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PRODUCTION OF BIODIESEL FROM MICROAlGAE

BY MENELIK GEBEYEHU

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School of Graduate studies

Faculty of Technology

Department of Chemical Engineering

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By

Menelik Gebeyehu

Adivsor

Dr. –Ing Nurelegne Tefera

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APPROVED BY BOEARD OF EXAMINERS:

Dr. –Ing Zebene Kifle	_____	_____
Chairman, Department's Graduate Committee	Signature	Date
Dr. -Ing. Nurelegne Tefera	_____	_____
Advisor	Signature	Date
Ato Teshome Mitku	_____	_____
External Examiner	Signature	Date
Dr. Tassisa Kaba	_____	_____
Internal Examiner	Signature	Date

Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for a degree at this or any other university, and that all reference materials contained therein have been duly acknowledged.

_____ _____

Menelik Gebeyehu (Candidate) Date

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge

_____ _____

Dr. –Ing Nurelegne Tefera (Thesis advisor) Date

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Contents

List of Tables

List of Figures

Acronyms

ARARI	Amhara Regional Agricultural Research Institute
ASTM	American Society for Testing and Materials
AV	Acid Value
CO_2-e	Carbon dioxide equivalent of green house emission gases
CPBR	Closed Photo Bio reactors
CV	Calorific Value
DW	Dry weight
EN	European Committee for Standardization
EPA	Environmental Protection Agency
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FPPBRS	Flat Plate Photo Bio Reactors
GC	Gas Chromatography
ha	Hectares
HHV	Higher Heating Value
HPLC	High Performance Liquid Chromatography
NPV	Net Present Value
PBR	Photo Bio Reactors
PBP	Pay Back Period
PFR	Plug flow reactors
ROR	Rate on Return
RWOP	Race Way Open Ponds
SG	Specific Gravity
SV	Saponification Value
TAG	Triacylglycerols
TPBR	Tubular Photo Bio Reactors
VCPBR	Vertical Column Photo Bio Reactors

Abstract

Since petroleum resources are believed to last only for a few decades, alternative sources of biofuel production should be exploited. In order to replace all the fossil fuels consumed in the world, other sources of biodiesel which have higher productivity per unit area of land than vegetable and non edible oilseed feed stocks are required. One of the alternative sources which falls in to relatively higher productivity per unit area of land ($10g/m^2/day$ -$50g/m^2/day$) is the production of biodiesel from microalgae.

This study focuses on production of biodiesel from microalgae by transesterification reaction. Algal biomass of symbiotic blue green algae were collected from ARARI. After drying the biomass, algae oil was extracted by soxhlet extraction method using solvent, hexane. Then, purification of the oil was performed by degumming, neutralization, and bleaching to facilitate the characterization and biodiesel production process. The characterization test of the oil confirmed that oil can be produced from the algal biomass with the acceptable range of pyisco-chemical properties for biodiesel production. Then, biodiesel was produced by base catalyzed transesterification reaction and characterized by determining density, kinematic viscosity, acid value, saponification number, flash point and heating value. HPLC analysis was conducted to determine the conversion of oil to biodiesel. The characteristic test result of the biodiesel showed that the density, kinematic viscosity, acid value, saponification number, flash point and heating value conforms to all the standard specifications of ASTM D 6751 and EN 14214, except for its acid value (0.57mgKOH/g) which is 14 % above the EN 14214 specification.

The result showed that the symbiotic blue green algae in ARARI can be used to produce biodiesel with acceptable quality. However, the oil yield of the algal biomass was very low (5.4wt %) when compared with oil contents of algal strains (>15wt %) recommended for biodiesel production. Therefore, three different pure algal strains were selected and assessed based on their oil content and productivity with growth parameter requirements of climatic conditions which conform to the Ethiopian environment particularly to the specific area selected for cultivation. The results of the investigation showed that the strain Bortyococcus braunii gives the best result and recommended for cultivation of algal biomass for biodiesel production in Ethiopia.

1. Introduction

1.1. Background

Despite the recent financial and economic crises prevailed around the world, the price of petroleum is decently increasing. The global production of petroleum has slowly increased in the last decade, while the demand for petroleum is increasing at a faster rate than it is being consumed [1]. More over the price and consumption of hydrocarbons is expected to soar in the near future as the huge populations of India and China will require more fuel as their economies continue to grow. Africa, with a population of more than a billion, is growing at a faster rate than the average growth of the rest of the world. This will be an additional factor for increasing the world energy demand and consumption of fuels derived from petroleum. Due to the recent oil and gas price hike started in 2007/08, many nations such as Ethiopia and most of the Sub-Saharan African countries, which cannot supply their own petroleum needs, are affected by unfavorable balance of payments. This is the direct economical impact of petroleum apart from the high inflation rate and slowing down of the economy witnessed in many developing countries in Africa. A case in point is Ethiopia, where yearly average inflation rate was 64.1% as of July 2008 [2].

The environmental impact of fossil fuels is also well known. It contributes to global warming by transferring previously sequestered carbon molecules as carbon dioxide and other green house gases into the atmosphere. It is also a major source of air pollution through other combustion products like particulate matters, SO_X and NO_X. The Stern Report [3] on the economics of climate change provides the most comprehensive evaluation of the causes and effects of climate change currently available. According to the report, current levels of greenhouse gases are higher now than at any time in at least the past 650,000 years due to human activities predominantly as a result of burning fossil fuels and industrial green house gas emissions. Since pre-industrial times, carbon dioxide concentrations have increased by just over one third from 280 ppm to 380 ppm in 2006. Coupling with the rising concentrations of other greenhouse gases, particularly methane and nitrous oxide, the report stated that the warming effect due to all the Kyoto greenhouse gases emitted by human activities in the same year is equivalent to around 430 ppm

of carbon dioxide (CO_2-e) and rising at around 2.3 ppm per year. Based on this projection, the review concluded that the dangerously high range atmospheric CO_2 levels above 450 ppm CO_2-e could be reached before 2015. Therefore, global warming, induced by increasing of greenhouse effect gases concentrations in the atmosphere, has become an important environmental concern [3].

In order to achieve environmental and economic sustainability, fuel production processes are required which are not only renewable, but also capable of sequestering atmospheric CO_2. Hence, the environmental and energy factors mentioned above were considered to be the important trigger for many initiatives in the developed and developing nations to search for alternative sources of energy. Biofuel production technologies, which are economically competitive with the current price of petroleum, are therefore rapidly being developed in different areas. Bioethanol from corn in the US and from sugar in Brazil has been used in blends with gasoline. It has been reported that bioethanol in Brazil is price competitive with petroleum above a value of 40 dollar per barrel of crude oil. However, due to the similarities in physical and chemical properties it has with petroleum-based diesel, biodiesel production increased at an average rate of 32% per year between 2000 and 2005 [1]. This is attributed to the fact that biodiesel can be used in conventional diesel engines alone or blended with petro diesel without significant modifications and can be used in existing infrastructures. Conventional biodiesel mainly comes from soybean and vegetable oils, palm oil, sunflower oil, rapeseed oil as well as restaurant waste cooking oil. However, current supplies from oil crops and animal fats account for only approximately 0.3% of the current demand for transport fuels. But increasing biofuel production on arable land could have severe consequences for global food supply. Farm crops to produce plant-derived ethanol or biodiesel precursor oils require large arable lands in a suitable climate, irrigation or sufficient natural precipitation. Coupling with the increased price and demand of land for agricultural products for food consumption around the world, it creates unfavorable conditions with its own economical and political implications in a given country.

In contrast to producing biodiesel from the above sources, algae is widely regarded as one of the most efficient ways (in terms of land requirement) of generating biofuels and also appears to represent the only current renewable source of oil that could meet the global demand for

transport fuels. Algae are grown either in open culture systems or closed PBR. It may be possible in the future to produce enough oil by farming microbes, such as algae, whose oil yields per unit land area could be two orders of magnitude higher than the conventional oil crops [1].

In additions to these facts, second generation (biofuel feedstock resources that do not compete for food items and agricultural arable lands, for example lignocellulosic technologies) microalgal systems have the advantage that they can produce a wide range of feed stocks for the production of biodiesel, bioethanol, biomethane, biohydrogen and fuel gases.

1.2. Problem statement

Ethiopia is the second largest country in Africa in terms of population. But the usage of petroleum fuel per capita is the smallest compared to other African nations. However, if it was not for the money transfer, loan and aid Ethiopia received in the first nine months of the year 2008, the little over one billion dollar revenue collected from its exports would have been consumed by the import of petroleum which took over 97% of the country's earnings from exports of mainly agricultural products [4]. This has severely affected the country's purchasing capacity of goods and machineries which will otherwise be used to improve the life of the people and infrastructure and the overall economy of the country.

Nowadays, many African nations have given a considerable attention for the development of biofuels from oil producing crops. Ethiopia also has allocated more than two million ha available for investors in the biofuel sector. As of 2008 a total of 698,100 ha land area is given to investors for the production of Jatropha, castor seed and other oil producing seeds which will be used for producing biofuel feedstocks, mainly for biodiesel production. Some of the investors have already begun production of oil from their farm. Indeed, Ethiopia has ample opportunities and potential for the production of varieties of both edible and non-edible oilseeds and oil fruits, due to the country's favorable agroecology (climate and soil) [5]. Furthermore, bioethanol produced by Fincha sugar factory, is used in Addis Ababa for automobile transportation after blended with 95% gasoline. Besides, the state owned sugar factories including the huge projects currently being undertaken in Afar region are expected to increase the ethanol production capacity of the

country by more than 10 folds in the near future [5]. These are some of the positive measures implemented by the government to reduce dependency on imported petroleum oil and increase the amount of currency earned through export.

However, in contrast to the above measures taken to increase biofuel productivity, there is an urgent need for the government to increase the production of agricultural food items in order to be self sustained and eradicate famine from the country. Bearing in mind that the population of the country will be around 120 million by 2025 [6] a vast area of land, which is currently unexploited should be made available for food crop production. The development of biofuel, therefore, will inarguably compute for the available land which will otherwise be used for the aforementioned purposes.

Therefore, it is the utmost important to search for the development of feedstock for biodiesel which is both able to grow in areas extremely unfavorable for conventional agriculture and has a very high biomass and/or oil productivity per unit area of land. Among the available alternatives, the best biofuel feed stocks which can perfectly fit in to the above criteria is the production of algal biomass as a source of biofuel feed stock. In terms of oil produced per unit area of land, algae have a 5- to 31-fold advantage over the next best oil producing crop, oil palms, depending on the species of algae and growth conditions [1].

Table 1.1 below shows the comparison of land requirement of different source of oil for producing biodiesel in order to replace the global fossil fuel demands in 2008 [1].

Table 1.1: Comparison of crop-dependent biodiesel production efficiencies from plant oils.

Plant source	Biodiesel (l/ha/a)	Area required to produce global oil demand(hectares*10^6)	Area required as percent global land mass	Area as percent global arable land
Cotton	325	15002	100.7	756.9
Soybean	446	10932	73.4	551.6
Mustard seed	572	8524	57.2	430.1
Sunflower	952	5121	34.4	258.4
Rapeseed	1190	4097	27.5	206.7
Jatropha	1892	2577	17.3	130
Palm oil	5950	819	5.5	41.3
Algae(10g/m^2day at 30% TAG	12000	406	2.7	20.5
Algae(10g/m^2day at 50% TAG	98500	49	0.3	2.5

Source [1].

1.3. Objective of the study

1.3.1. General objective

- To produce biodiesel from algae and to determine if biodiesel production from algae is feasible in Ethiopia.

1.3.2. Specific objectives

- To select suitable strains of microalgae for Ethiopian climate.
- To perform financial analysis for biodiesel production from selected algal strains
- To characterize oil and biodiesel from the microalgae.
- To perform sensitivity analysis over some key variables on biodiesel production from algal oil.

1.4. Limitation of the study

The limitation of this study was the quantity of oil yield of the algal biomass was very low so that all the characteristic tests and transesterification reaction at different conditions could not be performed.

2. Literature review

2.1. Classification of microalgae

The word *algae* represent a large group of different organisms from different phylogenetic groups, representing many taxonomic divisions. In general *algae* can be referred to as plant-like organisms that are usually photosynthetic and aquatic, but do not have true roots, stems, leaves, vascular tissue and have simple reproductive structures. They are distributed worldwide in the sea, in freshwater and in moist situations on land. Most are microscopic, but some are quite large, e.g. some marine seaweeds that can exceed 50 m in length. All microalgae are unicellular and microscopic unlike the other classes of algae and they usually contain higher lipid content than macro algae. Biologists have categorized microalgae in a variety of classes, mainly distinguished by their pigmentation, life cycle and basic cellular structure. The four most important classifications of microalgae are the following [7].

I. The diatoms (Bacillariophyceae). These algae dominate the phytoplankton of the oceans, but are also found in fresh and brackish water. Approximately 100,000 species are known to exist. Diatoms contain polymerized silica (Si) in their cell walls. All cells store carbon in a variety of forms. Diatoms store carbon in the form of natural oils or as a polymer of carbohydrates known as chyrsolaminarin [7].

II. The green algae (Chlorophyceae). These are also quite abundant, especially in freshwater. They can occur as single cells or as colonies. Green algae are the evolutionary progenitors of modern plants. The main storage compound for green algae is starch, though oils can be produced under certain conditions [7].

III. The blue-green algae (Cyanophyceae). Much closer to bacteria in structure and organization, these algae play an important role in fixing nitrogen from the atmosphere. There are approximately 2,000 known species found in a variety of habitats [7].

IV. The golden algae (Chrysophyceae). This group of algae is similar to the diatoms. They have more complex pigment systems, and can appear yellow, brown or orange in color. Approximately 1,000 species are known to exist, primarily in freshwater systems. They are similar to diatoms in pigmentation and biochemical composition. The golden algae produce natural oils and carbohydrates as storage compounds [7].

2.2. Algae as a feed stock for biodiesel

The idea of making biodiesel from algae is not a new phenomenon. It started during the Second World War, where transportation fuel shortage was high. The principle is based on the fact that most microalgae have natural lipid composition 15%-75% (see Table 2.4) of their dry mass. In fact oil contents of some microalgae can exceed 80% of the dry weight of algae biomass [8].

Biodiesel production from microalgae has gained an interest because of its higher biomass productivity and oil yield. As discussed above in the introduction section, microalgal biodiesel is the only renewable biodiesel that has the potential to be able to completely displace petroleum-derived transport fuels without adversely impacting supplies of food and other agricultural products. For example, an average annual productivity of microalgal biomass in a well designed production system located in a tropical zone can be as much as 1.535 $kg/m^3/day$ in optimized conditions [9].

However, unlike the lower area requirement and the higher biomass productivity, the cost of producing oil from microalgae is not as optimistic as that of vegetable and oil seed biodiesel feed stocks. Benemann and Oswald [9] estimated the cost of algal oil to be in the range of $39–$69 US/barrel in 1996. This estimate was based on 400 hectares of open ponds and productivity assumptions of 30–60 $g/m^2/day$ with 50% algal lipid yield. And based on the works of Benemann and Oswald, it is [1] estimated algae oil production costs to be $84 US/barrel (in 2006) for a hybrid system of open pond and PBR with a productivity of 70.4 $g/m^2/day$ and 35% algal lipid yield. Nevertheless, the data taken for the productivity and yields assumed in their work are taken from the laboratory results, they are not proven for large scale production and harvesting systems. The practical productivity and oil yield may be lower than those values used

in their assumptions. For example, Peer et al. reported that Seambiotic Ltd., an Israeli company, estimated that the production cost of its dried algae to be $0.34 US/kg (as of 2008) with a productivity of 20 g/m^2/day and total lipid content ranging from 8–40%. By taking the more optimistic 40% yield, they calculated that the lipid would cost $0.85 US/kg which equates to $126 US/barrel. This value is relatively higher than the current price of petroleum which staggers around $80 US/barrel. But this result shows that the competitiveness of the price of producing oil from micro algae would be imminent in the near future as methods of production systems are being improved and the cost of fossil fuel is increasing. For example, a more optimistic report has been recently (in May, 2009) released from the US Defense Advanced Research Projects Agency (DARPA) [10]. DARPA stated that it is producing algal oil at a cost of less than two dollars per US gallon and its final goal is to decrease the cost toward $1 dollar per gallon.

Microalgal oils differ from most vegetable oils in being quite rich in polyunsaturated fatty acids with four or more double bonds. Fatty acids and fatty acid methyl esters (FAME) with 4 and more double bonds are susceptible to oxidation and gum formation during storage and this reduces their acceptability for use in biodiesel. Total unsaturation of oil is indicated by its iodine value. Standards EN 14214 and EN 14213 require the iodine value of biodiesel to not exceed 120 and 130 g iodine/100 g biodiesel, respectively. Furthermore, both the European biodiesel standards limit the contents of FAME with four and more double bonds, to a maximum of 1 mol%. In view of the composition of many microalgal oils, most of them are unlikely to comply with the European biodiesel standards, but this need not be a significant limitation. The extent of unsaturation of microalgal oil and its content of fatty acids with more than 4 double bonds can be reduced easily by partial catalytic hydrogenation of the oil, the same technology that is commonly used in making margarine from vegetable oils. Table 2.1 shows fatty acid (those at levels exceeding 5% of the total) compositions some microalgae [11].

Table 2.1: Fatty acid composition of some microalgae.

Strain	Fatty acid composition *
Ankistrodesmus	16:0, 16:4, **18:1**, **18:3****
Botryococcus braunii	**16:0**, **18:1**, 18:2, **18:3**
Dunaliella salina	14:0/14:1, **16:0**, 16:3, 16:4, 18:2, **18:3**
Isochrysis sp.	14:0/14:1, 16:0, 16:1, **18:1**,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, 16:2,16:3, 20:6

*Fatty acids in bold are present at levels of 15% or higher.

**The first number indicates the total number of carbon atom and the second number indicates the number of carbon atom with double bonds in the hydrocarbon chain. Source [11].

2.3. Algae cultivation

2.3.1. Open ponds

The only practicable methods of large-scale production of microalgae are raceway ponds and tubular photobioreactors. However, the vast bulk of microalgae cultivated today are grown in open ponds. Open ponds can be built and operated very economically and hence offer many advantages as long as the species for cultivation can be maintained. Open ponds have a variety of shapes and sizes but the most commonly used design is the raceway pond. An area is divided into a rectangular grid, with each rectangle containing a channel in the shape of an oval; a paddle wheel is used to drive water flow continuously around the circuit (see Figure 2.1). They usually operate at water depths of 15–20 cm, as at these depths biomass concentrations of 1 g dry weight per liter and productivities of 10–25 g/m^2/day are possible. However, such productivities are not the rule and cannot be maintained on an annual average. Weismann et al. studied the capture of carbon dioxide by large pond-type systems. When operating under optimum conditions, the capture efficiency has been shown to be as high as 99%. [12, 13]

During daylight, the culture is continuously fed to the pond in front of the paddlewheels where the flow begins (Fig. 2.1). The biomass is harvested behind the paddle wheel after completion of the circulation loop. The paddlewheel operates all the time to prevent sedimentation. Raceway ponds for mass culture of microalgae have been used since the 1950s. Extensive experience

exists on operation and engineering of raceways. The largest raceway-based biomass production facility occupies an area of 440,000 m^2. [14]

Figure 2.1: Shallow open raceway pond facility with paddle wheels.

Source: [14]

2.3.1.1. Flue Gas Delivery Systems in Ponds

There are three types of flue gas delivery systems to open ponds. The first one is using bubble covers. This method enhances atmospheric and flue gas CO_2 intake of algal strains by improving the mass transfer from the gas phase to the pond water. A membrane covered structure submerged at its edges employed for covering a small percentage of the pond area. The pond water is pumped and flow over the plate returning to the pond with a higher dissolved CO_2 than that can be obtained from passive gas transfer over the pond surface. The percent pond coverage depends on the transfer rate of CO_2. [15]

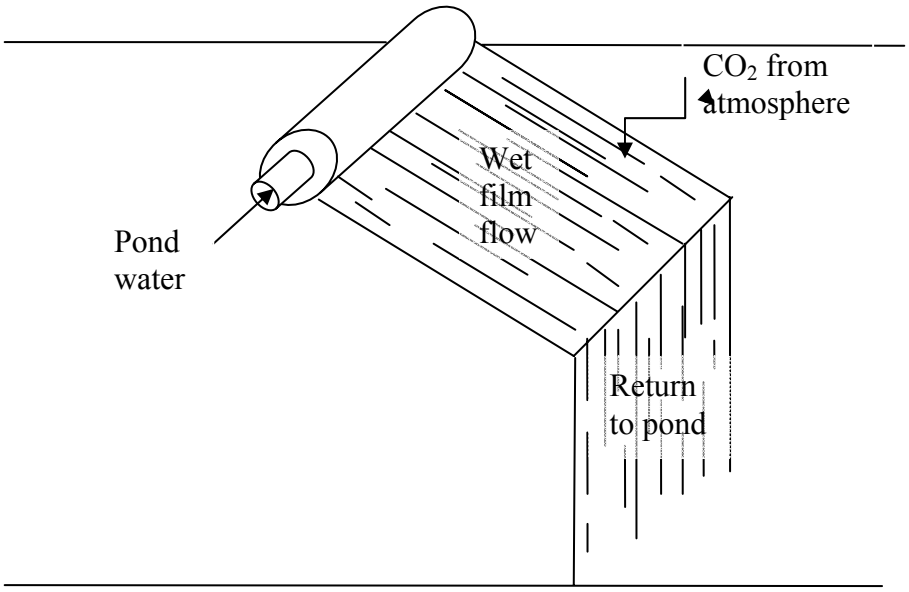

Figure 2.2: Bubble cover

Source: [16]

The second type is using Sumps. A blower is used to inject the gas at or near the bottom of a sump that spans all or part of the channel. Capital and operating costs are sensitive to sump depth, which determines both transfer efficiencies and pressure drops. The carbonation sump may be feasible for both pure CO_2 and flue gases because gas transfer is quantitatively higher than the above methods [15]. The third method is to employ a carbonation pit (a separate scrubber). The scrubber usually with a height of one meter greatly facilitates the gas absorption. Water from the pond continuously circulates through the pit. This method helps to dissolve CO_2 to the saturation point 5.6mol CO_2 per m^3. Since carbon content of algal biomass can be as high as 50%, this method will greatly improves the productivity of the pond. [16]

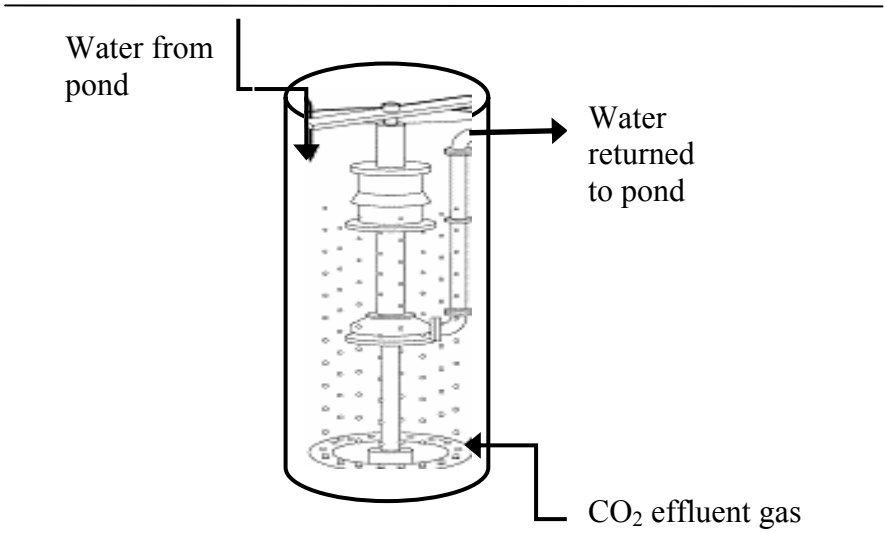

Figure 2.3: Carbonation pit

Source: [16]

2.3.2. Closed photobioreactors

Basically there are three types of closed photobioreactors for algal biomass production system. These are vertical-column, flat-plate, and tubular photobioreactors. Each of these closed photobioreactors have their own merits and demerits, depending on the mass culture type, the geography of location, and various operating parameters selected for operation. Vertical column photobioreactors are known to their high mass transfer, good mixing with low shear stress, low energy consumption, high potentials for scalability, easy to sterilize, good for immobilization of algae, reduced and photoinhibition . Those advantages are mainly attributed to their high small surface are to volume ratio. On the contrary, they require sophisticated material of construction and their relatively smaller diameter decrease illumination surface area upon scale-up. Flat-plate photobioreactors have large illumination surface area due to their relatively larger diameter. Therefore, they are relatively cheap, easy to clean up, suitable for outdoor cultures, good for immobilization of algae, and have higher biomass productivities. However, they require many compartments and support materials during scale up, and there is a difficulty in controlling culture temperature. On the other hand, tubular photobioreactors like the flat plate ones have large illumination surface area but they have lower resistance to fluid circulation inside the tube.

Therefore, it is easier to maintain the required pH, CO_2, O_2 and nutrient gradient. It is suitable for outdoor cultures, fairly good biomass productivities, but they require large land space [17].

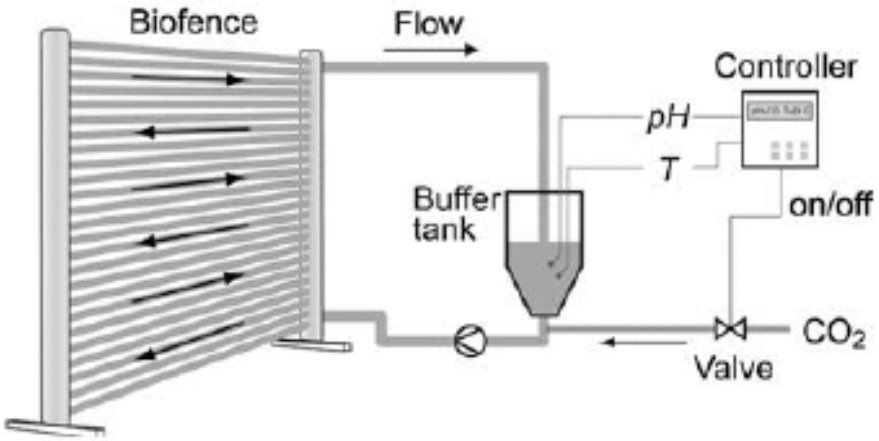

Figure 2.4: Biofence tubular photobioreactors.

Source: Cellpharm Ltd. UK [18]

Producing microalgal biodiesel requires large quantities of algal biomass. To minimize expense, the biomass must be produced using freely available sunlight and is thereby affected by fluctuations such as daily and seasonal variations in light levels. Generally speaking, tubular photobioreactor seems to be most satisfactory for producing algal biomass on the scale needed for biofuel production [8]. For large scale cultivation of algae in photobioreactors, the tubes should be constructed with a diameter as large as possible to decrease the cost of material construction. However, when photobioreactor with larger diameter operated with high-density culture for attaining high productivity, the tubes will inevitably contain a photolimited central dark zone. It is reported that light intensity in the photolimited zone is lower than the saturation light level of many micro algal cultures. Creating turbulence is the common method used to overcome the problem. This fact will impose an additional pumping cost and may create damages to the culture (depending on the species) due to the shear stress caused by the higher fluid circulation. Under conditions of sufficient and excess external irradiance, light–dark cycling of above a certain frequency can increase biomass productivity relative to the case when the same quantity of light is supplied continuously over the same total exposure time. [13]

2.4. Algae growth kinetics and nutrient requirement

2.4.1. Growth kinetics

The growth and productivity of algae depends on a number of external factors. Among the factors, availability of dissolved CO_2, temperature, light intensity, and nutrients such as nitrogen, phosphorous and potassium greatly affect the yield of algal biomass. In addition to the above factors, availability of trace minerals such as iron, calcium, and other metals sometimes may be important in limiting the growth of algae. The optimal amounts of growing factors such as light, CO_2, and nutrients differ from species to species, and the information, especially those of algae with high lipid content is not available for public use due to patent related issues. Generally the productivity of algal biomass is given by the following formula.

For open pond

$$\frac{P}{D} = \mu * C \qquad (2.1)$$

where P is the growth rate, $g/m^2/day$

D is the depth of the pond

C is the algal biomass concentration, g/m^3 or it is equivalent to ppm

μ is the specific growth rate, day^{-1}

And for closed bioreactor and batch systems, the kinetics would be

$$P = \mu * C \qquad (2.2)$$

where P is the growth rate, $g/m^3/day$

C is the algal biomass concentration, g/m^3 or it is equivalent to ppm

μ is the specific growth rate, day^{-1}

The specific growth rate, which is the number of doublings per day, is calculated by the following formula [19].

$$\mu = \frac{0.693}{t} \quad (2.3)$$

where 0.693 refers to the natural logarithm of the exponential growth of microbial cells.

t is the number of days required to double the cell.

2.4.2. Nutrient requirement for algal growth

In the estimation methods of nutrient requirement by the algal cell growth, determination of the maximum amount useful for optimal growth, below which the value will be growth limiting, is the usual concern. The specific growth rate (μ) of algal culture is a function of various parameters, such as CO_2, temperature, nitrogen, phosphorous, and other trace metals.

The relationship between specific growth rate and nutrient uptake rate is given by the Monod equation. The Droop's growth kinetics equation based on the nutrient concentration in the cell and Michaelis-Menten nutrient uptake kinetics at a given nutrient concentration in the culture medium are also important models for understanding the cell growth kinetics and nutrient requirement. The Droop's equation, Michaelis-Menten and the Monod equations, for example, for phosphorous are shown below. [20].

Droop's growth kinetics

$$\mu = \mu_{max}\left(1 - \frac{Q_o}{Q_P}\right) \quad (2.4)$$

Michaelis-Menten nutrient uptake kinetics

$$V = V_{max}\frac{P_i}{K_s + P_i} \quad (2.5)$$

Monod's model of kinetics growth

$$\mu = \mu_{max}\frac{P_i - P_t}{K_S + P_i - P_t} \quad (2.6)$$

where μ is specific cell growth rate at specific cellular phosphorous concentration, h^{-1} *or* day^{-1}.

μ_{max} is the maximum cell specific growth rate under no phosphorous limitation condition, h^{-1} *or* day^{-1}.

P is phosphorous

P_i is phosphorous nutrient concentration in the culture medium, μmol/liter

Q_P is the cell quota of P at the given steady state condition, *(μg P)/(mg DW)*

Q_o is the minimum cell quota (cellular concentration) or Q_P at $\mu = 0$ of phosphorous *(μg P)/(mg DW)*

K_s is half saturation constant for growth.

V is phosphorous uptake rate by the cell at the given phosphorous concentration P_i in the culture medium, $(\mu mol\ P)/(\ mg\ protien * h)$

V_{max} is the maximum phosphorous uptake rate by the cell at the given phosphorous concentration P_i in the culture medium, $(\mu mol\ P)/(\ mg\ protien * h)$

At steady state condition the rate of cell quota increase due to uptake equals the dilution of cell quota due to growth. Therefore,

$$V=\mu * Q_P \qquad (2.7)$$

However, the parameter constants for specific growth rate and nutrient uptake constants, and the optimal growth nutrient concentration is not available for high lipid content algal species which are suitable for biodiesel production. But there is a rough estimate of nitrogen and phosphorous requirement as a concentration in open ponds, and as a percentage of dry cell algal biomass products. For example, in pond system, the nitrogen is required in the form of ammonia or nitrate and must compose 0.8% of the volume of the pond solution to ensure maximum algae production. Likewise phosphorus is in the form of ammonium or other phosphate and must compose 0.6% of the pond. [9]. In terms of unit biomass productivity, *CO_2, N and P requirements for Chlorella sp.* is shown in Table 2.2

Table 2.2: Nutrient requirements of Chlorella sp.

Element (nutrient)	Algae content	
	Actual	Normalized to carbon
Carbon	52%	100%
Nitrogen	9%	17%
Phosphorus	1%	2%

Source [16]

Similarly, Table 2.3 shows a general guideline for nutrient requirements of strains as biomass wt % for the purpose of economic evaluation of RWOP given by Benemann [9].

Table 2.3: Nutrient requirements of strains as biomass wt%.

Element (nutrient)	Algae content
Carbon	50%
Nitrogen	4%
Phosphorus	0.4%

2.4.3. CO_2 requirements for algae growth

The supply and availability of CO_2 to the biomass production system is most crucial factor in algal biomass production systems, in both open pond and CPBR. This is due to the fact that composition of carbon, in the form of lipid and carbohydrate, in algal biomass accounts for more than 50% of dry weight [21]. Furthermore, the carbon utilization efficiency of algae is not more than 50% when operated under normal conditions. Navid [19] has reported that the highest carbon utilization efficiency C_{util} (see the equation below) for P. carterae was 27.9% at pH value

$$C_{util}=\frac{C_{uptake}}{C_{in}} \qquad (2.8)$$

where C_{util} is carbon utilization efficiency

C_{uptake} is the amount of carbon utilized by the microalgal cells.

C_{in} is amount of carbon fed to the raceway pond or the PPBR

of 8.1 in the plate photobioreactor and 12.7% at a pH value of 9.6 in the race way pond [20]. However, operating under optimized conditions such as careful control of pH, salinity and other physical conditions for introducing CO_2 into the ponds allowed utilization of injected CO_2 a as high as 99%[9].

2.4.4. Light and temperature requirements for algae growth

Light may have a positive and a negative outcome in the productivity of algal biomass. Increasing the intensity of light up to certain accepted level, depending on the species being cultivated, may increase the productivity of the system. However, increasing irradiance beyond the optimum point results a decrease in the specific growth rate of the species, thereby decreasing the productivity of the pond and the bioreactor. For example, the optimal light intensity requirement for *Botryococcus braunii* lies between 30-60 W/m^2. The temperature requirement of microalgae greatly varies depending on the particular species. Like the effect of light intensity on algal growth, the effect of temperature on algal growth shows the same behavior of peak specific growth and temperature inhibition regime. For example, the optimal temperature requirement of *Botryococcus braunii* lies between 23 and 27 degree Celsius. [15]

Temperature and light intensity have interrelated effect on the algal specific growth rate. For example, in Sandness' [22] study, the optimum temperature for growth of Chlorella increased from 25 ^{O}C (at 14.5μmol photon/m^2/s) to 28 ^{O}C (at 29.1 μmol photon/m^2/s). However, at lower light intensities (approximately below 20 ^{O}C), the specific growth rate was less affected by temperature.

2.5. Algae harvesting and oil extraction

2.5.1. Harvesting

The final goal of growing algae is to extract the oils that are present inside the cells. This extraction process could take place while the algae are still in the growth solution, but more

efficient and effective extraction can take place if the algae are separated from the growth medium first. This separation process is called harvesting.

Generally speaking, in order for oil extraction to take place, algae mass concentrations must be greater than 15%. Unfortunately, algae in growth solution typically have a concentration of less than 1% [23]. There are several approaches to raising concentration levels of algal biomass and they are discussed below.

Microfiltration uses filters to separate the algae from the growth medium. The process consists of running the growth medium with algae through microfilters, which retains the algae, and allows the water and nutrients to pass through. This allows for recycling of the growth medium, and collects the algae in an extremely concentrated paste on the filter. Some single-celled algae are smaller than 5 microns in diameter, so it is important that sufficiently small filters are used for this approach to be effective. This is a particularly good for harvesting on a pilot scale. [23]

A second method for algae harvesting is centrifugation. Centrifugation involves spinning the growth medium extremely rapidly, exaggerating the effects of gravity. It can be used to accomplish two things. The first is to simply rapidly separate the algae cells from the growth medium. The growth medium can be drained, leaving much denser (about 20% mass concentration) algae. Another approach combines centrifugation with microfiltration, spinning the growth medium and algae against microfilters/microscreens which allow the growth medium to pass through and retain the algae. While both approaches are effective, the use of centrifuges requires large quantities of electrical power, which can increase costs substantially. [23].

A third method is to cause the algae to flocculate. The flocculated algae are heavier and will fall out of suspension, settling to the bottom. The growth medium can be pumped off, and the remaining higher concentration algae solution can be collected from the bottom of the flocculation vessel. Flocculation is an approach borrowed from waste-water treatment. Flocculation can be induced using two approaches. The first is the use of chemical. Chemicals such as alum or ferric chloride can be introduced to the solution, and will cause the algae to

clump together. An alternative approach is to cut off the algae's CO_2 supply. This results in autoflocculation (flocculation induced without chemicals). [23]

2.5.2. Algal oil extraction

Oil is obtained from algae through extraction. There are generally three methods of oil extraction from the algae biomass. All three methods destroy the algae cell walls, allowing access to the oils inside. Each of these extraction methods are elaborated below.

Oil presses, or expellers, are used to extract many kinds of oils, such as those derived from nuts and seeds. The same equipment and process can be used to extract oil from algae. In order for this process to be effective, the algae must first be dried. Pressing breaks the cell walls and squeeze out the oils. This method is simple, but extracts at most 75% of the oils. [23]

Oils can also be extracted from algae with the use of chemical solvents. Generally solvents, such as benzene, cyclo-hexane, hexane, acetone, or dimethylformamide (DMF), are added to high-concentration algae paste. The solvents destroy the algae cell walls, allowing the oils to escape. The solvent and oil mixture is distilled, leaving behind the oils. The evaporated solvent can be reclaimed for further use. This method extracts 99% of the oil, but relies on those expensive and hazardous chemicals mentioned above. [23]

Another approach that seems particularly promising is ultrasonic cell disruption. This method exposes the algae to high intensity ultrasonic waves, which create tiny cavitation bubbles around the cells. The collapse of the bubbles emits shockwaves, shattering the cell walls. The destroyed cells release the oils inside into the solution. This method is already in widespread use on a smaller scale in laboratories. [23]

2.6. Selection of biomass production methods

Open pond versus PBR

Raceway open ponds need relatively lower capital cost requirement compared to tubular photobioreactors. For example an initial assessment made for Biofence 1200 liters of PBRs, produced by Biofence (shown in Figure 2.4), for a daily production of 8000 kg algal oil was done. Based on the data obtained from Sadness [22], 45 g of dry biomass of Chlorella was collected per day for optimized condition. For a 60 % lipid content of the Bortyococcus braunii and purchasing cost of $40000 per 1200 liters of PBR, the total purchasing cost of the reactors would be grater than seven billion dollar for the above mentioned daily capacity. This cost would be higher when considering installation and other related costs. However, the total capital cost required for the construction of raceway open ponds is a little more than four million dollar as shown in section 5.3. Hence, due to the higher capital cost of PBR, this study will focus on estimation of the production cost for raceway open ponds.

Carbon dioxide delivery systems

As discussed in section 2.3.1.1. there are three methods of carbon dioxide delivery system to open ponds apart from the passive gas transfer from the atmosphere. In order to select the appropriate delivery system, evaluation of efficiency, running and capital costs are the determinant factors.

When it comes to efficiency, the maximum flux of CO_2 that could be achieved from the air to pond with passive mass transfer is [16]

$$N = 0.35 \frac{gCO_2}{m^2 d} \qquad (2.9)$$

The maximum algae productivity (P) that could be supported, based on the assumption that microalgal biomass contains approximately 50% carbon by dry weight [14], with this flux is

$$P = 0.18 \frac{gAlgae}{m^2 d} \qquad (2.10)$$

Similarly, for a ramp of 2m height and area 1.65% of the area of the pond, the maximum flux of CO_2 that could be achieved is [16]

$$N = 13 \frac{gCO_2}{m^2 d} \quad (2.11)$$

The maximum algae productivity (P) that could be supported, based on the assumption that algae is 50% weight carbon, with this flux is

$$P = 0.65 \frac{gAlgae}{m^2 d} \quad (2.12)$$

Furthermore, Ron Putt [16] compared CO_2 delivery systems using carbonation pits for algal biomass productivity of 20g/m^2/day. It was shown in the study that, for 80 kg daily production using carbonation pit for atmospheric carbon dioxide and with flue gases from combustion required a column area of 87 m^2 and 0.32 m^2 respectively. In addition to this the pumping power requirement by the two systems is 15kW and 1.3kW for 3 meter water head respectively. Therefore, the second method is preferred from technical point of view (area of column) and cost of pumping power, if flue gas is available from combustion source close to the production site.

CO_2 delivery system using sumps is another alternative. Although it may be more efficient than the passive atmospheric gas transfer mechanism and the ramp [15], it is far less competitive than the carbonation pit. The limitation of this mechanism and the main reason for its inefficiency, when compared to the carbonation pit, is the relatively lower (maximum 0.3 meter depth of pond) level of water in which the mass transfer between the gas and water takes place. This depth is far shorter than the 3 meter height (which is used to achieve 90% of the saturation concentration of carbon dioxide 5.6mol/m^3 in water [19]) usually used in carbonation pits. Therefore, based on the above reasons flue gas delivery system with carbonation pit is selected for this study.

Size of raceway open pond

Increasing the size of a pond and production capacity has a positive effect on the cost of algal biomass production. Yusuf [8] estimated that, for an open pond of 100 ton/a dry biomass production facility, the cost of producing a kilogram of microalgal biomass is $3.80. However, if the annual biomass production capacity is increased to 10,000 t, the cost of biomas production per kilogram reduces to $0.80. Furthermore, Ron Putt [16] estimations resulted in a 3 year decrement of pay back period by using a pond area of 10 acre (40000 m^2) instead of 1 acre pond (4000m^2). For those reasons outlined here and for the purpose mentioned in the simulation of biodiesel section, 40000m^2 pond area and oil production of approximately 8000 ton algal oil production for the base case is used.

Harvesting method

Although auto flocculation of algae can be used instead of chemical (ferric) flocculation and it is cheaper, the factors that cause the strains to auto flocculate are different and depend on the particular species of interest. It needs specific research data for a specific Bortyococcus braunii and can not be used for a general purpose. Therefore, for initial concentration up to 1-3% dry algal biomass, ferric ion flocculation is selected. For final concentration of algae biomass either centrifugal force or filtration followed by drying can be used. While both approaches are effective, the use of centrifuges requires large quantities of electrical power, which will increase costs substantially [19]. Therefore, the latter method, filtration followed by drying is selected.

Oil extraction

Generally the two methods chemical (hexane) method and oil press can be used in extraction of oil from dried algae biomass. Although the use of the former relies on expensive and hazardous chemicals, it extracts 99% of the oil. The second method is simple, but extracts at most 75% of the oils [23]. A combination of the two can also be used, but requires relatively higher capital cost than using each of the two systems used separately. Since the major expense of biodiesel production from algae is the cost of oil production, the 25% of the oils that is not extracted by the oil press will greatly reduce the profitability of the biodiesel plant as well as the biomass production system. Therefore, chemical extraction method is selected for this study.

2.7. Selection of algal strains suitable for biodiesel production

2.7.1. Overview of algal strains suitable for biodiesel production

Selection of algal strains suitable for biodiesel production for a particular geographical location is a very difficult task. The strains of particular interest must have high lipid content, be obtainable in purest form, fairly enough quantities in culture for cultivation, good growth and productivity rate, compatible temperature, pH, light, and nutrient requirements for the given geographical location and easy for downstream processing. Furthermore, there is a lack of available information on growth rates, nutrient, and downstream processing parameters, especially for those strains with higher lipid content and productivity rate, mainly due to patent related issues. Even with the availability of growth kinetics and some of the other parameters mentioned above, the availability of pure strains from public sources for research and investigation is not certain. [23]

In selecting and evaluating the strains from the financial point of view, lipid content has the utmost importance. Then depending on the selected strains based on the lipid content, selection of the suitable cultivation method that would give higher productivity and lower production cost is the next task. Table 2.4 lists some of the promising higher oil content algal strain candidates for biodiesel production.

Table 2.4: Oil content of some microalgae

No	Microalga	Oil content (%dry wt)	No	Microalga	Oil content (%dry wt)
1	Botryococcus braunii	25-75	8	Nannochloris sp.	20-35
2	Chlorella sp.	28-32	9	Nannochloropsis sp.	31-68
3	Crypthecodinium cohnii	20	10	Neochloris oleoabundans	35-54
4	Cylindrotheca sp.	16-37	11	Nitzschia sp.	45-47
5	Dunaliella primolecta	23	12	Phaeodactylum tricornutum	20-30
6	Isochrysis sp.	25-33	13	Schizochytrium sp.	50-77
7	Monallanthus salina	>20	14	Tetraselmis sueica	15-23

Adapted from (Yusuf, 2007). [8]

Among the algal strains listed above Schizochytrium sp., Botryococcus braunii, Nannochloropsis sp., Neochloris oleoabundans, Nitzschia sp., Chlorella sp. and Nannochloris sp. have higher oil

content in their order respectively. Although algal strains with higher lipid contents are generally preferred for biodiesel production, their growth kinetics should be determined from experiment in order to use the strains for detail economic evaluation. Further more, some of the strains with lower oil content may have higher growth and biomass productivity rate so that the overall oil yield per unit land area could be higher. In addition to the above facts, environmental conditions in a given geographical location such as temperature and light intensities that fall with in the range of the growth requirements by the strains would give optimum productivities. Therefore, it is the utmost importance to search for algal strains of higher lipid content with higher biomass productivity and growth parameters in line with the specific location of interest.

Higher oil content algal strains with their respective growth kinetics that are collected from different sources are listed below.

Botryococcus braunii: - is a green algae and can produce hydrocarbons which represent 25-75% of its dry weight [8]. The lipid content can be as high as 86% [14]. Botryococcus is rumored to be a descendant of the organic compounds that make up most of the world's fossil fuel deposits. According to research done at Flinders University in Australia [24], the strain cells double approximately every two days. In contrast to this value, Abayomi et al. [25] reported the doubling time for Bortyococcus braunii to be 13.3 hours. The following conditions should be satisfied for optimum growth. Ambient temperature of 23 ^{O}C, light intensity of 30-60 W/m^2 a photoperiod of 12 hours light and 12 hours dark. However, Botryococcus would not be able to sustain high agitation intensities of growth techniques and the growth rate may decrease if the mass production system employed uses this technique. [23]

Chlorella sp. double in cell count every 8 hours or less if they have adequate nutrients and light, for pond temperatures in the range 20-35 °C. This corresponds to a specific growth rate constant *u* of 2.5 day^{-1}. A lipid content of chlorella sp. is in the 20-30 weight percent range. [16]

Scenedesmus Dimorphus:- Categorized as a heavy bacterium, scenedesmus has a lipid content of 16-40%. The strain must be constantly agitated while grown because of the ease of sediment buildup which hinders growth. The optimal growth temperature falls between 30-35 degrees.

Scenedesmus will use any and all light it is given. However, information on its growth rate is not given from this source. [23]

Table 2.5 shows the growth parameters of 4 different high oil content strains selected from the list provided by Abayomi et al.,[25].

Table 2.5: Growth parameters of some microalgae

Strain	Generation (doubling) time (hrs)	Optimal culture temperature	Protein (%dry weight)	Carbohydrate (%dry weight)	Lipid (%dry weight)
Chlorella vulgaris	8.7	22-26	51-58	12-17	14-22
Tetraselmis suecica	11.3	18-22	41-44	10-13	30-32
Botryococcus braunii	13.3	18-22	22	14.1	44.5
Dunaliella Salina	6.7	22-26	29.3	16.3	25.3

Source [25].

2.7.2. Selection of algal strains suitable for Ethiopian environments

The next task of the algal strain selection is to narrow down the number of strains to at least three that will be more compatible for cultivation to the selected specific location in Ethiopia .However, before the strain selection, the specific location should be determined first before continuing on further screening. The next subsections deals with this problem.

2.7.2.1. Selection of specific site for cultivation

In section 2.7, comparison and selection of biomass production methods, it is suggested that using free CO_2 supply from external combustion sources is the best alternative for optimum algal biomass production.

Kadam [26] made life cycle assessment on micro algae production using a source of CO_2 from coal fired power generation flue gases. The study showed the importance and concluded that there are potentially significant environmental and economic benefits of using power-plant flue

gases as a source of CO_2 for microalgae cultivation. It further demonstrates that a 50 MW power plant generates approximately 414 000 tons/a of CO_2, which can support 1000 ha of open pond microalgal production system. For this study, which is going to evaluate a production facility of around 80 separate open ponds of area 40000m^2 each (320 ha), a source of CO_2 flue gases from 16MW power plant would suffice.

Although, there is no a single coal fired power plant in Ethiopia, there are some places in the country with a proven quantity of mineral coal deposit. Among the specific locations with confirmed coal deposits are Yayu (Iluababora), Chilga (Gondar), and Wuchale (Dessie). The economic evaluation of this study confirmed that Yahu (Iluababora) deposit is the most economical and also preferred for its higher average heating value (5930 cal/g) and reliable reserve amount. The lignite to subbituminous coal in the Yayu can be gasified and used in making fertilizers and power generations [27].

Therefore based on the above study and the recent project activities being considered in Yayu (Iluababora) by the Ethiopian government [5] for fertilizer production and power generation, Iluababora area is selected for the location of the algal biomass production system in this study.

2.7.2.2. Selection of algal strains

The temperature and sunlight radiation data for the selected Iluababora area, obtained from the NASA surface weather data [28] is shown in appendix L. The temperature and sun light intensity requirements of algal strains which are short listed in section 2.7.1. were evaluated and compared with data provided for this particular area. Hence, strains with relatively higher oil content and growth rate with operating parameter requirements more suitable to the temperature and light intensities of the Iluababora area are selected and the list of the selected strains with their corresponding growth parameters is shown in Table 2.6.

Table 2.6: List of selected algal strains

Starins	Average lipid content	Optimum light intensity	Optimum temperature	Photo period	Average Doubling time	Specific growth rate
Botryococcus braunii,	70%	30-60 W/m^2	23°C	12 hours light	1.27 days	0.8 day^{-1}
Chlorella sp.	25%	-	20-35 °C	-	-	2.5day^{-1}
Tetraselmis suecica	31%	-	18-22°C	-	11.3 hrs	1.47 day^{-1}

2.8. Description of important processes in biodiesel production from algal biomass

2.8.1. Production of biodiesel

2.8.1.1. Pretreatment prior to biodiesel production

Many low cost feed stocks are available for biodiesel production. Unfortunately, many of these feed stocks contain large amounts of free fatty acids (FFAs). These free fatty acids will react with basic catalysts to produce soaps that inhibit the reaction. Generally, when the FFA level is less than 1%, and certainly if it is less than 0.5%, the FFAs can be ignored. Catalyst amount requirement for sodium hydroxide and potassium hydroxide is 1% of the triglyceride weight while for sodium methoxide it is 0.25% [23].

Soaps may allow emulsification that causes the separation of the glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. Further, catalyst that has been converted to soap is no longer available to accelerate the reaction. When FFA levels are above 1%, it is possible to add extra alkali catalyst. This allows a portion of the catalyst to be devoted to neutralizing the FFAs by forming soap, while still leaving enough to act as the reaction catalyst. Since it takes one mole of catalyst to neutralize one mole of FFA, the amounts of additional catalyst can be calculated by the requirements mentioned above plus the stoichiometric amount which is used to neutralize the

FFA. This approach to neutralize the FFAs will sometimes work with FFA levels as high as 5 – 6%. The actual limit can depend on whether other types of emulsifiers are present. It is especially important to make sure that the feedstock contains no water. 2-3% FFA may be the limit if traces of water are present. For feed stocks with higher amounts of FFA, the addition of extra catalyst may create more problems. The large amount of soap prevents the separation of the glycerol from the ester. Moreover, this technique converts the FFAs to a waste product when they could be converted to biodiesel. When working with feed stocks that contain 5-30% FFA or even higher, it is important to convert the FFAs to biodiesel. Otherwise, the process yield will be low if the FFAs are neutralized instead of converting them to biodiesel. [23]

2.8.1.2. Transesterification reaction

The term transesterification reaction refers to the alcoholysis of fatty acids, namely triglycerides. If the reaction is between the alcohol and free fatty acid, it is simply called esterification. The principal ways of making biodiesel are by transesterification of triglycerides and esterification of free fatty acids. The stoichiometry of transesterification reaction of triglycerides and esterification of FFA is shown as follows:

$$3\text{Alcohol} + \text{Triglyceride} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} 3\text{Biodiesel} + \text{Glycerol} \qquad (2.13)$$

$$\text{Alcohol} + \text{FFA} \overset{\text{Catalyst}}{\rightleftharpoons} \text{Biodiesel} + \text{Glycerol} \qquad (2.14)$$

The alcohols used for alcoholysis of triglycerides can be methanol, ethanol, 1-propanol, and 1-butanol. Ethanol is easily obtained from plant sugars, while methanol is commonly produced from natural gas, using ethanol makes a more sustainable fuel. 1-propanol and 1-butanol are not usually considered because of their higher molecular weight and cost. Due to their weight, biodiesel from these higher alcohols do not satisfy the requirements imposed by the various standards like ASTM. However, ethanol is also harder to use because it forms emulsions easily, making the separation of end products more difficult [29]. Furthermore, the cost of ethanol is usually higher than that of methanol. Hence, methanol is becoming the most commonly used feedstock to make biodiesel. Therefore, the transesterification reaction that will be discussed here is based on methanol.

Another key factor to consider in transesterification reaction is the selection of catalyst. Transesterification reactions can be base-catalyzed, acid catalyzed, or enzymatic. If the contents of free fatty acid (FFA) and water in oil are <1 and <0.5 wt %, respectively, then an alkaline catalyst is more suitable for the ester production. If the FFA content of oil is high (>1 wt %), then an acid catalyst is a good choice [30]. Alkali-catalyzed transesterification is about 4000 times faster than the acid catalyzed reaction [31] and it is most often used commercially. The base-catalyzed reaction takes about one hour at room temperature. It suffers from competing saponification reactions, which convert the same ingredients as well as any free fatty acids to soap. Acid-catalyzed and enzymatic transesterification are relatively very slow, they require three to four days to complete. The acid-catalyzed reaction also requires heat. But there is no competing saponification reaction with the acid-catalyzed and enzymatic reactions. In fact, even free fatty acids are converted to biodiesel by esterification. Esterification reaction of FFA by acid-catalyzed requires only about two hours to completion. Therefore, for oil feed stocks with a higher FFA content such as waste vegetable oil and animal fats, a two-stage reaction process can be used to maximize the amount of biodiesel produced, while minimizing the amount of soap produced. The first stage is acid-catalyzed esterification of the free fatty acids followed by base-catalyzed transesterification. [29]

In base catalyzed reaction systems, either NaOH or KOH is widely used. When the catalyst dissolves in the alcohol, the base forms an ionic solution, in which the K+ or Na+ ions and the OH- ions are not directly bound to each other. When a base catalyst is dissolved in methanol (alcohol), the catalyst completely dissociate in to its corresponding ions. The hydroxide ion reacts with the alcohol and removes the hydrogen atom from water as depicted in the reaction below. The alkali ion also associates partially with the methanol ion to form methoxide as it shown below.

$$CH_3OH+OH^- \rightleftharpoons CH_3O^-+H_2O \qquad (2.15)$$

The active ingredient is the hydroxide ion, OH^-. Hydroxide ion is the catalyst for base-catalyzed transesterification. It is also a reactant in the competing saponification reactions, in which it is consumed. Thus, saponification robs the transesterification reaction not only of reactants that

could be made into biodiesel, but also of the catalyst needed for the reaction to proceed [29]. Although a potassium phosphate fertilizer could be obtained from the neutralization of KOH by phosphoric acid, NaOH is usually selected due to its higher conversion yield [30] and lower purchasing cost. Catalyst requirement per weight of oil is also lower for NaOH because of its molecular weight [31].

For transesterification (reversible reaction), the higher the concentration of products, the slower the reaction rate. Since the contents of the CSTR are always equal to the final product concentrations, the transesterification reaction will run slowly. From this standpoint, the batch reactor and the PFR are favored. In the contrary, for the irreversible reaction of saponification, the reaction rate depends only on the concentrations of the reactants. Saponification will also run slower in the CSTR, due to the lower concentration of the saponification reactants. The net result is that the CSTR requires a longer reaction time without providing any advantage for transesterification over saponification. [29].

2.8.1.3. Post transesterification reaction processing

The excess methanol is usually separated and recovered by a distillation column. Almost all excess methanol from the transesterification reaction can be recovered with four or five stage column, owing to the relatively high boiling difference between methanol and FAME. After methanol separation biodiesel can be cleansed through washing. Washing consists of vigorously mixing water into biodiesel, and then allowing the mixture to separate again. Excess reactants and glycerol fall out of suspension in the biodiesel and are absorbed into the water. The water, along with contaminants, will settle to the bottom, allowing for easy separation. The washing process should be repeated several times. During the first washes, caution should be exercised to avoid creating an emulsion of biodiesel, water, and any soap that may present as a byproduct of the reaction. This emulsion could take weeks to separate out. Washing can be performed on batch systems or continuous extraction column techniques. Further purification should be completed by distilling the biodiesel to get rid it of excess methanol. The biodiesel should be heated to above 65˚C to allow for excess methanol to boil off. [23]

Following washing and distillation, the biodiesel must be dried. Drying can be completed over a longer period of time by being covered and exposed to sunlight. Alternatively, it can be heated to 50˚C for roughly three hours. Washed, distilled, and dried biodiesel will be free of impurities, chemically neutral, and relatively clear. This diesel can now be used in any diesel engine. Prior to use or sale, however, a gas chromatography or HPLC analysis should be performed on a sample to verify that the diesel meets all 15 of ASTM's requirements for biodiesel. [23]

2.9. Simulation of biodiesel production

Zhang et al. [31] compares 4 different routes of biodiesel production technologies using Hysys 3.2 process simulation software. In his study , for a biodiesel production rate of 8000 tons/a, four different flow sheets for continuous alkali- and acid-catalyzed processes using virgin vegetable oil or waste cooking oil as the raw material were designed and simulated. The article discussed the technical and economical feasibility of the four different routes followed to produce the biodiesel. These are, alkali-catalyzed process using virgin vegetable oil (process I), the alkali-catalyzed process using waste cooking oil (process II), Acid-catalyzed process using waste cooking oil (process III), and acid-catalyzed process using hexane extraction (process IV). He concluded that from technical point of view, the first process has been proved to be the simplest process and it requires the fewest unit operations. A more detail economic assessment and sensitivity analysis of the four processes (Zhang et al. [32]) has also proved the alkali catalyzed process using virgin vegetable oil had the lowest fixed capital cost. However if the raw material is not virgin oil, then the acid-catalyzed process using waste cooking oil is more economically and technically feasible, providing a lower total manufacturing cost, a more attractive after-tax rate of return and a lower biodiesel break-even price. Therefore, for the algal virgin oil being considered in this study, the alkali catalyzed system (process 1 is preferred).

Zhang et al. [32] also showed that the credit for the glycerol byproduct has a significant impact on the net value of the total manufacturing cost. The high value (high purity) glycerol led to a reduction in total production costs of 6 and 6.5% of biodiesel from Ethiopian mustard oil and used olive oil, respectively.

There are three parameters that have a major effect on the transesterification and the economics of biodiesel process, which are temperature (T), reaction time (t) and ratio of oil to alcohol. A proper selection of these three parameters has consequently a major effect in determining the production cost of biodiesel.

Effects of Reaction Time: - Fukuda [33] showed that increasing reaction time by decreasing feed flow rate, increased the product purity. Additionally, the percent purity increased exponentially from 0 to 20 minutes. After 20 minutes, the purity slightly increased and almost reached a steady state after 60 minutes. This can be concluded that the process operation using the reaction time higher than 20 minutes is waste of energy. However, lower conversions at lower temperatures have a negative effect on downstream processing such as washing and FAME purification.

Effect of temperature: - The reaction temperature plays an important role on the quality of the products. Increasing the temperature from $50^{O}C$-$65^{O}C$ will significantly increase the reaction rate. However, after 65 ^{O}C, the reaction stayed in equilibrium, increasing temperature did not bring more products but that consumed more energy, as a result, the total cost per unit of biodiesel increases. A temperature which is higher than the normal boiling point of methanol (68 ^{O}C) also causes more vaporization of methanol. However, operating at higher pressure (for example at four bar is used to overcome this problem in recent studies. On the other hand, the temperature which is lower than 50 ^{O}C causes higher viscosity of biodiesel. [33]

Effect of methanol to oil ratio: - The ratio of methanol to oil also affects that, the higher molar ratio, the higher conversion of alcohol. The ratios, normally used, are between 5:1 to 10:1. However using too high excess methanol can obstruct glycerin separation. Industrial processes use six mol of methanol for each mole of triglyceride. This large excess of methanol ensures that the reaction is driven in the direction of methyl esters, i.e. towards biodiesel. Yield of methyl esters exceeds 98% on a weight basis. [33]

3. Materials and Methods

3.1. Algae cultivation, harvesting and drying

The symbiotic blue green algae were cultivated in Adet at Amhara Regional Agricultural Research Institute (ARARI) by green houses and open ponds [34]. Wet biomass was collected from the open pond, sun dried and weighed. 3.8 kg of the dry biomass was obtained from the research center.

(a)*

(b)**

Figure 3.1: Cultivation of A. filiculoides and A. microphylla

*In green house
**In concrete tanks (open ponds) during June – October at ARARI

3.2. Oil extraction

The extraction was performed in a series of soxhlet extractors as shown in Figure 3.2. Each of the white filter bags in the soxhlet were filled with ground dry algal biomass. The temperature of the chiller was set to 10^{O}C. The outlet of the fist condenser was connected to the inlet of the second condenser and so on. The outlet from the last condenser was recycled back to the chiller. The recovery flask was filled with 250 ml of hexane. The setup was allowed to run at 60^{O}C for 3 hours to ensure complete (maximum) extraction. The oil extract was allowed to accumulate from 3 or 4 runs, before removing the product from the flask. Then the oil and hexane was partially separated by evaporation. Finally fractional distillation under vacuum pressure and hexane condenser was used to remove hexane from the total collected oil.

Oil Content = [Wo/Ws] 100 % (3.1)

where Wo = Weight of oil extracted

Ws = Weight of sample (dry base)

Figure 3.2: Algal oil extraction (soxhlet extraction)

At the analytical chemistry laboratory of Bahir Dar University. Photo by the author.

3.3. Oil purification

3.3.1. Degumming of oil

The crude oil was first heated to 70ºC under stirring at 1000 rpm in a beaker. 3wt% of distilled water (which was first heated to 90 ºC) and 0.2wt% of 85% purity phosphoric acid was added. The mixture was stirred for 1h. The precipitate was separated by centrifugation at 3500 rpm for 0.5h and the degummed oil was dried at 100 ºC for 0.5h under reduced pressure using rotary evaporator (fractional condenser). [35]

3.3.2. Neutralization of oil

The degummed oil was poured into a beaker and heated to 80°C, after which 0.1M of NaOH, 2ml for each 3 g of degummed oil, was added and stirred to a uniform solution. Sodium chloride, 10% of the weight of the oil, was added to help settle out the soap formed. This was transferred into a separating funnel and allowed to stand for 1h; the soap formed was separated from the oil. Hot water was added again and again to the oil solution until the soap remaining in solution was removed. The neutralized oil was then drawn off into beaker. [35]

3.3.3. Bleaching process

The neutralized oil was poured into a beaker and heated to 90°C. The mixture was stirred continuously for 30 minutes. Activated carbon, 2.0 wt% of oil, was added and the temperature was allowed to rise to 110°C with continuous agitation for additional 30 minutes. The content was filtered hot immediately. [35]

3.4. Oil characterization

3.4.1. Determination of specific gravity

Graduated cylinder and hydrometer was used for the SG measurement. Distilled water was used for calibration before the test. The sample was filled into graduated cylinder and its temperature was noted. The SG value was then recorded and according to ASTM D 1250-80 standards, temperature correction factor table was used to convert the measured specific gravity to the reference temperature of $60^{O}F$ recommended by the ASTM specification standards. [36]

3.4.2. Determination of viscosity

Vibro Viscometer (SV-10) was used for the measurement. The viscometer's cup was filled with the sample and placed into a holder. The cup was maintained in a $40^{O}C$ constant temperature bath for 30 min to reach equilibrium according to the ASTM D 445 standards. The measurement

was taken after steady state value was achieved. The kinematic viscosity of the oil was then recorded [36].

3.4.3. Determination of acid value

25ml of diethyl ether and 25ml of ethanol was mixed in a beaker. The resulting mixture was added to the sample in a conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M NaOH to the end point with consistent shaking for which a dark pink color was observed and the volume of 0.1M NaOH was noted. The acid value was calculated by equation 3.2 and 3.3. [35]

$$FFA=\frac{V_O*2.83*100}{W_O} \quad (3.2)$$

$$\text{Acid value}= FFA*2 \quad (3.3)$$

where 100ml of 0.lM NaOH = 2.83g of Oleic acid

W_O is sample weight

V_O is volume of NaOH solution

3.4.4. Determination of saponification value

2g of the sample was weighed into a conical flask; 25ml of 0.1N ethanolic potassium hydroxide of was then added. The content which was constantly stirred was allowed to boil for 60min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5M HCl to the end point until the pink color of the indicator just disappeared. The same procedure was used for blank. The saponification value (SV) was calculated by equation 3.4. [35]

$$SV=\frac{56.1N(V_O-V_1)}{M} \quad (3.4)$$

where V_O is volume of the solution used for blank

V_1 is volume of the solution used for the sample

N is actual normality of the HCl

M is mass of the sample

3.4.5. Determination of flash point

A laboratory modified tester was used. The cup was filled with biodiesel and continuously agitated to ensure uniform temperature. A small open flame was maintained from external source. The small flash was noted when the flash point has been achieved and the temperature was recorded. [36].

3.4.6. Determination of calorific value

The calorific value was determined by bomb calorimeter (C210 Junke & Kunkel K.G.). Benzoic acid with a heat value of merck=6324 cal/g was used to standardize the calorimeter. One gram of sample was taken in a crucible and made into a pellet and the initial weight was noted. It was placed in the bomb, which is pressurized to 18 atm. The bomb was placed in a vessel containing 2000g of distilled water. The ignition circuit was connected and the water temperature was noted. After ignition the temperature rise was noted every minute till a constant temperature was reached. The pressure was released and the length of unburned fuse wire was measured. And the determination of the biodiesel's calorific value was conducted following the same procedure for standardization, except for the sample preparation, which was liquid. [36]

$$HHV = \frac{[m_W c_W + (mc)_{APP}](t_m + c - t_O) - \sum b}{M} \quad (3.5)$$

$$(mc)_{APP} = \frac{HHV" * M + \sum b}{(t_m + c - t_O)} - m_W c_W \quad (3.6)$$

Where, HHV-higher heating value [cal/g]

$m_W c_W$ − mass and specific heat of calorimetric water. $c_W = 1 \frac{cal}{g.^oC}$

t_O – first temperature reading of main test [℃]

t_m – last temperature reading of main test [℃]

c- Correction for heat exchange between calorimeter and the surrounding.

∑ b-correction for observed heat which does not correspond to heat of combustion [cal]

3.5. Biodiesel production

The transesterification process was performed on a jacketed glass which was stirred continuously and kept at a temperature of 60 ^{O}C. KOH, 1% weight of oil, was combined and thoroughly mixed for 5 min with methanol to form CH_3O^- (methoxide). The molar ration of oil to methanol used was 1:12. The purified oil was poured in to the reactor and a steady state temperature of 60^{O}C at atmospheric pressure was achieved before mixing with the catalyst. The reaction was allowed for 80 minutes and the resulting mixture was poured in to funnel and allowed for overnight to settle in to layers, a separate phase of glycerol and biodiesel based liquid phases. Then biodiesel layer was separated and the product was washed repeatedly with hot water until a clear layer of biodiesel was obtained. Finally, the remaining methanol and water in the biodiesel were separated by a fractional condenser at 120^{O}C. [23].

3.6. Biodiesel characterization

The standard procedure described for the oil is used for the determination of the biodiesel SG, viscosity, acid value FP and CV.

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3.6.1. Biodiesel HPLC analysis

After the transesterification reaction, the Methyl ester was analyzed by the HPLC in the department. The experiment was performed using a combined linear gradient with aqueous–organic and non-aqueous mobile phase Acetonitrile, distilled water, and hexane/isopropyl alcohol with a ratio of 4:5 were used as a carrier liquid.. The first 10 min gradient elusion was started with 10% water and 90% acetonitrile until it reaches 100% acetonitrile. Then the experiment continued for another 10 min with 100% acetonitrile and 0% hexane/isopropyl

alcohol until the gradient elusion reaches 50% acetonitrile and 50% hexane/isopropyl alcohol. The final 10 min was isocratic elusion with 50% acetonitrile and 50% hexane/isopropyl alcohol. Calibration curve was prepared (appendix K) and used to evaluate the conversion of oil to methyl ester [37].

4. Results and discussions

The results of oil characterization showed that the oil extracted from the algal biomass from the ARARI is suitable for the production of biodiesel. However, in terms of biomass oil yield, the oil content was found to be lower by more than two folds than the oil content of most of the algal strains recommended for biodiesel production (see Table 2.4).

The results of the of the biodiesel characterization showed that the characteristics of biodiesel product obtained from the algal oil comply with the ASTM standards (except the conversion) and most of the EN specifications, limited to the characteristic tests taken in this study.

4.1. Oil extraction and purification

From the symbiotic algae strain obtained from ARARI, 228 ml (205.312g) of algal oil was obtained by hexane extraction. Therefore, the oil content of the algal biomass was 5.4% on mass basis. This amount of oil content, however, is very low when compared with algal strains which are recommended for biodiesel production (see Table 2.4). The reason is that the algal strains being cultivated at ARARI were not selected for the purpose of lipid production. In fact, the biomass of the strains is used for the replacement of nitrogen based chemical fertilizers at the Fogera rice farm. The use of biomass as a fertilizer for nitrogen source indicates that the strains have relatively higher protein content, which reduces the oil content of the strains.

After the degumming was performed, the sample was centrifuged and the oil was poured in to a beaker leaving behind the settled phosphatids. The phosphatids sludge was weighed to be 4.8g. But this amount do not account totally for phosphatids since there is also some oil residue in the sample. The next step in the purification of oil was neutralization. This was used to remove FFAs and the phosphoric acid residue, if any, used for degumming purpose. After the neutralization, the sample was poured in to a conical flask decanter and left for over 1 hour. The white soap and oil layer was formed. The oil was separated and washed 5 times with hot water until no more soap layer was noted. The soap was collected and weighted to 9.7 grams. However, water as visible droplets and an emulsion form was present in the sample. Therefore,

the soap was dried in the oven and weighed to be 4.2 grams. Then the next step, bleaching gives a clear white and lower viscosity (12.9 mm^2/s) oil.

4.2. Physicochemical Properties

Density and viscosity

The results of the specific gravity measurement showed SG for oil 0.9 and for biodiesel 0.87. The SG result for FAME was in agreement with the EN standard specification [38] for density of biodiesel, i.e., between 0.860-0.900 g/ml. The transesterification process has resulted in decreasing of the density of the oil, as expected.

The main objective of transesterification is the reduction of viscosities of fatty acids to acceptable values for use with out modifications diesel engines. The recorded kinematic viscosities (KV) the raw oil, purified oil and biodiesel were 20.1, 12.9 and 4.3 mm^2/s respectively. A significant reduction in KV was observed after transesterification. The KV result of the biodiesel was found to be with in the limit of ASTM standards [63] i.e. between 1.9 -6 mm^2/s. the result shows that the biodiesel from the algal oil is a little more viscous than No. 2 diesel fuel (3.5 mm^2/s) as expected.

Acid value and saponification value

The recommended Acid value of biodiesel is ≤ 0.8 and ≤ 0.5 mgKOH/g for ASTM D 6751 and EN 14214 specification respectively. The AV result from the experiment was recorded to be 0.41 mgNaOH/g. Since NaOH has lower molecular weight than KOH, the AV obtained would be higher if KOH was used for the experiment. However, since both alkalis give equal anion on dissociation, the result could be converted to equivalent mgKOH/g by multiplying with the ratio of the molecular weights of the alkalis. The converted AV is 0.57mgKOH/g. The result indicates that the AV for the FAME satisfies the ASTM D 6751 specification, while it is 14 % above the EN 14214 specification (≤ 0.5). The acid value of the oil before degumming and bleaching was 0.84 mgNaOH/g, which is equivalent to 1.2mgKOH/g.

The saponification value of the oil calculated was 185 mg/g. Saponification number is used for an indication of average molecular weight of the fatty acids composition of the oil.

Flash point and calorific value

Flash point for the oil was not done because of the low amount of oil obtained from extraction and purification. The FP temperature of the biodiesel was found to be 142 ^{O}C. The minimum flash point requirement is 120 ^{O}C and 130 ^{O}C according to ASTM and EN standards and specification respectively. Therefore, the flash point of the biodiesel satisfies both the American and European standards and the quality of biodiesel produced is acceptable with this regard.

The calculated gross heat content (Hg) of the FAME was found to be 38.21 MJ/kg. The calorific value (CV) of the FAME was less than the energy content of No.2 diesel which has a CV of 42.7 MJ/kg, as expected. Biodiesel from vegetable oil sources have lower heating value than the conventional diesel fuel. For example the CV of Jatropha curcas is 38.71 MJ/kg [39].

4.3. Biodiesel production and characteristic test

Reaction and separation

After transesterification reaction and purification of the product, 92g (80 ml) of biodiesel was obtained from 102 g (113ml) of purified oil. Approximately equal mass of biodiesel to that of oil was expected, since oil to biodiesel conversion gives 1 to 1 on mass basis if there is complete conversion. The yield of oil to biodiesel from the experiment was 9.8% lower than the expected value. The discrepancy surely comes from waste of products and reactants during the reaction, washing and separation steps and also from an incomplete conversion.

HPLC analysis

The chromatogram result of the purified biodiesel from the micro algae oil is shown in the appendix K below. Due to the shortage of HPLC grade acetonitrile the test was run only for one time. Therefore, the result would have been more reliable if more tests were performed. For this reaction the yield of FAME was found to be 60% by weight. The conversion of the triglycerides into FAME was less than the expectation based on literature values for a reaction taking place under similar conditions. Chromatogram result and Calibration curve prepared for the HPLC experiment is shown in appendix K and the calibration curve was used to evaluate the conversion of oil to methyl ester.

5. Financial analysis of algal biomass and biodiesel production

In this subsection, project evaluation of algal biomass production from the three algal strains selected in section 2.7.2.2. were performed. The evaluation encompasses determination of productivity and number of required ponds, amount of material and energy intakes, sizing and selection of appropriates processing equipment, and chemical engineering economic evaluation including total income, total production cost, total capital investment, pay back period and rate on return. Comparison of efficiencies, profitability and advantages and disadvantages, based on the investment criterions, will be used to select the best suitable candidates of the three algal strains. In order to demonstrate the effect of the economics of scale on the financial analysis, production capacities of 25500 kg oil/day and 51,000 kg oil/day, which is two fold of the base case, were investigated for all cases.

5.1. Review of evaluation parameters selected for biomass production facility

Due to the main reasons elaborated on literature review, especially in the Algae growth kinetics section, it is very difficult to accurately predict and evaluate large scale biomass productivity and production cost and of a specific strain with growth parameters reported from a laboratory or small scale experimental results. Despite the availability of some growth kinetic parameters for the strains selected, exact estimation or prediction of productivity for project evaluation is difficult due to various reasons. The following points outline some of the main reasons that make the estimation very difficult. .

- Presence of photoinhibition or light saturation during clear day and strong sunlight (the extent is not the same for different geographical locations due to the differences in light intensity and temperature variations)
- If the strain is not native, there may be a danger of wash out by wild strains which are native to the particular location.
- There may be a difference in the mineral content and turbidity of the water that will be used for cultivation. The amount of the concentrations of trace metal ions in the water

may affect the strain growth positively or negatively. The turbidity of the water along with the strain concentration in the pond determines the degree of light penetration towards the bottom, thereby reducing or limiting the depth of the productivity zone.

- If the concentrated CO_2 source is from power plant effluent, there may be a variation of the effluent temperature, CO_2, NO_X, and SO_X content which have effects on the growth rate of the strains.

For those main reasons mentioned, the rate of biomass productivity calculated based on the reported values of strains specific growth rate by Equation 2.1. is not directly used.

$$\frac{P}{D} = \mu * C \qquad (2.1)$$

Rather, a lower value of algae biomass productivity is used to account for the lower efficiency of large scale open pond production systems. According to the recommendations based on the works of Benemann and Oswald [9] and Ron Putt [16] for open pond biomass weight concentration of 250ppm and depth of 0.2-0.3m, 20% efficiency for the biomass productivity is assumed for all strains used in this study. Furthermore, supply of carbon dioxide at no cost is assumed since effluent gases from power plant combustion sources are generally regarded as a waste.

In order to assess the economics of scale, the project evaluation is done for two different annual oil production capacities of 7650 ton/a and 15300 ton/a The summary of the parameters used for the project evaluation are summarized in Table 5.1 below and overview the flowsheet for the biomass production facility is shown in Figure 5.1.

Table 5.1: Summary of parameters used for project evaluation of biomass production

No	Strains	Specific growth rate	Corresponding productivity	20% productivity	Oil content
1	Bortyococcus braunii	0.8 day^{-1}	$50\frac{grams}{m^2.day}$	$10\frac{grams}{m^2.day}$	70%
2	Chlorella sp.	2.5 day^{-1}	$156.25\frac{grams}{m^3.day}$	$31.25\frac{grams}{m^2.day}$	25%
3	Tetraselmis suecica	1.47 day^{-1}	$91.8\frac{grams}{m^2.day}$	$18.36\frac{grams}{m^2.day}$	31%

	Equipment used				
1	Purpose	Type	Method	Specification	Description
2	Carbonation	Bubble column pit	absorption	Increases CO_2 concentration in water to 5.6mol CO_2/m^3	Pond water is circulated through the carbonation pit by using pump.
3	Biomass concentration	Settling tank	Flocculation	From 0.25 g/m^3 (250 ppm) to 20 g/m^3 (2% wt)	Employs chemical flocculants with static pre mixers
4		Belt filter press	Filtration	From 2wt% to 20%	-
5	Drying	Drum drier	-	From 20wt% to 90wt%	-
6	Biomass production	Open pond	-	-	Area 40000m^2 and depth 0.25m

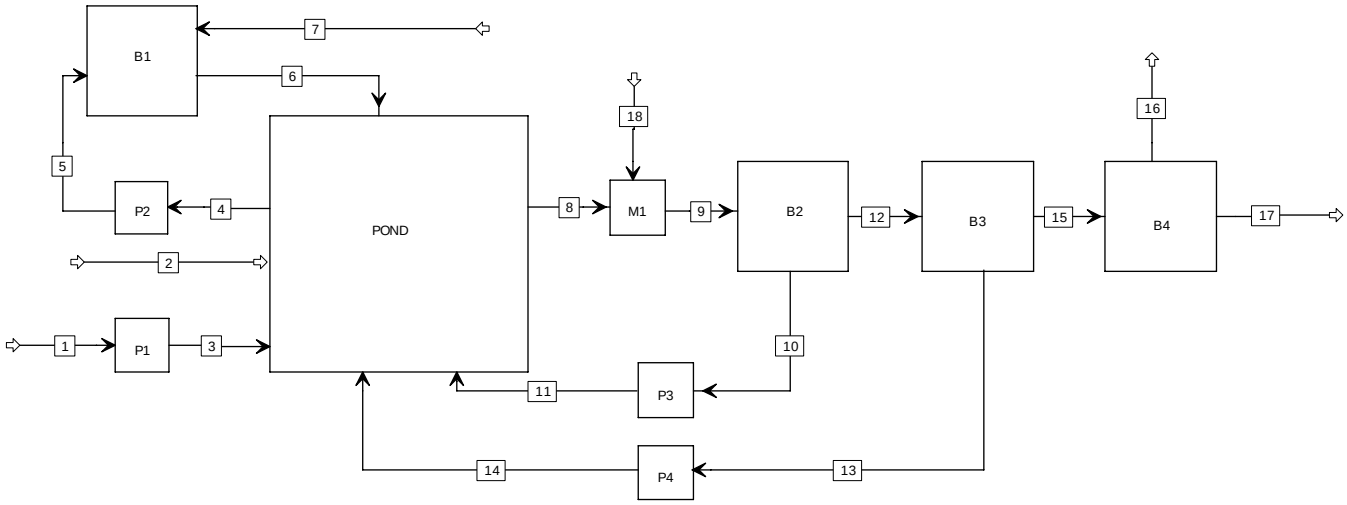

Figure 5.1: Process flow sheet for the algal biomass production facility

5.2. Results of material and energy balance for ponds

The details of material balance, energy balance and economic evaluation of the open pond biomass production facility systems are shown in Appendix A, B, C, D, E, F, G, H, and I. Summary of material and energy balance is shown in the following Table 5.2.

Table 5.2: Summary of material and energy balance results.

Strains	Oil content	Productivity kg per pond per day	Required annual oil production in ton	Required daily oil production in kg	Require daily algal biomass in kg	No ponds required
Bortyococcus b.	70%	400	7650	25500	36429	91
		800	15300	51000	72857	182
Chlorella sp.	25%	1250	7650	25500	102000	81.6≃82
		2500	15300	51000	204000	163.2≃163
Tetraselmis s.	31%	732	7650	25500	85000	116.1≃116
		1464	15300	51000	170000	232.2≃232

Material consumption				Energy consumption			
kg/day per pond	Bortyococcus braunii	Chlorella sp.	Tetraselmis suecica	kW per pond	Bortyococcus braunii	Chlorella sp.	Tetraselmis suecica
Ammonia	44	126.9	69.98	Carbonation pump	0.668	2.156	1.274
Ammonium phosphate	13.15	41	23.96	Static mixers	0.08	0.08	0.08
Ferric ion	0.4	1.25	0.732	Power for drying	43.96	137.5	80
Water (m^3/day)	17.58	80	80	Water recycling pump	0.000408	0.00127	0.00074
CO_2				Water return pump	0.03626	0.117	0.0663

5.3. Discussions on project and economic evaluation results

Costing of algal biomass was evaluated for two different oil production line capacities, 7650 ton per year and 15300 ton per year. The first production line capacity was selected in order to compare the results of project evaluation on biodiesel production and process simulation with previous studies on the subject. Many studies [31, 32, 33, 41] conducted on modeling and simulation are based on daily oil feed flow rate of 1.19kmol per hour and annual biodiesel production capacity of 8000 tons.

The pay back period for Bortyococcus braunii was 2.82 and 3.27 years for 1300ton/a and 7650ton/a capacity respectively. The rate on return (ROR) was 35.3% and 30.5% for the larger and smaller capacity respectively. For Tetraselmis suecica the resulting PBP was calculated to be 6.36 and 6.08 years for the larger and smaller capacity respectively. And the ROR was 1.9 and 16.4% and 15.7% respectively. For Chlorella sp., the bay back period for the larger capacity was above 100 years.

The major production cost for the biomass production facilities is the cost of energy. Approximately 68%, 77%, and 71% of the total production cost comes from the cost of energy for Bortyococcus, Chlorella sp and Tetraselmis respectively. As it can be seen from the figures, the energy cost of Chlorella, which has the lowest oil content and higher productivity, accounts for the highest percentage of the total production cost. It is because, the relatively lower oil content of the strain yields higher biomass per lipid content. The higher biomass in turn results in a higher burden on the downstream processing. In terms of pond area requirement, lower number of ponds was obtained for Bortyococcus braunii. The biomass from Chlorella left after extraction was 2.5 fold higher than that of Bortyococcus braunii . Since the left over can be sold as a meal for animals or as a fuel, it can increase the total income significantly if the market for such product finds higher value. However due to the high downstream processing cost involved in the larger biomass, it turned out to be a disadvantage in terms of the overall economic analysis.

The payback period for Bortyococcus braunii was found to be in the acceptable range i.e. between 2-5 years. Since the ROR is higher than 20%, it is found to be very attractive. The ROR and PBP for Tetraselmis suecica, are very close to the recommended values of 20% and 2-5

years. Therefore, biomass production from this strain may be proved to be feasible with further analysis and better alternatives of low cost production techniques and recommended for further investigations. The ROR and PBP for Chlorella sp, based on any investment financial criteria, are very low and not recommended for further consideration according to the results of this study.

6. Conclusion and recommendations

6.1. Conclusion

The result of the physico-chemical characteristic test showed that the symbiotic blue green algae from ARARI can be used to produce biodiesel with acceptable quality complying with the ASTM D 6751 standards. However, the oil yield of the algal biomass was very low (5.4wt %) when compared with oil contents of algal strains (>15wt %) recommended for biodiesel production. According to the results of this study, production of biodiesel from Algae in Ethiopia is recommended. Owing to the fact that Ethiopia has strong sunlight and clear days throughout most of the year, higher average productivity and yield of algal biomass could be obtained.

The land requirement per biomass yield obtained was lower when compared with other biodiesel feeds stock land requirements. Although land in Ethiopia can be easily acquired from the government for agricultural investment purposes, the average size of farming land acquired by farmers is small, around 1.1 hectare per family. Further more, there is the prevalent and recurrent drought and shortage of food in the country. Therefore, each and every piece of lands available should be used effectively. The result of this study shows that algae falls in to high range of productivity per unit land mass. For example, the forecasted sum amount of petroleum that will be imported at the end of 2010by the Ethiopian Petroleum Agency is around 1, 964, 464.276 ton. Therefore, 89384 hectare is enough to produce a biodiesel that will substitute all the imported petroleum for 2010. This is less than the amount of land (100000 hectare) allocated to a single company (the Israeli company LHBCHATZ) in the Oromia region for Jatropha plantation [5].

The production facilities for biomass and biodiesel production are not capital intensive. Therefore, investments for higher capacity of biodiesel are preferred. Further more, algal strains, according to the results from this study, with higher lipid content and lower biomass productivity, are better than those of algal strains with higher productivity but lower lipid content. This was mainly found to be due the associated higher cost in the downstream biomass processing section. In general, algal strains with higher lipid content were obtained to be more feasible.

6.2. Recommendations

Although it was concluded that biodiesel can be produced in Ethiopia, there was a lack of pure algal strains to select species which have higher lipid content among different alternatives. There is a lack of enough research in the area. Especially, a major emphasis should be given to the cultivation of algal strains, which are native to Ethiopia to prevent the danger of washout by wild strains in open pond systems. These includes selection and isolation of specific species of algal strains from the colonies, determination of fatty acid compositions, investigation on the productivity of isolated species, determination of optimal temperature, sun light intensity, and nutrients requirement for optimal growth of strains with higher fatty acid yield per unit area of land is required. For researches involved in open pond cultivation of microalgae, the facility at ARARI could be used since there are open ponds already constructed with and without green houses. Future studies in algal cultivation should focus on obtaining strains with higher lipid content than higher productivity strains.

The processing cost of algal biomass, especially the energy cost was found to be significant. Drying and carbonation water pump operation are the major energy consuming parts. However, the energy cost of drying can be reduced if the oil can be extracted wet. There are recent developments for this method of extraction. Ultrasonic cell disruption system is one of them. But the details should be investigated for the running cost and if the technology is available for use. Alternative processes for the drying with minimal cost should be investigated. In this study, flocculation units, and carbonation pits were designed for each pond. This may have resulted in increments of capital and running costs. Therefore, future studies are required to determine if using single carbonation pit and flocculation unit would give lower capital and running costs.

Another key factor that will play an important role on the economic performance of biomass production is the left over biomass after the oil extraction process. Finding a better market or looking for processes that could convert the biomass by product in to a more valuable item can play a positive role in making the overall process more profitable.

It should be noted that algal biomass and hence oil production from algae should not be considered as an industrial practice only. Rather, it should also be considered as an agricultural practice and as an investment on agriculture. Therefore, if the algae biomass production receives the incentives given for agricultural investments, it would be more profitable and attractive business in Ethiopia.

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Appendices

A: Material balance for biomass production of Bortyococcus braunii

Mass balance around the pond

Basis, 40000 m^2 of pond area.

- ***Algae production rate***

From equation 2.1,

$$\frac{P}{D} = \mu * C$$

Where P is the growth rate, $g/m^2/day$

D is the depth of the pond

C is the algal biomass concentration, g/m^3or it is equivalent to ppm

Therefore, for a target pond concentration 250 ppm ($250g/m^3$) the equation becomes

$$\frac{P}{D} = 0.8 * 250 \frac{grams}{m^3.day} \quad \text{(A.1)}$$

Substituting for the value of depth 0.25 meter of the pond being considered in this study,

$$P = 0.25m * 0.8 * 250 \frac{grams}{m^3.day} = 50 \frac{grams}{m^2.day}$$

Therefore, productivity (P_r) for the 40000 m^2 pond

P_r=growth rate * total area of the pond (A.2)

$P_r = 40000m^2 * 50\frac{grams}{m^2.day} = 2000 \frac{kg}{day}$ per pond

However, this is the maximum theoretical productivity of biomass that could be achieved under optimum theoretical specific growth. This optimum growth rate is a function of various parameters including optimum T, carbon dioxide concentration, and light intensity throughout the depth of the pond. The maximum specific growth rate, generally, cannot be achieved by an open pond, even by closed photo bioreactors for that matter. Therefore, according to Ron Putt

[16], 20% efficiency for productivity is assumed for this study. Therefore, for the 40000m^2 pond, adjusted productivity rate will be

$P_r = 0.2 * 2000 \frac{kg}{day} = 400 \frac{kg}{day}$ per pond

- ***Water Harvesting rate from the pond***

$$\text{Harvesting rate } (Q_h) = \frac{\text{production rate}}{\text{Algal biomass concentration in the pond}} \quad \text{(A.3)}$$

$$Q_h = \frac{400 \frac{kg}{day}}{\frac{250g}{m^3}} = \frac{400 \frac{kg}{day}}{\frac{0.25kg}{m^3}} = 1600 \frac{m^3}{day}$$

- ***Water residence time (τ)in the pond***

Pond volume = Pond area*pond depth (A.4)

=40000m^2*0.25m=10000m^3

Residence time (τ) = (pond volume)/(water harvesting rate (Q_h)) (A.5)

$$\tau = \frac{10000m^3}{1600m^3/day} = 6.25\text{days}$$

- ***Make up water requirement***

A typical pond evaporation rates are about 3 centimeters per day in arid situations [9]. Therefore it is very reasonable to assume at least a 2 cm evaporation rate per day for a pond in Ethiopia under medium daily temperature.

Make up water flow rate (Q_w) = Pond area*evaporation rate (A.6)

$Q_w = 0.002\frac{m}{d} * 40000 m^2 = 80\frac{m^3}{d}$ or $0.0556\frac{m^3}{min}$ per pond

- ***CO_2 requirement of the pond***

Based on the data tabulated in Table 2.3, carbon content is 52% of actual dry biomass.

400 kg of algae per day requires 208 kg of carbon per day (52% carbon in algae)

208 kg of Carbon requires, based on stoichiometry, 832 kg/day of CO_2

- ***Nutrient requirement***

The data from Table 2.3 is used for this calculation

Nitrogen requirement is 17% of carbon requirement, this gives

208kg*0.17=35.36kg of nitrogen

This would give, based on stoichiometry, 46.24kg of ammonia

Phosphorus requirement is 2 % of carbon requirement, this gives

208kg*0.02=4.16kg/day of phosphorus

This would give, based on stoichiometry, 13.15kg of ammonium phosphate. From this value ammonia amounts to, based on stoichiometry, 2.18 kg. Adjusted amount of ammonia would be 44.06kg.

Mass balance on flocculation unit

Harvesting is done by a flocculation unit. The flocculation process agglomerates individual micro-algae cells into macroscopic entities which are easily dewatered through settling, filtration, and pressing. The flocculation starts with addition of ferric nitrate.

- ***Ferric nitrate requirement***

The basis for calculating the required flocculants is that around 0.1% of algal biomass would give the required 1-3% solid algae mass concentration.

Therefore, mass of ferric nitrate ($mass_{fn}$) required

$Mass_{fn}$=0.001*400kg/day=0.4kg/day

- ***Underflow (concentrated algae) mass balance***

For the purpose of mass balance, the average 2% (from 1%-3%) dry weight concentration can be assumed. Mass of algae produced=P=400kg/day. Therefore, mass of water with the algae can be calculated as, based on the fair assumption that alga biomass and water have equal density.

$$2\text{wt\%}=\frac{2g\ of\ algae}{100g\ of\ water}*\frac{1000g}{L}*\frac{1000L}{m^3}=\frac{20000g}{m^3}$$

W_{uflow} =mass of dry algae/concentration (A.7)

$$W_{uflow}=\frac{400kg/day}{20000g/m^3}=\frac{400kg/day}{20kg/m^3}=20\ m^3/day$$

- ***Overflow water mass balance***

Over flow water flow rate (W_{oflow}) would be the difference between the flowrate of inlet and underflow outlet.

W_{oflow}=Feed flow (Q_h) – under flow (W_{oflow}) (A.8)

=1600m^3/day-20m^3/day=1580m^3/day

Mass balance on filtration and drying

- ***Mass of water removed by filtration***

Concentration by filtration is from 2% - 20 %

$$20\text{wt\%}=\frac{20g\ of\ algae}{100g\ of\ water}*\frac{1000g}{L}*\frac{1000L}{m^3}=\frac{200000g}{m^3}=\frac{200kg}{m^3}$$

Therefore, mass of water leaving the filtration with biomass (entering to the drier) W_{fout} is calculated by

W_{fout}=dry algal biomass/concentration (A.9)

$$W_{fout} = \frac{\frac{400kg}{day}}{\frac{200kg}{m^3}} = 2m^3$$

Therefore, total mass of water entering to the drier is,

$W_{massin} = 2m^3$/day*1000kg/m^3 = 2000kg/day

Hence, mass of water removed by filtration (W_{fr}) is given as

Wfr=mass of water from flocculation unit-mass of water entering to the drier (A.10)

= W_{uflow}- W_{fout}

= $20m^3 - 2m^3$ = 18m^3 = 18000kg/day

- **Mass of water and algal biomass entering to the drier**

W_{massin} + W_{algae} = 2000kg/day+400kg/day = 2400kg/day

- **Mass of algal biomass leaving the drier.**

For facilitating the oil extraction process, the algal biomass should at least be dried to 90%.
For 90% dry alga of mass 400kg product per day

$$0.9 = \frac{mass\ of\ dry\ algal\ biomass}{total\ mass\ of\ water\ and\ biomass} \quad (A.11)$$

$0.9 = \frac{\frac{400kg}{day}}{\frac{400kg}{day}+W_{mass}}$, therefore W_{mass} would be

$W_{massout}$=44.5kg/day

Total mass=400kg/day+44.5kg/day=444.5kg/day

- **Mass of water removed by drying (**M_{water})

M_{water} = mass of water entering-mass of water leaving with biomass (A.12)

$M_{water} = W_{massin} - W_{massout}$

M_{water} = 2000kg/day-44.5kg/day=1955.5kg/day

B: Energy balance for biomass production of Bortyococcus braunii

Energy balance for the carbonation pit

For assumption of 208 kg carbon required per day for the 40000m^2 growth pond (algae assumed to be 52 wt% carbon), and CO_2 supply from power plant exhaust gas (20 mole % carbon dioxide) with a bubble column a pit of downward pond water flow and upward carbon-dioxide containing gas flow, was considered for the scrubbing operation. The saturation concentration of carbon dioxide in water at normal condition is 5.6molCO_2/m^3 [16].

Since 208kg/day per pond of C in the 20% mol carbon dioxide effluent gas is required, the carbon dioxide concentration in 20% mol effluent can be calculated by Equations B.1 and B.2. Although the temperature and pressure of effluent gases from a power plant may be higher and varies depending on the type of the power plant and processes conditions employed, constant temperature and pressure values of 300K and 1 atmosphere is assumed for this study.

$$PV=nRT \quad \text{(B.1)}$$

$$[CO_2]_{effluent} = \frac{nM}{V} = \frac{P}{RT} \quad \text{(B.2)}$$

$$= \frac{1\ atm}{0.082\frac{L.atm}{mol.K}300K}$$

$$= 0.35\frac{kg}{m^3}_{exhuast}$$

For 208 kg of carbon requirement per day, assuming 12 working hours per day for carbonation column, the volumetric flow rate (V_m) is equal to

$$V_m = \frac{mass\ flowrate\ of CO_2}{effluent\ CO_2 concentration} \quad \text{(B.3)}$$

$$V_m = \frac{208kg\ C}{0.5d} * \frac{44kg\ CO_2}{12kg\ C} * \frac{1m^3}{0.35kg} * \frac{1d}{24*3600S} = 0.05\frac{m^3}{s}$$

Therefore, the molar rate of carbon dioxide intake (M_r) is calculated as

$$M_r = mass\ flow\ rate\ of\ CO_2 * \frac{1\ mol\ CO_2}{44g\ CO_2} \quad \text{(B.4)}$$

$$M_r = Volumteric\ flowrate * mass\ concentration\ of\ CO_2\ \ \frac{1\ mol\ CO_2}{44g\ CO_2} \quad \text{(B.5)}$$

$$M_r = 0.05\frac{m^3}{s} * 0.35\frac{kg}{m^3_{exhust}} * \frac{1\ mol\ CO_2}{44g\ CO_2} = 0.398\frac{mol\ CO_2}{s}$$

For 10% gas volume fraction in the column to ensure good mass transfer rate for the bubble column [16], and bubble rise velocity $0.3\frac{m}{s}$, the minimum column area (A) required would be

A=Volumetric flow rate/velocity (B.6)

$$A = \frac{0.05\frac{m^3}{s}}{0.3\frac{m}{s} * 0.1} = 1.67 m^2$$

For a 10-fold reduction in partial pressure (and hence concentration) of carbon dioxide in the gas phase (90% carbon dioxide recovery), 10 second of gas residence time was required by detail mass transfer calculations by Ron Putt [16]. Hence, height of column (H_{column}) can be calculated by,

H_{column}= velocity * residence time (B.7)

$H_{column} = 0.3\frac{m}{s} * 10s = 3m$

Water flow (W_f) in the carbonation column is calculated by a liquid flow rate which is 10 times more than the stoichiometry amount of the CO_2 saturation concentration [16]. Therefore, volumetric flowrate of water (W_f) required for saturation can be calculated as,

W_f= molar intake of CO_2 / saturation concentration (B.8)

$$W_f = \frac{0.398\frac{mol\ CO2}{s}}{5.6\frac{mol\ CO2}{m^3}} = 0.07\frac{m^3}{s}$$

Adjusted water flowrate 10 times the stoichiometric requirement

$W_f = \frac{0.398 \frac{mol\ CO2}{s}}{5.6 \frac{mol\ CO2}{m^3}} * 10 = 0.7\ \frac{m^3}{s}$

Hence, the velocity of water (V_w) in the column is

V_w = water flowrate/column area (B.9)

$V_w = \frac{W_f}{A} = \frac{0.7 \frac{m^3}{s}}{1.67 m^2} = 0.41 \frac{m}{s}$

Then the liquid pumping power, assuming frictional loss negligible, is calculated by

P=Mass flow rate of water*height*gravitational acceleration (B.10)

However, the carbonation water enters to the pit from the top and after circulating leaves through the same elevation. Therefore, it can be assumed that the pump should not provide the 3 meter head loss (height). For the purpose of overcoming the frictional loss a pumping power for 0.2m head loss is assumed.

$$P = 0.7 \frac{m^3}{s} * 1000 \frac{kg}{m^3} * 0.2m * 9.8 \frac{m}{s^2} = 0.668\ kW\ for\ 24\ hours$$

For the gas phase it is assumed that the pressure from the exhaust (outlet) gas is enough to circulate through the column

Column pit volume = column area * column height (B.11)

Column pit volume=A*H=$1.67 m^2$*3m=$5.01 m^3$

For10% volume allowance=$5.01 m^3$+$0.501\ m^3$=$5.51\ m^3$

Energy balance for static mixer and settling tank (flocculation unit)

Static pre mixers instead of stirred tanks was selected because of their better uniformity of mixing and lower installed and operating and maintenance costs were recommended by Ronn put [16]. 3 inch diameter, six-element mixers for each of the two additives, which would provide the required mixing at a lower pumping power were used. Water flow rate to the static mixers from material balance is $1600m^3$/day=$1.108m^3$/min. The mixers power rating is 80watt for each. Therefore, 160watt per pond is the total power requirement per pond.

Three flocculation units and a residence time of 1 hour is proposed for each pond.

Therefore, volume of settling tank= $1.108m^3$/min*1/3*60min/h=$22.16m^3$

The water return pumping power requirement assuming 0.2 m head loss will be, based on equation B.10.

$$P = 0.0185\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 36.26w$$

Energy balance for filtration (for water recycling)

A power requirement for water recycled by filtration ($18m^3$/day) equivalent to 0.2 m head loss is assumed. Then, based on equation B.10, P would be

$$P = 0.0002\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 0.408w$$

Energy balance for Drying

The amount of water removed by drying is 1955kg/day per pond

Energy required for drying=W_{mass}*$H_{vaporization}$ (B.12)

=$1955\frac{kg}{day}$*$0.54\frac{kW.h}{kg}$=1055kW.h.=43.96kW for 24 hrs

C: Economic evaluation for biomass production of Bortyococcus braunii

Costing of raceway open ponds for Bortyococcus braunii

No	Item	unit cost $	Bases	quantity	total Cost $ for 91ponds	total cost $ for 182ponds
land and builings						
1	Land	0				
2	Office and process building	615	meter sq.	000&1200	615000	738000
Down stream processing						
5	Belt filter press		ton per hr	1.52t&3.04t	140000	195000
6	Drum drier		ton per hr	1.52t&3.04t	145000	210000
7	Water recycling pump	1000	1600m3/d	91&182	91000	182000
				subtotal	991000	1325000
Pond system						
9	Pond	1900	pond	91&182	172900	345800
11	Carbonation pit	3500	5.5 m3	91&182	318500	637000
12	Static mixer	500	number	91&182	45500	91000
13	Static mixer	500	number	91&182	45500	91000
14	carbonation water pump	8500	0.7 m3/s	91&182	773500	1547000
15	Harvesting water pump	1000	0.037 m3/s	91&182	91000	182000
16	Ferric metring pump	200	small	91&182	18200	36400
18	Settling tank	1500	21.16m3	91&182	136500	273000
19	Settling tank	1500	21.16m3	91&182	136500	273000
20	Settling tank	1500	21.16m3	91&182	136500	273000
21	Water return pump	1000	0.018m3/s	91&182	91000	182000
				Subtotal	1965600	3931200
			Equipment total		2956600	5256200
	Installation 10% of equipment total.				295660	525620
				Installed Cost	3252260	5781820
				Working Capital 10%	325226	578182
		Total Capital Investment (installed +working)			3577486	6360002
22	Materials	line 1	line 2	unit cost $/kg	cost $/a	cost $/a
23	Ammonia (kg/day)	4004	8008	0.12	144144	288288
24	Ammonium phosphate(kg/d)	1196.65	2393.3	0.25	89748.75	179497.5
25	Ferric ion (kg/day)	36.4	72.8	0.16	1747.2	3494.4
26	Water make up (m3/day)	1600	3200	0.02	9600	19200
				Total	245239.95	490479.9

table continued….

	Energy per pond			cost $/kwh		
27	Carbonation pump power (kW)	0.668		0.03	13130.208	26260.416
28	Static mixers power (kW)	0.08		0.03	1572.48	3144.96
29	Power for drying (kW)	43.96		0.03	864077.76	1728155.52
30	Water recycling pump (kW)	0.000408		0.03	8.019648	16.039296
31	Water return pump (kW)	0.03626		0.03	712.72656	1425.45312
				Total	879501.1942	1759002.39
		Salary				
		Quantity	$ Per month	$ Per year		
	Labour	95 &186	100	1200	114000	223200
32	Forman	9 & 14	200	2400	21600	33600
33	Technicians	4 & 6	300	3600	14400	21600
34	Finance	2&3	200	2400	4800	7200
35	Adminstration	2&3	200	2400	4800	7200
				Total Labor	159600	292800
			Total Prodction cost		1284341.144	2542282.29
	Algae production	kg/d		Price ($) per kg	price $/a	price $/a
		91 pond	182 pond			
36	Biomass	36429	72858			
37	Lipid	25500.3	51000.6	0.4	3060036	6120072
38	Meal (or fuel)	7650.09	15300.18	0.05	229502.7	459005.4
				Total Income	3289538.7	6579077.4
			Gross profit		2005197.556	4036795.11
			Depreciation 10% of installed		325226	578182
			Net profit (35% tax)		1091981.511	2248098.52
			Pay Back Period		3.276141549	2.8290584

D: Material balance for biomass production of Chlorella sp

Mass balance around the pond

Basis, 40000 m^2 of pond area.

- ***Algae production rate***

For a target pond concentration of 250 ppm (250g/m^3) and specific growth rate of chlorella 2.5 day^{-1}, the growth rate based on Equation 2.1 would be

$$\frac{P}{D} = 2.5 * 250 \frac{grams}{m^3.day}$$

Substituting for the value of depth 0.25 meter of the pond being considered in this study,

$$P = 0.25m * 2.5 * 250 \frac{grams}{m^3.day} = 156.25 \frac{grams}{m^2.day}$$

Therefore, productivity (P_r) for the 40000 m^2 pond, based on Equation A.1

P_r=40000*156.25=$6250 \frac{kg}{day}$ per pond

Since 20% efficiency for productivity is assumed for this study, then adjusted productivity rate will be

P_r=$0.2 * 6250 \frac{kg}{day}$=$1250\frac{kg}{day}$ per pond

- ***Water Harvesting rate***

Water harvesting rate from Equation A.3 is

$$Qh = \frac{1250\frac{kg}{day}}{\frac{250g}{m^3}} = \frac{400\frac{kg}{day}}{\frac{0.25kg}{m^3}} = 5000 \frac{m^3}{day}$$

- ***Water residence time (τ)in the pond***

Water residence time from Equation A.4 and A.5 is

$$\tau = \frac{10000m^3}{5000m^3/day} = 2\text{days}$$

- ***Make up water requirement***

Make up water flowrate from Equation A.6 is

$$Q_w = 0.002\frac{m}{d} * 40000m^2 = 80\frac{m^3}{d} \text{ or } 0.0556\frac{m^3}{min} \text{ per pond}$$

- ***CO_2 requirement of the pond***

Based on the data tabulated in Table 2.3, carbon content is 52% of actual dry biomass.

1250 kg of algae per day requires 650 kg of carbon per day (52% carbon in algae)
650 kg of Carbon requires, based on stoichiometry, 2600 kg/day of CO_2

- ***Nutrient requirement***

The data from Table 2.3 is used for this calculation
Nitrogen requirement 17% of carbon requirement, this gives

650kg*0.17=110.5kg of nitrogen

This would give, based on stoichiometry, 134 kg of ammonia
Phosphorus requirement 2 % of carbon requirement, this gives

650kg*0.02=13kg of phosphorus

This would give, based on stoichiometry, 41 kg of ammonium phosphate. From this value ammonia amounts to, based on stoichiometry, 7.12 kg of ammonia. Adjusted amount of ammonia would be 126.88kg.

Mass balance on flocculation unit

Harvesting is done by a flocculation unit. The flocculation process agglomerates individual micro-algae cells into macroscopic entities which are easily dewatered through settling, filtration, and pressing. The flocculation starts with addition of ferric nitrate.

- ***Ferric Nitrate requirement***

The basis for calculating the required flocculants is that around 0.1% of algal biomass would give the required 1-3% solid algae mass concentration.

Mass of ferric nitrate (mas_{fn}) required, based on the data found from the experiment

$Mass_{fn}$=0.001*1250kg/day=1.25kg/day

- ***Underflow (concentrated algae)***

For the purpose of mass balance, the average 2% (from 1%-3%) dry weight concentration can be assumed. Mass of algae produced=P=1250kg/day. Therefore, mass of water with the algae can be calculated as, based on the fair assumption that alga biomass and water have equal density.

$$2\text{wt\%}=\frac{2g\ of\ algae}{100g\ of\ water}*\frac{1000g}{L}*\frac{1000L}{m^3}=\frac{20000g}{m^3}$$

From Equation A.7

$$W_{uflow}=\frac{1250kg/day}{2000g/m^3}=\frac{1250kg/day}{20kg/m^3}=62.5\ m^3$$

- ***Overflow water mass balance***

Over flow water flow rate (W_{oflow}) would be the difference between the flowrate of inlet and underflow outlet. From Equation A.8

W_{oflow} =5000m^3/day-62.5m^3/day=4937.5m^3/day

Mass balance on Filtration and drying

- ***Mass of water removed by filtration***

Concentration by filtration is from 2% - 20 %

$$20\text{wt}\% = \frac{20g\ of\ algae}{100g\ of\ water} * \frac{1000g}{L} * \frac{1000L}{m^3} = \frac{200000g}{m^3} = \frac{200kg}{m^3}$$

Therefore, mass of water entering to the drier (leaving the filtration with biomass) W_{fout} is calculated by Equation A.9

$$W_{fout} = \frac{\frac{1250kg}{day}}{\frac{200kg}{m^3}} = 6.25m^3$$

Therefore, total mass of water entering to the drier is,

W_{massin} =6.25m^3/day*1000kg/m^3=6250kg/day

Mass of water removed by filtration (W_{fr}) from Equation A.10

W_{fr}==62.5m^3 − 6.25$m^3$3=56.25m^3=56250kg

- ***Mass of water and algal biomass entering to the drier***

W_{massin} + W_{algae} =6250kg/day+1250kg/day=7500kg/day

- ***Mass of algal biomass leaving the drier***

For facilitating the oil extraction process, the algal biomass should at least be dried to 90%.
For 90% dry alga of mass 1250kg product per day, Equation A.11 becomes

$0.9 = \frac{\frac{1250kg}{day}}{\frac{1250kg}{day}+W_{mass}}$,therefore W_{mass} would be

$W_{massout}$=138kg/day

Total mass=1250kg/day+138kg/day=1388kg/day

- ***Mass of water removed by drying***

From Equation A.12

$M_{water} = W_{massin} - W_{massout}$

M_{water} = 6250kg/day-138kg/day=6112kg/day.

E: Energy balance for biomass production of Chlorella sp.

Energy balance for the carbonation pit

Since 650 kg/day per pond of C in the 20% mol carbon dioxide effluent gas is required, the carbon dioxide concentration in 20% mol effluent can be calculated by Equations B.1 and B.2.

$$[CO_2]_{effluent}=0.35\frac{kg}{m^3}_{exhuast}$$

For 650kg of carbon requirement per day, assuming 12 working hours per day for carbonation column, the volumetric flow rate (V_m) is equal to (Equation B.3)

$$V_m\frac{650Kg}{0.5d}*\frac{44kg\ CO2}{12kg\ C}*\frac{1m3}{0.35kg}*\frac{1d}{24*3600S}=0.157\frac{m^3}{s}$$

Therefore, the molar rate of carbon dioxide intake (M_r) from Equation B.4 and B.5 is

$$M_r=0.157\frac{m^3}{3}*0.35\frac{kg}{m^3}_{exhust}*\frac{1\ mol\ CO2}{44g\ CO2}=1.248\frac{mol\ CO2}{s}$$

The minimum column area, and height required as given by Equation B.6 and B.7 are

$$A=\frac{0.157\frac{m^3}{s}}{0.3\frac{m}{s}*0.1}=5.23m^2$$

$$H_{column}=0.3\frac{m}{s}*10s=3m$$

Water flow in the carbonation column is calculated by equation B.8 is calculated as

$$W_F=\frac{1.248\frac{mol\ CO2}{s}}{5.6\frac{mol\ CO2}{m^3}}*10=2.2\frac{m^3}{s}$$

Hence, the velocity of water in the column from Equation B.9 is

$$V_W=\frac{W_F}{A}=\frac{2.2\frac{m^3}{s}}{5.23m^2}=0.42\frac{m}{s}$$

Then the liquid pumping power, assuming frictional loss negligible, is calculated by equation B.10

$$P = 2.2\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 2.156kW\ for\ 24\ hours$$

For the gas phase it is assumed that the pressure from the exhaust (outlet) gas is enough to circulate through the column

Column pit volume=A*H=5.23m^2*3m=15.69m^3

For10% volume allowance=15.69m^3+0.1569 m^3=17.2 m^3

Energy balance for static mixer and settling tank (flocculation unit)

Static pre mixers instead of stirred tanks is selected because of their better uniformity of mixing and lower installed, operating and maintenance costs were recommended by Ronn put [16]. 6 inch diameter, six-element mixers for each of the two additives, which would provide the required mixing at a lower pumping power were used. Water flow rate to the static mixers from material balance is 5000m^3/day=3.46m^3/min. The mixers power rating is 80 watt for each. Therefore, 160 watt per pond is the total power requirement per pond.

Three flocculation units and a residence time of 1 hour is proposed for each pond.
Therefore, volume of settling tank= 6.94m^3/min*1/3*60min/h=138.8m^3

The pumping power requirement for water return based on Equation B.10 is

$$P = 0.057\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 111.72W$$

Energy balance for filtration

A power requirement for water recycling (56.25m^3/day) equivalent to 0.2 m head loss is assumed. Then P , based on Equation B. 10 would be

$$P = 0.00065\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 1.27w$$

Energy balance for Drying

The amount of water removed by drying is 6112kg/day per pond, then based on equation B.12

E =$6112\frac{kg}{day}$*$0.54\frac{kW.h}{kg}$=3300kW.h=137.5kw for 24 hrs

F: Economic evaluation for biomass production of Chlorella sp.

`						
		unit cost $	Bases	quantity	total Cost $	total cost $
No	Item				for 91ponds	for 182ponds
land and buildings						
1	Land	0				
2	Office and process building	615	meter sq.	000&1200	615000	738000
Down stream processing						
5	Belt filter press		ton per hr	4.25t&8.5t	280000	395000
6	Drum drier		ton per hr	4.25t&8.5t	300000	430000
7	Water recycling pump	2200	5000m3/d	82&163	180400	358600
				subtotal	1375400	1921600
Pond system						
9	Pond	1900	Pond	82&163	155800	309700
11	Carbonation pit	8000	17.2 m3	82&163	656000	1304000
12	Static mixer	800	Number	82&163	65600	130400
13	Static mixer	800	Number	82&163	65600	130400
14	carbonation water pump	17000	2.2 m3/s	82&163	1394000	2771000
15	Harvesting water pump	6500	0.116 m3/s	82&163	533000	1059500
16	Ferric metring pump	200	Small	82&163	16400	32600
18	Settling tank	3000	138.8 m3	82&163	246000	489000
19	Settling tank	3000	138.8 m3	82&163	246000	489000
20	Settling tank	3000	138.8 m3	82&163	246000	489000
21	Water return pump	2200	0.058m3/s	82&163	180400	358600
				Subtotal	3804800	7563200
			Equipment total		5180200	9484800
	Installation 10% of equipment total.				518020	948480
				Installed Cost	5698220	10433280
				Working Capital 10%	569822	1043328
		Total Capital Investment (installed +working)			6268042	11476608
22	Materials	line 1	line 2	unit cost $/kg	cost $/a	cost $/a
23	Ammonia (kg/day)	10404.16	20681.44	0.12	374549.76	744531.84
24	Ammonium phosphate(kg/d)	3362	6683	0.25	252150	501225
25	Ferric ion (kg/day)	102.5	203.75	0.16	4920	9780
26	Water make up (m3/day)	6560	13040	0.02	39360	78240
				Total	670979.76	1341959.52

table continued…

	Energy			cost $/kwh		
27	Carbonation pump power (kW)	21.56		0.03	381870.72	759084.48
28	Static mixers power (kW)	0.04		0.03	708.48	1408.32
29	Power for drying (kW)	137.5		0.03	2435400	4841100
30	Water recycling pump (kW)	0.00127		0.03	22.49424	44.71416
31	Water return pump (kW)	0.117		0.03	2072.304	4119.336
				Total	2820074	5605756.85
		Salary				
		Quantity	$ Per month	$ Per year		
	Labour	85 &167	100	1200	102000	200400
32	Forman	8 & 13	200	2400	19200	31200
33	Technicians	3 & 5	300	3600	10800	18000
34	Finance	2&3	200	2400	4800	7200
35	Adminstration	2&3	200	2400	4800	14400
				Total Labor	141600	271200
			Total Prodction cost		3632653.76	7218916.37
	Algae production	kg/d		Price ($) per kg	price $/a	price $/a
		81 pond	163 pond			
36	Biomass	102000	205259.26			
37	Lipid	25500	51314.815	0.4	3060000	6157777.78
38	Meal (or fuel)	76500	152067.07	0.05	1147500	2281006.1
				Total Income	4207500	8438783.88
			Gross profit		574846.242	1219867.51
			Depreciation 10% of installed		569822	1043328
			Net profit (35% tax)		3265.75714	114750.678
			Pay Back Period		1919.32276	100.013422

G: Material balance for biomass production of Tetraselmis suecica

Material balance around the pond

Basis, 40000 m^2 of pond area.

- ***Algae production rate***

For a target pond concentration of 250 ppm (250g/m^3) and specific growth rate of chlorella 1.47 day^{-1}, the growth rate based on Equation 2.1 would be

$$\frac{P}{D} = 1.47 * 250 \frac{grams}{m^3.day}$$

Substituting for the value of depth 0.25 meter of the pond being considered in this study,

$$P = 0.25m * 1.47 * 250 \frac{grams}{m^3.day} = 91.8 \frac{grams}{m^2.day}$$

Therefore, productivity (P_r) for the 40000 m^2 pond, based on Equation A.1

$$P_r = 40000m^2 * 91.8 = 3664 \frac{kg}{day} \text{ per pond}$$

Since 20% efficiency for productivity is assumed for this study, then adjusted productivity rate will be

$$P_r = 0.2 * 3664 \frac{kg}{day} = 732 \frac{kg}{day} \text{ per pond}$$

- ***Water Harvesting rate***

Water harvesting rate from Equation A.3 is

$$Q_h = \frac{732 \frac{kg}{day}}{\frac{250g}{m^3}} = \frac{732 \frac{kg}{day}}{\frac{0.25kg}{m^3}} = 2928 \frac{m^3}{day}$$

- ***Water residence time (τ))in the pond***

Water residence time from Equation A.4 and A.5 is

$$\tau = \frac{10000m^3}{2928m^3/day} = 3.415 \text{days}$$

- ***Make up water requirement***

Make up water flowrate from Equation A.6 is

$Q_w = 0.002\frac{m}{d} * 40000m^2 = 80\frac{m^3}{d}$ or $0.0556\frac{m^3}{min}$ per pond

- ***CO_2 requirement of the pond***

Based on the data tabulated in Table 2.3, carbon content is 52% of actual dry biomass.

732 kg of algae per day requires 380 kg of carbon per day (52% carbon in algae)

380 kg of Carbon requires, based on stoichiometry, 1520 kg/day of CO_2

- ***Nutrient requirement***

The data from Table 2.3 is used for this calculation

Nitrogen requirement 17% of carbon requirement, this gives

380kg*0.17=110. kg of nitrogen

This would give, based on stoichiometry, 78.3kg of ammonia

Phosphorus requirement 2 % of carbon requirement, this gives

380kg*0.02=7.6kg of phosphorus

This would give, based on stoichiometry, 23.96kg of ammonium phosphate. From this value ammonia amounts to, based on stoichiometry, 4.16 kg of ammonia. Adjusted amount of ammonia would be 69.98kg.

Mass balance on flocculation unit

Harvesting is done by a flocculation unit. The flocculation process agglomerates individual micro-algae cells into macroscopic entities which are easily dewatered through settling, filtration, and pressing. The flocculation starts with addition of ferric nitrate.

- ***Ferric Nitrate requirement***

The basis for calculating the required flocculants is that around 0.1% of algal biomass would give the required 1-3% solid algae mass concentration. [16].Mass of ferric nitrate ($mass_{fn}$) required,

$Mass_{fn}$=0.001*732kg/day=0.732kg/day

- ***Underflow (concentrated algae) mass balance***

For the purpose of mass balance, the average 2% (from 1%-3%) dry weight concentration can be assumed. Mass of algae produced=P=732kg/day. Therefore, mass of water with the algae can be calculated as, based on the fair assumption that alga biomass and water have equal density.

$$2\text{wt\%}=\frac{2g\ of\ algae}{100g\ of\ water}*\frac{1000g}{L}*\frac{1000L}{m^3}=\frac{20000g}{m^3}$$

From Equation A.7

$$W_{uflow}=\frac{732kg/day}{2000g/m^3}=\frac{732kg/day}{20kg/m^3}=36.6m^3$$

- ***Overflow water mass balance***

Over flow water flow rate (W_{oflow}) would be the difference between the flowrate of inlet and underflow outlet. From Equation A.8,

W_{oflow} =2928m^3-36.6m^3=2891.4m^3

Mass balance on Filtration and drying

- ***Mass of water removed by filtration***

Concentration by filtration is from 2% - 20 %

$$20wt\%=\frac{20g\ of\ algae}{100g\ of\ water}*\frac{1000g}{L}*\frac{1000L}{m^3}=\frac{200000g}{m^3}=\frac{200kg}{m^3}$$

Therefore, mass of water entering to the drier (leaving the filtration with biomass) W_{fout} is calculated by Equation A.9

$$W_{fout}=\frac{\frac{732kg}{day}}{\frac{200kg}{m^3}}=3.66m^3$$

Therefore, total mass of water entering to the drier is,

W_{massin}=3.66m^3/day=3660kg/day

Mass of water removed by filtration (W_{fr}) from Equation A.10,

W_{fr} =36.63m^3 − 3.66$m^3$3=32.97m^3=32970kg

- ***Mass of water and algal biomass entering to the drier***

Wmass + Walgae =3660kg/day+732kg/day=4392kg/day

- ***Mass of algal biomass leaving the drier***

For facilitating the oil extraction process, the algal biomass should at least be dried to 90%.
For 90% dry alga of mass 1250kg product per day, Equation A.11 becomes

$$0.9= \frac{\frac{732kg}{day}}{\frac{732kg}{day}+W_{mass}}$$

$W_{massout}$=81.3kg/day

Total mass=732kg/day+81.3kg/day=813.3kg/day

- **Mass of water removed by drying (**M_{water})

From Equation A.12

$M_{water} = W_{massin} - W_{massout}$

M_{water} = 3660kg/day-81.3kg/day=3578.7kg/day.

H: Energy balance for the biomass production of Tetraselmis suecica

Energy balance for the carbon pit

Since 380kg/day per pond of C in the 20% mol carbon dioxide effluent gas is required, the carbon dioxide concentration in 20% mol effluent can be calculated by Equations B.1 and B.2.

$$[CO_2]_{effluent}=0.35\frac{kg}{m^3}_{exhuast}$$

For 380kg of carbon requirement per day, assuming 12 working hours per day for carbonation column, the volumetric flow rate (V_m) is equal to (Equation B.3)

$$V_m=\frac{380kg}{0.5d}*\frac{44kg\ CO2}{12kg\ C}*\frac{1m3}{0.35kg}*\frac{1d}{24*3600S}=0.092\frac{m^3}{s}$$

Therefore, the molar rate of carbon dioxide intake (M_r) from Equation B.4 and B.5 is

$$M_r=0.092\frac{m^3}{s}*0.35\frac{kg}{m^3}_{exhust}*\frac{1\ mol\ CO2}{44g\ CO2}=0.732\frac{mol\ CO2}{s}$$

The minimum column area, and height required as given by Equation B.6 and B.7 are

$$A=\frac{0.092\frac{m^3}{s}}{0.3\frac{m}{s}*0.1}=3.06m^2$$

$$H_{column}=0.3\frac{m}{s}*10s=3m$$

Water flow in the carbonation column is calculated by equation B.8 is calculated as

$$W_F=\frac{0.732\frac{mol\ CO2}{s}}{5.6\frac{mol\ CO2}{m^3}}*10=1.3\frac{m^3}{s}$$

Hence, the velocity of water in the column from Equation B.9 is

$$V_W=\frac{W_F}{A}=\frac{1.3\frac{m^3}{s}}{3.06m^2}=0.42\frac{m}{s}$$

Then the liquid pumping power, assuming frictional loss negligible, is calculated by equation B.10

.

$$P = 1.3\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 1.274\ kW\ for\ 24\ hours$$

For the gas phase, it is assumed that the pressure from the exhaust (outlet) gas is enough to circulate through the column

Column pit volume=A*H=3.06m2*3m=9.18m^3

For10% volume allowance=9.18m^3+0.918m^3=10.1m^3

- ***Energy balance for static mixer and settling tank (flocculation unit)***

Static pre mixers instead of stirred tanks is selected because of their better uniformity of mixing and lower installed and operating and maintenance costs were recommended by Ronn put [16]. 3 inch diameter, six-element mixers for each of the two additives, which would provide the required mixing at a lower pumping power were used. Water flow rate to the static mixers given from the material balance is 2928m^3/day=2.03m^3/min=0.0338m^3/s. The mixers power rating is 80 watt for each. Therefore, 160watt per pond is the total power requirement per pond. Three flocculation units and a residence time of 1 hour is proposed for each pond.

Therefore, volume of settling tank

V_t= 2.03m^3/min *1/3*60min/h=40.6m^3

The pumping power requirement for water return based on Equation B.10 is

$$P = 0.0338\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 66.248W$$

- ***Energy balance for filtration***

A pumping requirement for water recycled from the filtration (32.97m^3/day) equivalent to 0.2 m head loss is assumed. Then P, based on Equation B. 10 would be

$$P = 0.00038\frac{m^3}{s} * 1000\frac{kg}{m^3} * 0.2m * 9.8\frac{m}{s^2} = 0.74W$$

- ***Energy balance for Drying***

The amount of water removed by drying is 3578.7kg/day per pond, then based on equation B.12

E=3578.7$\frac{kg}{day}$*0.54$\frac{kW.h}{kg}$=1932.49kW.h.=80kW for 24 hrs

I: Economic evaluation of biomass production for Tetraselmis suecica

No	Item	unit cost $	Bases	quantity	total Cost $ for 91ponds	total cost $ for 182ponds
land and builings						
1	Land	0				
2	Office and process building	615	meter sq.	1000&1200	615000	738000
Down stream processing						
5	Belt filter press		ton per hr	3.54t&7.08t	235000	360000
6	Drum drier		ton per hr	3.54t&7.08t	245000	390000
7	Water recycling pump	1800	3660m3/d	116&232	208800	417600
				subtotal	1303800	1905600
Pond system						
9	Pond	1900	pond	116&232	220400	440800
11	Carbonation pit	6000	10.1 m3/s	116&232	696000	1392000
12	Static mixer	650	number	116&232	75400	150800
13	Static mixer	650	number	116&232	75400	150800
14	carbonation water pump	14000	1.3 m3/s	116&232	1624000	3248000
15	Harvesting water pump	3000	0.067m3/s	116&232	348000	696000
16	Ferric metring pump	200	small	116&232	23200	46400
18	Settling tank	1800	40.6m3	116&232	208800	417600
19	Settling tank	1800	40.6m3	116&232	208800	417600
20	Settling tank	1800	40.6m3	116&232	208800	417600
21	Water return pump	1500	0.033m3/s	116&232	174000	348000
				Subtotal	3862800	7725600
			Equipment total		5166600	9631200
	Installation 10% of equipment total.				516660	963120
				Installed Cost	5683260	10594320
				Working Capital 10%	568326	1059432
		Total Capital Investment (installed +working)			6251586	11653752
22	Materials	line 1	line 2	unit cost $/kg	cost $/a	cost $/a
23	Ammonia (kg/day)	8117.6	16235.2	0.12	292233.6	584467.2
24	Ammonium phosphate(kg/d)	2779.3	5558.6	0.25	208447.5	416895
25	Ferric ion (kg/day)	84.9	169.8	0.16	4075.2	8150.4
26	Water make up (m3/day)	9280	18560	0.02	55680	111360
				Total	560436.3	1120872.6

table continued…

	Energy per pond			cost $/kwh		
27	Carbonation pump power (kW)	1.274		0.03	31921.344	63842.688
28	Static mixers power (kW)	0.08		0.03	2004.48	4008.96
29	Power for drying (kW)	80		0.03	2004480	4008960
30	Water recycling pump (kW)	0.00074		0.03	18.54144	37.08288
31	Water return pump (kW)	0.0663		0.03	1661.2128	3322.4256
				Total	2040085.578	4080171.156
			Salary			
		Quantity	$Permonth	$ Per year		
	Labour	116 &332	100	1200	139200	398400
32	Forman	9 & 14	200	2400	1800	33600
33	Technicians	4 & 6	300	3600	14400	21600
34	Finance	2&3	200	2400	4800	7200
35	Adminstration	2&3	200	2400	4800	24000
				Total Labor	165000	484800
			Total Production cost		2765521.878	5685843.756
	Algae production		kg/d	Price ($) per kg	price $/a	price $/a
		116 pond	332 pond			
36	Biomass	85000	170000			
37	Lipid	25500	51000	0.4	3060000	6120000
38	Meal (or fuel)	59500	119000	0.05	1785000	3570000
				Total Income	4845000	9690000
				Gross profit	2079478.122	4004156.244
				Depreciation 10% of installed	568326	1059432
				Net profit (35% tax)	982248.8791	1914070.758
				Pay Back Period	6.364564147	6.088464572

J: Costing of oil extraction

Capital cost =7650 ton/a*1000kg/ton*0.9liter/kg*0.359gal/liter*$0.5/gal=$1235857.5

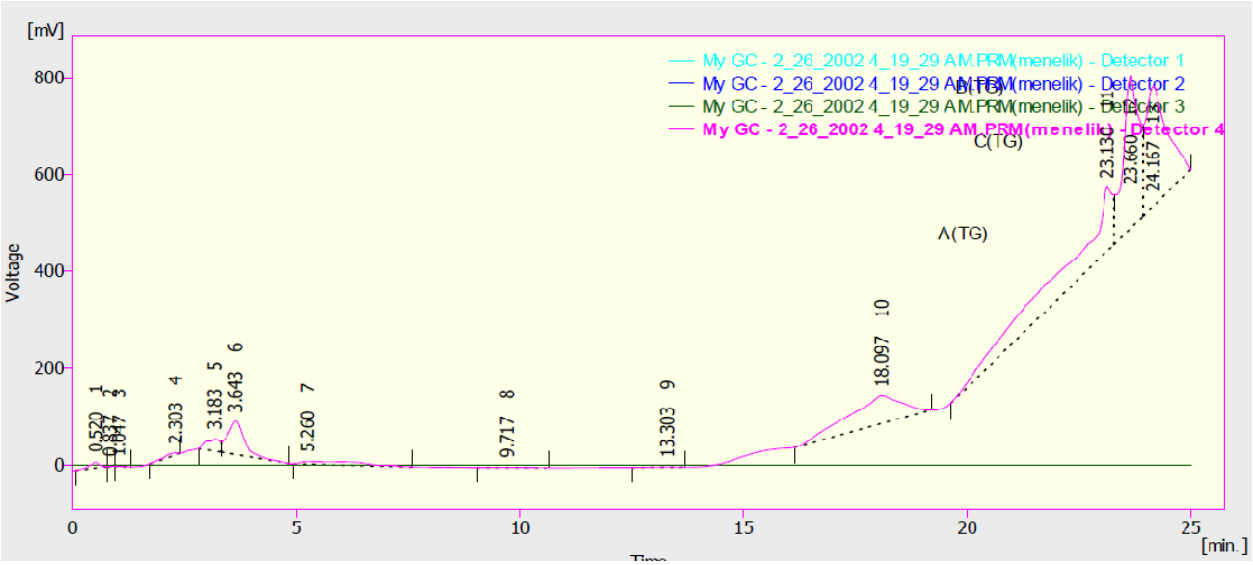
Operating cost=7650*$35=$267750

For the production line of 15300 ton per year

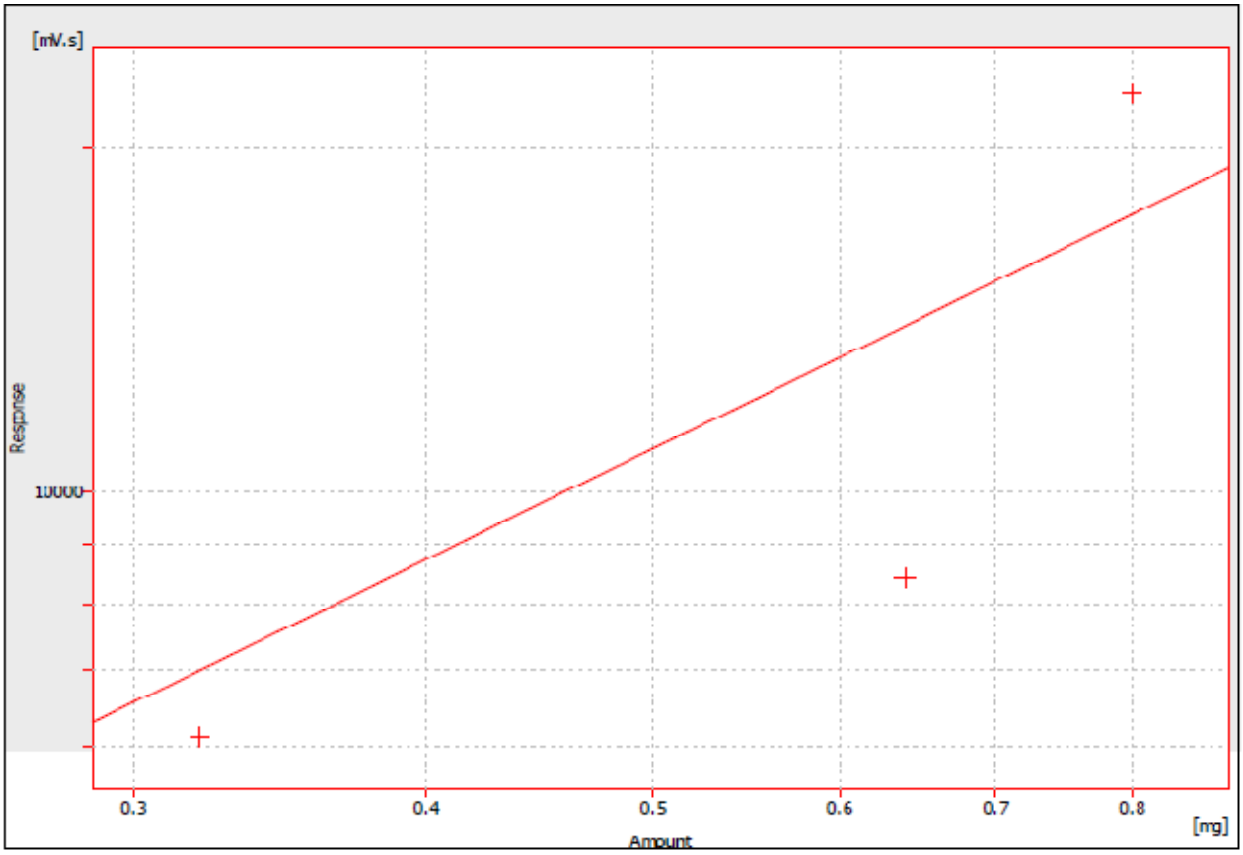
Capital cost =15300 ton/a*1000kg/ton*0.9liter/kg*0.359gal/liter*$0.5/gal=$2471715

Operating cost= 15300*$35=$535500

K: Chromatogram result and Calibration curve for the HPLC



a. Chromatogram result



b. Calibration curve

L: Serface weather condition of Iluababora (Yayu) area.

	Unit	Climate data location
Latitude	°N	7.667
Longitude	°E	36.833
Elevation	m	1942
Heating design temperature	°C	12.96
Cooling design temperature	°C	27.39
Earth temperature amplitude	°C	12.84
Frost days at site	day	0

Month	Air temperature	Relative humidity	Daily solar radiation - horizontal	Atmospheric pressure	Wind speed	Earth temperature	Heating degree-days	Cooling degree-days
	°C	%	kWh/m^2/d	kPa	m/s	°C	°C-d	°C-d
January	21.2	40.2%	5.43	83.3	3.1	23.5	0	343
February	22.2	38.8%	5.82	83.3	3.0	24.9	0	340
March	22.0	50.8%	5.87	83.2	2.8	24.6	0	372
April	20.5	67.5%	5.64	83.3	2.8	22.2	0	319
May	19.2	76.9%	5.39	83.4	2.5	20.2	0	290
June	18.4	75.8%	4.87	83.5	2.4	19.3	4	258
July	17.7	75.9%	4.41	83.5	2.1	18.4	16	242
August	17.9	75.9%	4.64	83.5	1.9	18.5	11	249
September	18.3	74.2%	5.21	83.4	2.0	19.0	4	257
October	18.4	71.5%	5.39	83.4	2.4	19.0	2	272
November	18.9	58.5%	5.40	83.4	2.9	19.5	1	274
December	19.9	47.1%	5.41	83.4	3.1	21.3	0	310
Annual	19.6	62.8%	5.29	83.4	2.6	20.9	38	3526
Measured at (m)					10.0	0.0		

M: Financial analysis of biodiesel production

Simulation of biodiesel production

The simulation and modeling of the biodiesel production process was performed using Aspenplus simulation and modeling software. Two different biodiesel production capacities were analyzed. Thermodynamic packages, ELECNRTL, UNIFAC and UNIFACDMD were used for property and parameter calculation. NRTL for processes involved with electrolytes (ELECNRTL), referenced with UNIFAC was selected as the main thermodynamic package since the process of biodiesel production involves electrolytes (NaOH, HCl, and NaCl). Electrolytes behave differently and have different property parameters in solution from their pure component states. For example, Na^+ and OH^- have different parameters from NaOH. The referenced UNIFAC package is used for determination of properties that will not be calculated (or can not be calculated accurately) by NRTL. The UNIFACDMD (UNIFAC modified by DORTMUND) was particularly used for evaluation of the property parameters for the washing column block by overriding the main property package ELECNRTL. The sensitivity analysis calculation of the washing column by the ELECNRTL referenced with UNIFAC was never converged easily and the result was not in consistent with experimental reported values.

Although the kinetic data was available for the transesterification reaction, a conversion reactor (with 96.6 %conversion of oil) was used in the model for three reasons. The first one is that the kinetics of the transesterification reaction does not give the same yield of biodiesel reported by experimental results. Because, there is a side reaction of saponification among the catalyst, the FFAs and methanol. This reduces the extent of the transesterification reaction by consuming the catalyst and the reactants. The second reason is that the soap that is formed by the saponification reaction reduces the rate of the reaction by forming an emulsion between the reactants and the products. Thirdly, modeling the reaction kinetics accurately for both transesterification and saponification on the reactor is a difficult task since the reaction interaction between the catalyst, soap, the anions, the cations, and reactants of the transesterification reaction involves more than 10 reaction paths. [29].

The process for the neutralizer was modeled by the procedure in the Aspenplus simulation for process involved with reactants which interact between reaction and electrolyte chemistry. In the neutralization reaction, there are basically three kinds of reaction taking place. The reaction involving are the irreversible complete salt precipitation reaction between Na^+ and Cl^- in aqueous solution, the complete dissociation of NaOH in to Na^+ and OH^-, and the reversible partial dissociation of HCl in to H^+ and Cl^-. The equilibrium kinetic constants for the electrolyte chemistry were available in the Aspenplus electrolyte chemistry data base system.

Biodiesel purity of 99.8% w/w and glycerol 99.7% percent was obtained. Glycerol with a composition above 99.4 %w/w is regarded as a high purity of glycerol. Therefore, the process system that gives a high value product of glycerol was used. The price of glycerol is a strong function of its purity. High purity glycerol can be sold as high as $1.7 per kg, more than two folds of the value for low quality glycerol [40]. The process flow sheet used for the biodiesel production was adopted from Velosa and Gomez [41] and is shown in Figure M 1. The inputs to the process simulations based on the data obtained from Velosa and Gomez [41] and from the discussions above and sensitivity analysis are tabulated in Table M 1

Table M 1: Inputs to the simulation of material and energy balance for biodiesel

Equipment				Material input	
Name	Pressure and/or Temperature	Reflux ration & No of stages	Thermodynamic package	Name	Flow rate (kmol/h)
Mixer	4 bar		ELECNRTL referenced with UNIFAC	Oil	1.2
Oil heater	4 bar, 80^OC		ELECNRTL referenced with UNIFAC	Methanol	3.529
Reactor	4 bar, 80^OC		ELECNRTL referenced with UNIFAC	NaOH	0.25
Methanol dist.	0.2 bar	0.1 and 4	ELECNRTL referenced with UNIFAC	HCl	0.25
Cooler	60^OC		ELECNRTL referenced with UNIFAC	Water	0.666
Wash colm.	60^OC	4	UNIFACDMD		
Neutralizer	1 bar		ELECNRTL referenced with UNIFAC		
Separator	1 bar		ELECNRTL referenced with UNIFAC		
Biodiesel dist.	0.04 bar	0.4 and 8	ELECNRTL referenced with UNIFAC		
Glycerol dist.	0.04 bar	1 and 4	ELECNRTL referenced with UNIFAC		

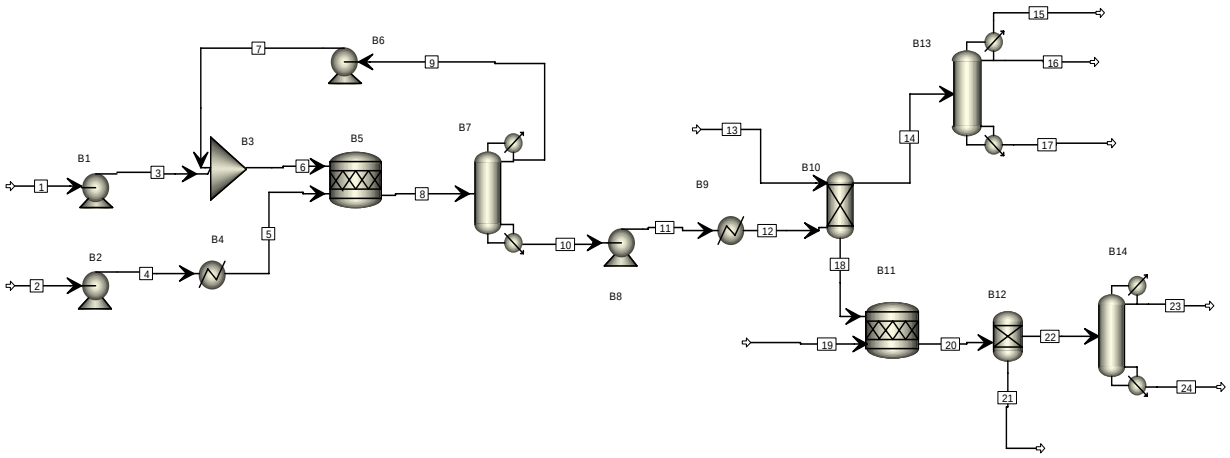


Figure M 1: Process flow sheet for biodiesel production.

Sensitivity analysis of methanol and biodiesel distillation columns

Sensitivity analysis for unit operation of methanol and biodiesel distillation columns were done to determine the block specifications that recover the excess methanol and give biodiesel purity higher than the minimum value specified by the ASTM D 6751 [36] and EN 14214 [38] biodiesel standards and minimum utility requirements.

Sensitivity analysis for methanol distillation column

The required molar stoichiometric ratio of methanol to oil for transesterification reaction is 3:1. However, in order to drive the reaction forward and to get higher oil conversion, methanol to oil molar ratio 6:1 was employed as a recommended value (see the transesterification section 2.8.1.2.). In order to recover the excess methanol and keep the 6:1 molar reactant ratio, methanol should be separated from the process as much as possible and recycled back to the transesterification reactor. A distillation column was used to recover the methanol according to the process flow sheet selected. The flow rate of the input process stream to the column cannot be altered since it is the out put of the transesterification reactor. Therefore, determination of the minimum reflux ratio and number of stages of the column that would give the best methanol separation efficiency with lower utility requirement was performed by sensitivity analysis. The effect of reflux ratio on methanol distillate purity, methanol mass fraction in the bottom product (recovering efficiency), condenser duty, and reboiler duty was investigated. The distillate molar reflux ratio was only varied from a minimum value of 0.1 up to 1.5 since relatively methanol has higher relative volatility to biodiesel, oil and glycerol. The result of the sensitivity analysis is shown in Table M 2.

Table M 2: Sensitivity analysis result for methanol distillation column

Molar reflux ratio	Methanol purity in distillate	Methanol composition in bottom product	Condenser duty	Rebioler duty
Molar	Mass fraction	Mass fraction	Gcal/h	Gcal/h
0.1	0.99840682	0.001474	-0.03866	0.288797
0.2	0.99843034	0.001474	-0.04215	0.292278
0.3	0.99845985	0.001474	-0.04564	0.29575
0.4	0.99849341	0.001475	-0.04912	0.299205
0.5	0.99852963	0.001475	-0.05259	0.302649
0.6	0.99856753	0.001475	-0.05605	0.306083
0.7	0.99860639	0.001475	-0.05951	0.309506
0.8	0.99864569	0.001476	-0.06295	0.312915
0.9	0.99868504	0.001476	-0.06639	0.31632
1	0.99872418	0.001476	-0.06982	0.319716
1.1	0.99876289	0.001476	-0.07324	0.323104
1.2	0.99880102	0.001477	-0.07666	0.32649
1.3	0.99883846	0.001477	-0.08006	0.329863
1.4	0.99887514	0.001477	-0.08346	0.333227
1.5	0.99891099	0.001477	-0.08685	0.336585

According to Table M 2, increasing the molar reflux ratio did not significantly increase the methanol distillate purity. Furthermore, the amount of unrecovered methanol left with the bottom product didn't show a decrement; in fact it shows a very little increment (in the sixth significant digit). Increasing the reflux ratio beyond the value of 0.1 resulted in higher condenser and reboiler duties with out bringing any advantage in the methanol recovery. Therefore reflux value of 0.1 for the methanol distillation column was selected and the corresponding minimum number of column stages that would give methanol distillate purity above 99.8% was 4.

Sensitivity analysis for biodiesel distillation column

The minimum biodiesel purity required by **EN 14214** [44] is 96.4%. Therefore sensitivity analysis was done to determine the minimum number of stages and reflux ratio that would give the biodiesel specification and purity. The result of the sensitivity analysis is shown in Table 5.5.

Table M 3: Sensitivity analysis result for biodiesel distillation column

Reflux ratio (molar)	Biodiesel distillate mole fraction	Biodiesel bottom flow rate kg/h	Condenser duty Gcal/h	Reboiler duty Gcal/h
0.1	0.99648	1.372702	-0.3811	0.82906
0.2	0.997461	1.031244	-0.41903	0.866906
0.3	0.997875	0.887589	-0.45698	0.904836
0.4	0.998098	0.809832	-0.49494	0.94279
0.5	0.998238	0.761228	-0.53291	0.980751
0.6	0.998334	0.72791	-0.57088	1.018725
0.7	0.998404	0.703625	-0.60885	1.056702
0.8	0.998458	0.6851	-0.64683	1.094681
0.9	0.9985	0.670472	-0.68481	1.132661
1	0.998534	0.658604	-0.72281	1.170663
1.1	0.998562	0.648785	-0.76079	1.208645
1.2	0.998586	0.640507	-0.79877	1.246628
1.3	0.998606	0.633427	-0.83675	1.284612
1.4	0.998624	0.627297	-0.87473	1.322597
1.5	0.99864	0.621935	-0.91272	1.360583

According to the results tabulated in Table M 3, the purity of biodiesel increases with molar reflux ratio. However increasing the molar reflux ratio above 0.4 did not increase the purity of biodiesel significantly. Furthermore, increasing the reflux ratio beyond 0.4 did not decreases the biodiesel bottom mass flow rate (which is a waste) while it increased the condenser and reboiler duty. Therefore, reflux ratio value 0.4 was used for simulation and the value of minimum stage number that brought stability and the required biodiesel purity was 8.

Process simulation

The biodiesel production process was simulated based on the data in Table M 1 and the flowsheet in Figure M 1. The material and energy balance result of the simulation for the two different capacity production lines are shown in Table 5.6 and 5.7 in the next pages. .

Table M 4: Results of Material and Energy balance for lower capacity biodiesel production

Table M 5: Results of Material and Energy balance for higher capacity biodiesel production

Costing and financial analysis of biodiesel production

Process simulation and costing was done using a product of Aspen tech simulation softwares. Aspen Plus process modeling and simulation and Aspen Icarus process evaluator was used for calculating the material and energy balance and the project evaluation respectively.

Project costing and evaluation of the biodiesel production was done by Aspen Icarus Process Evaluator, a product of Aspen tech. The project evaluation was done after a complete mapping and investment criteria input specification was performed. The results of the over all financial analysis of the two different capacity production facilities and the inputs of the project evaluation criteria are shown in Table 5.8. Detail project evaluation, including all quantities and costs of site clearing, construction, and installation phases of the process is included in the CD attached with the back of this paper. Since the project evaluation report for each line is prepared with a document which contains more than 1200 pages of detail analysis, it can not be presented in this paper. However, a Microsoft word version of the Aspen Icarus report file was prepared and included in the CD for ease of access and reference.

The price of raw materials was obtained from ICS pricing [40]. The price of the oil was determined based on the financial analysis of the algal biomass production facilities.

The payback period of the smaller and larger capacities was 4.94 and 3.96 respectively, as it is generally expected for chemical processes. This was mainly because the cost of equipment did not increase linearly with size. Running costs and utility requirement also shows similar behavior.

Table M 6: Executive summary for the financial analysis of the two production lines.

PROJECT NAME:	Biodiesel production from algae
CAPACITY:	7410960 kg/a biodiesel at $ 0.8/kg
PLANT LOCATION:	Ethiopia
Start Date for Engineering	1-Jan-10
Duration of project completion phase	41 weeks
Length of Start-up Period	20 weeks
Completion Date for Construction	October 18, 2010
Currency Conversion Rate	1
Total Project Capital Cost	$4.18E+06
Total Operating Cost	$4.08E+06
Total Raw Materials Cost	$3.60E+06
Total Utilities Cost	$94840.3
Total Product Sales	7$.21E+06
Desired Rate of Return	20%
P.O. Period	4.94
PROJECT NAME:	Biodiesel production from algae, larger capacity.
CAPACITY:	14853319 kg/a biodiesel at $ 0.8/kg
PLANT LOCATION:	Ethiopia
Start Date for Engineering	1-Jan-10
Duration of project completion phase	44 weeks
Completion Date for Construction	November 06, 2010
Length of Start-up Period	20 weeks
Currency Conversion Rate	1
Total Project Capital Cost	$5.64E+06
Total Operating Cost	$7.96E+06
Total Raw Materials Cost	$7.28E+06
Total Utilities Cost	$13263.3
Total Product Sales	$1.45E+07
Desired Rate of Return	20%
P.O. Period	3.93