Nutrients, water, and CO_2 demand have been calculated based on this TEA algal biofuels model. Table 3.8.2.7a presents nutrients, water, and CO_2 requirement to generate 1 kg lipid.

Table 3.8.2.7 a: Nutrients, water, and CO_2 demand.

	Demand for 10 MM gal/yr Lipid (ton/yr)		Demand for 1 kg Lipid (kg)	
	Open Pond	PBR	Open Pond	PBR
P nutrient	1256		3.3E-02	
P nutrient as DAP	5351		0.14	
N nutrient	3283		8.6E-02	
N nutrient as NH_3	3987		0.10	
Water	45,023,232	3,049,611	1173	79
CO_2	289,907		7.6	

3.9 Aspen Plus Simulation Development

3.9.1 Introduction to Aspen Plus simulation

From 1976 to 1979 the researchers at MIT developed a process simulation system named ASPEN (Advanced System for Process Engineering). This software was commercialized in 1980s by the foundation of Aspentech (Fogler and Gurmen, 2002). Aspen Plus is one of the core computer programs which was developed by Aspentech. It is a rigorous steady state simulation tool which is used for chemical process modeling, process plant design and simulation (Luyben and Chien, 2010).

Aspen Plus is based on techniques for solving flowsheets. A flowsheet can be defined as a part of blue print of an engineering system. It identifies all streams, unit operations and operation conditions (Fogler and Gurmen, 2002; Aspentech, 2011). Flowsheets are solved by both Sequential Modular and Equation Oriented modeling strategies in Aspen Plus (Venkatarathnam et al., 2008; Aspentech, 2010; Schefflan, 2011). The Sequential Modular strategy solves each unit operation block in sequence. Flowsheet iteration is required when recycling is present and Sequential Modular is used to solve a large number of blocks. Equation oriented modeling can

solve all of the model equations simultaneously. The combination of these two strategies is effective for calculation in Aspen Plus. (Aspentech, 2010)

Aspen Plus has some basic functions including (Aspentech, 2011):

- Developing a process simulation model by using basic engineering relationships, such as mass and energy balances, chemical equilibrium.
- Predicting stream flow rates, compositions and properties.
- Predicting operating conditions and equipment sizes.
- Allowing designers to quickly test various plant configurations to reduce plant design time.
- Conducting “what if” analysis and determine optimal process conditions within given constraints.

This software package can be used in almost every aspect of a process model for design. The Aspen Plus process simulation model can be performed by the following steps (Aspentech, 2011):

1. The flowsheet shows inlets streams entering into and continuing through unit operations and going through product streams. Aspen Plus has a model library including mixers, separators, heat exchangers, columns, reactors, etc. Custom or proprietary models can extend the model library so that the designer can create user models by Fortran subroutines or Excel Worksheets (Schefflan, 2011).
2. After building the flowsheet, the process model specifies chemical components in the process. Aspen Plus stores physical property parameters for a large number of components in several databanks (Aspentech, 2000). Thermodynamics models can be built in Aspen Plus to represent the properties of the components and mixtures in the process.
3. Then Aspen Plus can evaluate the effect of component’s flow rates, thermodynamic conditions and operation conditions to the outcome of the system. In addition to process simulation, Aspen Plus can be used to perform a wide range of other tasks such as conducting sensitivity studies and optimizing processes.

Therefore, Aspen Plus can create a process model, build a flowsheet and specify the chemical components and operation conditions (Aspentech, 2011). Then the software can execute all of the

necessary calculations needed to solve the outcome of the system. When the calculations are complete, Aspen Plus lists the results stream by stream.

3.9.2 Aspen Plus simulation for algal biofuel

Rigorous mass balances, equipment sizing and process economics of full-scale processes can be performed using the software Aspen Plus. An Aspen Plus simulation of the algae to lipid process was created (Figure 3.9.2a). Several of the unit operations used in the process (cultivation, AD, settling, and etc.) is not rigorously modeled in terms of performance and equipment design by Aspen Plus; therefore, approximations of the systems were used with simpler blocks (e.g. separator and reactor). Regardless, this simulation presents an accurate mass balance for lipid production from algae. Table 3.9.2a to Table 3.9.2c displays component mass balances derived from the Aspen Plus simulation.

The algae grow by the inputs of nutrients and water. The demand of CO_2 is 285000 ton/yr, NH_3 is 4200 ton/yr, and DAP is 4800 ton/yr. The concentration of algae is 1% in the settling tank. Algae are thickening to 10% by dissolved air flotation (DAF). The algae are further concentrated to 20% by using a centrifugation. The harvesting efficiency of each unit is 90% efficiency in settling, 90% in DAF, and 95% in centrifugation. Then the algal cells are disrupted by homogenizer. The homogenization efficiency for modeling is 90%. The lipid content is 25% on a dry weight basis and the lipids were treated as 100% triglyceride (TAG). Assuming a 5% carryover loss of oil into the water phase which results in a combined 95.5% overall extraction efficiency. This model uses hexane for lipid extraction. Finally, the hexane solvent was recycled via a stripping column. Hexane offers a lot of advantages because of its lower boiling point and lower water miscibility and lower cost. The spent algae and wastewater are sent to AD. This model assume75% capture of nitrogen and 50% capture of phosphorus recycled in AD.

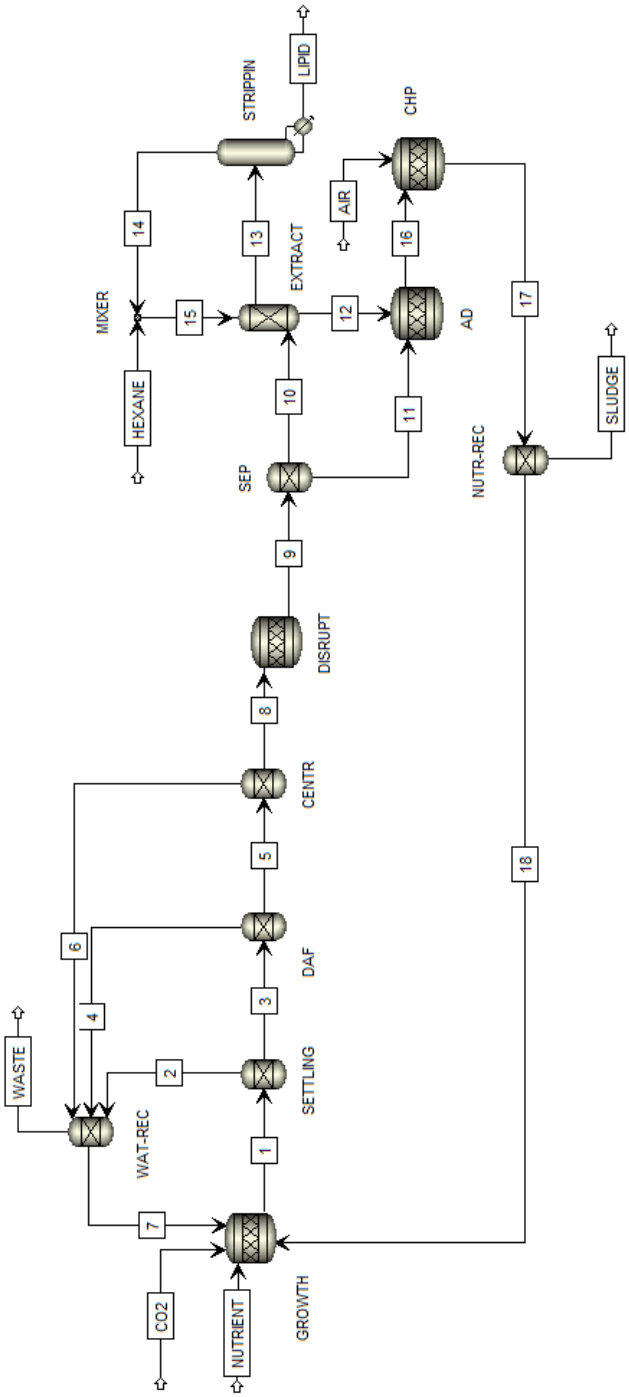


Figure 3.9.2 a Algal biofuel process modeled in Aspen Plus.

Table 3.9.2 a: Results of algal biofuel process modeled in Aspen Plus.

	AIR	CO2	HEXANE	LIPID	NUTRIENT	SLUDGE	WASTE
Temperature K	298.1	293.1	293.1	419.4	293.1	298.1	266.5
Pressure atm	1	1	1	1.1	1	1	1
Vapor Frac	1	1	0	0	0	0.529	0.07
Mole Flow kmol/hr	4000	670.177	1.441	5.63	16806.08	7317.809	14012.38
Mass Flow kg/hr	115401.6	29494.37	124.187	4288.68	303208.4	175637.2	267969.1
Volume Flow l/min	1.63E+06	268682.3	3.125	94.745	5062.991	1.58E+06	361794.7
Enthalpy MMBtu/hr	0	-250.078	-0.272	-8.377	-4554.91	-1068.81	-3577.04
Mass Flow kg/hr							
H2O	0	0	0	0	302187.9	63732.18	233855.2
CO2	0	29494.37	0	0	0	12922.67	4090.818
NH3	0	0	0	0	476.463	430.381	20.298
DAP	0	0	0	0	544.042	515.122	13.541
HEXANE	0	0	124.187	75.06	0	0	0
O2	26878.99	0	0	0	0	9514.265	29989.19
C57H1-01	0	0	0	4213.62	0	0	0
N2	88522.6	0	0	0	0	88522.6	0
CH4	0	0	0	0	0	0	0
Mole Flow kmol/hr							
H2O	0	0	0	0	16773.98	3537.674	12980.94
CO2	0	670.177	0	0	0	293.632	92.952
NH3	0	0	0	0	27.977	25.271	1.192
DAP	0	0	0	0	4.12	3.901	0.103
HEXANE	0	0	1.441	0.871	0	0	0
O2	840	0	0	0	0	297.332	937.197
C57H1-01	0	0	0	4.759	0	0	0
N2	3160	0	0	0	0	3160	0
CH4	0	0	0	0	0	0	0
Mass Flow kg/hr	115401.6	29494.37	124.187	4288.68	303208.4	175637.2	268250.5
Enthalpy MMBtu/hr	0	-250.078	-0.272	-8.377	-4554.91	-1068.81	-5.36E+08
Temperature K							266.5
Pressure atm	1	1	1	1.1	1	1	1
Vapor Frac							0
Mole Flow kmol/hr	0	0	0	0	0	0	0.116
Mass Flow kg/hr	0	0	0	0	0	0	281.441
Volume Flow l/min	0	0	0	0	0	0	0.03
Enthalpy MMBtu/hr							-5.36E+08
Mass Flow kg/hr							
ALGAE	0	0	0	0	0	0	281.441
DEBRIS	0	0	0	0	0	0	0
Mole Flow kmol/hr							
ALGAE	0	0	0	0	0	0	0.116
DEBRIS	0	0	0	0	0	0	0

Table 3.9.2 b: Results of algal biofuel process modeled in Aspen Plus.

	1	2	3	4	5	6	7	8	9
Temperature K	266.5	266.5	266.5	266.5	266.5	266.5	266.5	266.5	293.1
Pressure atm	1	1	1	1	1	1	1	1	1
Vapor Frac	0.002	0.004	0	0	0	0	0	0	0
Mole Flow kmol/hr	263920.4	153507	110413.4	101580.3	8833.071	5564.835	246639.8	3268.236	3272.995
Mass Flow kg/hr	4.77E+06	2.78E+06	1.99E+06	1.83E+06	159138.2	100257.1	4.44E+06	58881.14	63094.77
Volume Flow l/min	248027.9	291311.3	32376.38	29786.27	2590.11	1631.77	72321.87	958.341	1155.85
Enthalpy MMBtu/hr	-71750.4	-41630.5	-30119.8	-27710.2	-2409.58	-1518.04	-67281.1	-891.545	-895.127
Mass Flow kg/hr									
H2O	4.74E+06	2.75E+06	1.99E+06	1.83E+06	159129	100251.3	4.44E+06	58877.73	58877.73
CO2	4090.818	4090.818	0	0	0	0	0	0	0
NH3	20.298	20.298	0	0	0	0	0	0	0
DAP	274.229	159.053	115.176	105.962	9.214	5.805	257.279	3.409	3.409
HEXANE	0	0	0	0	0	0	0	0	0
O2	29989.19	29989.19	0	0	0	0	0	0	0
C57H1-01	0	0	0	0	0	0	0	0	4213.627
N2	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	0	0	0
Mole Flow kmol/hr									
H2O	262887	152474.4	110412.5	101579.5	8833.002	5564.791	246637.8	3268.211	3268.211
CO2	92.952	92.952	0	0	0	0	0	0	0
NH3	1.192	1.192	0	0	0	0	0	0	0
DAP	2.077	1.204	0.872	0.802	0.07	0.044	1.948	0.026	0.026
HEXANE	0	0	0	0	0	0	0	0	0
O2	937.197	937.197	0	0	0	0	0	0	0
C57H1-01	0	0	0	0	0	0	0	0	4.759
N2	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	0	0	0
Mass Flow kg/hr	4.79E+06	2.78E+06	2.01E+06	1.83E+06	178918.4	101246.1	4.45E+06	77672.36	77672.39
Enthalpy MMBtu/hr	-4.65E+10	-4.65E+09	-4.19E+10	-4.19E+09	-3.77E+10	-1.88E+09	-1.02E+10	-3.58E+10	-6.68E+10
Temperature K	266.5	266.5	266.5	266.5	266.5	266.5	266.5	266.5	293.1
Pressure atm	1	1	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0	0	0	0
Mole Flow kmol/hr	10.105	1.01	9.094	0.909	8.185	0.409	2.213	7.776	70.759
Mass Flow kg/hr	24420.04	2442.004	21978.04	2197.804	19780.23	989.012	5347.379	18791.22	14577.63
Volume Flow l/min	2.609	0.261	2.348	0.235	2.113	0.106	0.571	2.007	18.279
Enthalpy MMBtu/hr	-4.65E+10	-4.65E+09	-4.19E+10	-4.19E+09	-3.77E+10	-1.88E+09	-1.02E+10	-3.58E+10	-6.68E+10
Mass Flow kg/hr									
ALGAE	24420.04	2442.004	21978.04	2197.804	19780.23	989.012	5347.379	18791.22	1879.122
DEBRIS	0	0	0	0	0	0	0	0	12698.5
Mole Flow kmol/hr									
ALGAE	10.105	1.01	9.094	0.909	8.185	0.409	2.213	7.776	0.778
DEBRIS	0	0	0	0	0	0	0	0	69.982

Table 3.9.2 c: Results of algal biofuel process modeled in Aspen Plus.

	10	11	12	13	14	15	16	17	18
Temperature K	293.1	293.1	341.1	319	341.9	341.3	293.1	298.1	298.1
Pressure atm	1	1	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	1	0.992	0.149	0.545	0.988
Mole Flow kmol/hr	3272.969	0.026	3268.042	182.884	177.254	177.957	3656.87	7656.87	339.061
Mass Flow kg/hr	63091.36	3.409	58874.7	19301.03	15012.35	15084.38	73455.7	188857.3	13220.08
Volume Flow l/min	1155.797	0.056	1031.254	558.202	82874.17	82486.67	219101.4	1.70E+06	136612.5
Enthalpy MMBtu/hr	-895.098	-0.029	-880.418	-42.102	-27.246	-27.422	-954.634	-1175.34	-104.426
Mass Flow kg/hr									
H2O	58877.73	0	58874.7	70.643	70.643	67.612	53955.86	63732.18	0
CO2	0	0	0	0	0	0	12395.13	24336.48	11413.81
NH3	0	0	0	0	0	0	1721.525	1721.525	1291.144
DAP	0	3.409	0	0	0	0	1030.243	1030.243	515.122
HEXANE	0	0	0	15011.92	14936.86	15011.92	0	0	0
O2	0	0	0	0	0	0	0	9514.265	0
C57H1-01	4213.627	0	0	4218.471	4.851	4.844	0	0	0
N2	0	0	0	0	0	0	0	88522.6	0
CH4	0	0	0	0	0	0	4352.947	0	0
Mole Flow kmol/hr									
H2O	3268.211	0	3268.042	3.921	3.921	3.753	2995.005	3537.674	0
CO2	0	0	0	0	0	0	281.645	552.979	259.347
NH3	0	0	0	0	0	0	101.084	101.084	75.813
DAP	0	0.026	0	0	0	0	7.802	7.802	3.901
HEXANE	0	0	0	174.198	173.327	174.198	0	0	0
O2	0	0	0	0	0	0	0	297.332	0
C57H1-01	4.759	0	0	4.764	0.005	0.005	0	0	0
N2	0	0	0	0	0	0	0	3160	0
CH4	0	0	0	0	0	0	271.334	0	0
Mass Flow kg/hr	63091.36	14581.04	58874.7	19301.03	15012.35	15084.38	73455.7	188857.3	13220.08
Enthalpy MMBtu/hr	-895.098	-6.68E+10	-880.418	-42.102	-27.246	-27.422	-954.634	-1175.34	-104.426
Temperature K		293.1							
Pressure atm	1	1					1	1	1
Vapor Frac		0							
Mole Flow kmol/hr	0	70.759	0	0	0	0	0	0	0
Mass Flow kg/hr	0	14577.63	0	0	0	0	0	0	0
Volume Flow l/min	0	18.279	0	0	0	0	0	0	0
Enthalpy MMBtu/hr		-6.68E+10							
Mass Flow kg/hr									
ALGAE	0	1879.122	0	0	0	0	0	0	0
DEBRIS	0	12698.5	0	0	0	0	0	0	0
Mole Flow kmol/hr									
ALGAE	0	0.778	0	0	0	0	0	0	0
DEBRIS	0	69.982	0	0	0	0	0	0	0

3.10 Economics

There have been no algal biofuel facilities constructed at scales relevant to national transportation fuel scales. In addition, much of the cultivation and separation equipment is novel and not commercially available. Therefore, capital and manufacturing costs are based on many assumptions and generally not validated with commercial experience. The cultivation operation costs (open ponds or PBRs) are especially not well understood, and dominate the other capital costs. A cost analysis was performed on the 10 MM gal/yr facility using the few published studies on algal biofuel costs.

3.10.1 Capital costs

3.10.1.1 Cost index

The purchase cost of equipment is not constant due to inflation. Charts and equations are applied to convert the cost of equipment between different years. The purchase cost at a later date can be estimated by multiplying the cost from an earlier data by the ratio of a cost index (Seider et al., 2004):

$$Cost = Base\ Cost\left(\frac{I}{I_{base}}\right)$$

Where I is the later cost index, and I_{base} corresponds to the cost index applied to the purchase cost. Four common cost indexes have been used by chemical engineers, including the Chemical Engineering (CE) Plant Cost Index, the Marshall & Swift (MS) Equipment Cost Index, the Nelson-Farrar (NF) Refinery Construction Cost Index, and the Engineering News-Record (ENG) Construction Cost Index (Seider et al., 2004).

CE Plant Cost Index (Appendix A.9) is selected as the cost index in this TEA scenario. If equipment costs were found from 2006 or later, that equipment cost was used. Equipment costs prior to 2006 were converted to 2012 costs. The year 2006 was selected as the change in index, which was relatively flat from 2006 to 2012.

3.10.1.2 Capital investment costs

The total capital investment is a one-time expense for chemical plant design, construction, and start-up (Seider et al., 2004). In order to put an industrial plant into operation, the necessary

equipment must be purchased and installed. And then the plant will be erected complete with piping, control, and services (Peters and Timmerhaus, 1991). The capital needed to provide manufacturing and plant facilities for chemical plant operation is called the fixed-capital investment (Peters and Timmerhaus, 1991). Table 3.10.1.2a summarizes the typical variation in costs as percentages of fixed capital cost.

Table 3.10.1.2 a: Typical percentages of fixed capital investments values for cost of chemical plants (Peters and Timmerhaus, 1991; Molina et al., 2003).

	Range (%)	Percentage of MEC in this Scenario (%)
Equipment installation	30-40	35
Instrumentation	10-30	20
Piping	30	30
Electrical	10-20	15
Buildings	20-30	25
Yard improvements	8-10	9
Service facilities	20-60	40
Land	6	0
Engineering and supervision	25-40	30
Construction expenses	10-40	25
Constructor's fee	5	5
Contingency	6-10	8
Total fixed capital rate (%)		**242**

3.10.1.3 Capital costs for algal biofuel process

The methodology to determine the capital costs consists of summing the major equipment costs, and using the sum to estimate the other capital costs. Table 3.10.1.2a presents the percentage of the major equipment costs for the other categories in capital cost. The major equipment costs (MEC) includes the cost of settling, DAF, centrifuge, homogenizer, LLE, stripping, and AD equipment. The cultivation bioreactor or ponds were not included in the equipment costs to use as a multiplier as they are very large and estimates for their construction include the associated cost. The total direct cost of tubular PBR for 10 MM algal lipid scale is calculated to be $2520 MM (Table 3.3a), which is much more than $522 MM estimated by NREL (Davis et al., 2011). In this

scenario, a direct capital cost of $522 MM for tubular PBR is selected (Davis et al., 2011). The major equipment costs are summarized in Table 3.10.1.3a, Figure 3.10.1.3a and Figure 3.10.1.3b. The total FCI project for algal lipid production using open ponds is $431 MM.

Table 3.10.1.3 a: TEA major equipment cost details for open pond system.

Capital	Direct Capital Cost ($MM)	Fixed Capital Cost Rate (%)	Capital Cost ($MM)	% of Cost
Land	7.5	--	7.5	1.7%
Ponds (excluding liners)	61	--	61	14.3%
Pond liners	127	--	127	29.5%
Tubular PBR	522	--	522	--
Flue gas off-site delivery	19	--	19	4.4%
Settling for PBR	3.2	242% of MEC	11	--
Settling	26		88	20.7%
DAF	3.6		12	1.4%
Centrifuge	11		38	9.6%
Homogenizer	4.3		15	3.4%
LLE column	2.8		9.6	2.2%
Stripping Column	3.6		12	2.9%
AD	9.9		34	7.8%
CHP	8.0	--	8.0	1.9%
Total	**283**		**431 (open pond)** **688 (PBR)**	**100%**

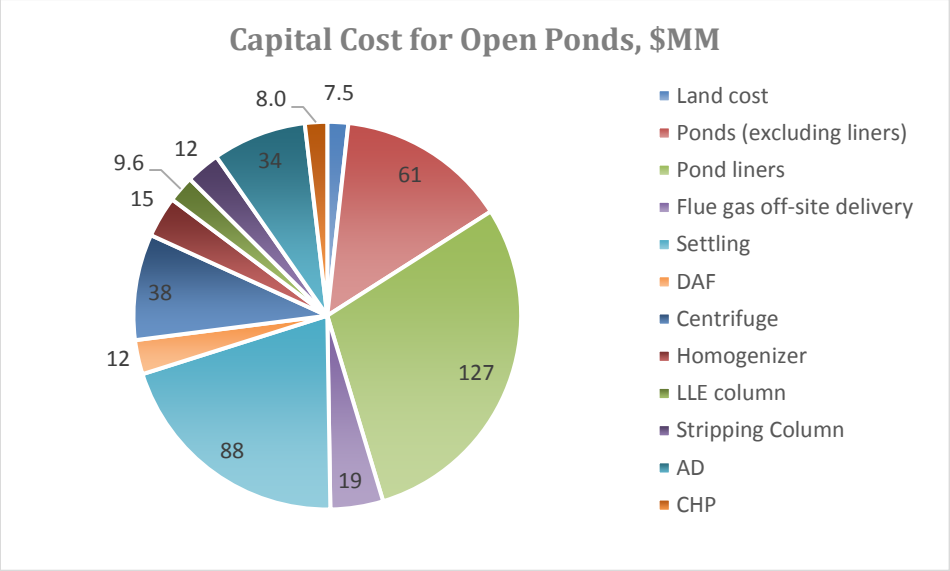


Figure 3.10.1.3 a: Capital cost of an open pond algal lipid facility for 10 MGY lipid productions.

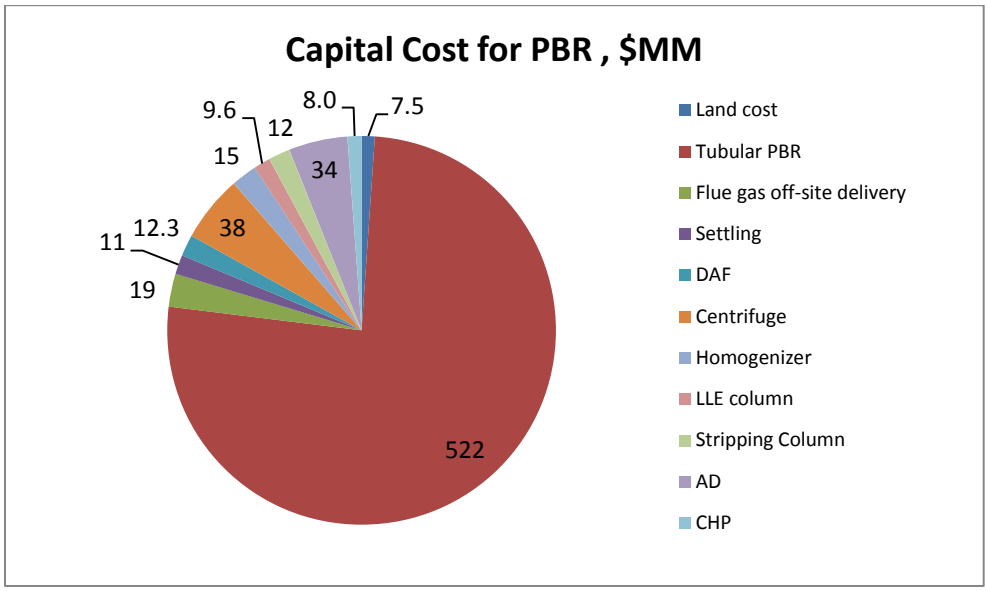


Figure 3.10.1.3 b: Capital cost of a PBR algal lipid facility for 10 MGY lipid productions.

3.10.2 Operating costs

Operating costs includes the expenses for raw materials, power for equipment, labor, and maintenance. Fixed operating cost is a method to estimate some operating costs, including labor and various overhead items, maintenance and taxes. Generally overhead is about 60% of labor which covers some costs for labor, such as safety, general engineering, general plant maintenance, and payroll overhead (Aden et al., 2002). Annual maintenance material and insurance and taxes are 2% and 1.5% of the total installed cost, respectively (Aden et al., 2002). Labor and overhead costs are complicated to analyze. This TEA study assumed a cost of $8.2 million for labor and overhead costs which is based on the results from Davis et al. (2012). The power cost is assumed to be $0.08/kWh (Davis et al., 2011). Table 3.10.2a presents the raw materials and economics for open ponds and PBR. Table 3.10.2b presents the power consumption of major equipment. The electric consumption by airlift column is not evaluated for PBR system in this scenario. Table 3.10.2c presents the total operating cost for this TEA study.

Table 3.10.2 a: The operating costs for open ponds and PBR algal biofuel facilities.

	Demand	Cost ($MM)
Lipid production (MM gal/yr)	10	--
Land use (acre) *Only for algae growth	4880	7.5
Open pond water demand (MM gal/yr)	10,790	0.54
PBR water demand (MM gal/yr) *Exclude water spray for PBR cooling	731	0.037
CO_2 demand (ton/yr)	289,963	12
NH_3 demand (ton/yr)	2595	2.4
DAP demand (ton/yr)	5351	3.5
Hexane (gal/yr)	86,082	0.36
Total resources cost for open pond	**--**	**18**
Total resources cost for PBR	**--**	**18**

Table 3.10.2 b: Major equipment power consumption.

	Power (kW)
Water pump from off-site	619
Open pond paddle wheel	10751
DAF	3609
Centrifuge	480
Homogenizer	3182
Extraction, heat	4397
Extraction, electricity	290
Stripping column, heat	1450
AD, heat	6146
AD, electricity	1779
CHP power generation	-10000
Total major equipment power	**22704**
Power cost ($MM)	**14.4**

Table 3.10.2 c: Total operating costs.

	Operating Cost ($MM/yr)
Raw materials	18
Power	14
Labor and overhead	8.2
Maintenance for open pond	8.6
Maintenance for PBR	14
Gross operating costs for open pond	**49**
Gross operating costs for PBR	**55**

3.10.3 Algal lipid selling price

Given the capital and manufacturing costs, a 20 year lifetime cash flow spreadsheet was developed to calculate the minimum lipid sales price (Table 3.10.3a and Table 3.10.3b). A tax rate of 35% and an internal rate of return of 10% are selected. The minimum lipid selling prices is the price at which the discounted present value for 20 years of operation is zero. The open pond minimum lipid sales prices was determined to be $11.3/gal and the PBR prices was 15.5 $/gal.

The conversion from lipid to biodiesel has been projected to cost about $2/gal of lipid (Davis et al., 2012).

Table 3.10.3 a: The selling price calculation for open pond algal lipid.

year	Sales income	Before tax cash flow	Depreciation	Taxable income	Income tax	Cumulate. cash flow
0	0	0	0	0	0	-431
1	79.1	30	62	0	0	-404
2	113	64	106	0	0	-351
3	113	64	75	0	0	-304
4	113	64	54	0	0	-260
5	113	64	38	0	0	-221
6	113	64	38	0	0	-185
7	113	64	38	0	0	-152
8	113	64	19	44	16	-130
9	113	64	0	64	22	-112
10	113	64	0	64	22	-97
11	113	64	0	64	22	-82
12	113	64	0	64	22	-69
13	113	64	0	64	22	-57
14	113	64	0	64	22	-46
15	113	64	0	64	22	-36
16	113	64	0	64	22	-27
17	113	64	0	64	22	-19
18	113	64	0	64	22	-12
19	113	64	0	64	22	-5
20	113	64	0	64	22	1.3

Table 3.10.3 b: The selling price calculation for PBR algal lipid.

year	Sales income	Before tax cash flow	Depreciation	Taxable income	Income tax	Cumulate. cash flow
0	0	0	0	0	0	-688
1	108.5	54	98	0	0	-639
2	155	100	169	0	0	-556
3	155	100	120	0	0	-481
4	155	100	86	0	0	-412
5	155	100	61	0	0	-350
6	155	100	61	0	0	-293
7	155	100	61	0	0	-242
8	155	100	31	70	24	-206
9	155	100	0	100	35	-179
10	155	100	0	100	35	-153
11	155	100	0	100	35	-130
12	155	100	0	100	35	-110
13	155	100	0	100	35	-91
14	155	100	0	100	35	-74
15	155	100	0	100	35	-58
16	155	100	0	100	35	-44
17	155	100	0	100	35	-31
18	155	100	0	100	35	-19
19	155	100	0	100	35	-8
20	155	100	0	100	35	1.3

3.10.4 Sensitivity analysis

The basic goal of this study is to produce 10 MM gal of lipid per year from microalgae. Open ponds have an algae productivity of 25 g m^{-2} d^{-1}, and biomass productivity of PBR is 1.25 kg m^{-3} d^{-1}. Figure 3.10.4a explores the TEA implication of algae productivity changes in response to algal lipid selling price. Lipid content was assumed to be 25%. The figure indicates that the costs are highly sensitive to the algae productivity, especially for PBR system.

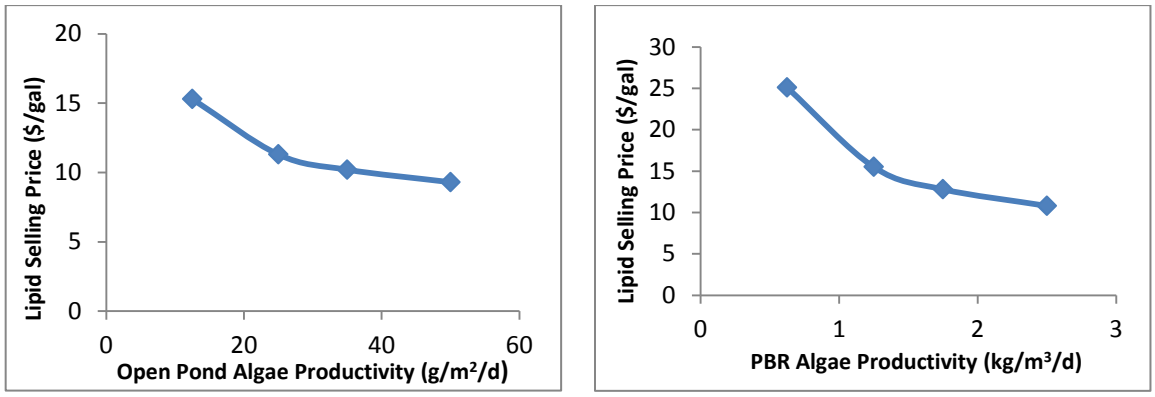


Figure 3.10.4 a: Algal lipid selling price as a function of algae productivity. The left plot is open pond system and the right plot is PBR system.

The basic model has a lipid content of 25% for microalgae. Figure 3.10.4b evaluates lipid cost modification as a function of lipid content. The biomass productivity was assumed to be 25 g m^{-2} d^{-1} for open pond and 1.25 kg m^{-3} d^{-1} for PBR. As with algae productivity, the study demonstrated that the costs are highly sensitive to the assumption of lipid content. Therefore, maximizing the overall productivities of algae systems and increasing lipid fraction are considered central and critical subjects for improvement in the production of biofuel from algae.

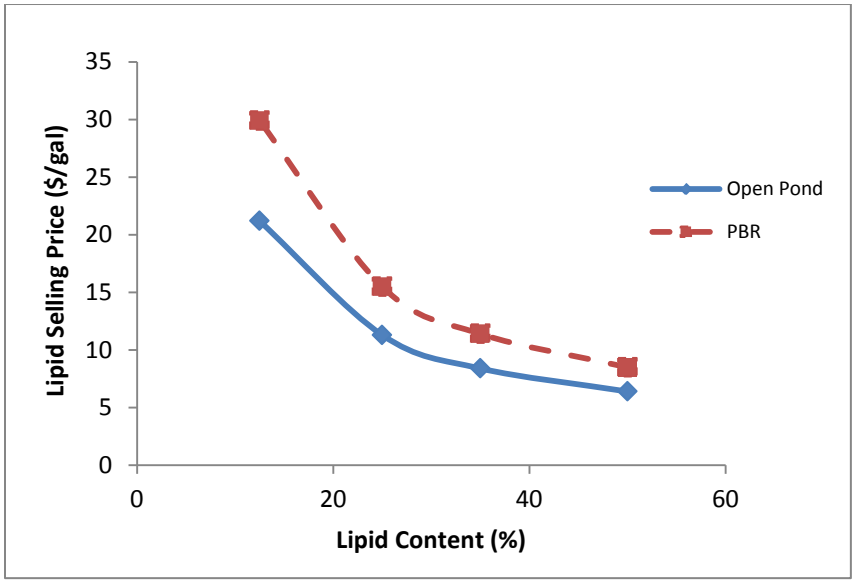


Figure 3.10.4 b: Algal lipid selling price as a function of lipid content.

In this scenario, chemical and flocculants in the harvesting process should be controlled in order to recover water that is unaffected by accumulation of chemicals. The recovery of water effluent from the harvesting process can dramatically reduce the raw material demand, including nutrients and water. Figure 3.10.4c explores the effect of water recycle rate on algae lipid cost. The figure demonstrates that water recycle after harvesting has a small impact on algal lipid selling price.

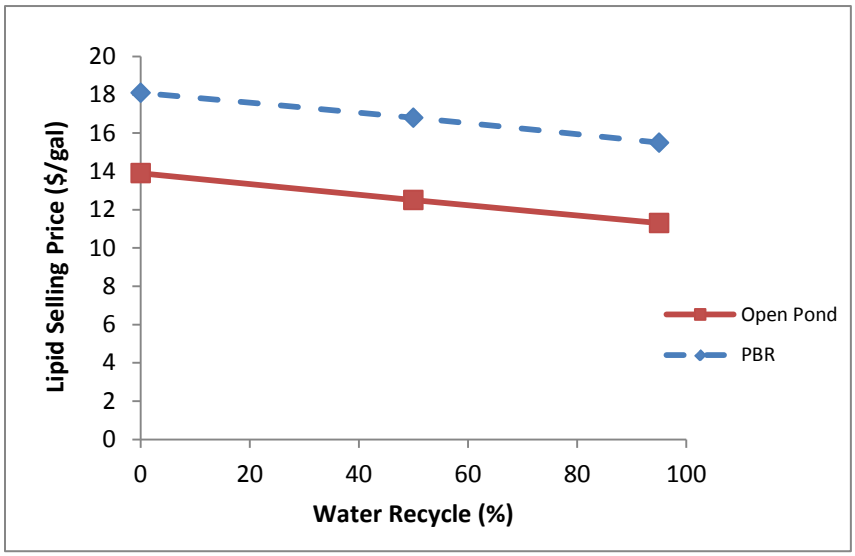


Figure 3.10.4 c: Algal lipid selling price as a function of medium recycle rate.

4 CONCLUSION

Although there are no algal biodiesel facilities at scales relevant to transportation fuel use in the U.S., Sapphire Energy Inc. (2013) has a commercial demonstration scale algae fuel production farm with the first 100 acres of pond systems. The studies that are published regarding industrial scale technology and economics are hypothetical, and often the details and assumptions necessary for calculation are missing. An excel model was developed, and validated partially with an Aspen Plus simulation, for a 10 MM gal lipid/year facility. The TEA developed by NREL (Davis et al., 2012) was found to be relatively conservative, and subsequently considered to be highly reliable. Where possible the TEA completed in this study used assumptions from the NREL analysis. Table 4.1a compares the microalgal oil yield given by the NREL study, the industrial Sapphire Energy facility, and the TEA prepared for this thesis.

Table 4 a: Comparison of lipid yield from various published literature.

	Lipid Production (MM gal/yr)	Lipid Content (%)	Productivity ($g/m^2/day$)	Land Demand (acre)	Lipid Yield (gal/acre/yr)
TEA	10	25%	25	4880	2049
Davis et al., (2012)	10	25%	25	4820	2075
Sapphire Energy (2013)	1[a]	--	--	300	3333

[a] Assume the finished product is lipid (biodiesel productivity is slightly smaller than lipid production)

In this thesis, an integrated technology and cost model has been analyzed based on technology published by NREL. A model of lipid production from algae is simulated by filling in the details that are not published, and further refining assumptions. The modeled facility will produce 10 MM gal of lipid per year from microalgae. It was assumed that both open ponds and PBR have an algae productivity of 25 $g\ m^{-2}\ d^{-1}$ and land use of 4880 acre for algae cultivation. The study demonstrated that the costs and lipid production are highly sensitive to the assumption of algae productivity and lipid content. A techno-economic model can be used to assess the effect of operational parameters on cost and performance, select approaches to maximize profits, and produce the input/output inventory required for a life cycle analysis.

This TEA model establishes a set of assumptions based on technology for the production of biodiesel from algae. Even though most of the technological data and assumptions were available from prior researches, there is still uncertainty in the recycling model, such as the efficiency of nutrient utilization for algae growth, water recycle rate after harvesting, and water recycle rate from anaerobic digestion.

The results from TEA show that the capital costs are high for 10 MM gal/yr of algal biodiesel productivity. The single largest cost for open ponds system is pond liner, which is about 30% of total capital cost. For PBR systems, the main contributor of capital cost is tubular photobioreactors. Large-scale PBRs are currently too expensive to build for the production of biofuel from algae.

Currently, the economics of producing biofuel from algae are not competitive with petroleum fuel. In the future, several strategies may have the potential to enhance algal biofuel economics, such as the production of high value co-products from algae, integrating wastewater treatment, and improvement of algal biofuel technologies.

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APPENDIX A

A.1 Algal Cultivation

A.1.1 Light utilization efficiency

According to Bush equation, the light utilization efficiency (Es) is a function of the incident light intensity (I_0) and light saturation factor (I_s), (Borowitzka, 2005)

$$E_s = \frac{Total\ Applied\ Light - Unutilizable\ Light}{Total\ Applied\ Light} = \frac{I_s}{I_0}\left(\ln\left(\frac{I_0}{I_s}\right) + 1\right)$$

This predicted efficiency can't be used for real culture because it is limited by the quantum efficiency of various wavelengths. The light efficiency for algae culture ranges from less than 1% to 5%.

A.1.2 Effect of light intensity to biomass productivity

The volumetric productivity of the biomass can be calculated by (Molina et al., 2001):

$$P = \mu C$$

where P is volumetric productivity of biomass, μ is the specific growth rate, C is the concentration of the biomass.

$$\mu = \frac{\mu_{max} I_{av}^n}{I_k^n + I_{av}^n}$$

- μ_{max} is the maximum growth rate
- I_{av} is the average irradiance inside the reactor
- I_k is an experimental constant
- n is an empirically established exponent

A.2 Nutrient, CO_2 and water

A.2.1 Dilution rate

At steady state the growth rate (μ) of continuous culture is determined by dilution rate D (d^{-1})"

$$\mu = F/V = D$$

where F is medium flow rate (m^3/d), V is volume of culture vessel (m^3).

This equation can evaluate the general growth rate of algae. But it may not correct for algal culture of low densities or under physiological stress from the environment (Wood et al., 2005).

A.3 Open Pond Design

A.3.1 Open pond water flow and head loss

The flow speed of water in open pond can be described by Manning's equation (Borowitzka, 2005).

$$V = \frac{R^{\frac{2}{3}} S^{\frac{1}{2}}}{n}$$

Where V is the mean velocity (m/s), R is mean hydraulic radius (m). S is water head loss per unit length, that is Δh/L (d is head loss and L is the channel length).

For raceway pond,

$$R = \frac{dw}{w + 2d}$$

Therefore, the head loss per unit length can be described as:

$$S = \frac{V^2 n^2}{R^{\frac{4}{3}}}$$

n is Manning's friction coefficient ($s \cdot m^{-1/3}$). Table A.3.1a estimates the value for Manning's n.

Table A.3.1 a: Manning's n for different liner material (Borowitzka, 2005).

Materials for Channel Liner	Manning's n
Smooth plastic on smooth concrete	0.008
Plastic with "scrim" on smooth earth	0.010
Smooth plastic on granular earth	0.012
Smooth cement concrete	0.013
Smooth asphalt concrete	0.015
Coarse trowelled concrete, rolled asphalt	0.016
Gunnite or sprayed membranes	0.020
Compacted smooth earth	0.020
Rolled coarse gravel, coarse asphalt	0.025
Rough earth	0.030

A.3.2 Open pond mixing depth

Oswald estimated the relationship between the concentration of algae, C (mg/L), and the light penetration depth, d_p (cm) (Becker, 1994; Borowitzka, 2005).

$$d_p = \frac{6000}{C}$$

Experience shows that the large scale cultures allow light to penetrate two third of the actual depth, that is

$$d_p = \frac{2}{3}d$$

$$d = \frac{9000}{C}$$

Therefore, the penetration depth is 18 cm for 0.5 kg/m^3 algae concentration.

This method cannot be used when the water has colored by organic matter or dyes (Becker, 1994).

A.3.3 Paddle wheel power

The hydraulic power of paddle wheel can be calculated from the following equation (Borowitzka, 2005):

$$P = \frac{QW\Delta d}{102e}$$

Where P is the power (kW), Q is the flow rate (m^3/s), Δd is the head loss of water which can be calculate by Manning's equation in Appendix A.3.1. W is the density of water (kg/m^3), 102 is conversion factor to convert m kg s^{-1} to kW. The efficiency of paddle wheel is about 17% (Borowitzka, 2005).

A.4 Water Deliver Equipment

A.4.1 Pump

A.4.1.1 Pump power

The ideal hydraulic power of pump depends on the mass flow rate, liquid density and head loss. The power of pump (P_h) can be calculated as

$$P_h = \frac{Q\rho g\Delta h}{3.6 \times 10^6}$$

- Q is mass flow rate of liquid (m^3/h)
- ρ is the liquid density (kg/m^3)
- g is gravitational acceleration (m/s^2)
- Δh is the head loss (m)

The shaft pump power (P_s) depends on the efficiency of pump and can be calculated as:

$$P_s = P_h/\eta$$

- η is the efficiency of pump

A.4.1.2 Centrifugal pump selection

The selected centrifugal pump has a flow rate of 1000 gpm and head of 30 m. The capital cost of centrifugal pump is calculated by equation from Seider et al. (2004).

The centrifugal pump size parameter (S) can be operate over a range of flow rate and head combinations,

$$S = Q(H)^{0.5}$$

- Q is mass flow rate of liquid (gpm)
- H is the hydraulic head (ft)

The base pump purchase cost at a CE cost index of 394.

$$C_B = \exp\{9.2951 - 0.6019[\ln(S)] + 0.0519[\ln(s)]^2\}$$

The purchase cost is given by

$$C_p = F_T F_M C_B$$

- F_T is pump-type factor (1-stage, 1800 rpm, HSC centrifugal pump, $F_T = 2.0$)
- F_T is material factor (cast steel is 1.35)

The power consumption of the motor is

$$P_c = \frac{QH\rho}{33000\eta_P\eta_M}$$

- ρ is the liquid density (lb/gal)
- η_P is the pump efficiency
- η_M is the motor efficiency

The base cost of the motor with CE index of 394 is

$$C_B = \exp\{5.4866 - 0.13141[\ln(P_c)] + 0.053255[\ln(P_c)]^2 + 0.028628[\ln(P_c)]^3 + 0.0035549[\ln(P_c)]^4\}$$

The purchase cost of motor is

$$C_p = F_T C_B$$

- F_T is motor-type factor (explosion-proof enclosure motor with 1800 rpm, $F_T = 1.7$)

A.4.1.3 Centrifugal pump for off-site water transportation

Table A.4.1.3 a: The parameters of centrifugal pump for off-site water transportation.

Parameters	Value	Source and Note
Pump flow rate (pgm)	1000	Seider et al. (2004)
Hydraulic head (ft)	98.4	Davis et al. (2012)
Pump size factor	9920	Calculation
Pump basic cost	3468	Calculation
Pump type factor F_T	2.0	Seider et al. (2004)
Pump material factor F_M	1.35	Seider et al. (2004)
Pump purchase cost ($)	9363	Calculation
Water density (lb/gal)	9.5	Seider et al. (2004)
Pump efficiency	75%	Davis et al. (2012)
Motor efficiency	90%	Davis et al. (2012)
Motor power consumption (Hp)	42	Calculation
$\ln(P_B)$	3.7	Calculation
Motor basic cost	1856	Calculation

A.5 Downstream Processing: Harvesting and Dewatering

A.5.1 Sedimentation

The velocity of sedimentation can be described by Stokes' law

$$v = \frac{g d^2 (\rho_s - \rho_l)}{18\mu}$$

- v is the particle settling velocity (m/s)
- g is gravitational acceleration (m/s^2)
- d is the particle diameter (m)
- ρ_s is the particle density (kg/m^3)
- ρ_l is the solution density (kg/m^3)
- μ is the dynamic viscosity (pa·s)

A.5.2 Centrifugation

The velocity of sedimentation in a centrifugal field can be described by Stokes' law. It is very similar to the sedimentation equation.

$$v = \frac{d^2(\rho_s - \rho_l)(r\omega^2)F_s}{18\mu\theta}$$

- r is the radius of rotation
- ω is the angular velocity in radians (s^{-1}) which is related to N (rpm) by $\omega = \frac{\pi N}{30}$
- $r\omega^2$is the acceleration factor (m/s^2, one g is equal to an acceleration of 9.81 m/s^2)
- F_s is corrosion factor which depends on the fraction of solids present; approximately equaling 1, 0.5, 0.1, and 0.05 for 1%, 3%, 12% and 20% solids volume fraction respectively.
- θ is the shape factor (use 1 for spherical particles)

The maximum throughput flow rate of centrifugation, ϕ (m^3/s) is given by Stoke's law:

$$\phi = \frac{d^2(\rho_s - \rho_l)(r\omega^2)(2\pi rL)F_s}{18\mu\theta}$$

- ϕ is the flow rate entering to the centrifugation
- L_{eff} is the centrifuge height (m)
- $2\pi rL$ is the effective clarifying surface (m^2)

A.6 Extraction of Production from Algae

A.6.1 Liquid-liquid extractors

A.6.1.1 Flow rate

The rotating-disk extractor has a maximum diameter of 25 ft (7.6 m) and maximum liquid throughout of 120 ft^3 (3.4 m^3) of liquid/hr-ft^2 of column cross-sectional area (Seider et al., 2004).

The maximum column cross-sectional area $= \frac{(25\text{ ft})^2}{4}\pi = 419\ ft^2$

The maximum LLE liquid flow rate $= 419\ \times 120\ ft^3/h = 58900\ ft^3/h = 1.67\ m^3/h$

A.6.1.2 Power requirement

The agitator power (P) for liquid-liquid extraction can be estimated from (Benitez, 2005)

$$P = \Omega^2 D_i^5 \rho_M$$

- Ω is the impeller rate of rotation (H_z)
- $D_i = \frac{1}{3} D_T$
- D_T is the diameter of LLE vessel
- ρ_M is the two-phase mixture density

$$\Omega = \left[1.03 \Phi_D^{0.106} \left(\frac{D_T}{D_i} \right)^{2.76} \left(\frac{\mu_M^2 \sigma}{D_i^5 \rho_M g^2 (\Delta\rho)^2} \right)^{0.084} \left(\frac{g \Delta\rho}{\rho_M D_i} \right) \right]^{0.5}$$

- Φ is the fractional holdup in the tank of the dispersed liquid phase (algae slurry is dispersed liquid phase)
- μ_m is the two-phase mixture viscosity
- σ is the interfacial tension between the liquid phases
- $\Delta\rho$ is the difference in density between the liquids

$$\rho_M = \rho_C \Phi_C + \rho_D \Phi_D$$

- Φ_C is the fractional holdup in the tank of the continuous liquid phase (hexane is dispersed liquid phase)
- ρ_C is density of the continuous liquid phase
- ρ_D is density of the dispersed liquid phase

$$\mu_m = \frac{\mu_C}{\Phi_C} \left(1 + \frac{1.5 \mu_D \Phi_D}{\mu_C + \mu_D} \right)$$

- μ_C is viscosity of the continuous liquid phase
- μ_D is viscosity of the dispersed liquid phase

The units for those equations are not given. Stephenson et al. (2010) calculated that the power is about 3.3 kW/m^3 for LLE with a rotation rate of 5.3 Hz.

A.6.1.3 Cost estimation

The purchase cost for a rotating-disk liquid-liquid extractor can be calculated from (Seider et al., 2004)

$$C_p = 250S^{0.84}$$

$$S = HD^{1.5}$$

- C_p is the purchase cost with CE index of 394
- S is the size parameter (3-2000 $ft^{2.5}$)
- H is the height of LLE column (ft)
- D is the diameter of LLE column (ft)

The LLE column has a dimension of 20 ft in height and 20 ft in diameter. The cost estimation is summarized in Table A.6.1.3a.

Table A.6.1.3 a: LLE main parameters.

Parameters	Value	Source and Note
LLE height (ft)	20	Seider et al. (2004)
LLE diameter (ft)	20	Seider et al. (2004)
Size parameter	1789	Calculation
Original purchase cost ($)	134,928	Calculation
Material factor for stainless-steel construction	2	Seider et al. (2004)
Original cost index	395	*Cost index for 2001
Cost index	585	*Cost index for 2012
Purchase cost ($)	399,661	Calculation

A.6.2 Stripping column

The solvent can be recovered by separation in the stripping column. Aspen Plus simulation is applied to analyze the heat and electricity demand and cost. The main parameters are summarized in Table A.6.2a and Table A.6.2b.

Table A.6.2 a: General parameters for stripping column.

Parameters	Value	Source and Note
Column stage	25	Assumption
Column diameter	1.73	Assumption
Reflux ratio	1.2	Assumption
Heat duty (kW)	1450	Calculated by Aspen Plus
Capital cost ($MM)	3.6	Calculated by Aspen Plus
Operating cost ($MM/yr)	1.0	Calculated by Aspen Plus

Table A.6.2 b: Flow rate of stream in stripping column.

Stream	Input	Bottom	Distillate
Temperature (K)	298.2	608.1	366
Pressure (atm)	10	2.5	2
Triolein mass flow (kg/h)	4397	4397	0
Hexane mass flow (kg/h)	13,371	26.742	13344.26

A.7 Anaerobic Digestion

A.7.1 CO_2 recycled

The carbon content being degraded can be calculated in the following equation:

$$\frac{0.30\ \text{L}\ CH_4}{\text{g VS}} \times \frac{100\%\ L\ CH_4\ \&\ CO_2}{70\%\ L\ CH_4} \div \frac{22.4\ \text{L}\ CH_4\ \&\ CO_2}{mol\ \text{C}} \times \frac{12\ \text{g C}}{mol\ C} \times\ 0.9\ \frac{\text{g VS}}{g\ organic}$$
$$= 20.7\% \frac{\text{g C}}{g\ organic}$$

The composition of algae is $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$ and lipid structure is $C_{57}H_{104}O_6$ (triolein). The homogenization and extraction efficiency is 85.5% and lipid content is 25%. The structure of debris and carbon content can be calculated in the following equation:

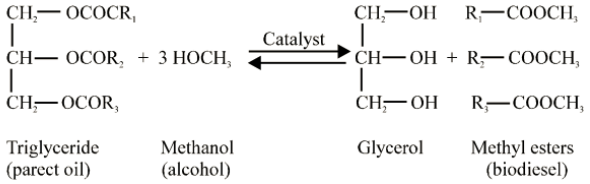
$$CO_{0.48}H_{1.83}N_{0.11}P_{0.01} - \frac{23.39\ \text{g algae}}{\text{mol algae}} \times 25\%\ \frac{g\ lipid}{g\ algae} \div \frac{885.24\ \text{g lipid}}{\text{mol lipid}} \times C_{57}H_{104}O_6$$
$$= C_{0.62}O_{0.44}H_{1.14}N_{0.11}P_{0.01}$$

$$\left(10\%\ \frac{g\ algae}{g\ organic}\times\frac{12\ g\ carbon}{23.39\ g\ algae}+90\%\ \frac{g\ algae}{g\ organic}\times 75\%\frac{g\ debris}{g\ algae}\times\frac{12\times 0.62\ g\ carbon}{17.48\ g\ debris}\right.$$
$$\left.+\ 90\%\ \frac{g\ algae}{g\ organic}\times 25\%\frac{g\ lipid}{g\ algae}\times(1-95\%)\times\frac{12\times 57\ g\ carbon}{885\ g\ debris}\right)$$
$$\div\left(1-90\%\ \frac{g\ algae}{g\ organic}\times 25\%\frac{g\ debris}{g\ algae}\times 95\%\right)=44.2\%\ \frac{\text{g C}}{g\ organic}$$

The carbon content is 51.8% and 43.8% for before and after extraction process respectively. Therefore, the carbon fraction of algae is 46.8% which calculating by 20.7% dividing 44.2%. Finally, 46.8% of carbon dioxide has been recycled for algal growth.

A.8 Kinetic of Lipid Transesterification in Batch Reactor

The fractions of algal lipid compose of triglyceride (TAG), diglyceride (DAG), monoglyceride (MAG) and free fatty acid (FFA). TAG is the main lipid for algae. In the algal biodiesel conversion process, transesterification reaction is employed to convert most of algal lipid to fatty acid methyl esters (FAME). The stoichiometry of reaction requires 3 mol of methanol and 1 mol of TAG to generate 1 mol of glycerol and 3 mole of FAME. Generally, this reaction is catalyzed by acid catalyst (Vicente et al., 2005). The intermediates, DAG and MAG, can be detected in three consecutive reactions (Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Vicente et al., 2005; Xu et al., 2005). The common ROH (M) is methanol with yield of glycerol (GL).



Stepwise reactions are:

$$TG + ROH \underset{k_2}{\overset{k_1}{\rightleftarrows}} DG + R'CO_2R$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\rightleftarrows}} MG + R'CO_2R$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\rightleftarrows}} GL + R'CO_2R$$

Several parameters can determine the reaction rate of transesterification, including impeller speed, temperature, and catalyst concentration. Two different methods are used to evaluate the kinetics of transesterification reaction, regarding catalyst concentration or not regarding catalyst concentration.

To build a mathematical model for the transesterification reaction without regarding the catalyst concentration, the following assumptions were adopted (Xu et al., 2005):

(1) Only small amounts of water in the reaction and then neglect hydrolysis reaction for free fatty acid.
(2) Mass transfer is neglected

The kinetic differential equation can be described as follows (Noureddini and Zhu, 1997; Xu et al., 2005):

$$\frac{d[TG]}{dt} = -k_1[TG][M] + k_2[DG][FA]$$

$$\frac{d[DG]}{dt} = k_1[TG][M] - k_2[DG][FA] - k_3[DG][M] + k_4[MG][FA]$$

$$\frac{d[MG]}{dt} = k_3[DG][M] - k_4[MG][FA] - k_5[MG][M] + k_6[GL][FA]$$

$$\frac{d[FA]}{dt} = k_1[TG][M] - k_2[DG][FA] + k_3[DG][M] - k_4[MG][FA] + k_5[MG][M] - k_6[GL][FA]$$

$$\frac{d[M]}{dt} = -\frac{d[FA]}{dt}$$

$$\frac{d[GL]}{dt} = k_5[MG][M] - k_6[GL][FA]$$

Xu et al. (2005) gave the reaction rate at specific is 5 g soybean oil, 5 g methyl acetate, 0.5 g Novozym 435, 40℃, 150 oscillations/min.

Table A.8 a: Reaction rate estimated by Xu et al. (2005).

Reaction	Rate Constants (l/mol min)	Value
TG→DG	k_1	0.0311
DG→TG	k_2	0.0176
DG→MG	k_3	0.1124
MG→DG	k_4	0.1271
MG→TA	k_5	0.1129
TA→MG	k_6	0.0915

Vicente et al. (2005) analyzed the catalyst concentration effect on the reaction rates. It assumed the reaction rates of transesterification are direct proportional to catalyst concentration. The kinetic differential equation can be described as follows (Vicente et al., 2005). C represents the concentration of catalyst.

$$\frac{d[TG]}{dt} = -k_1 C[TG][M] + k_2 C[DG][FA]$$

$$\frac{d[DG]}{dt} = k_1 C[TG][M] - k_2 C[DG][FA] - k_3 C[DG][M] + k_4 C[MG][FA]$$

$$\frac{d[MG]}{dt} = k_3 C[DG][M] - k_4 C[MG][FA] - k_5 C[MG][M] + k_6 C[GL][FA]$$

$$\frac{d[FA]}{dt} = k_1 C[TG][M] - k_2 C[DG][FA] + k_3 C[D][M] - k_4 C[MG][FA] + k_5 C[MG][M] - k_6 C[GL][FA]$$

$$\frac{d[M]}{dt} = -\frac{d[FA]}{dt}$$

$$\frac{d[GL]}{dt} = k_5 C[MG][M] - k_6 C[GL][FA]$$

Vicente et al. (2005) calculated the reaction rate at varying catalyst concentration (0.5, 1 and 1.5 wt% of sunflower) and varying temperature (25, 35, 45, 55, and 65℃). The based-catalyzed reaction of methanol and soybean has a 6:1 molar ratio. The impeller speed was set at 600 rpm.

The temperature influence on the reaction rate can be studied from the Arrhenius equation:

$$k = Aexp\left(-\frac{E_a}{RT}\right)$$

Where A is a constant called pre-exponential factor, E_a is the activation energy (J/mol), R is the gas constant which is 8.314 J/(mol·K), T is temperature (K).

Activation energy and pre-exponential factor can be calculated from a plot of reaction rate constant (k) vs the temperature from the following equation:

$$\log(k) = -\frac{E_a}{2.303RT} + \log(A)$$

Vicente et al. (2005) gave the estimations of activation energy and pre-exponential factor in Table A.8b. After rigorous analysis and calculation, activation energy (E_a) should multiple 2.303 to get the better estimated result. Reaction rate k_6 is very small that is negligible.

Table A.8 b: Estimation of activation energy and pre-exponential factor by Vicente et al. (2005).

Reaction	T → D	T ← D	D → M	D ← M	M → G
Activation energy (Ea) (J/mol)	31,656.2	31,014.3	41,557.8	41,107.2	5955.5
Right Activation energy (Ea) (J/mol)	72,904	71,426	95,708	94,670	13,716
Pre-exponential factor (A)	3.4×10^{12}	9.8×10^{12}	2.1×10^{17}	1.2×10^{17}	537.9
Regression coefficient (r^2)	0.9889	0.9817	0.9556	0.9053	0.9608

Matlab can be used to calculate the reaction rate by the parameters from Table A.8 b.

Matlab program:

```
% tran.m
% This file is used to calculate the kinetics of transesterification
% reaction
%
%
% TG + ROH = DG + R'CO2R
% DG + ROH = MG + R'CO2R
% MG + ROH = GL + R'CO2R
%
% (d[TG])/dt =-k1 C[TG][M]+k2 C[DG][FA]
% (d[DG])/dt =k1 C[TG][M]-k2 C[DG][FA]-k3 C[DG][M]+k4 C[MG][FA]
% (d[MG])/dt =k3 C[DG][M]-k4 C[MG][FA]-k5 C[MG][M]+k6 C[GL][FA]
% (d[FA])/dt =k1 C[TG][M]-k2 C[DG][FA]+k3 C[DG][M]-k4 C[MG][FA]
```

```
% +k5 C[MG][M]-k6 C[GL][FA]
% (d[M])/dt=-(d[FA])/dt
% (d[GL])/dt =k5 C[MG][M]-k6 C[GL][FA]
%
% k6 is very small that has been neglected
%
% k=Aexp(-E_a/RT)
%
% Reference: Vicente et al., (2005)
%
clear all
global C_c k1 k2 k3 k4 k5

C_c0 = input('Enter the catalyst concentration (0.5-1.5%):');
C_c = C_c0/10;
lipid = input('Enter the lipid concentration (< 0.85 mol/L):');
disp('Methanol to lipid mole ratio is 6:1, impeller speed is 600rmp')
%
% Assume lipid concentration is x, if 100% of lipid is triolein.
% (32 g/mol * 6x mol/L) / 791.8 g/L + (885.432 g/mol* x mol/L) / 950 g/L = 1
% The maximum concentration of triolein is 0.85 mol
%
% Assume lipid concentration is y, if 100% of lipid is monoglyceride (C21H40O4).
% (32 g/mol * 6y mol/L) / 791.8 g/L + (356.54 g/mol* y mol/L) / 958 g/L = 1
% The maximum concentration of triolein is 1.63 mol
%
TG0 = input('Enter the triglyceride fraction in the lipid (>0.9):');
DG0 = input('Enter the diglyceride fraction in the lipid:');
MG0 = input('Enter the monoglyceride fraction in the lipid:');
FA0 = 0;
M0 = 6;
GL0 = 0;

if TG0 + DG0 + MG0 > 1, error('Total mass of TG, DG, and MG cannot be larger
than 1'),end

E_a = [72904 71426 95708 94670 13715];
% Activation energy (J/mol)
A = [3.4e12 9.8e12 2.1e17 1.2e17 537.9];
% Pre-exponential factor
R = 8.314;
% Gas constant (J/mol/K)
T = input ('Enter the temperature of the reaction (298-338K):');

k = A.*exp(-E_a./(R*T));
k1 = k(1);
```

```
k2 = k(2);
k3 = k(3);
k4 = k(4);
k5 = k(5);

t = input ('Enter the retention time for the batch reactor (min):');

[tt C] = ode23('tran_fun', [0 t], [TG0*lipid DG0*lipid MG0*lipid FA0 M0*lipid
GL0]);
plot(tt,C(:,1),tt,C(:,2),'--',tt,C(:,3),'.',tt,C(:,4),'-
.',tt,C(:,5),tt,C(:,6),'linewidth',2)
xlabel('Time(t)')
ylabel('Concentration')
title('Kinetics of Transesterification Reaction')
legend('TG','DG','MG','FA','M','GL','Location','Best')

TG_final = C(end,1)
DG_final = C(end,2)
MG_final = C(end,3)
FA_final = C(end,4)
M_final = C(end,5)
GL_final = C(end,6)
TG_conv = 1 - TG_final/TG0
```

Function program:

```
function f = tran_fun(t,C);
global C_c k1 k2 k3 k4 k5
f(1,1) = -k1*C_c*C(1)*C(5) + k2*C_c*C(2)*C(4);
f(2,1) = k1*C_c*C(1)*C(5) - k2*C_c*C(2)*C(4) - k3*C_c*C(2)*C(5) +
k4*C_c*C(3)*C(4);
f(3,1) = k3*C_c*C(2)*C(5) - k4*C_c*C(3)*C(4) - k5*C_c*C(3)*C(5);
f(4,1) = k1*C_c*C(1)*C(5) - k2*C_c*C(2)*C(4) + k3*C_c*C(2)*C(5)...
 - k4*C_c*C(3)*C(4) + k5*C_c*C(3)*C(5);
f(5,1) = -(k1*C_c*C(1)*C(5) - k2*C_c*C(2)*C(4) + k3*C_c*C(2)*C(5)...
 - k4*C_c*C(3)*C(4) + k5*C_c*C(3)*C(5));
f(6,1) = k5*C_c*C(3)*C(5);
```

Matlab program result example:

```
Enter the catalyst concentration (0.5-1.5%):1.5
Enter the lipid concentration (< 0.85 mol/L):0.85
Methanol to lipid mole ratio is 6:1, impeller speed is 600rmp
Enter the triglyceride fraction in the lipid (>0.9):1
Enter the diglyceride fraction in the lipid:0
```

```
Enter the monoglyceride fraction in the lipid:0
Enter the temperature of the reaction (298-338K):318
Enter the retention time for the batch reactor (min):30
```

Result:

```
TG_final = 9.9560e-04
DG_final = 1.7542e-04
MG_final = 1.9178e-04
FA_final = 2.5465
M_final = 2.5535
GL_final = 0.8486
TG_conv = 0.9990
```

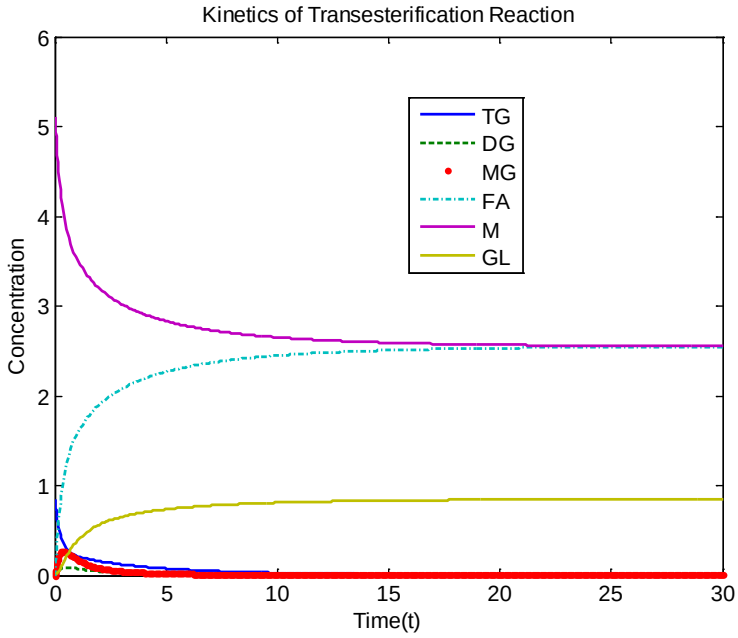


Figure A.8 a: Example of kinetic of transesterification

A.9 Cost Index

Table A.9 a: Chemical Engineering (CE) Plant Cost Index (Seider et al., 2004).

Year	CE Plant Cost Index	Year	CE Plant Cost Index	Year	CE Plant Cost Index
1980	261	1991	361	2002	396
1981	297	1992	358	2003	402
1982	314	1993	359	2004	444
1983	317	1994	368	2005	468
1984	323	1995	381	2006	500
1985	325	1996	382	2007	525
1986	318	1997	387	2008	575
1987	324	1998	390	2009	522
1988	343	1999	391	2010	551
1989	355	2000	394	2011	586
1990	358	2001	395	2012	585