ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL & BIO-ENGINEERING

BIODIESEL FROM MICROALGAE BASED ON CO_2 RELEASED FROM CEMENT INDUSTRIES

(CASE STUDY: - DANGOTE CEMENT PLANT)

BY

MEKONNEN ASSEFA

JUNE, 2016

ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL & BIO-ENGINEERING

BIODIESEL FROM MICROALGAE BASED ON CO_2 RELEASED FROM CEMENT INDUSTRIES

(CASE STUDY: - DANGOTE CEMENT PLANT)

BY

MEKONNEN ASSEFA

A Thesis Submitted to the School of Graduate studies of Addis Ababa University, Addis Ababa Institute of Technology, in Partial Fulfilment of the Requirements for the Degree of Masters of Science in Chemical Engineering (Process Engineering).

ADVISOR: DR.ING.ABUBEKER YIMAM

JUNE, 2016

ADDIS ABABA

ETHIOPIA

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL & BIO-ENGINEERING

BIODIESEL FROM MICROALGAE BASED ON CO_2 RELEASED FROM CEMENT INDUSTRIES

(CASE STUDY: - DANGOTE CEMENT PLANT)

BY

MEKONNEN ASSEFA

A Thesis Submitted to the School of Graduate studies of Addis Ababa University, Addis Ababa Institute of Technology, in Partial Fulfilment for the requirement of the Degree of Masters of Science in Chemical Engineering (Process Engineering).

Approved by the Examining Board

Name	*Signature*	*Date*
Chairman,Graduate committee		
Advisor		
Internal examiner		
External examiner		

ACKNOWLEDGEMENTS

I would like to thank my Advisor Dr Ing Abubeker Yimam for his instruction and direction in the success to finish my master thesis in chemical engineering. I thank also the senior lab technicians Ato Hintsa and Ato Feysal for their invaluable help and efforts in laboratory part.

Thanks and gratitude to my Spouse, Etagegn Yirsaw and my brothers Birhanu Tefera and Girmachew Hailu for their support and encouragement of my spirit in difficult times. I am grateful and have great appreciation to Cadila pharmaceuticals Quality control and Assurance manager Ato Tegene Aklilu and East African Deputy General Manager her honour W/o Muna who have supported me in giving laboratory material and space.

Thanks and gratitude to my children Henok Mekonnen and Nardos Mekonnen because they brought happiness always to my heart.

Thanks and gratitude to all the AAiT School of chemical and bioengineering instructors who taught me.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS & ACRONYMS

AR	Analytical reagent
ASTM	American standard for testing and materials
AV	Acid value
B100	Biodiesel, pure
B5	Biodiesel 5% and Diesel 95%
BD	Biodiesel
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CCD	Central composite design
CCS	Carbon capture and storage
CDM	Clean development mechanism
CER	Certified emission reduction
CKD	Cement kiln dust
CO_2	Carbondioxide
CO_2 e	Carbondioxide equivalent
d.b	Dry basis
DeNox	Denitrification
ECRGE	Ethiopian carbon resilient green economy
EF	Emission factor
EPA	Environmental protection agency of United states
EU	European union
GHG	Green house gas
FAME	Fatty acid methyl ester
FFA	Free fatty acid
g,gm	gram
Gt	Giga ton
IPCC	Intergovernmental panel on climate change

ISBT	International society of beverage technologists
Kg	Kilogram
LDPE	Light density poly ethylene
Lt	Litre
m^3	Cubic meter
MgCO3	Magnesium carbonate
MgO	Magnesium oxide
MF	Mass flow
MOI	Ministry of industry
Mt	Million ton
MRU	Methanol recovery unit
NEG	Net energy gain
NOx	Nitrogen oxides
NSFA	Nonsaturated fatty acid
O_2	Oxygen
OD	Optical density
PBR	Photo bioreactor
RSM	Rapid surface method
SCF	Supercritical fluid
SFA	Saturated fatty acid
SV	Saponification value
TAG	Triacyl glycerides
US	United states

ABSTRACT

Fossil fuels which are recognised as common sources of energy are continuously decreasing in quantity due to increasing demand, Moreover, the increase in atmospheric carbondioxide from chemical industries like cement plants is resulting in global climate change. In order to achieve environmental and economic sustainability, 3rd generation biofuel derived from microalgae are considered to be the best alternative energy resource compared to 1st and 2nd generation biofuels. Mixed species of microalgae was sourced locally from Kilole Lake at Bishoftu district and found suitable feed stock to produce algal biodiesel in the laboratory. Experiments were carried out using PVC jars of 3.5 litre capacity using 0.1 to 4% carbondioxide concentration, air bubbling rate of 0.1 to 7.0 litre per minute and pH ranged between 5 -7. The maximum biomass was obtained 0.44 gm/lt at pH 7, bubbling rate 3.5 lt/min and 2% carbondioxide feed. Oil was extracted from the algal biomass and analysed for water content, acid value, and fatty acid composition and saponification value. Algal oil fatty acid composition was very low and as a result of this no pre-treatment of algal oil was needed. Biodiesel produced by transesterfication of algal oil performed by using sodium methoxide as catalyst, and it was analysed for kinematic viscosity, specific gravity, acid value and sulphated ash. The properties of biodiesel tested were within limits of ASTM standard. Scale up of biodiesel plant in integration with the cement industry facility was studied as a way to mitigate the carbondioxide released from the plant flue gas as well as to address the shortage of fossil fuel in our country. Using the preliminary design of the biodiesel plant, a production capacity of 5,860 ton/year biodiesel was obtained and it was possible to capture 22,893.3 ton per year carbondioxide released from the cement industry. The net energy ratio of the proposed plant is 1.03; meaning 3% of energy can be produced more than required by the process.

Key words: - Algal biomass, carbon dioxide, lipid oil, Biodiesel, Raceway pond

CHAPTER ONE

INTRODUCTION

1.1 Background

The world demand of fuel becomes more and more increased in recent years and there is no indication for decreasing trend of demand for fuel supply. Most of the research works have reported that the world's oil and gas supply will disappear within three decades and also other natural resources such as coal will extinct within a century .The over exploitation of fossil fuels and the increasing greenhouse gases are considered to be the forthcoming crisis for human's population. Especially, carbon dioxide, which is the main component of greenhouse gas emissions, poses great challenge to the world (MayZaw H., et al., 2013).

Biofuels derived from microalgae are considered to be an alternative energy resource that is devoid of the major drawbacks associated with biofuel from terrestrial plants (jatropha, palm oil, oil seeds etc...). Microalgae are able to produce 15–300 times more oil for biodiesel production than terrestrial plants on an area basis. Furthermore compared with conventional terrestrial plants which are usually harvested once or twice a year, microalgae have a very short harvesting cycle (1– 10 days) depending on the process), allowing multiple or continuous harvests with significantly increased yields (Giuliano et al, 2010).

The cement industry is one of the largest carbon emitting industrial sectors in the world. The cement manufacturing process is not only a source of combustion related CO_2 emissions, but it is also a large source of industrial process related CO_2 emissions. CO_2 emissions in the cement industry will continue to rise, even if new ambitious CO_2 policies are put in place. Between 9 and 10% of the world CO_2 emissions can be attributed to cement production. This

makes cement production a key emissions source. Almost 2 gigatonnes of CO_2 (70% of the total cement industry CO_2 emissions) is process emissions which cannot be reduced through energy efficiency measures. Therefore effective CO_2 reduction policies must not only focus on energy efficiency and fuel substitution, but also address process emissions (Michael et al, 2006).

This study focused on the development of best available technology for biodiesel manufacturing with sequestration of CO_2 from cement flue gas by microalgal photosynthesis.

1.2 Significance of the study

Ethiopia is the most promising location in the world for microalgae production due to the steady climatic condition (sunlight and temperature), cheap land near by carbon emitting source(cement plant) and ample rainfall as identified by study in Abraham, et al,2013. The estimates obtained from the study confirm that, there is a realistic potential for microalgae biodiesel production and will serve the biofuel industry to achieve this target and reduce the losses occurring in the large-scale open pond cultivation system.

Biodiesel from microalgae can help the country in reducing the shortage of diesel to vehicles, which is believed to be the richest source of biofuel than the earlier 1st and 2nd generation biodiesel feed stocks.

Once the production system established, algae can be harvested daily, since they can double their numbers every few hours and have potential to produce a volume of biomass and biofuel many times greater than that of the other biofuel feed stocks.

Algae can grow in nutrient rich waters like industrial waste water at the same time purifies this waste effluent producing a biomass suitable for biofuel production.

Algae can be cultivated to produce a variety of products for large to small production of plastics, chemical feed stocks, lubricants, and fertilizer and even cosmetic.

Most importantly this envisaged project under study when it comes practical will create a wide variety of jobs in the area where this project is implemented, i.e from research to engineering, from construction to farming, from marketing to financial services.

1.3 Problem of the statement

Mainly one of the possible causes of atmospheric air pollution is the release of carbon dioxide from chemical industries. In Ethiopia, among the industry sectors, the main industry causing atmospheric air pollution is cement industry (ECRGE, 2011). Nowadays the cement industry sector of Ethiopia is growing at a fast rate than the past decades. According to the report of the Ethiopian Ministry of industry (MOI,2014),the production volume of the cement industry will reach to be more than 27 million metric ton cement in 2020, in parallel to this, these cement industries will release about 24.3 million tone carbon dioxide per year.

Ethiopia is importing large amount fossil fuel for vehicles and industries, which is consuming about 70% of the foreign exchange reserve of the nation (Tadele, et al, 2013).It is vital to produce biofuel from biomass and other feedstock for sustainability of the energy demand of the country in general and, in particular to satisfy the demand of diesel for vehicles. Therefore, this paper will give special attention to biodiesel manufacturing from microalgae in integration with sequestration of carbon dioxide released from cement industries having efficient desulphurisation, focusing on Dangote cement industry as case study which have a modern and efficient desulphurisation and deNOx unit .The qualitative and quantitative composition of the flue gas composition of the Dangote cement industry showed that the carbon dioxide obtained from the flue gas of the industry is relatively pure (Appendix VI I) and can be used as main nutrient for the algae biomass growth.

At the end of the study, this paper will answer the following questions

- What is the possible amount of biodiesel to be produced from microalgae and its role in reducing the shortage of diesel fuel to Ethiopian vehicles?
- What is the amount of carbondioxide to be mitigated from the flue gas of the cement industry and the percent decrease of release of CO2 pollution by the industry.
- What is the net energy ratio of this microalgae biodiesel plant output.

1.4 Objectives

1.4.1 General Objective

The general objective of this study is to produce biodiesel from micro algae in tandem with mitigating CO_2 released from cement industries.

1.4.2 Specific Objectives

The specific objectives of the study are to

- Demonstrate that locally selected strain of micro algae can be grown and cultured in suitable medium needed for the desirable biodiesel production and CO_2 mitigation.
- Characterize the effect of mixing , pH and Carbondioxide amount on the growth of the algal biomass.
- Demonstrate that use of purified CO_2 of cement industry flue gas can be used as supply of carbon dioxide for the growth of microalgal biomass.
- Characterize the quality of the biodiesel produced from the microalgal oil as per the international biodiesel quality standard (ASTM).
- Propose an appropriate microalgal biodiesel manufacturing plant in tandem with CO_2 mitigation system nearby the area of the cement industry.

CHAPTER 2

LITERATURE REVIEW

2.1 The Algae: - Overview

Microalgae, recognised as one of the oldest living organisms, are plants lacking roots, stems, and leaves that have chlorophyll 'a' as their primary photosynthetic pigment and lack a sterile covering of cells around the reproductive cells. While the mechanism of photosynthesis in these microorganisms is similar to that of higher plants, they are generally more efficient converters of solar energy because of their simple cellular structure (EPA, 2010).

2.1.1 Types of Microalgae

There are three general types of unicellular algae: green, brown, and red.

Green algae: - belong to the group *Chlorophyta* and inhabit freshwater, marine, and moist terrestrial ecosystems. Even though their main carbon reserve is starch, they are known to produce large amounts of lipids under nutrient stress. Abundant lipid producers in the group *Chlorophyta* include *Chlorella vulgaris* and *Chlorella protothecoides*.

Brown algae: - belong to the group *Chrysophyta* and include diatoms that have lipid, not starch, as their carbon reserve and do not require nutrient stress to produce it. Organisms in the group *Chrysophyta* inhabit the same ecosystems as *Clorophyta*. *Chaetoceros gracilis* and *Chaetoceros muelleri*, two diatoms, are known to be excellent lipid producers.

Red algae :- which lack flagella, are less known for lipid production and belong to the group *Rhodophyta*. Some examples of red algae include *Palmaria palmate* and Coralline algae. They inhabit mainly marine ecosystems (Abodeely et al,2013)

2.1.2. Composition and oil content

More than 50,000 species of microalgae species exist today, but only 30,000 are identified as potential species for the biodiesel production. Table 2.1 gives oil yields of some of the potential algae species (Kumar, Sharama, 2013).

Table 1. Oil contents of different microalgae

S.N	Microalgae	Oil content(% dry weight)
1	Botryococcus braunii	25-75
2	Chlorella sp.	28-32
3	Crypthecodinium cohnii	20
4	Cylindrotheca sp.	16-37
5	Dunaliella primolecta	23
6	Isochrysis sp.	25-33
7	Monallanthus salina	>20
8	Nannochloris sp.	20-25
9	Nannochloropsis sp.	31-68
10	Neochloris oleoabundans	45-47
11	Nitzschia sp.	45-47
12	Phaeodactylum tricornutum	20-30
13	Schizochytrium sp.	50-77
14	Tetraselmis sueica	15-23

2.2 Global and regional carbondioxide emission

Climate change is one of the greatest and probably most challenging of environmental, social and economic threats facing the world this century. Carbon dioxide is the most important of the greenhouse gases released by human activities. It is the main contributor to climate change because of the quantities released. On a worldwide basis the primary sources of CO_2 generated from anthropogenic activities are fossil fuel combustion from industry and industrial processes such as cement production, transportation, space heating, electricity generation and cooking, vegetation changes in natural ecosystems.

Carbon dioxide is considered to be the major source of GHG responsible for global warming; Global CO_2 emissions more than doubled between 1971 and 2007.In 2007, global total CO_2 emissions due to human activities were more than 29.3 Gt. In 2009, total global CO_2 emissions were estimated to be 31.3 Gt, which represented an increase of 25% since 2000 and almost a 40% increase since 1990. Figure 1 shows the estimated CO_2 emissions from the world's top 25 largest emitting countries in 2008 and 2009. In 2009, the shares of the CO_2 emissions from developing countries were 53% of the global total compared to 44% for developed countries.

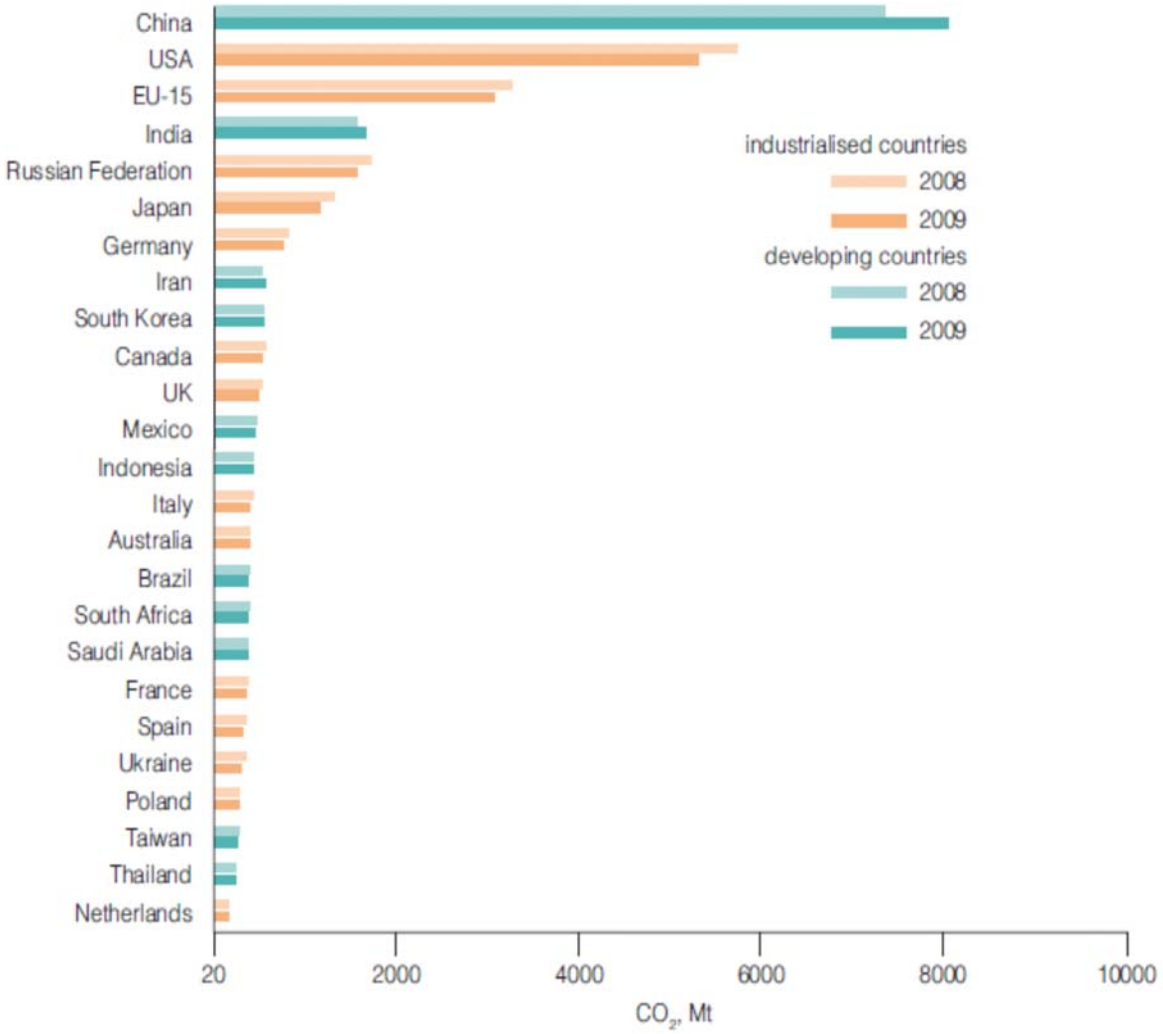


Figure 1 Carbondioxide emission from world top 25 emitters (2008-2009),Qian Zhu,2011

The world's top five largest emitters China, USA, India, Russia, Japan plus the EU ,15 countries comprise two thirds of total global emissions whereas the top-25 emitting countries emitted more than 80% of the world total (Qian Zhu,2011).

2.2.1 Carbondioxide emission by the Global cement industries

The cement industry is responsible for approximately 5% of the global anthropogenic carbon dioxide emissions. The cement industry emits nearly 900 kg of CO_2 per metric ton of cement produced. Because of the significant emissions per unit of cement produced, atmospheric concentrations of greenhouse gases cannot be stabilized without addressing this important

emissions source. The cement industry is faced with the prospect of sharp increases in global demand over the coming decades, as well as the prospect of climate change policies that could simultaneously call for reductions in emissions of greenhouse gases. The global cement demand is projected to increase by 60% to 105% over current levels by 2020. By 2050 the cement demand will increase approximately by 225% from current levels. Most of the increase in demand is in developing regions of the world, where the industry's current capital stock is relatively old and inefficient.

Cement related greenhouse gas emissions come from fossil fuel combustion at cement manufacturing operations (about 40% of the industry's emissions); transport of raw materials (about 5%); and combustion of fossil fuel required to produce the electricity consumed by the cement manufacturing operations (about 5%). The remaining cement related emissions (about 50%) originate from the process that converts limestone ($CaCO_3$) to calcium oxide (CaO), the primary precursor to cement. Based on worldwide cement production and associated CO_2 emissions, the average gross unit-based emissions for the industry is approximately 0.87 kg CO_2 per kg of cement. Regionally, however, unit-based emissions vary from 0.73 kg CO_2 per kg of cement (in Japan) to 0.90 kg CO_2 per kg of cement (in the United States).

2.2.2 The current carbondioxide emission level of Ethiopia

According to the Ethiopian green economy strategy, Ethiopia's current contribution to the global increase in GHG emissions since the industrial revolution has been practically negligible. Even after years of rapid economic expansion, to days per capita emissions of less than 2 ton CO_2 are modest compared with more than 10 ton per capita on average in EU and more than 20 ton per capita in the US and Austaralia.In 2011 Ethiopia's total emissions of around 150 Mt CO_2 represent less than 0.3% of global emission. Of the 150 Mt CO_2 in 2010, more than 85% of GHG emissions came from the agricultural and forestry (ECRGE, 2011).

They are followed by power, transport, industry and buildings, which contributed 3% each.(Figure 2)

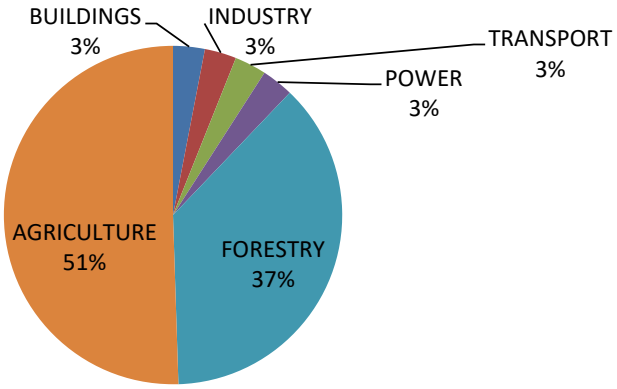


Figure 2. Major sources of emissions in Ethiopia. Source: - ECRGE, 2011

2.2.3 Preliminary evaluation of CO_2 release by Dangote cement (Ethiopia)

Due to lack of country specific CO_2 emission measurements of the cement industries in Ethiopia, the exact amount of carbondioxide released from cement industries cannot be obtained. Thus a general approach of intergovernmental panel on climate change(IPCC) guide line to estimate process CO_2 emissions from cement industries is used (IPCC,1996).

As per the IPCC guide lines, there are two methods to estimate preliminarily the process CO_2 emission in cement industries.i.e the cement based methodology and clinker based methodology. Several researches agreed that clinker based methodology is more reliable than cement based (Shen et al, 2014). Table 2 below provide recent available data of clinker production by Dangote cement industry since June 2015 to February 2016.

Table 2. Clinker productions in ton/month for Activity data of clinker based CO_2 estimation of the Dangote (Ethiopian) cement industry.

SN	Month	Average Clinker production, ton/day
1	June 2015	4162
2	July 2015	3493
3	August 2015	3965
4	September 2015	4448
5	October 2015	5163
6	November 2015	4146
7	December 2015	2812
8	January 2016	2837
9	February 2016	4420
	Average production per day	3,938

Source : Dangote cement(Ethiopia) production data base

Basically, the process- related emissions mainly come from calcinations of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) in the feed meal for clinker production, which could be expressed by the following stoichiometric equations:

$$CaCO_3(+950^oC) = CaO + CO_2 \uparrow \qquad \text{eq. 1}$$

$$MgCO_3(+950^oC) = MgO + CO_2 \uparrow \qquad \text{eq. 2}$$

Where CaO and MgO denote calcium oxide and magnesium oxide, respectively .CaO is the main content of clinker. According to the law of conservation of matter, each mole of CaO remained in the clinker emits one mole of CO_2. As a result, the clinker emission factor is the product of the fraction of lime in the clinker multiplied by the ratio of the relative mass of CO_2 released per unit of lime as below:

$$\text{EF clinker} = \boldsymbol{Fraction\ CaO}\ \frac{(\frac{44.01g}{mole}CO2)}{(56.08\frac{g}{mole}CaO)} \qquad \text{eq. 3}$$

= Fraction CaO x 0.785

The CaO content can vary from country to country. Thus, the IPCC Guide line recommends the default value for the fraction of lime in the clinker could be 64.6 % (IPCC, 2006), then the clinker emission factor is 0.646 x 0.785 = 0.5071.The IPCC also recommends that the above factor should be adjusted by the emission of the lost cement kiln dust (CKD) with around 2 to 6%, which represents additional CO_2 emissions not accounted for in the clinker emissions estimate. As a result the above EF clinker should be at least 0.5071 x 1.02 = 0.5172.

Therefore, the preliminary estimation of CO_2 emitted by the Dangote (Ethiopia) cement industry is calculated as

Total process CO_2 emitted per day = EF clinker X average daily production of clinker

= 0.5172 x 3,938 ton clinker

= 2,036 ton CO_2/day

Therefore it can be estimated that Dangote cement industry of Ethiopia is currently releasing 2,036 ton carbondioxide to the atmosphere per day.

It is crucial to find a means to mitigate the amount of carbondioxide released by cement industries in our country. This study focuses on Dangote cement industry in particular. The study proposed to implement a solution, based on algae culture and biomass production, which would allow for the CO_2 capture of cement flue gas and the production of biodiesel that can be used within and outside the industry.

2.3 Biofuels

Biofuels are referred to solid, liquid or gaseous fuels derived from organic matter. They are generally divided into primary and secondary biofuels (figure 3). While primary biofuels such as fuel wood are used in an unprocessed form primarily for heating, cooking or electricity production, secondary biofuels such as bioethanol and biodiesel are produced by processing biomass and are able to be used in vehicles and various industrial processes. The secondary biofuels can be categorized into three generations: first, second and third generation biofuels on the basis of different parameters, such as the type of processing technology, type of feedstock or their level of development.

2.3.1 First generation biofuel

First generation biofuels, also known as conventional biofuels, are made from sugar, starch or vegetable oil. First generation biofuels are produced through well-understood technologies and processes, like fermentation, distillation and transesterfication. These processes have been used for hundreds of years in many uses, such as making alcohol. Sugars and starches are fermented to produce primarily ethanol, and in smaller quantities, butanol and propanol. Ethanol has one-third of the energy density of gasoline, but is currently used in many countries, including Ethiopia, as an additive to gasoline. A benefit of ethanol is that it burns cleaner than gasoline and therefore produces less greenhouse gases. Another 1st generation biofuel, called biodiesel, is produced when plant oil or animal fat goes through a process called transesterfication. This process involves exposing oils with an alcohol such as methanol in the presence of a catalyst. The distillation process involves separating the main product from any of the by products of the reactions. Biodiesel can be used in place of petroleum diesel in many diesel engines or in a mixture of the two.

2.3.2 Second generation biofuel

The biomass sources for 2nd generation biofuels include wood, organic waste, food waste and specific biomass crops. Fast growing trees such as poplar trees need to undergo a pre-treatment step, which is series of chemical reactions that break down lignin, the “glue” that holds plants together, in order to make fuel. This pre-treatment step involves thermochemical or biochemical reactions that unlock the sugars embedded in fibers of the plant. After this step, the process to generate plant ethanol resembles that of 1st generation ethanol production. Additionally, straw and other forest residues can go through a thermochemical step that produces syngas (a mixture of carbon monoxide, hydrogen and other hydrocarbons). Hydrogen can be used as a fuel and the other hydrocarbons can be used as additives to gas oil.

2.3.3 Third generation biofuel

Third generation biofuels use specially grown plants such as algae as the energy source. These algae are grown and harvested to extract oil within them. The oil can then be converted into biodiesel through a similar process as 1st generation biofuels, or it can be refined into other fuels as replacements to petroleum-based fuels. Third generation biofuels are more energy dense than 1st and 2nd generation biofuels per area of harvest. They are cultured as low-cost, high-energy, and completely renewable sources of energy. Algae are advantageous in that it can grow in areas unsuitable for 1st and 2nd generation crops, which would relieve stress on water and arable land used. It can be grown using sewage, wastewater, and saltwater, such as oceans or salt lakes. Because of this, there wouldn't be a need to use water that would otherwise be used for human consumption. However, further research still needs to be done to further the extraction process in order to make it financially competitive to petro diesel and other petroleum-based fuels.

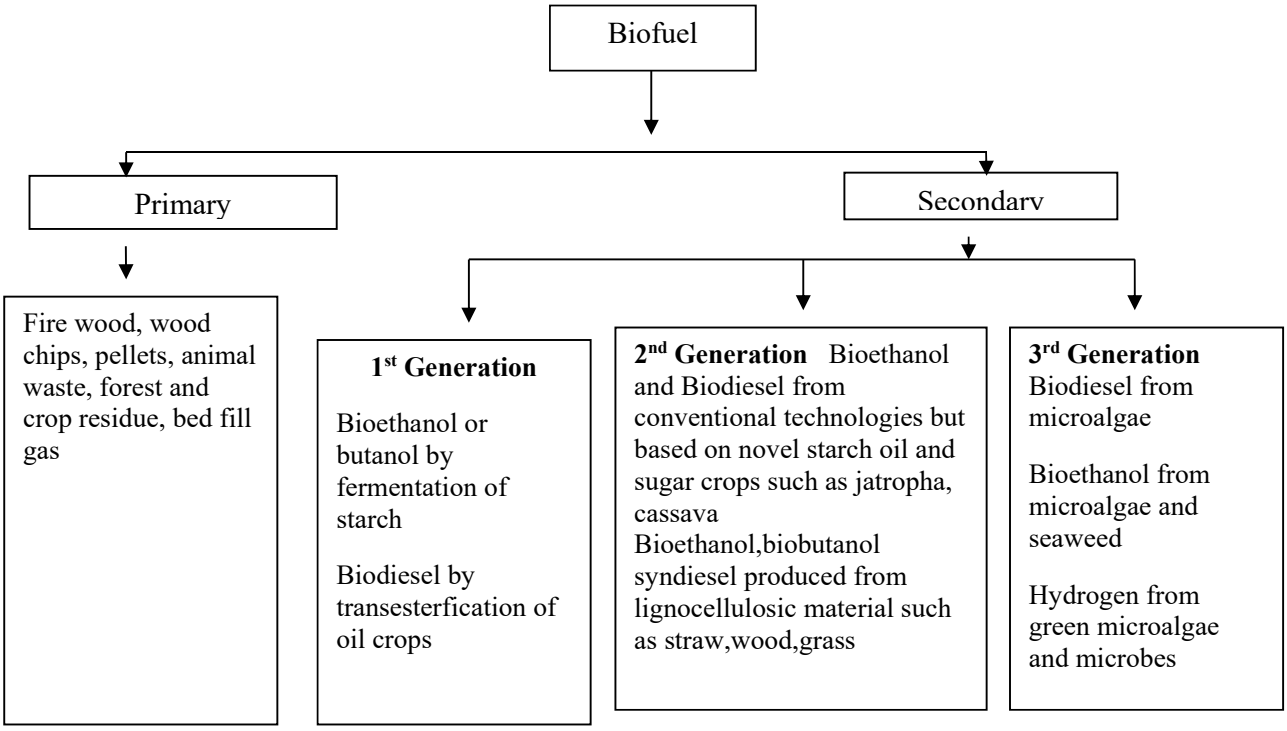


Figure 3. Classification of biofuel

2.3.4 Biodiesel over view

Biodiesel is a liquid biofuel obtained by chemical processes from plant oils or animal fats and an alcohol that can be used in diesel engines, alone or blended with diesel oil. ASTM International (originally known as the American Society for Testing and Materials) defines biodiesel as a mixture of long-chain mono-alkylic esters from fatty acids obtained from renewable resources, to be used in diesel engines. Blends with diesel fuel are indicated as ‘‘Bx’’, where ‘‘x’’ is the percentage of biodiesel in the blend. For instance, ‘‘B5’’ indicates a blend with 5% biodiesel and 95% diesel fuel; in consequence, B100 indicates pure biodiesel.

Biodiesel is produced from oils or fats and an alcohol, through a transesterfication reaction. This chemical reaction converts an ester (oil or fat) into a mixture of esters of the fatty acids that makes up the oil (or fat). Biodiesel is obtained from the purification of the mixture of

fatty acid methyl esters (FAME). A catalyst is used to accelerate the reaction (Figure 4). According to the catalyst used, transesterfication can be basic, acidic or enzymatic, the former being the most frequently used.

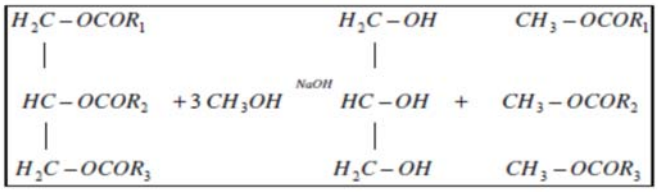


Figure 4. Basic transesterfication reactions with methanol

A generic transesterfication reaction is presented in the equation below

RCOOR' +R''OH $\xleftrightarrow{\text{cat.}}$ OH + RCOOR'' eq. 4

RCOOR' indicates an ester, R'OH an alcohol, R''OH another alcohol (glycerol), RCOOR'' an ester mixture and a catalyst: When methanol is the alcohol used in the transesterfication process, the product of the reaction is a mixture of methyl esters; similarly, if ethanol were used, the reaction product would be a mixture of ethyl esters. In both cases, glycerine will be the co-product of the reaction.

Although transesterfication is the most important step in biodiesel production (since it originates the mixture of esters), additional steps are necessary to obtain a product that complies with international standards. In consequence, once the chemical reaction is completed and the two phases (mix of esters and glycerine) are separated, the mix of methyl esters must be purified to reduce the concentration of contaminants to acceptable levels. These include remnants of catalyst, water and methanol; the latter is usually mixed in excess proportion with the raw materials in order to achieve higher conversion efficiency in the transesterfication reaction.

The mixture of fatty acids methyl esters (FAME) obtained from the transesterfication reaction must be purified in order to comply with established quality standards for biodiesel. Therefore, FAME must be washed, neutralized and dried. Successive washing steps with water remove the remains of methanol, catalyst and glycerine, since these contaminants are water-soluble. Care must be taken to avoid the formation of emulsions during the washing steps, since they would reduce the efficiency of the process. The first washing step is carried out with acidified water, to neutralize the mixture of esters. Then, two additional washing steps are made with water only. Finally the traces of water must be eliminated by a drying step. After drying, the purified product is ready for characterization as biodiesel according to international standards.

2.4 Manufacturing biodiesel from microalgae

Microalgae have great potential for biodiesel production, since the oil could be one to two orders of magnitude higher than that of other raw materials. Oil content is usually from 20 to 50%, although in some species it can be higher than 70 % (Chisti, 2007). However, it is important to note that not all microalgae are adequate for biodiesel production. High levels of CO_2, water, light, nutrients and mineral salts are necessary for the growth of microalgae. Production processes take place in photo biological reactors.

Algal biomass is one of the emerging sources of sustainable energy. Recent research has proved that oil production from microalgae is clearly superior to that of terrestrial plants such as palm, rapeseed, soybean or jatropha. Microalgae commonly double their biomass within 24h. Biomass doubling time during exponential growth is commonly as short as 3.5hr, can double their biomass in mean times that range from 2-5 days, achieving large yields, without the need for the application of pesticides, herbicides or fungicides. Microalgae are capable of synthesizing more oil per acre than the terrestrial plants which are currently used for the

fabrication of biofuels and using microalgae to produce biodiesel will not compromise production of food, fodder and other products derived from crops (Table 3).

Table 3. Comparison of sources of biodiesel

Crop	**Oil yield(L/ha)**	**Land area needed(M/ha)**
Corn	172	1540
Soy bean	446	594
Canola	1190	223
Jatropha	1892	140
Coconut	2689	99
Oil palm	5950	45
Microalgae	136,900	2

Source:-Adapted from Chisti Yusuf, 2007

Manufacturing steps of microalgal biodiesel

The production of microalgal biodiesel requires large quantities of algal biomass. Currently there are four major important steps in the production of biodiesel from microalgae.

- Culturing
- Harvesting
- Lipid extraction
- Transesterification

The biodiesel manufacturing process from microalgae using the carbondioxide release from the cement flue gas is shown below in the figure 5.

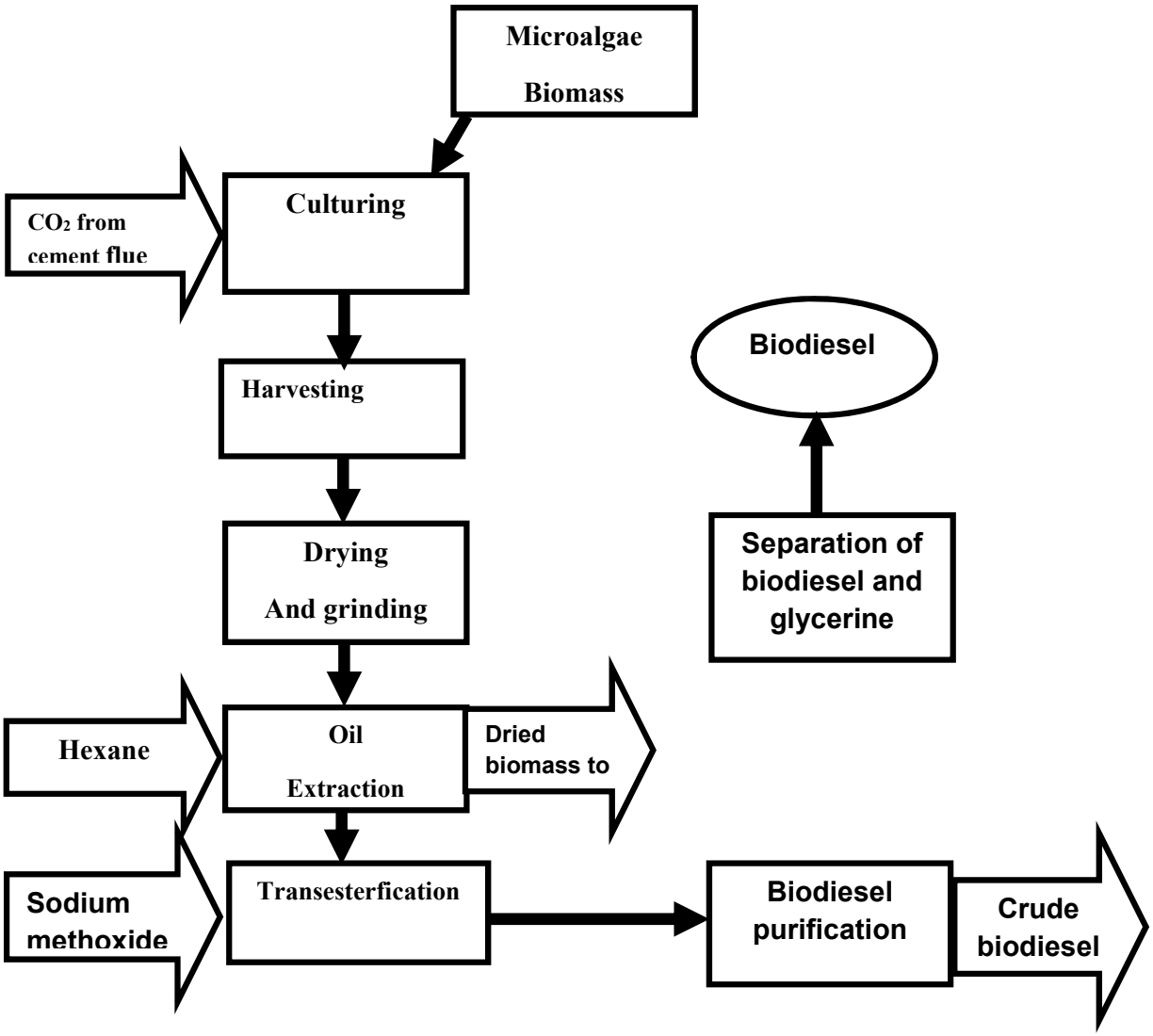


Figure 5. Flow diagrams for Biodiesel manufacturing from microalgae

2.4.1 Microalgae cultivation system

There are three distinct micro algae cultivation mechanisms.

- photoautotrophic
- heterotrophic and
- Mixotrophic cultivation mechanism.

Organisms that produce energy through photosynthesis are called photoautotrophs. Heterotrophic production requires organic substances (e.g. glucose) to stimulate growth, while some algae strains can combine autotrophic photosynthesis and heterotrophic assimilation of organic compounds are called mixotrophic.

2.4.1.1 Photoautotrophic cultivation

Photosynthesis is the most important biochemical process in which plants, algae, and some bacteria harness the energy of sunlight to produce food. Photosynthesis is a process in which green plants utilize the energy of sunlight to manufacture carbohydrates from carbon dioxide and water in the presence of chlorophyll.

Currently, photoautotrophic production is the only method which is technically and economically feasible for large-scale production of algae biomass for non-energy production. Two systems that have been deployed are

- open pond cultivation system
- Closed photobioreactor system.

Open pond cultivation system

Open-pond systems are shallow ponds in which algae are cultivated. Nutrients can be provided through runoff water from nearby land areas or by channelling the water from sewage/water treatment plants. The water is typically kept in motion by paddlewheels or rotating structures, and some mixing can be accomplished by appropriately designed guides (Demirbas, 2010).

Raceway ponds usually lined with plastic or cement, are about 15 to 35 cm deep to ensure adequate exposure to sunlight. They are typically mixed with paddlewheels, are usually lined with plastic or cement, and are between 0.2 to 0.5 ha in size. Paddlewheels provide motive

force and keep the algae suspended in the water. The ponds are supplied with water and nutrients, and mature algae are continuously removed at one end. Figure 6 shows a raceway pond (Chisti 2007).

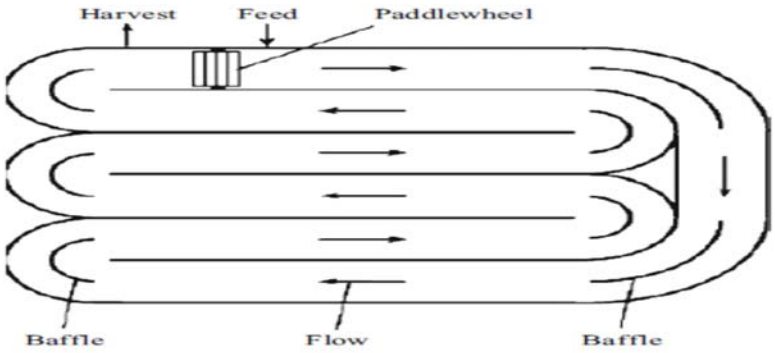


Figure 6. Raceway pond

Closed photobioreactor system

Microalgae production based on closed photobioreactor technology is designed to overcome some of the major problems associated with pollution and contamination risks of the described open pond production systems. (Richmond, 2004).

Closed systems include three basic types of photobioreactor

- the tubular photobioreactor,
- flat plate photobioreactor, and
- Column Photobioreactors.

The tubular photobioreactor

The most widely used photobioreactor is a tubular design, which has a number of clear transparent tubes, usually aligned with the sun's rays. Figure 7 depicts a tubular photobioreactor with parallel run horizontal tubes. A tubular photobioreactor consists of an

array of straight transparent tubes that are usually made of plastic or glass. This tubular array or the solar collector is where the sunlight is captured as seen in Figure 7. The solar collector tubes are generally 0.1m or less in diameter. Tube diameter is limited because light does not penetrate too deeply in the dense culture broth, which is necessary for ensuring a high biomass productivity of the photobioreactor (Demirbas, 2010).

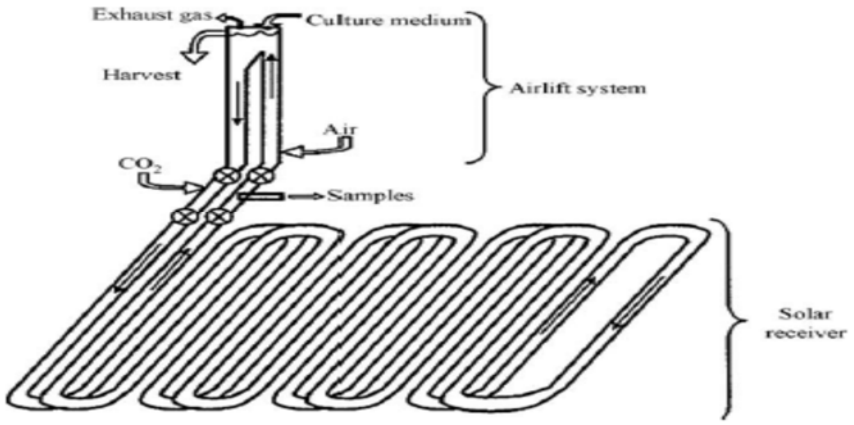


Figure 7. a horizontal tubular photobioreactor

Figure 8 shows another type of tubular photobioreactor with parallel run horizontal tubes (Chisti 2007).

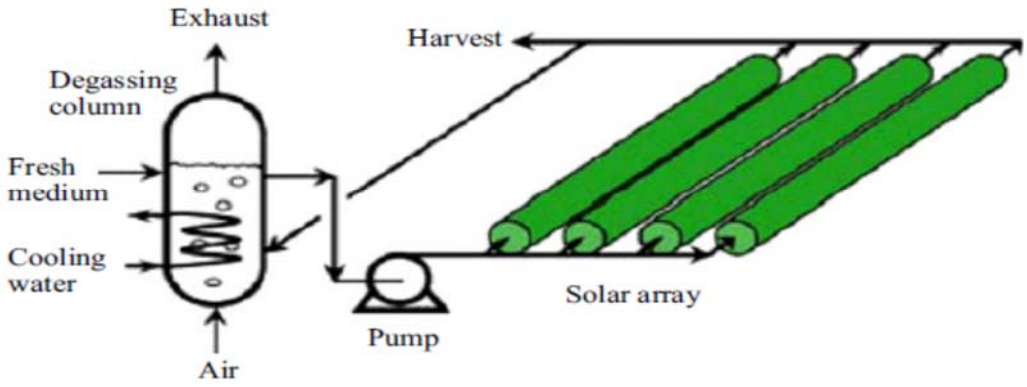


Figure 8.A tubular photobioreactor with parallel run horizontal tubes,

Flat plate photobioreactor

Flat-plated Photobioreactors are usually made of transparent material. The large illumination surface area allows high photosynthetic efficiency, low accumulation of dissolved oxygen concentration, and immobilization of algae. The reactors are inexpensive and easy to construct and maintain. However, the large surface area presents scale-up problems, including difficulties in controlling culture temperature and carbon dioxide diffusion rate and the tendency for algae adhering to the walls (Demirbas, 2010).

Column Photobioreactors

Column Photobioreactors offer the most efficient mixing, the highest volumetric mass transfer rates and the best controllable growth conditions. They are low-cost, compact and easy to operate. The vertical columns are aerated from the bottom, and illuminated through transparent walls, or internally. Their performance compares favourably with tubular Photobioreactors (Richmond,2004).

Hybrid system (Photobioreactor + raceway pond)

In hybrid systems, both open ponds as well as closed bioreactor system are used in combination to get better results. Open ponds are a very proficient and lucrative method of cultivating algae, but they become contaminated with superfluous species very quickly. A combination of both systems is probably the most logical choice for cost-effective cultivation of high yielding strains for biofuels. Open ponds are inoculated with a desired strain that was invariably cultivated in a bioreactor, whether it be as simple as a plastic bag or a high tech fiber optic bioreactor. Importantly, the size of the inoculums needs to be large enough for the desired species to establish in the open system before an unwanted species. Therefore to minimize contamination issues, cleaning or flushing the ponds should be part of the

aquaculture routine, and as such, open ponds can be considered as batch cultures (Roy et.al, 2014).

2.4.1.2 Factors affecting algal growth

The most important parameters regulating algal growth are nutrient quantity and quality, light, pH, turbulence, salinity and temperature. The most optimal parameters as well as the tolerated ranges are species specific and a broad generalization for the most important parameters is given in Table 4. Also, the various factors may be interdependent and a parameter that is optimal for one set of conditions is not necessarily optimal for another.

Culture medium/nutrients

Concentrations of cells in phytoplankton cultures are generally higher than those found in nature. Algal cultures must therefore be enriched with nutrients to make up for the deficiencies in the seawater. Macronutrients include nitrate, phosphate (in an Approximate ratio of 6:1), and silicate. Silicate is specifically used for the growth of diatoms which utilize this compound for production of an external shell.

Table 4. A generalized set of conditions for culturing microalgae

Parameter	Range	Optima
Temperature(°C)	16-27	18-24
Salinity(gm/lt)	12-40	20-24
Light intensity(Lux)	1,000-10,000	2,500-5,000
Photoperiod(light:dark,hrs)	-	Min 16:8 Max 24:0
pH	7-9	8.2-8.7

Source: - www.ftp.fao.org/docrep

Micronutrients consist of various trace metals and the vitamins thiamine (B1), cyanocobalamin (B12) and sometimes biotin. Two enrichment media that have been used extensively and are suitable for the growth of most algae are the Walne medium (Appendix II) and the Gaillard's F/2 medium (Appendix III).

The complexity and cost of the above culture media often excludes their use for large scale culture operations. Alternative enrichment media that are suitable for mass production of microalgae in large scale extensive systems contain only the most essential nutrients and are composed of agriculture grade rather than laboratory grade fertilizers (Appendix IV).

Light

As with all plants, micro-algae photosynthesize, i.e. they assimilate inorganic carbon for conversion into organic matter. Light is the source of energy which drives this reaction. Light intensity plays an important role, but the requirements vary greatly with the culture depth and the density of the algal culture: at higher depths and cell concentrations the light intensity must be increased to penetrate through the culture (e.g. 1,000 lux is suitable for erlenmeyer flasks, 5,000-10,000 is required for larger volumes). Light may be natural or supplied by fluorescent tubes. Too high light intensity (e.g. direct sun light, small container close to artificial light) may result in photo-inhibition. Also, overheating due to both natural and artificial illumination should be avoided. Fluorescent tubes emitting either in the blue or the red light spectrum should be preferred as these are the most active portions of the light spectrum for photosynthesis. The duration of artificial illumination should be minimum 18 h of light per day, although cultivated phytoplankton develop normally under constant illumination.

pH

The pH range for most cultured algal species is between 7 and 9, with the optimum range being 8.2-8.7. Complete culture collapse due to the disruption of many cellular processes can result from a failure to maintain an acceptable pH. In the case of high-density algal culture, the addition of carbon dioxide allows to correct for increased pH, which may reach limiting values of up to pH 9 during algal growth.

Aeration/mixing

Mixing is a key parameter for acceptable performance of culturing in microalgal bioreactors. Low mixing rates hamper gaseous mass transfer and might even permit biomass settling. In either case, poor mixing leads to emergence of stagnant zones, where light and nutrients are insufficiently available and anoxic/anaerobic conditions will thus prevail, which results in a decrease of productivity (Kumar and Sharma, 2013).

The most common methods of mixing in microalgal bioreactors are pumping, mechanical stirring and gas injection. Gas injection (bubbling) produces lower hydrodynamic stress, while providing good gas transfer and reasonable mixing efficiency; however, cell damage in sparged cultures increases as the biomass concentration increases, because exponentially higher degrees of stirring are needed to maintain a high-density culture at a predefined level of mixing. One approach to minimize this problem is to maintain a low gas input per nozzle, so as to reduce shear stress and consequent cell damage.

Temperature

The optimal temperature for phytoplankton cultures is generally between 20 and 24°C, although this may vary with the composition of the culture medium, the species and strain cultured. Most commonly cultured species of micro-algae tolerate temperatures between 16

and 27°C. Temperatures lower than 16°C will slow down growth, whereas those higher than 35°C are lethal for a number of species.

Salinity

Marine phytoplanktons are extremely tolerant to changes in salinity. Most species grow best at a salinity that is slightly lower than that of their native habitat, which is obtained by diluting sea water with tap water. Salinities of 20-24 g/lt have been found to be optimal.

2.4.1.3 Growth dynamics of microalgae

The growth of an axenic culture of micro-algae is characterized by five phases

Lag or induction phase

This phase, during which little increase in cell density occurs, is relatively long when an algal culture is transferred from a plate to liquid culture. Cultures inoculated with exponentially growing algae have short lag phases, which can seriously reduce the time required for up scaling. The lag in growth is attributed to the physiological adaptation of the cell metabolism to growth, such as the increase of the levels of enzymes and metabolites involved in cell division and carbon fixation.

Exponential phase

During the second phase, the cell density increases as a function of time t according to a logarithmic function:

$$C_t = C_0.e^{mt} \qquad \text{eq. 5}$$

with C_t and C_0 being the cell concentrations at time t and 0, respectively, and m = specific growth rate. The specific growth rate is mainly dependent on algal species, light intensity and temperature.

Phase of declining growth rate

Cell division slows down when nutrients, light, pH, carbon dioxide or other physical and chemical factors begin to limit growth.

Stationary phase

In the fourth stage the limiting factor and the growth rate are balanced, which results in a relatively constant cell density.

Death or "crash" phase

During the final stage, water quality deteriorates and nutrients are depleted to a level incapable of sustaining growth. Cell density decreases rapidly and the culture eventually collapses.

In practice, culture crashes can be caused by a variety of reasons, including the depletion of a nutrient, oxygen deficiency, overheating, pH disturbance, or contamination. The key to the success of algal production is maintaining all cultures in the exponential phase of growth. Moreover, the nutritional value of the produced algae is inferior once the culture is beyond phase 3 due to reduced digestibility, deficient composition, and possible production of toxic metabolites (www.fao.org).

2.4.2 Microalgae harvesting system

Choice of harvesting technique is dependent on characteristics of microalgae, e.g. size, density, and the value of the target products. Generally, microalgae harvesting is a two stage process, involving:

Bulk harvesting: - aimed at separation of biomass from the bulk suspension. The concentration factors for this operation are generally 100–800 times to reach 2–7% total solid

matter. This will depend on the initial biomass concentration and technologies employed, including flocculation, flotation or gravity sedimentation.

Thickening; - the aim is to concentrate the slurry through techniques such as centrifugation, filtration and ultrasonic aggregation, hence, is generally a more energy intensive step than bulk harvesting.

2.4.2.1. Harvesting by Flocculation

This is the first stage in the bulk harvesting process that is intended to aggregate the microalgal cells in order to increase the effective ‘‘particle’’ size. Flocculation is a preparatory step prior to other harvesting methods such as filtration, flotation or gravity sedimentation. Since microalgae cells carry a negative charge that prevents natural aggregation of cells in suspension, addition of flocculants such as multivalent cations and cationic polymers neutralises or reduces the negative charge. It may also physically link one or more particles through a process called bridging, to facilitate the aggregation. Multivalent metal salts like ferric chloride ($FeCl_3$), aluminium sulphate ($Al_2(SO_4)_3$ and ferric sulphate $Fe_2(SO_4)_3$ are suitable flocculants (Jing et al, 2013).

2.4.2.2. Harvesting by Gravity and centrifugal sedimentation

Gravity and centrifugation sedimentation methods are based on Stoke’s Law, i.e. settling characteristics of suspended solids is determined by density and radius of algae cells (Stoke’s radius) and sedimentation velocity. Gravity sedimentation is the most common harvesting technique for algae biomass in wastewater treatment because of the large volumes treated and the low value of the biomass generated. However, the method is only suitable for large (ca. >70 mm) microalgae such as Spirulina.

2.4.2.3 Drying of microalgal oil

The harvested biomass slurry (typical 5–15% dry solid content) is perishable and must be processed rapidly after harvest; dehydration or drying is commonly used to extend the viability depending on the final product required. Methods that have been used include sun drying, low-pressure shelf drying, spray drying , drum drying, fluidised bed drying, freeze drying, and Refractance Window technology drying (Jing et al, 2013).

2.4.3 Extraction process

The next step after harvesting and drying the microalgae biomass is liquid extraction i.e. algal oil extraction. Although the energy consumed in lipid extraction from dried microalgae biomass contributed a relatively small portion to the overall energy life cycle of microalgae biofuels (around 5–10%), the usage of appropriate extraction method is still vital as part of production practice. Using effective lipid extraction is essential in particularly for microalgae with low lipid content as reducing the lipid contents during extraction process may bring a significant impact towards the production cost of microalgae biofuels. There are three different categories of extraction:

- Chemical extraction
- mechanical extraction and
- biological extraction.

Chemical solvent extraction is the most common method used to extract lipid from microalgae biomass. This is because chemical solvent has high selectivity and solubility towards lipid and therefore, even inter-lipid can be extracted out through diffusion across the cell wall. The disadvantages of using chemical solvent are mostly related to their high toxicity towards human beings and the surrounding environment. Chemical solvents such as n-hexane, methanol, ethanol and mixed methanol–chloroform (2:1 v/v) (Bligh and Dyer

method) are effective to extract microalgae lipid, but the extraction efficiency is highly dependent on microalgae strains.

2.4.4 Microalgal Biodiesel production

After the extraction processes, the resulting microalgal oil can be converted into biodiesel through a process called transesterfication. The transesterfication reaction consists of transforming triglycerides into fatty acid alkyl esters, in the presence of an alcohol, such as methanol or ethanol, and a catalyst, such as an alkali or acid, with glycerol as a by-product. For user acceptance, microalgal biodiesel needs to comply with existing standards, such as ASTM Biodiesel Standard D 6751 (United States) or Standard EN 14214 (European Union). The triglycerides in microalgae are in the form of lipids. A lipid content of 20 – 50 wt-% of dry biomass is common, but by adjusting the cultivation the lipid content can reach up to 80 % (Chisti 2007). Process flow diagram of the biodiesel production process can be seen in figure 9.

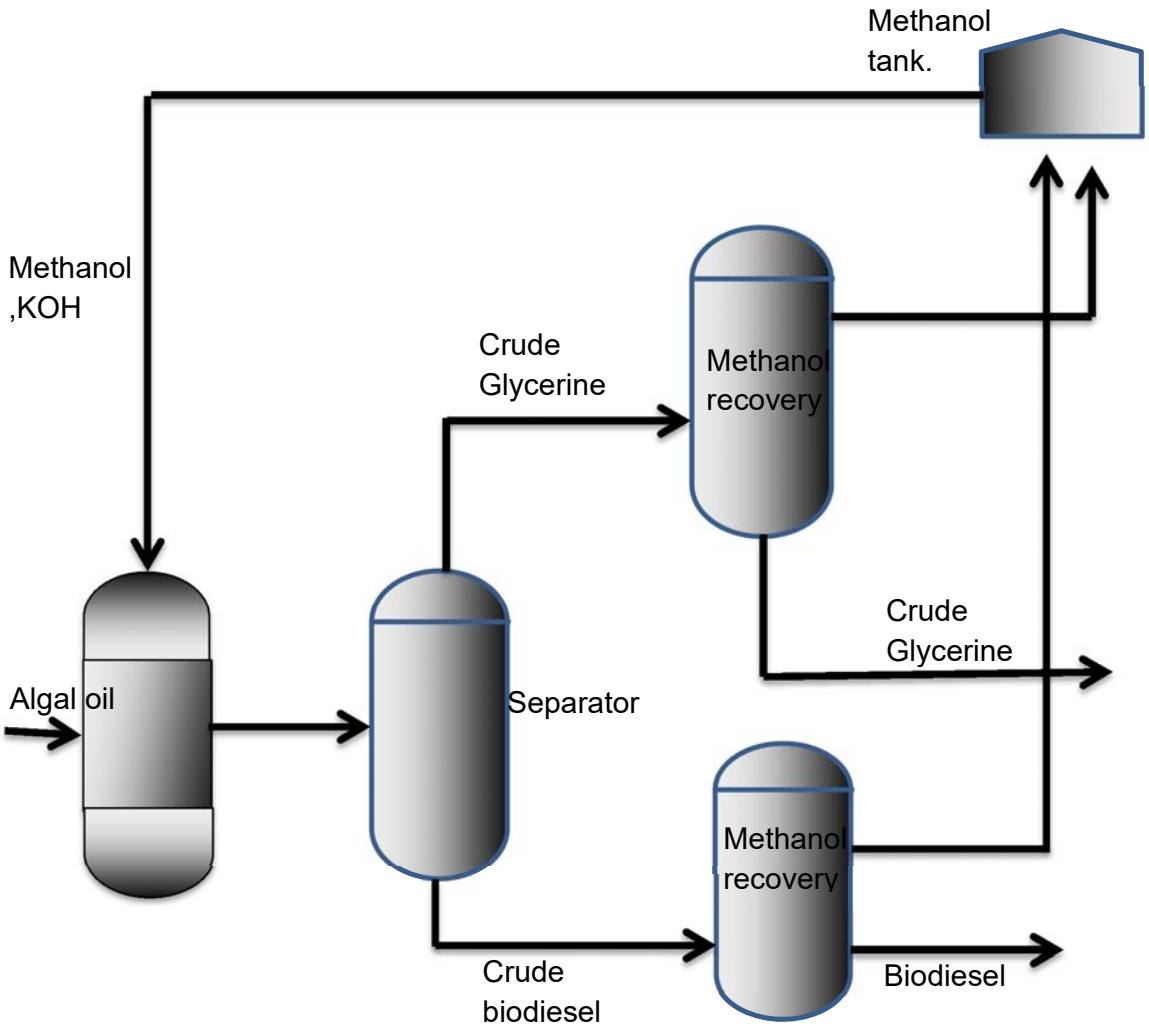


Figure 9

Figure 9.The process flow diagram biodiesel production process

CHAPTER THREE

MATERIALS AND METHODS

To satisfy the objectives of this study, the carbon dioxide gas that represent the purified carbondioxide of cement flue gas collected from G.Global gas manufacturing factory in Addis Ababa. Laboratory experiment were conducted below in order to generate data that are require.

- To identify the strain of microalgae used for maximum biodiesel yield and capturing of carbon dioxide
- To select best optimum conditions for maximum algal biomass productivity
- To select best flocculants for harvesting the algal biomass
- To characterise the quality of algal oil extracted
- To characterise the quality of biodiesel produced as per ASTM standard

3.1 Experiment on Identification of algal species for biodiesel and CO_2 mitigation

Samples of fresh water microalgae were collected from Hora Kilole Lake, near Bishoftu town, 14 kilometre distance east to the town. The fresh water algae sample was identified for algal strain type using standard method described by Sanet et al, 2006 at the laboratory of ALERT hospital in Addis Ababa (figure 10).

3.1.1 Materials

Materials used in this experiment were, microscope, Haemocytometer, pipet, cover slip and dropper.

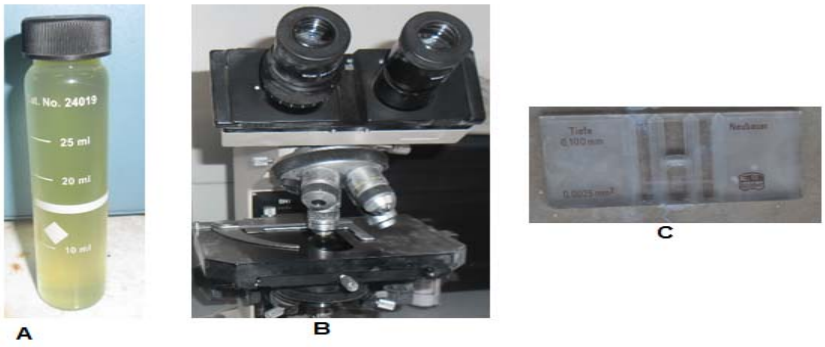


Figure 10. Identification of microalgae strain using light microscope: - A-specimen tube, B-Olympus light microscope C–Haemocytometer

3.1.2 Method

The Haemacytometer used has a Neubauer ruling with two counting grids in to which the samples was placed. Each counting grids consists of 4 squares, measuring 1mm along a side. The Haemacytometer chamber is 0.1 mm deep. The volume of sample in 1 square is taken 0.00025mm^3.The samples were thoroughly mixed and one drop, withdrawn from test sample was applied to the Haemacytometer grid at a position of application (figure 10).A total of 64 squares were counted resulting in count of algal strains per mm^3 (0.001 ml).The unit counts of each strain identified as per sanet et al, 2006, and the unit counts used to calculate the percent colony of each identified species in units per ml.

3.2 Experiment on determination of algal biomass productivity (Input for biodiesel)

3.2.1 Material

The major raw material used during this experiment is the fresh water green micro algae collected from Kilole Lake near Bishoftu town. The sample collected was transferred to the closed photobioreactor system (Figure 11) immediately before 2 hour after sampling to avoid contamination since the microalgae is sensitive to be affected by bacteria and protozoa.

The other solution used to this experiment is the BG11 media prepared (Appendix II) used as nutrient for the biomass growth and compressed CO_2 gas purchased from G.Global gas company in Addis Ababa, that represent the carbon dioxide purity of desulfurized flue gas of Dangote cement industry.

Apparatus

The equipment used to conduct this study are carbon dioxide containing cylinder, Air compressor, five plastic(PET) bottles of 3.5 litre capacity, plastic tubes(6 mm diameter),Perkin elmer spectrophotometer

Chemicals and reagents used

Chemicals used to prepare the media BG 11 were, sodium nitrate, potassium phosphate, iron sulphate, citric acid, manganese chloride, Zinc sulphate, copper sulphate, ammonium molybdate, ammonium vanadate,EDTA,cobalt chloride, Vitamin B12,sodium hydroxide , Ethanol and distilled water. All chemicals obtained from Cadila (Ethiopia) pharmaceutical industry plc given for the research.

3.2.2 Methods

Factors affecting algal biomass growth

The algae biomass is the main raw material and input for the production of biodiesel and bio-sequestration of carbon dioxide released from the cement industry. Therefore study on factors for affecting the Growth and productivity of algal biomass is important. Algal biomass productivity can be affected by different factors such as pH, mixing rate, time, amount of light, salinity, Temperature etc. But none of this equally contributes to the algal biomass growth. Depending on their relative effect and nature of the algae, this experiment has only considered three factors at three levels that have significant influence on biomass growth.

- pH at 5±0.5 ,7±0.5 and 9±0.5
- Mixing rate/Aeration – 7 litres/min, 3.5 litres/min, and 0.1 litres/min
- Amount of carbon dioxide – <0.1% ,2% and 4%

The study has been carried out with one response, biomass growth in gm. /lt. A total of 20 runs has been conducted. Dynamic biomass growth was determined by optical density(Absorbance) measurement at 515 nm using perkin elmer spectrophotometer at 515 (figure 11). Gas flow rate of the compressed air and carbon dioxide flow rate measured using gauge setting of the air compressor and carbon dioxide cylinder by simple positive displacement method.

Figure 11. Laboratory set up for closed PBR culturing for determination of optimum algal biomass productivity (AAIT post graduate research lab)

Experimental design

To conduct this experiment and optimise these variables, response surface with central composite design has been used. Because ,response surface methodology is a collection of mathematical and statistical technic that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimise these responses(Douglas c.montegomery,2001).The response surface

methodology(RSM) based on statistical principles can be employed as an interesting strategy to implement the microalgal biomass growth condition by performing a minimum number of experiments.

Therefore, in this work, optimisation of algal biomass growth condition for the design of photo bioreactor (pH,mixing rate,CO_2 supply amount) using RSM of biomass growth for

Figure 12. Perkin Elmer spectrophotometer for measurement of optical density of algal biomass at 515 nm.

The optimum condition for the photo bioreactor has been chosen and the influence of variables analysed using central composite design experiments, to do so design expert 9.0 software has been used.

Table 5. Experimental design using design expert (RSM of CCD)

	Factor 1	Factor 2	Factor 3	Response 1
Run	**A:pH**	**B:Mixing/Aeration**	**C:Carbondioxide supply**	**Algal biomass productivity**
	pH	**Litre/min.**	**%**	**gm/litre**
1	7	4	2.5	
2	9	7	4	
3	5	7	4	
4	9	1	1	
5	7	1.05	2.5	
6	7	4	2.5	
7	7	4	0.02	
8	5	7	1	
9	7	4	2.5	
10	7	4	2.5	
11	4	4	2.5	
12	5	1	1	
13	9	1	4	
14	7	9.05	2.5	
15	7	4	2.5	
16	9	7	1	
17	7	4	5.02	
18	7	4	2.5	
19	5	1	4	
20	10	4	2.5	

Experiment

Determination of optimum biomass growth condition for production of biodiesel feed stock.

Carbon dioxide gas that thought to represent the purity of carbon dioxide composition of flue gas of the Dangote cement plant was used to cultivate the microalgae (Appendix VII, VIII). Direct use of the Dangote cement industry flue gas for laboratory experiment was not possible due to financial constraint to compress the flue gas in gas container. The carbon dioxide gas that represent the cement flue gas (containing 99.9%v/v CO_2, 1.3 ppm SO_2 ,2.5 ppm NOx and remaining trace gases) was diluted with air mixture at different ratios using compressed air and supplied daily for each plastic containers. The mixing and aeration was provided by bubbling the carbon dioxide gas and compressed air in to microalgae systems with different Air gas volumetric flow rate per unit time (litres/minute) of 7,3.5 and 0.1 with ratio of 0.1%,2% and 4% carbon dioxide in combination. Gas tubes were connected from both the CO_2 and Air compressor to the containers inlet (Figure 11).

Culturing experiment of algae prepared in 5 transparent PET bottles having 3.5 litres capacity exposed to 6×15 W fluorescent day light equal to 3000 lumen in 8:16 hours (day, night) cycles at room temperature. All the culturing experimentation last 23 days.

The culture media BG11 (Appendix II) in addition to the supply of CO_2 gas used as nutrient for the algal culture (Ahmad,et al,2013).Algal growth was analysed in terms of optical density (absorption) which was periodically read at 515nm (Pooja and Himabindu ,et al) using a spectrophotometer (Perkin elmer,uv/visible, model CT06484,USA). A growth curve was generated based on the Optical Density (OD) readings. Algal dry cell weight was determined gravimetrically correspondingly by using oven at 50^0C to constant weight, using pre-weighed Petri dishes. In order to determine the dry weight of the algal biomass,dry

biomass was immediately transferred to desiccators over silica gel for dehydration overnight (24 hours) before weighing. Cell or biomass dry weight productivity was calculated at the end of the experiment, and correlation of dry weight versus optical density made based on the calibration produced optical density versus biomass quantity in gram/litre,

3.3 Experiments on Harvesting:

Determination of flocculation efficiency

Flocculation is one of the cheapest and principal steps in harvesting microalgae. In this experiment of harvesting microalgae using flocculation method, the flocculation efficiency of different types of flocculants was investigated. This flocculation experiment was carried out in stationary growth phase of microalgae. The experiment was conducted in measuring glass cylinder (500 ml capacity) with 500 ml testing volume, containing microalgae and flocculants ,Al_2SO_4(1.0 gm./lt) and FeCl3(1.0g/lit) efficiency investigated at pH=10.

3.3.1 Materials

Materials used in this experiment are measuring cylinder (500 ml),Aluminium sulphate(1gm/lt),Ferric chloride(1 gm./lt),and sodium hydroxide(1.0M) and sulfuric acid(1.0M)

3.3.2 Method

Flocculation efficiency of two known inorganic flocculants (Alum and ferric chloride) were carried out by adjusting the pH of 500ml of culture medium at pH 10 using 1M sodium hydroxide. The medium was mixed rapidly until the required pH value was achieved and then slowly for 1 minutes. After sedimentation under gravity for different sedimentation times

(30min,60min,90min,120min,240min and 480 min), an aliquot of 10 ml medium was withdrawn for measuring the dried sample weight.

The flocculants efficiency was measure at the end of each period by taking sample from half of the height of the clear zone. The flocculation efficiency was evaluated by comparing the amount of total suspended solids (TSS) gravimetrically. The flocculation or harvesting efficiency (%) was calculated using the following equation.

$$\text{Flocculation/harvest efficiency \%} = \frac{Wi - Wf}{Wf} * 100 \qquad \text{eq. 6}$$

Where, Wi the net weight of cell in suspension before flocculation, and W_f is the final net weight of suspension after flocculation

3.4 Experiment on Extraction of Algal oil

3.4.1 Materials

Apparatus used: - Soxhlet extraction set up containing condenser, thimble, water bath, round bottom flask (500 ml).

Materials used: - water, acetone, dried Algae powder

3.4.2 Methods

In this experiment algal oil was extracted from powdered biomass using solvent extraction method with acetone. Two Soxhlet extraction set up made using acetone. (Figure 13). The dry algae powder was put directly in the glass round bottom flask of 500 ml capacity containing acetone solvent and extracted using Soxhlet extractor water bath was used because

it makes controlling the temperature of the extraction,56^{O}C, easy and it ensured uniform heating.

Figure 13 .Soxhlet extraction set up for extraction of algal oil

300 ml of acetone was used for 80 gm of dried algae for extraction. The extraction was carried out in a Soxhlet extractor for 4 hour. After extraction time completed the round bottom flask containing the algae oil was removed from the hot water bath and allowed to cool.Then,the solvent was evaporated which left the lipids in the flask. The mass of algal oil recovered were determined and used to calculate the extraction yield. After extraction time is up, the solvent was used in the next batch of reaction.The oil yield of the algal biomass recovered from each flask were determined using the following equation.

$$\text{Oil yield} = \frac{\boldsymbol{Mass\ of\ algal\ oil\ obtained}}{\boldsymbol{Mass\ of\ dried\ algae\ powder}} \qquad \text{eq. 7}$$

3.5 Experiment on characterisation of algal oil

3.5.1 Determination of acid value and fatty acid of algal oil

To determine the acid value of the extracted algal oil,2 gm of oil was measured and poured in to a beaker. A neutral solvent containing equal volume of mixture of 25 ml diethyl ether and 25 ml methanol was taken and poured in to a beaker containing the oil. The mixture was stirred vigorously for 30 minutes.0.56 gm of potassium hydroxide(KOH) pellet was measured and placed in a separate beaker and 0.1 M potassium hydroxide was prepared,3 drop of phenolphthalein indicator was added to the sample and was titrated against 0.1M KOH till the colour change observed turned pink and persisted for 15 minutes. Titration against the standard alkali repeated three times.

The acid value calculated using the following formula (equation 8) and free fatty acid value determined by equation 3.4.

$$AV = \frac{\mathbf{56.1} * \boldsymbol{V} * \boldsymbol{N}}{\boldsymbol{W_{oil}}} \qquad \text{eq. 8}$$

Where

V= volume of standard alkali used

N= normality of standard alkali used

W_{oil} = weight of oil used

AV = acid value

$$FFA = \frac{\boldsymbol{AV}}{\mathbf{2}} \qquad \text{eq. 9}$$

3.5.2 Determination of saponification value

Saponification value represents the number of milligrams of KOH required to saponify 1 gm of fatty acid under the conditions specified. It is a measure of the average molecular weight or chain length of all the fatty acid present.

Therefore, the saponification value of the algal oil is determined by, first preparing the fresh alcoholic 0.5N KOH in ethanol.2 gm of algal oil weighed and transferred to a conical flask.25 ml of alcoholic KOH was added to it. A blank solution and treated similarly without sample is prepared alongside. The flask containing the sample well covered and placed in a steam water bath for 30 minutes shaking it periodically.1 ml of phenolphthalein added to sample and blank. Titration against 0.5 N HCL to get the point (Indhumathi et al, 2014).Titration against sample done three times. The saponification value calculated using formula 3.5.

$$SV = \frac{\mathbf{56.1}*(\boldsymbol{B}-\boldsymbol{A})*\boldsymbol{N}}{\boldsymbol{W_{oil}}} \qquad \text{eq. 10}$$

Where

B = volume of standard HCl consumed by blank

A = volume of standard HCL consumed by sample

N= normality of standard used

W_{oil} = weight of oil used

3.5.3 Determination of moisture content of algal oil

In order to determine the moisture content in the algal oil,10 gm of algal oil weighed in crucible and dried in an oven for 3 hours at 450^{O}C.after 3 hours the samples was cooled and

weighed. Sample redried in the oven for two consecutive 15 minutes until constant weight obtained.

3.6 Experiment on transesterfication of algal oil

3.6.1 Materials

Apparatus: - One reaction flask (250 ml), beaker (250 ml), Mixer,

Materials used: - Algal oil, sodium hydroxide, methanol (anhydrous),

3.6.2 Methods

58 gm of algal oil was measured (weighed) and poured in to a 150 ml reaction flask. A solution of sodium methoxide was prepared in a 250 ml beaker using 0.25 gm of NaOH pellet and 10.5 ml of anhydrous methanol. The solution was properly stirred until the NaOH pellet was completely dissolved in it. The sodium methoxide solution was then poured in to the reactor. Reaction was conducted at 60^0C temperature for 1 hour with constant stirring at 110 rpm (figure 14). After this process the reaction mixture was cooled to room temperature and the mixture was left to settle for 24 hours in a separatory funnel. After settling, the upper layer which was biodiesel was decanted in to a separate beaker while the lower which comprises of glycerol and soap was collected from the bottom of the separatory funnel (figure 15). The quantity of biodiesel collected was measured and recorded.

Figure 14. Transesterfication of algal oil to biodiesel

Washing and drying

Biodiesel must be washed to remove any remaining methanol, glycerine, catalyst, soaps and other impurities. Water used is warmed to about $45^{O}C$ and is passed through the esters to allow soluble material, excess catalyst and other impurities to stick to the water and be settled to the bottom of the vessel. The water is removed from the vessel periodically until the wash water drained out is clear or the pH of the biodiesel becomes relatively neutral. The biodiesel washing sometimes leaves the biodiesel looking a bit cloudy. This means there is still a little water in it.It was heated slowly to $100^{0}C$ and held there until all moisture present was evaporated.

Figure 15. Separation of biodiesel using separatory funnel

The biodiesel yield is calculated based on the following equation.

$$\text{Biodiesel yield} = \frac{\boldsymbol{Biodiesel\ collected}}{\boldsymbol{Weight\ of\ algal\ oil}} \qquad \text{eq. 11}$$

3.7 Experiment on characterisation of algal biodiesel.

3.7.1 Determination of specific gravity

To measure the specific gravity of the algal biodiesel, a clean dry empty density bottle (50 ml) is empty weighed and mass recorded. Then it is filled with distilled water and mass M1 recorded. Subsequently, it is filled with algal biodiesel and mass M2 recorded. The specific gravity is calculated using equation 3.7

$$\text{Specific gravity} = \frac{\boldsymbol{M2-M}}{\boldsymbol{M1-M}} \qquad \text{eq. 12}$$

3.7.2 Determination of kinematic viscosity

Viscosity is determined using a rotational viscometer.First,the viscometer spindle is inserted in position inside the device and made to be immersed fully in the 100 ml capacity beaker containing biodiesel sample at 40^{O}C and left to rotate at 100 rpm for few minutes until constant reading (Figure 16).

Figure 16. Rotational viscometer, Fungi lab alpha series, East African pharmaceuticals, Addis Ababa

The kinematic viscosity (v) is calculated by dividing the dynamic visicsity (η) with density of the biodiesel(ρ)

$$\text{Kinematic viscosity} = \frac{\boldsymbol{\eta}}{\rho} \qquad \text{eq. 13}$$

3.7.3 Determination of acid value

The acid value of the biodiesel is determined similarly as the procedure described in 3.5.1

3.7.4 Determination of pH

A pH meter (DBK digital pH meter) electrode inserted in to a buffer solution of pH 7 and calibrated. Then the pH electrode cleaned carefully and then inserted in to the beaker containing the biodiesel.pH measurement reading taken and recorded carefully.

3.7.5 Determination of ash content

A suitable platinum crucible is ignited below 550^{O}C for 30 minutes. Then it is allowed to cool in a desiccator over silica gel. The empty crucible weight recorded as M.Then about 1.0 gm of biodiesel placed inside the crucible and weighed as M1. The substance is first charred

using small amount of sulfuric acid (AR).Then it is ignited in the muffle furnace (Figure 17) at 550^{O}C to constant weight and Weight recorded M_2.Then the sulphated ash is calculated using equation 3.9.

$$\text{Sulphated ash content} = \left(\frac{\boldsymbol{M2-M}}{\boldsymbol{M1-M}}\right) * 100 \qquad \text{eq. 14}$$

Figure 17. Muffle furnace for sulphated ash determination, East African pharmaceuticals

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Identification of microalgae strain

4.1.1 Result

Identification of microalgae strain was made using Olympus binocular microscope at 40X as per the reference guide by sanet et al, 2006.With this magnification scale, it was only possible to identify two algal genera based on the guide taken from the identification manual of microscopic algae by sanet et al, 2006.These identified micro algae strain were Chlorella (phylum chlorophyta) and Diatom (phylum Bacilarophyta).In fact there were few other genera of microalgae being observed, but too difficult to identify using ordinary microscope used. Using haemocytometer of size $0.0025mm^2$ *0.1mm, about 64 quadrats has been counted. Based on this count the following genera of microalgae had been counted (Table 6).

Table 6 . Identification and count estimation of microalgae using microscope

SN	Genera of microalgae	Class of microalgae	Count Per ml	Percent colony
1	Chlorella	Chlorophyta (green algae)	$4.736x10^6$	67.77%
2	Diatoms	Bacillarophyta (Golden brown algae)	$1.792x10^6$	25.45%
3	Others	-	$0.512x10^6$	7.27%

4.1.2 Discussion

The result showed that the mixed sample taken from the lake consist of 67.7 % chlorella, 25.45% diatom and 7.27% other microalgae genera. Chlorella is the genus of single cell green algae belonging to the class chlorophyta (Appendix V). Diatom is class of Bacillariophyceae that includes a very conspicuous number of golden brown unicellular organisms.

The dominant strain of this mixed algae sample i.e. chlorella vulgaris having lipid content of (14-22%) which has been used to produce 68% of the biodiesel of this experiment, whereas diatom having lipid content of 12 to 45 %(Ayhan Demirbas,2010),which has been used to produce 26% of the biodiesel.Demirbas,2010 indicated that chlorella can fix carbon dioxide to 20-30%,NOx to 100ppm and SOx to 50-100 ppm.It also added that, there is no one strain or species of algae that can be said to be best in terms of oil yields for biodiesel,However,firstly diatom and secondly green algae have shown the most promise. This makes the mixed microalgae sampled from Kilole Lake near Bishoftu town to be best selective to this study to produce biodiesel and to mitigate the carbon dioxide released by cement industries.

4.2 Characterization of algal biomass growth condition (a feedstock for biodiesel production and CO_2 capture).

4.2.1 Result

Experiment on determination of algal biomass productivity has taken 23 days. Samples for optical density measurement taken at the 5^{th}, 7^{th}, 14^{th}, 18^{th}, and 23^{rd} day at wave length of 515 nm (Saddam et al, 2014), using UV-VIS spectrophotometer (Perkin elmer) and the result is recorded carefully in table 7.

Table 7 . Result of Optical density measurement of algal biomass cultured at room temperature (20^0C) and light illumination of 3000 lumen

SN	Growth condition			Optical density(measurement)					
	pH	Mixing (air flow rate lt/min)	CO_2 supply (%)	Day 1	Day 5	Day 7	Day 14	Day 18	Day 23
A	5±0.5	3.5	2	0.049	0.088	0.9	0.77	0.86	0.79
B	7±0.5	3.5	2	0.049	0.092	0.71	1.11	1.50	1.18
C	9±0.5	3.5	2	0.049	0.089	0.91	1.20	1.12	1.03
D	7±0.5	0.1	0.1	0.049	0.048	0.64	0.85	0.62	0.65
E	7±0.5	7.0	4	0.049	0.088	0.98	1.12	1.16	0.95

During the optical density measurement, 10ml of sample was taken from each culture vessels and diluted to 100 ml with distilled water. Then optical density (absorbance) measured by scanning between 450 nm and 700nm (Appendix I).Optical density measurement for green microalgae was taken at 515nm (Sadam et al,2014),and actual optical density(absorbance) measured based on equation 4.1

$$A_{actual} = A_{measured} + \frac{\mathbf{100}}{\mathbf{10}} \qquad \text{eq. 15}$$

To determine the algal biomass productivity in terms of grams per litre, calibration curve was produced by correlating optical density with dry weight at different concentration of the algal culture (table 8). A linear regression equation was derived to describe the relationship between the optical density and the cell density.

Table 8. Optical density versus biomass productivity

Sample Id	Optical density@515 nm	Algal biomass(gm/lt)
1	0.62	0.148
2	0.84	0.249
3	1.06	0.289
4	1.28	0.318
5	1.5	0.452

In the first day of the culturing experiment, the absorbance of all the culture vessels was uniform, as the same media was poured to each culture system before pH adjustment. Just at the 5th day, content turbidity seen almost in all culture vessels. Figure 18.Then At the 7th day faint green colour observed on each culture vessel except vessel D, at the 15th day deep green coloration of content with varying intensity observed which showed exponential growth of microalgal biomass in each culture vessel at different growth rate. Until the 18th day the growth rate continued rising and reached stationary phase. At the 23 rd day growth of all the vessels declined.

Maximum algal biomass growth observed on culture vessel B (0.44 gm/lt),the next higher value of growth observed on vessel E (0.326 gm/t),and after wards values of C (0.313 gm/lt) and A(0.086 gm/lt) observed.

Day 1 Day 5

Day 15 Day 18

Figure 18. View of culture condition of mixed microalgae at different level of pH ,mixing rate and CO_2 suplly,At research lab of AAIT,school of chemical and bioengineering

4.2.2 Discussion

4.2.2.1 Growth dynamics of the algal biomass growth

Optical density and cell biomass weight measurement were correlated to estimate the biomass productivity. This linear regression model (figure 19) yields an easy analytical method to estimate the mass of the microalgae in each culture vessel within 18 days of complete cycle.

Table 9. Biomass productivity of culture vessels at the 18th day.

Sample Id	Optical density@515 nm	Algal biomass(gm/lt)
A	0.86	0.23
B	1.50	0.44
C	1.12	0.31
D	0.62	0.15
E	1.16	0.33

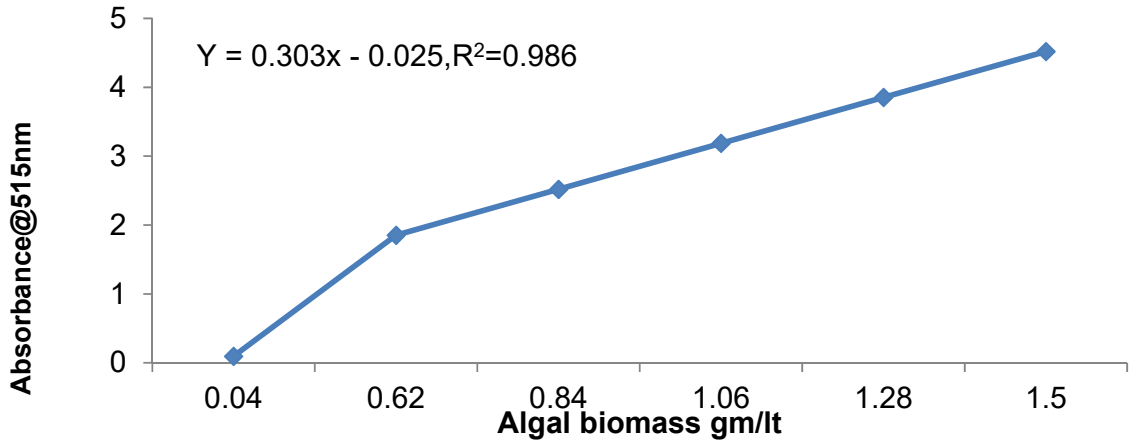


Figure 19.Calibration curve for correlating optical density with biomass productivity in gm/lt

The correlation is strongly tied with the coefficient of determination (R^2) greater than 0.986.Therefore optical density measurement was used to correlate cell density in gm/lt and equation 4.1 shows governing relationship.

$$Y = 0.303X - 0.025 \qquad \text{eq. 16}$$

Where Y = Algal biomass productivity in gm/lt

X = optical density (Absorbance) at 515 nm

The growth dynamics of each culture vessel is shown in figure 20 and the specific growth rate, doubling rate and time is discussed briefly in the following section

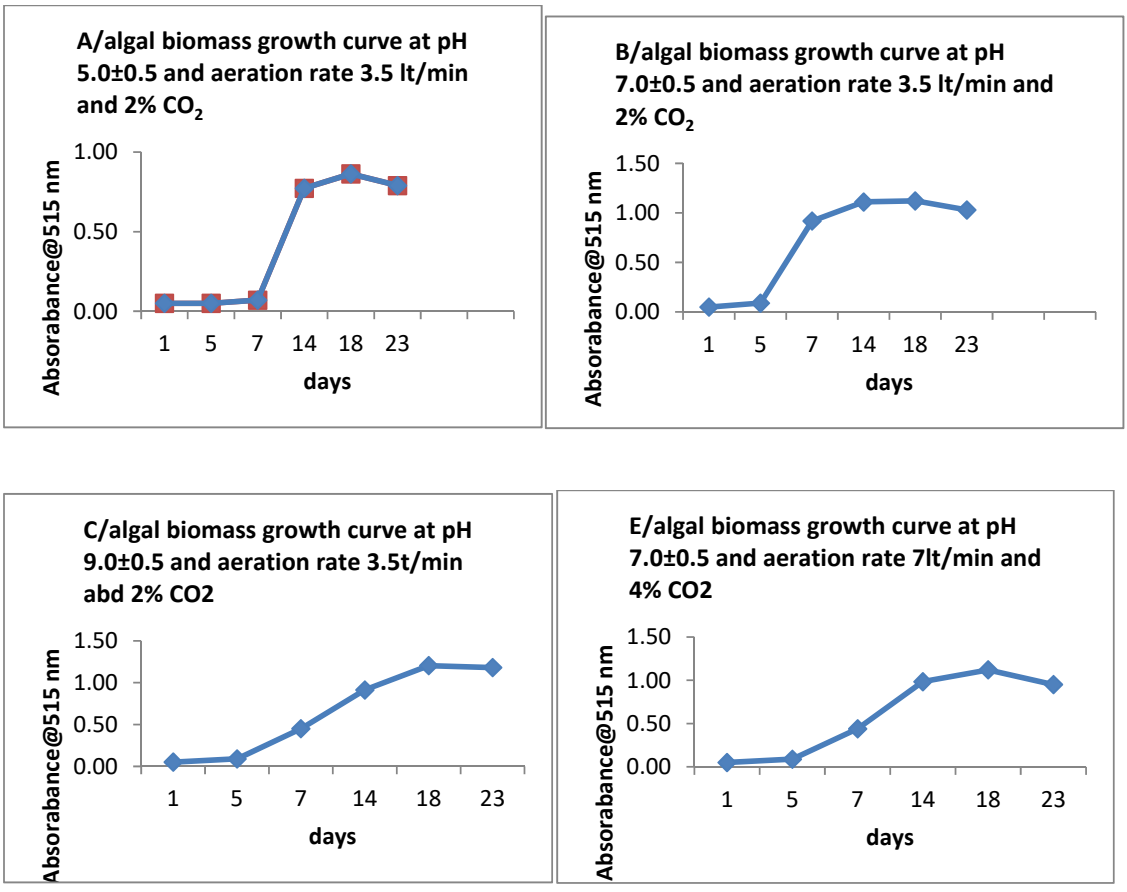


Figure 20. Algal biomass growth curve of the culture vessels conducted at room temperature and illumination of 3000 lumen fluorescent light.

4.2.2.2 Discussion on Carbondioxide sequestration effect of the algal biomass

The experiment result showed that maximum growth rate is 0.44 gm/lt and obtained at pH=7, Mixing rate=3.5 lt/min, 3000 lumen light intensity and at 20^0C temperature. To produce one gram algal biomass needs 1.83 gm carbondioxide (Demirbas,2010). Therefore from this experiment it possible to conclude that the maximum carbondioxide absorbed by this algal biomass is 0.8 gm/lt.i.e this strain showed its best strength for biodiesel production and bio mitigation at pH=7, 3.5 lt/min and 2% carbondioxide supply.

4.2.2.3 Determination of optimum process conditions for algal biomass production

The laboratory results of the experiment have been collected depending on the run order recommended by the software and tabulated as in the table 10 below. The experiments are conducted and these results are collected according to the experimental design output of the software to minimize equipment and human error of the experiment.

Table 10. Algal biomass productivity prediction based on Design expert software 9

Std	Run	A:pH	B:Air flow rate(for mixing)	C:CO_2 supply(nutrient)	Algal biomass productivity
		PH	litre/min	Percent (%)	gram/litre
1	1	7	4.0	2.5	1.56
2	2	9	7.0	4.0	1.12
3	3	5	7.0	4.0	0.86
4	4	9	1.0	1.0	0.83
5	5	7	1.05	2.5	0.74
6	6	7	4.0	2.5	1.02

7	7	7	4.0	0.02	0.89
8	8	5	7.0	1.0	1.06
9	9	7	4.0	2.5	1.02
10	10	7	4.0	2.5	1.02
11	11	4	4.0	2.5	0.77
12	12	5	1.0	1.0	0.51
13	13	9	1.0	4.0	0.98
14	14	7	9.05	2.5	1.50
15	15	7	4.0	2.5	1.02
16	16	9	7.0	1.0	0.83
17	17	7	4.0	5.02	1.15
18	18	7	4.0	2.5	1.56
19	19	5	1.0	4.0	0.65
20	20	10	4.0	2.5	1.28

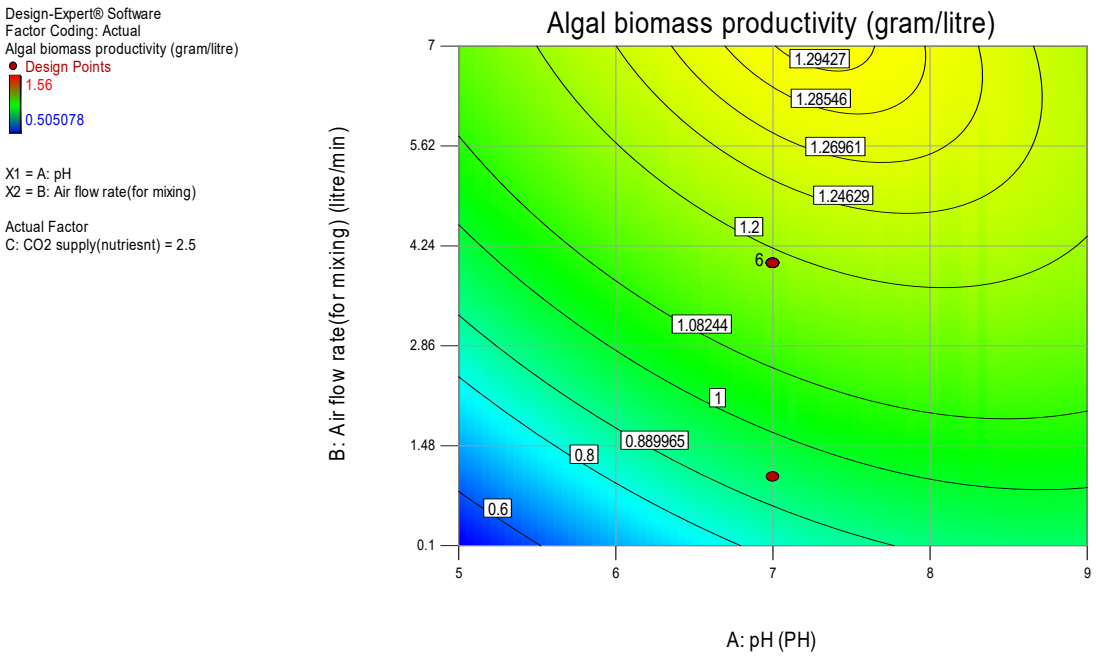
From over view of the results, the maximum biomass productivity and carbondioxide sequestration occurred at pH 7, gas aeration of 3.5 lt/min and 2% carbondioxide supply. The minimum biomass growth and carbondioxide sequestration occurred at pH 5, gas aeration of 0.1 lt/min and 0.1% carbondioxide supply.

In order to determine the optimal levels of each variables for maximum biomass productivity response (gm/lt) contour plots and 3D response surface of the results obtained were constructed by plotting (gm/lt) biomass on the Z-axis, against two independent variables, while maintaining other variables at their optimal levels which is helpful for understanding both the main and the interaction effects of these three factors. The response surface can be

used to predict the optimum range for different values of the test variables and the major interactions between the tests variables can be identified from the circular or elliptical nature of the contours. The contour plot and 3 D response surface plots based on independent variables were obtained using the software package design 9.0 as follows.

Effect of pH and aeration rate (mixing) on Algal biomass productivity

a)



b)

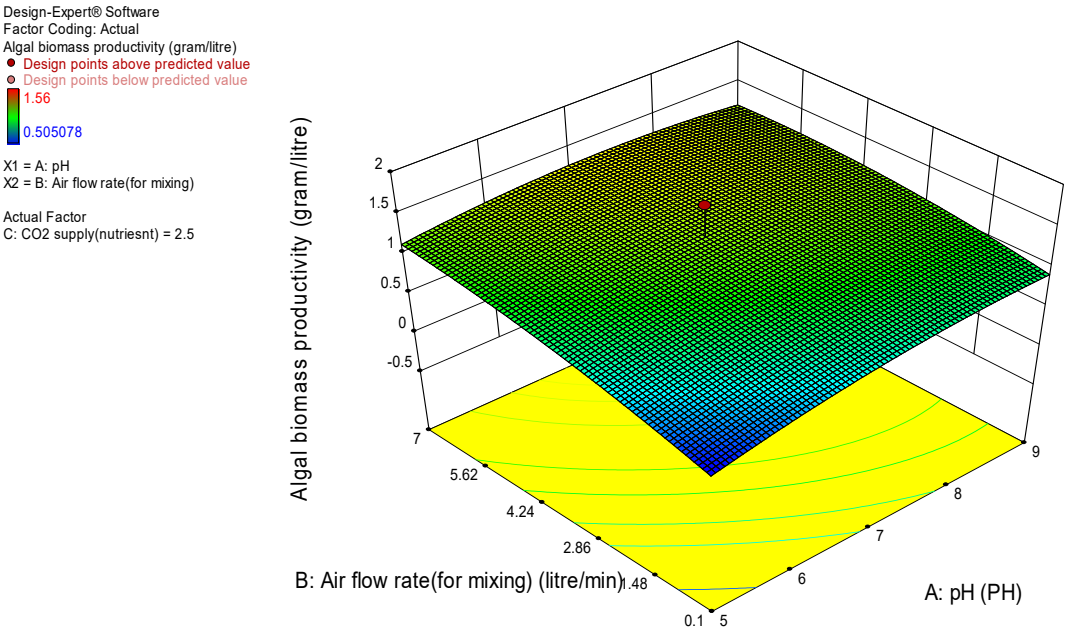
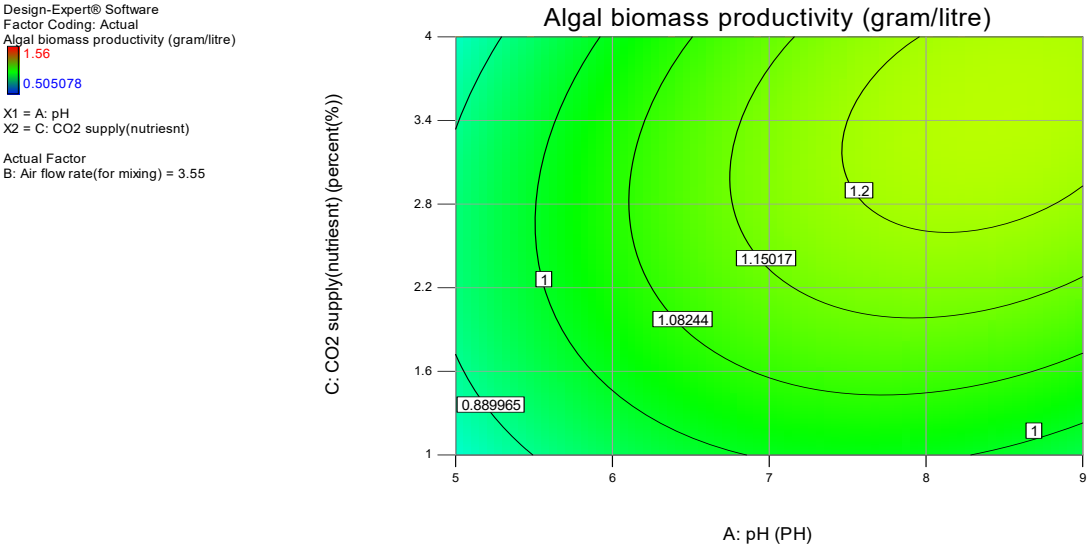


Figure 21 the effect of pH and aeration rate (mixing) on algal Biomass productivity at room temperature and constant illumination of 3000 lumen a) contour plot b) 3-D surface plot

Effect of pH and carbondioxide supply on algal biomass productivity



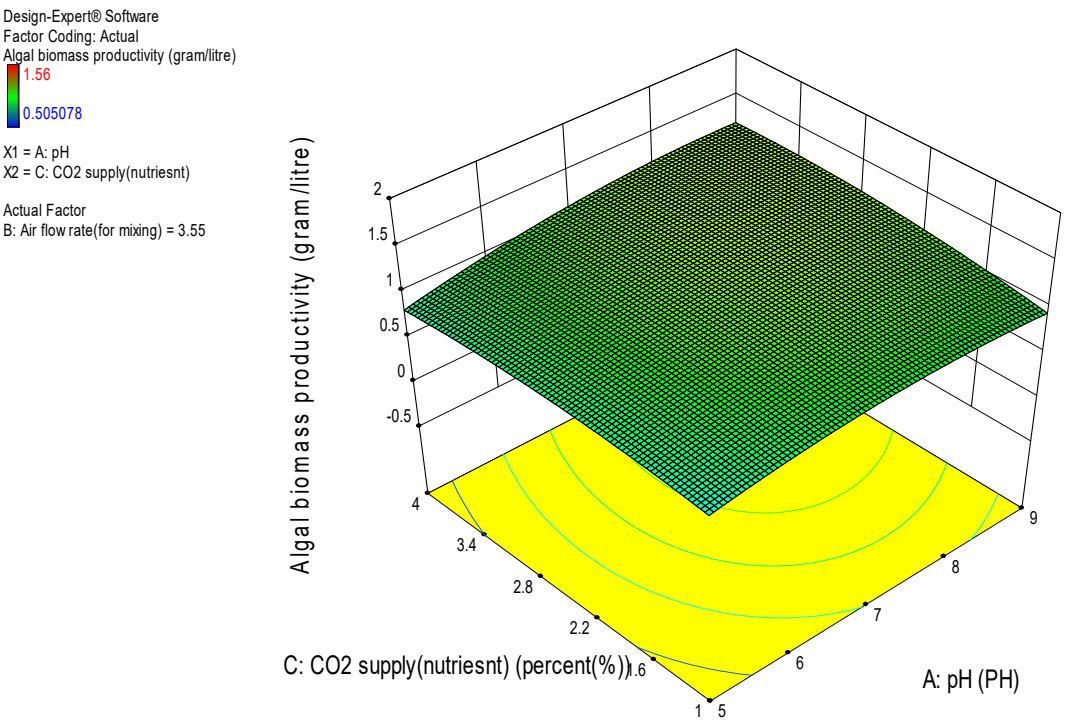
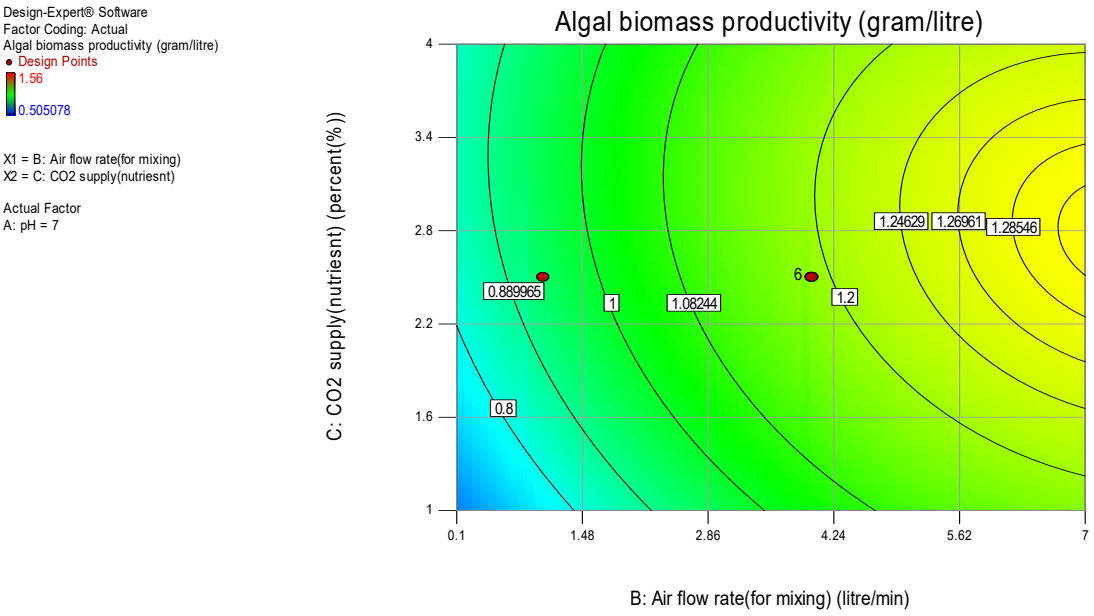


Figure 22. The effect of pH and carbondioxide rate on algal Biomass productivity at room temperature and constant illumination of 3000 lumen a) contour plot b) 3-D surface plot

Effects of Air flow rate and Carbondioxide supply



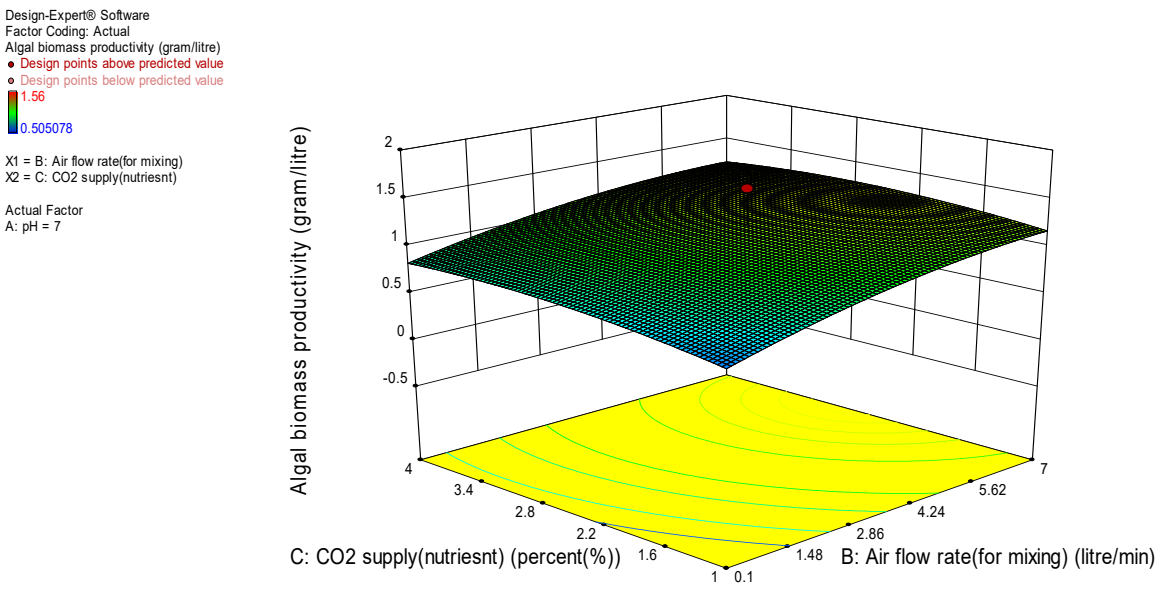


Figure 23. The effect of airflow rate versus CO_2 supply on algal biomass productivity.

The above Figures 21 , 22 and 23 a) contour and b) 3-D plots show interaction effects of pH,mixing rate and CO_2 supply rate on the response variable of Algal biomass productivity. The circular natures of the contours shows that the interaction effects between the test variables are not significant and therefore optimum values of the test variables can be easily obtained.

From the figures above, it can be seen that as one goes from pH 7 on both directions with in the given range of pH, biomass productivity reached optimum between 6.5 and 8.5 and noticeably decrease as the pH goes further in both side. This means that pH favours the biomass productivity within range between pH 6.5 and pH 8.5.The same effect is observed on the other two factors i.e. Mixing by aeration between 2 litres/minute to 5 litres/min and carbondioxide rate between 1.5 – 3.0% favours the biomass productivity.

4.2.2.4 Development of regression model equation

The model equation that correlates the response (biomass productivity) to process variables, pH, mixing rate and CO_2 supply rate was given below.

Biomass productivity (gm/lt) = 1.16+0.13A+0.24B+0.065C+0.089AB

$$+0.062AC-0.03BC- 0.12A2-0.1B^2-0.088C^2 \quad \text{eq. 17}$$

Where: - A=pH of biomass

B= Mixing rate by aeration (lt/min)

C=Carbon dioxide supply rate (%)

From this model it can be seen that these factors affect the growth rate positively in the 1st order term until it reaches maximum and affects negatively in the 2nd order term. Even if their effects are relatively different, the individual effects of all factors are significant. The interaction effects are minimum to 2nd order term.

4.2.2.5 Effects of individual process variables

Effects of pH on biomass productivity

The experimental result shows the biomass productivity increased with increased pH until pH=8.5 and declined below pH=5(figure 24).

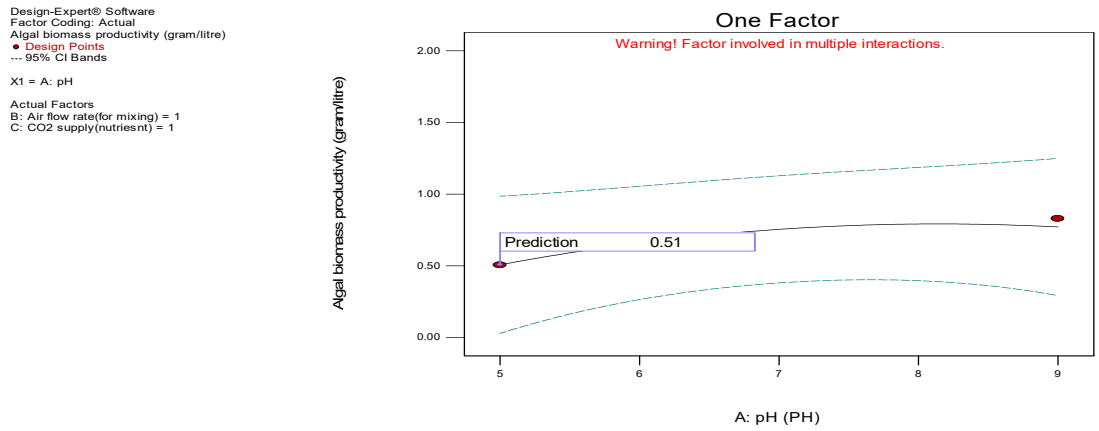


Figure 24 .Effect of pH on biomass productivity

Figure 24 gives the profile of pH effect on the growth of microalgae cultured at constant aeration rate (3.5 lt/min aeration),CO_2 concentration (2% with air),light intensity(3000 lumen).The vessels show difference in cell biomass productivity based of difference in pH.At pH=7 Maximum productivity of 0.44 gm/lt observed and at pH=5 productivity of 0.228 gm/lt observed. Therefore this result showed that the optimum pH value for maximum algal growth is between 7.0 and 9.0.We can learn from this experiment that this strain of microalgae are tolerant to wide pH range between 7 and 9.

A low pH value may inhibit microalgal growth, whereas pH change due to CO_2 has just a minor influence on algal growth. Therefore pH drop should be prevented with buffered medium and active pH control. This experiment showed that when pH was 6.5 to 7.5 ,mixed algae gained maximum growth rate, while under acidic condition (pH 4.5 to 5.5) the growth was reduced to 52% in comparison to the optimum condition. Of particular interest is that the alkaline pH=8.5 to 9.5 the growth shows no noticeable change, indicating optimum pH condition falls between 6.5 to 9.5.

Effect of aeration rate on biomass productivity

Figure 25 gives the mixing effect profile at constant pH (7),CO_2 supply(2%),light intensity(3000 lumen) and room temperature. The most common method of common mixing is gas aeration (bubbling) which offers reasonable mixing efficiency and gas transfer with low hydrodynamic stress. Culture vessel with 3.5 litre/min (average) showed maximum biomass growth, whereas culture vessel with 7.0 lt/min showed slight decrease in biomass growth due to high aeration rate. The culture vessel with aeration of 0.1 lt/min showed significantly least biomass growth due to absence of mass transfer between algal cells i.e nutrient, light and gas supply.

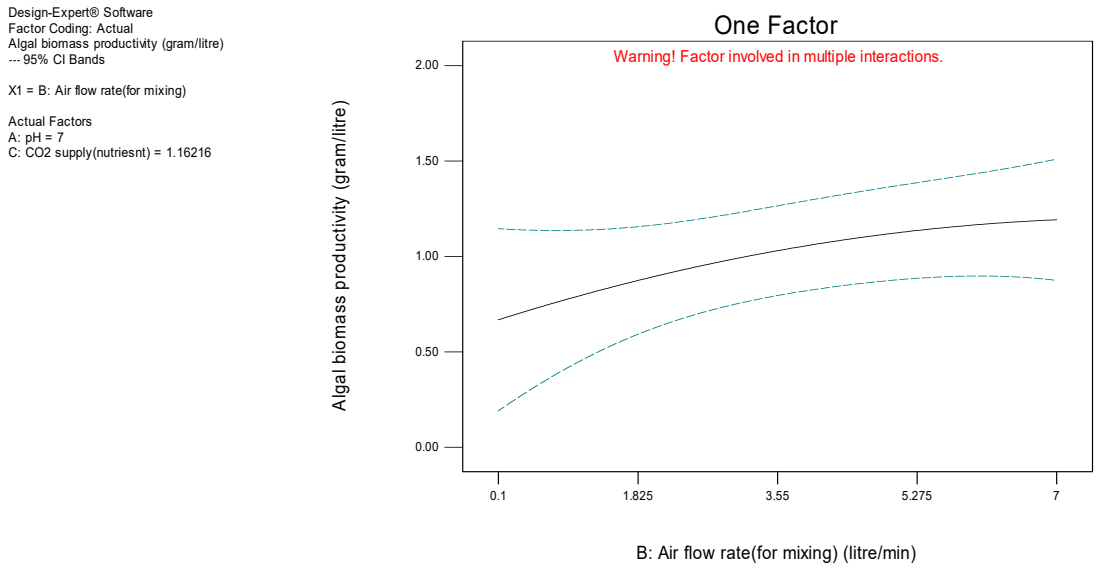


Figure 25. Aeration rate effect on algal biomass

We learned from this, that an appropriate turbulence caused by an appropriate aeration is helpful to increase microalgal production. But an extremely high aeration rate increases shear stress especially in the process of bubble generation. For most closed cultivation the recommended aeration is 1.5 lt/min to 3.5 lt/min

.

Effects of carbondioxide supply rate

Figure 26 shows the experiment that was carried out in laboratory culture flasks using 0.1%,2% and 4% carbondioxide gas -air mixture at a flow rate of 3.5 litre/min periodically for every four hour. The maximum biomass 0.44 gm/lt were obtained in 2 % carbondioxide gas concentrations aerated into culture flasks at 3.5 lt/min.

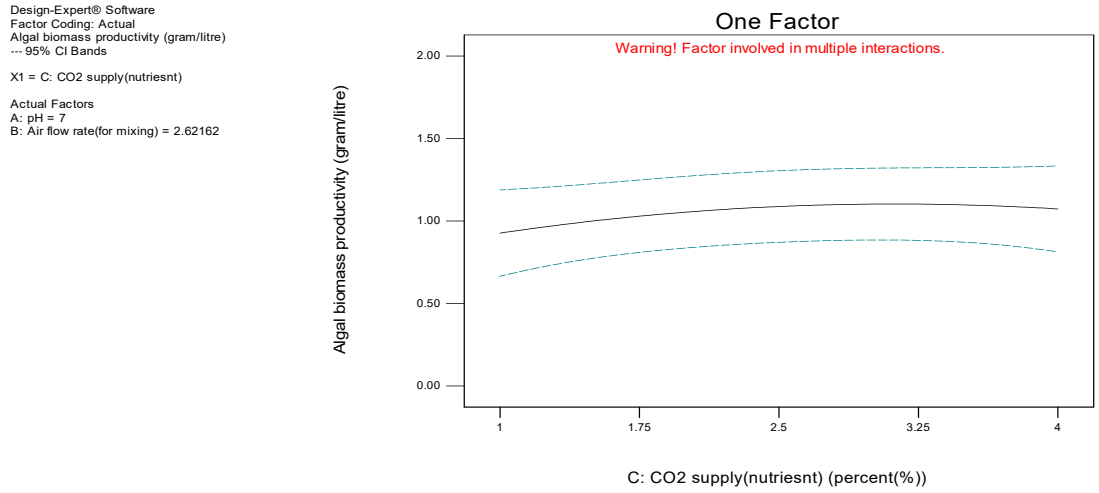


Figure 26. The effect of CO_2 supply on algal biomass productivity

The maximal biomass productivity and lipid productivity can be obtained when aerating with 2% of CO_2.The result of this experiment agrees with the conclusion given by Pooja et al,2013.

4.2.2.6 Interaction effect between process variables

Interaction between process variables can affect the performance of the photobioreactor. But, as it already seen, in this case, the interaction effects of the variables are not siginificant.In this section, these effects are going to be seen statistically and graphically (figure 27) as follows.

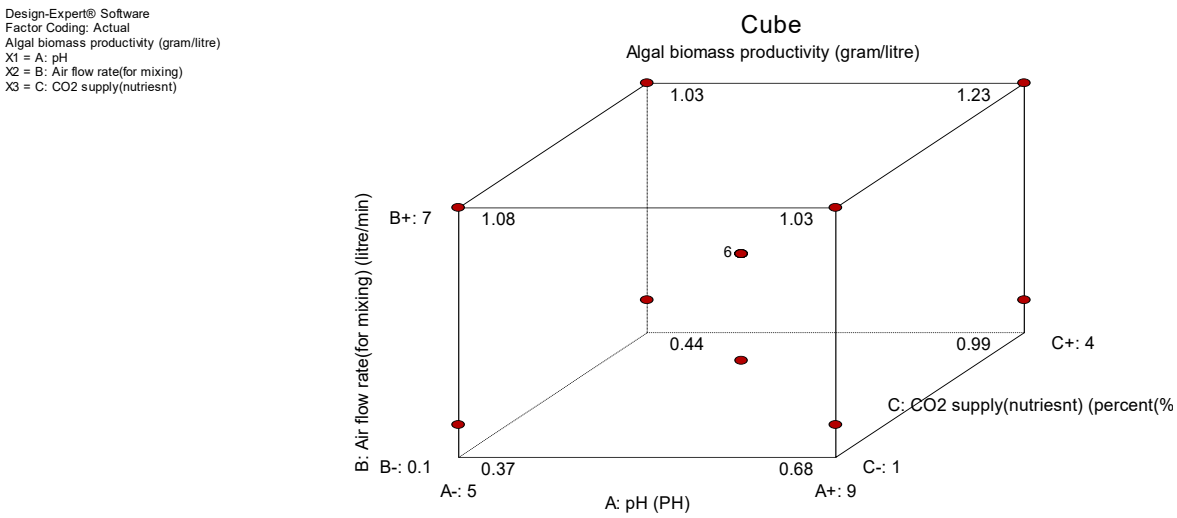


Figure 27. Cubic representation of interaction effects of pH, mixing rate and CO2 supply rate.

pH – Mixing rate interaction effect

$$=\frac{\mathbf{1}}{\mathbf{4}\boldsymbol{X}\mathbf{2}} \quad (0.99-0.44-0.68+0.37+1.23-1.03-1.03+1.08) = 0 \qquad \text{eq. 18}$$

This result shows that mixing rate - pH interaction has no effect on algal biomass productivity. This is shown graphically in figure 28 below. From the graph, it can be seen that the lines are almost parallel that shows there is no significant interaction effect between the two factors.

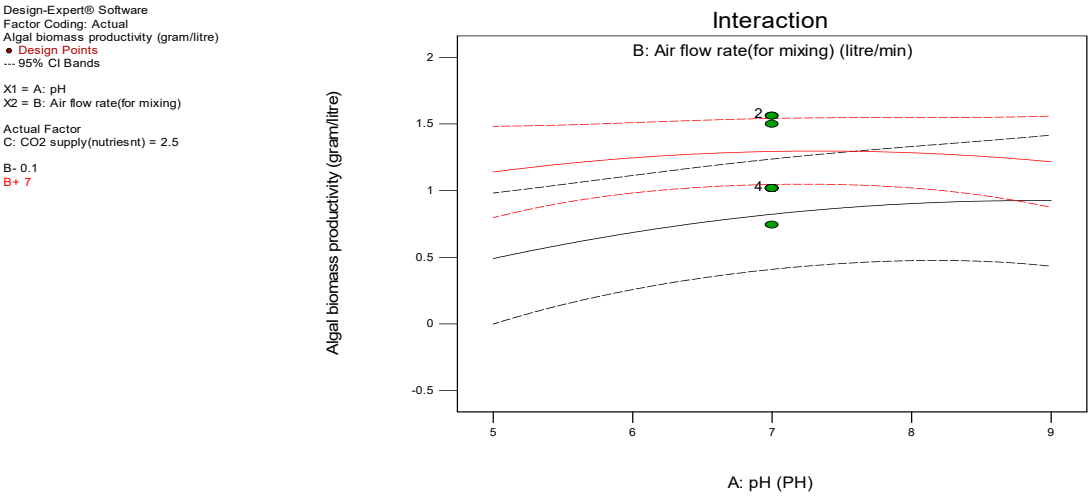


Figure 28. *Mixing rate - pH interaction effect on algal biomass productivity*

pH versus carbondioxide supply rate

$$=\frac{\mathbf{1}}{\mathbf{4}\boldsymbol{X2}} \quad (0.37-0.68+0.44-0.99-1.08+1.03-1.03+1.23) = 0 \qquad \text{eq. 19}$$

Similarly, pH-carbondioxide supply rate interaction has no effect on biomass productivity. This is shown graphically in figure 29 below. In this graph also, the lines are almost parallel which shows that there is no interaction effect between pH and CO2 supply rate .

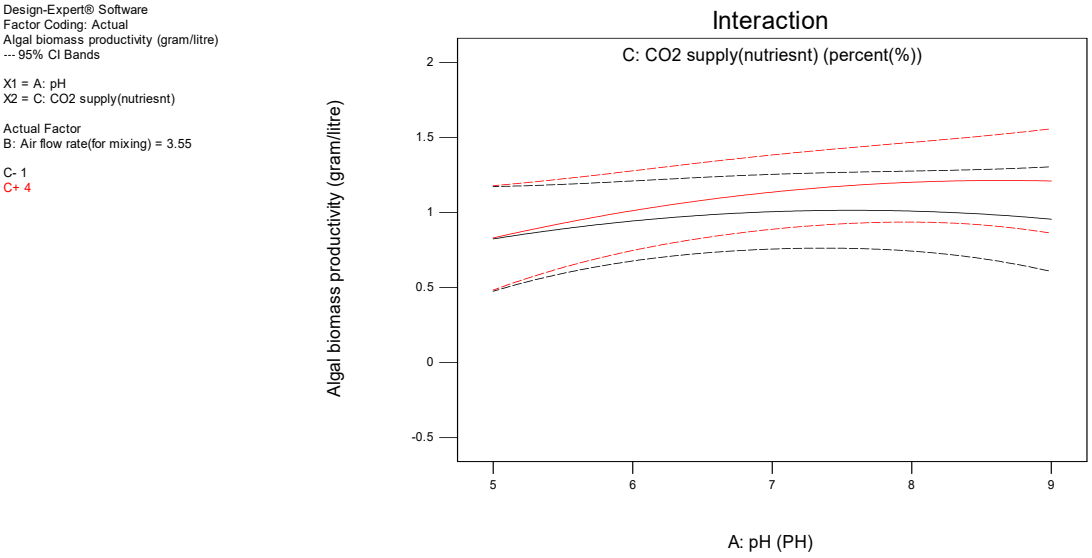


Figure 29. pH versus CO2 supply rate interaction

Interaction between Mixing rate and CO_2 supply rate

$$=\frac{\mathbf{1}}{\mathbf{4X2}} \quad (0.37+0.68-0.44-0.99-1.08-1.03+1.03+1.23) = 0 \qquad \text{eq. 20}$$

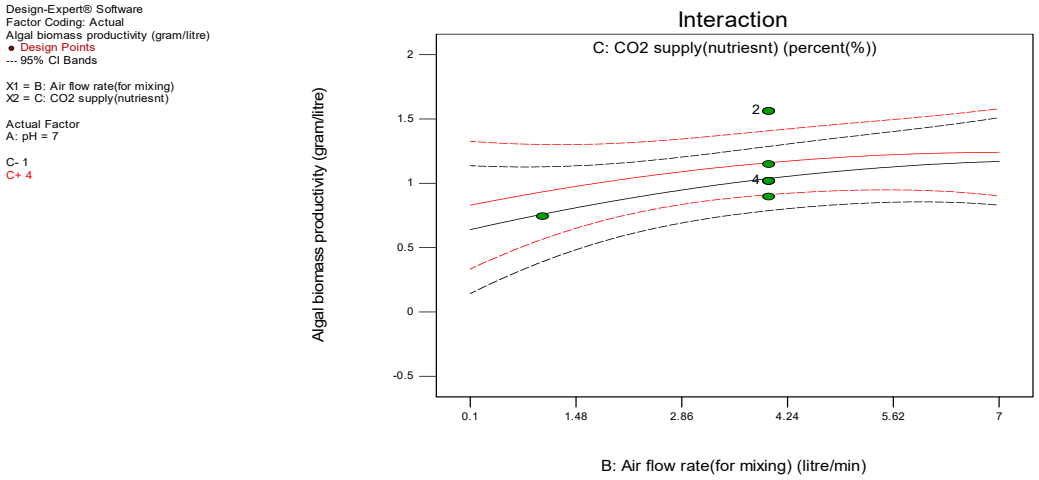


Figure 30. Aeration rate versus CO_2 supply rate

Mixing rate – CO_2 supply rate interaction also has a no effect on biomass productivity. As shown in figure 30 above, the lines are parallel lines which indicated that the interaction effect of the factors is zero.

4.2.2.7. Optimisation of process variable

Our interest is to maximize the biomass productivity as much as possible so that maximum algal oil and Carbondioxide sequestration rate obtained. The results above have shown that the above selected algal biomass growth factors affect the biomass productivity and carbondioxide sequestration rate. Therefore the next step is to optimise the process variables in order to obtain highest algal biomass using the model regression developed.

Using the optimisation function in design expert software package, it was predicted that at the condition of 7 pH media, 4.0 lt/min aeration rate, 2.5% carbondioxide supply optimum algal biomass can be obtained that is 0.44 gm/lt.In order to verify this prediction, experiments were

conducted at condition of pH 7, 3.5 lt/min aeration rate, 2%carbondioxide supply with result of 0.44 gm/lt biomass productivity .

Therefore, this study shows that, maximum algal Biomass for biodiesel production and carbondioxide sequestration can be obtained at pH between 6.5 – 8.5, aeration 3.5 lt/min,1.5-2.5% carbondioxide supply.

4.3 Flocculation experiment

4.3.1 Result

The study focuses on two coagulants: ferric chloride and aluminum sulfate (alum), which are most common in use for coagulation in water treatment.Table 11 and shows the flocculation efficiency of these two coagulants.

Table 11. Experiment result on flocculation efficiency of aluminium sulphate/Alum

Time minute	Empty weight	weight with sample	Final weight	Initial net weight	Final net weight	Flocculation Efficiency,%
30	44.8565	45.8371	44.9488	0.9806	0.8883	9.41
60	44.8565	45.8307	45.0733	0.9742	0.7574	22.25
90	44.8565	45.8321	45.0926	0.9756	0.7395	24.2
120	44.8565	45.8296	45.2567	0.9731	0.5729	41.13
240	44.8565	45.8265	45.4460	0.9700	0.3805	60.77
480	44.8565	45.7535	45.4029	0.8970	0.3506	60.91

Table 12. Experiment result on flocculation efficiency of Ferric Chloride

Time minute	Empty weight	weight with sample	Final weight	Initial net weight	Final net weight	Flocculation Efficiency,%
30	42.1173	42.21503	42.1838	0.09773	0.0665	yie
60	42.1173	42.9450	42.38001	0.8277	0.262712	68.26
90	42.1173	42.9690	42.30476	0.8517	0.187459	77.99
120	42.1173	42.9467	42.24959	0.8294	0.132289	84.05
240	42.1173	42.9451	42.19056	0.8278	0.07326	91.15
480	42.1173	42.9896	42.19459	0.8723	0.077286	91.14

4.3.2 Discussion

During the process of flocculation, the positively charged flocculants attracted to negatively charged walls of microalgal cells(Demirbas,2010),there by particle collision and neutralisation of charges occur followed by deteriorating the intra particle repulsion and thus formation of flocs is achieved.

Ferric Chloride exhibited maximum flocculation efficiency than Aluminium sulphate. It showed an efficiency of 91.1% at the end of 240 minutes whereas aluminium sulphate showed 61% flocculation efficiency (Figure 31). Therefore efficient flocculation of microalgae cells were observed with the ferric chloride salt.

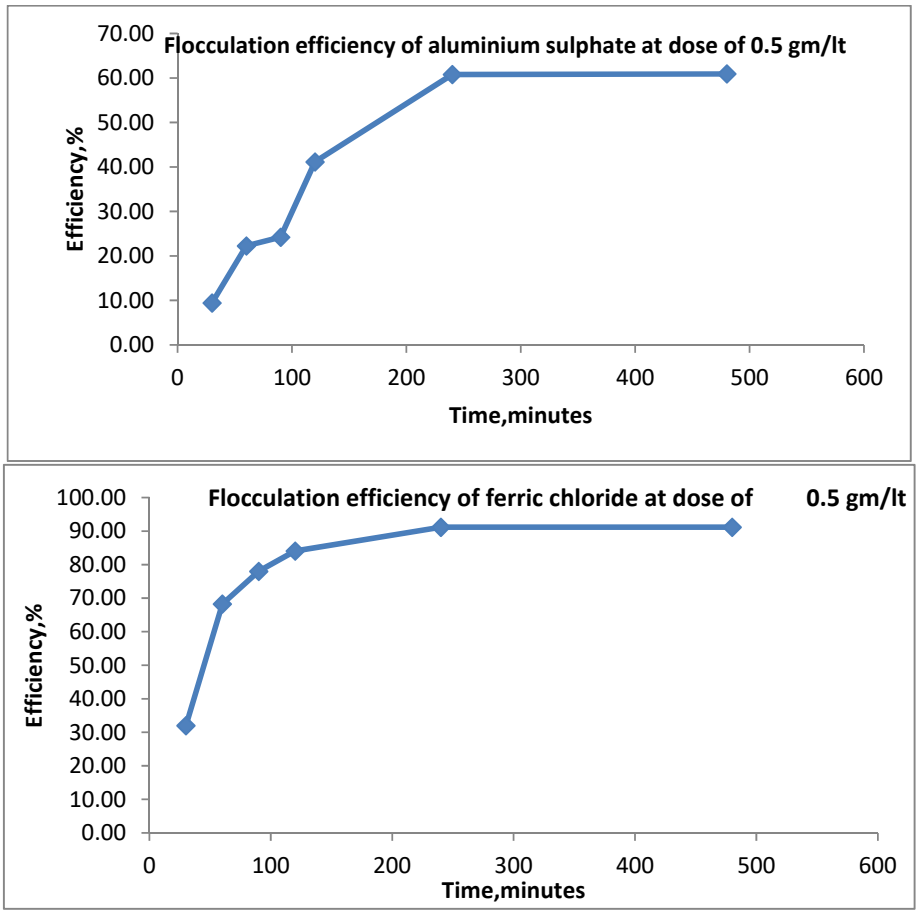


Figure 31 . Effect of time on flocculation of 0.5 g/lt Aluminium sulphate (A) and 0.5 g/lt Ferric chloride

Though ferric ions showed maximum efficiency, the color change or brick red pigmentation of culture due to the addiction of ferric ions, showed that use of ferric salt for flocculation may not be attractive for commercial green algae production.

In this study, the effect of varying concentration of aluminium sulphate on flocculation of the microalgae cells is not studied due to financial and time constraint,how ever due to the study conducted by Surendhiran et al,2013,Aluminium sulphate showed 82.27% efficiency at 0.8 g/lt concentration after 4 hours of time.There for the pigmentation problem of ferric chloride can be avoided by the use of aluminium sulphate at dose of 0.8 gm/lt.

4.4 Result and discussion on Algal oil extraction

4.4.1 Algal oil yield

The yield of algal oil extracted from algal biomass powder was recorded in the table below.

Table 13. Algal oil yield

Run No	Mass of oil obtained In gram	Mass of dried algae taken In gram	Oil yield In percent
1	15.1	80	18.88
2	15.7	80	19.63
3	15.8	80	19.73
4	16.68	80	20.85
		Average	19.78

Depending on the species and growth condition, microalgae can contain up to 60% algal oil of total algal biomass taken using solvent extraction. Solvent extraction using hexane was chosen for solvent extraction. However it was difficult to obtain hexane solvent, and acetone taken as alternative solvent to extract the algal oil. The average oil yield obtained is approximately 20.0%.The low value of extraction yield is due to the fact that the algal biomass is obtained from mixed species microalgal cells. The presence of low lipid content species and unfavourable conditions (pH fluctuation, unbalanced nutrient supply, aeration disturbance due to intermittent electric failure) that hinder the lipid activity of the cells may affect the lipid content of the algal biomass consortium. The other reason is the growth condition of biomass was not well controlled due to lack of automatic control devices.

4.4.2 Acid value

The acid value of the oil determined using the method discussed in section3.5.1 and the results were presented in the Table 14

Table 14. Acid values of algal oil

Run No	Weight of oil,gm	Volume of titrant, ml KOH	Normality of titant	Acid value mgKOH/gm oil	FFA
1	4	1.50	0.1	2.1	1.05
2	4	1.45	0.1	2.03	1.01
3	4	1.45	0.1	1.96	0.98
			Average	2.03	1.01

The average acid value of the oil was calculated using equation 3.3 and the result was obtained to be 2.03 mg KOH/g oil.The acid value measures the content of free fatty acid value(1.01),which has influence on fuel aging. This value is small, and it showed that it is the free fatty acid of the algal oil is too low and needs no pre-treatment.

4.4.3 Saponification value of algal oil

The saponification value of the algal oil determined using the method discussed in section 3.5.2.and the results are presented in Table 15

Table 15. Saponification value of algal oil

Run No	**Mass of oil In gram**	**Volume HCl in blank**	**Volume HCl In sample**	**Difference**	**Normality Of HCl**	**Saponification value**
1	2.0	38.5	25.0	13.50	0.5	189.34
2	2.0	38.5	24.5	14.00	0.5	196.35
3	2.0	38.5	23.0	15.50	0.5	217.39
					Average	201.03

The average saponification value is 201.03.The soap in the biodiesel can reduce fuel lubricate and can cause injector coking and other deposits in engine motors (Indhumathi et al, 2014).Therefore, during scale up and large scale design of biodiesel plant, it is essential that the downstream processing of the biodiesel shall be well washed cleaned and dried in post operation of transesterfication to remove the soap.

4.4.4 Moisture content of oil

Moisture content of algal oil determined using the method discussed in section 3.5.3.The result obtained is found to be 0.65%.This indicated that further drying of the algal oil is required.

4.5 Result and discussion on Algal biodiesel transesterfication

4.5.1 Biodiesel yield

Yield of biodiesel transesterfied from algal oil is calculated using equation 3.7, and the result obtained is 98.0%.

4.5.2 Specific gravity of algal biodiesel

Specific gravity is an important property of biodiesel. It is observed that the specific gravity of the biodiesel obtained is 0.87 kg/lt, which is in well agreement with the ASTM D6751 standard.

4.5.3 Kinematic viscosity

To define kinematic viscosity it is essential to determine viscosity or simply called dynamic viscosity, which is the ease with which a fluid will flow.Viscosity is the most important parameter of biodiesel, since it affects the operation of fuel injection equipment, particularly at low temperature when the increase in viscosity affects the fluidity of the fuel. Kinematic viscosity is determined as per equation 3.8.The result on viscosity and kinematic viscosity of the biodiesel obtained is shown on table 16.

Table 16. Kinematic viscosity result of biodiesel determined at 40^0C

Run no	Viscosity(cp)	Density(g/cc)	Kinematic viscosity( )
1	4.3	0.87	4.94
2	4.25	0.87	4.89
3	4.3	0.87	4.94
Average	4.28	0.87	4.92

The viscosity of the biodiesel is high (4.92 cs) which is in well agreement with the limit given by ASTM D 6781.

4.5.4 pH

The pH of biodiesel determined using the method discussed in section 3.7.3 and found to be 7.2, which is within the limit given by ASTM D6751.

4.5.5 Acid value of Biodiesel

The acid value of biodiesel determined similarly with the method discussed in section 3.5.1.The result was recorded in table 17.

Table 17. Acid value of algal biodiesel

Run No	Weight of biodiesel	Volume of KOH, ml	Concentration of KOH,N	Acid value
1	2	0.80	0.1	0.90
2	2	0.75	0.1	0.84
3	2	0.80	0.1	0.90
			Average	0.88

As can be seen from the table,the acid value of the produced biodiesel was 0.88 mg KOH/g, while that of the algal oil was 0.44 mg KOH/g with lowering of 56.4 % indicating good transesterfication process.

4.5.6 Sulphated ash

The amount of sulphated ash determined and the result indicated that it is free of ash. Ash can deposit up on the engine parts causing abrasion. If abrasive it may cause excessive wear of closely fitting parts of fuel pumps and injectors.

Table 18. Summary of the characterisation of algal biodiesel

SN	Property	Value	Limits,ASTM D6751
1	pH	7.2	7-9
2	Specific gravity	0.87	0.86-0.89
3	Viscosity@44^{O}C(mm2/s)	4.3	1.9-6.0
4	Acid value.mg KOH/g	0.88	-
5	Free fatty acid value	1.01	-
6	Moisture content(%)	0.05	0.05,max
7	Sulphated ash	Nil	0.001%

CHAPTER FIVE

DESIGN OF THE ALGAL BIODIESEL PLANT INTEGRATED WITH THE CEMENT MANUFACTURING PLANT

5.1 Process design assumption

The design in the present study was developed to estimate the scaled up algal biodiesel manufacturing plant to produce 9,792 ton crude algal oil per year. It is believed that combining open and closed reactors is the most effective configuration for growing algae(Demirbas,2010).The facility featured 125 m^3 closed photo bioreactors for inoculation and 1250 m^3 open ponds.

The two-stage culturing process began with growth in an industrial scale closed photo bioreactor. The highly controlled environment in this step maximized cell growth. Next, the algae were exposed to nutrient deprivation by being transferred to an open pond reactor. Finally, the stress increased the lipid content of each cell. An important guideline to adhere to when considering a hybrid reactor scheme is minimizing the residence time of the algae in the open pond, where they are vulnerable to contamination.

The algal biodiesel manufacturing plant under study will be integrated with the cement industry plant (Figure 32).The cement plant flue gas from the Dangote cement plant in Mugher area ,which is treated from dust, Nox, SOx at optimum level will supply carbondioxide to the closed photobioreactor and open raceway pond. To reduce the risk of contamination, for a higher biomass productivity and reduction of power consumption the algal strain will be pre-cultured in closed PBR before being transferred to the open pond.

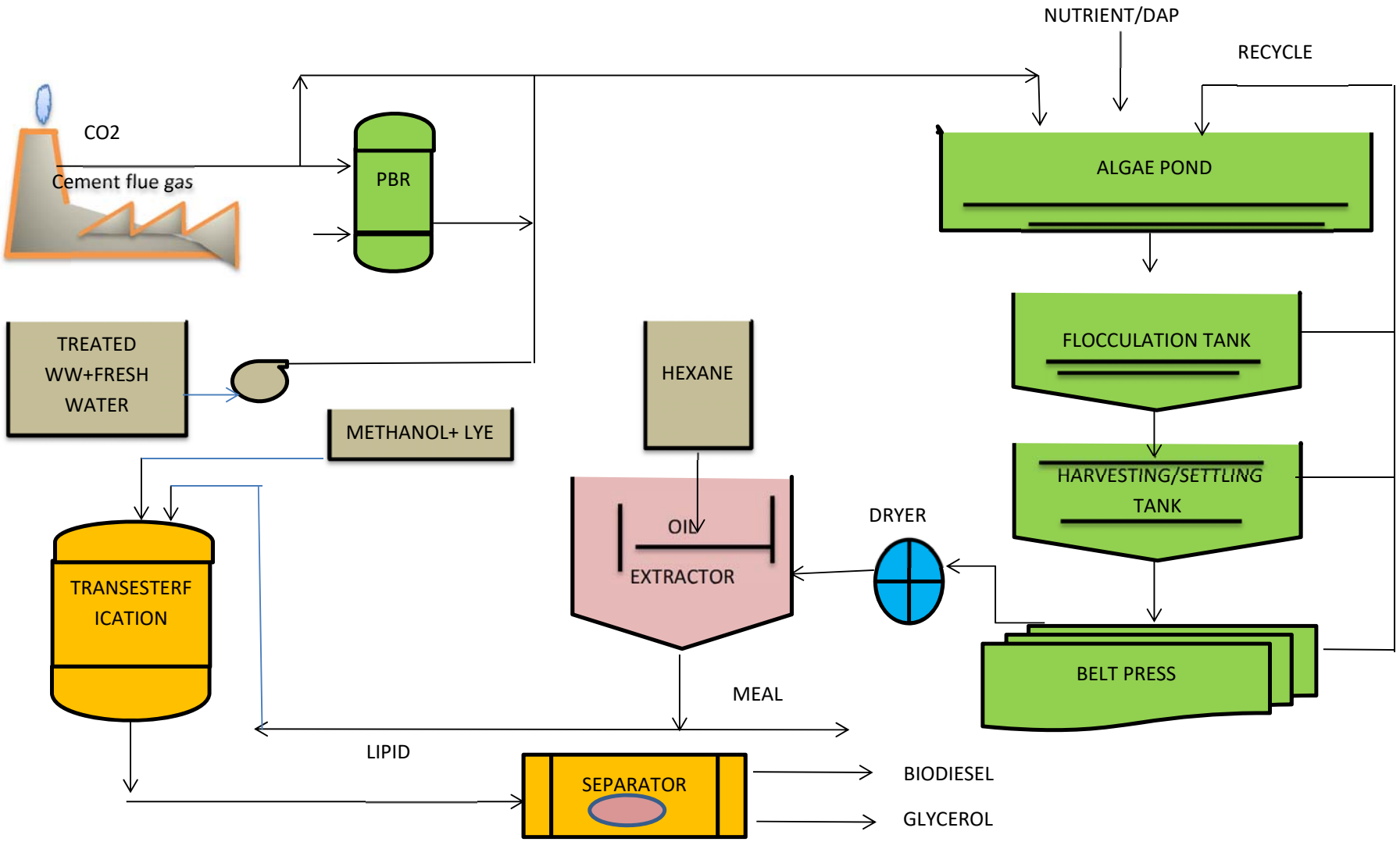


Figure 32 Process description of the algal biodiesel plant integrated with cement industry flue gas

5.2 Algae cultivation

To make the algal biodiesel production economically viable and to keep the production cost low, the algae cultivation is chosen to be done in open raceway ponds. Nutrient chosen for the biomass growth is the use of inexpensive fertilizer of DAP. The water supply to the PBR and raceway ponds is treated industrial, municipal waste water and fresh water. Fresh water is available from nearby rivers and shall be treated before use. The nutrient uptake quantity taken from literature (Chisti,2007),based on the elemental formula $C_{106}H_{181}O_{45}N_{15}p_7$.

The corresponding dimension of the individual pond selected is 42 m by 120m long and the resulting area of each pond is 5000 m^2(0.5 hectar).see figure 33

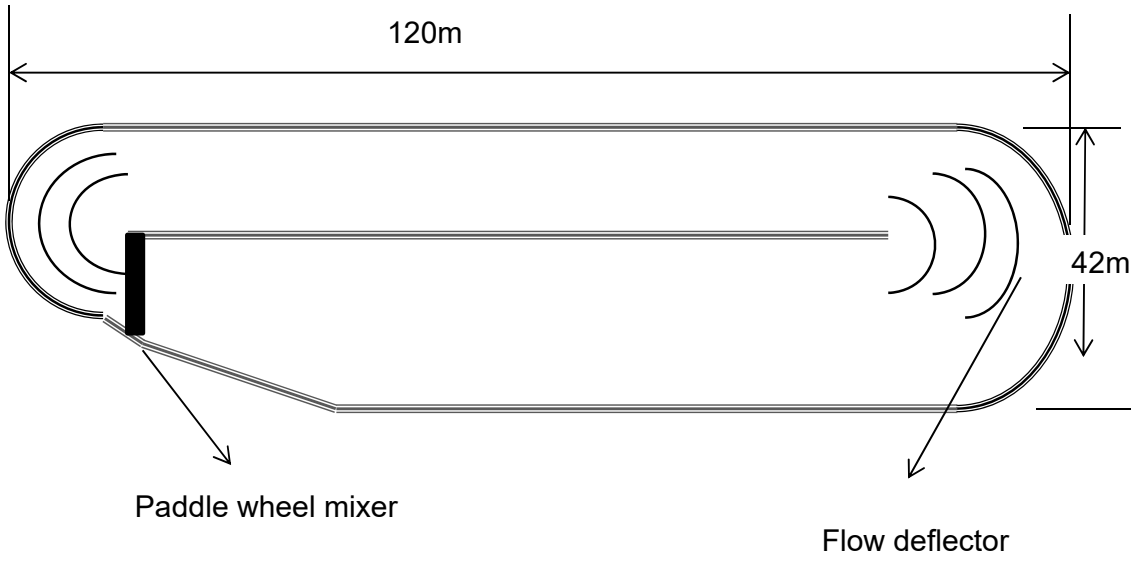


Figure 33.Plan view of an individual raceway pond(Source :- Lundquist et al,2010)

The Raceways proposed will be equipped with a paddle wheel and aeration system to Ponprevent settling, allow adequate movement for light absorption, and enhance mixing of nutrients and CO_2

with the media. A closed photobioreactor system is integrated into the cultivation system for, providing a continuous flow of culture to the larger production ponds.

5.2.1 Material requirement of the race way pond

Basis: - one raceway pond = 5,000 sq. meter area

Because of their rapid growth rates the mixed chlorella will be allowed to dominate the open ponds here. Lipid contents in the 20-25 weight percent range have been verified in the experiment for Chlorella based mixed species. The Chlorella mixed species under study double in cell count every 8 hours, This corresponds to a specific growth rate constant u of 2.4 day $^{-1}$ (Ron put, 2007) in the expression

$$\frac{P}{D} = uC \qquad \text{eq. 21}$$

Where, P is the growth rate, grams/m^2.day

D is the pond depth,

C is the algal concentration, grams/m^3(experimentally determined that 0.0695 gm/lt)

For a specific growth rate constant of 2.4 per day and our target pond concentration of 69.5 gm/m^3,

$$\frac{P}{D} = uC$$

$$= 2.4*69.5 = 166.8 \text{ gm/m}^3 \text{ (ppm)}$$

For a pond depth of 0.25 meters, the areal productivity is

$$= (166.8 \ \frac{gram}{m^3.d}) \ (0.25) = 41.7 \text{ g/m}^2\text{.d}$$

For one raceway pond designed to have 5,000 sq. meter area, the production rate (P) of a single pond is

$$P = (41.7 * \frac{\boldsymbol{g.algae}}{\boldsymbol{m^2 d}})(\frac{\boldsymbol{1\ kg}}{\boldsymbol{1000 g}})\ (5{,}000 \boldsymbol{m^2}) = 208.5\ \frac{\boldsymbol{kg\ Algae}}{\boldsymbol{day}} \qquad \text{eq. 22}$$

The harvesting flow rate (Q_H) at an algae concentration of 168.8 ppm for the single pond at 10% harvesting rate per day is

$$QH = (208.5 * \frac{\boldsymbol{kg.algae}}{\boldsymbol{d}})(\frac{\boldsymbol{1x10^6 kg\ pond\ water}}{\boldsymbol{166.8 kg}}(\frac{\boldsymbol{1 m^3}}{\boldsymbol{1000 kg}}) * 0.1 = 125\ \frac{\boldsymbol{m^3 pond\ water}}{\boldsymbol{d}} \qquad \text{eq. 23}$$

Therefore, $(1{,}25\ \frac{m^3}{d})(\frac{980\ kg}{m^3})(\frac{1d}{24\ hr}) = 5{,}043.7$ kg/hr ≈ 5,000 kg/hr

The pond water residence time (t)

$$\text{Pond volume} = A * h = 5{,}000\ m^2 * 0.25 = 1250\ m^3 \qquad \text{eq. 24}$$

$$\text{Residence time} = t = \frac{\boldsymbol{1{,}250\ m^3}}{\boldsymbol{125\ \frac{m^3}{d}}} = 10.0\ \text{day} \qquad \text{eq. 25}$$

Make up water requirement

The average pond evaporation rate is 0.1 cm per day (Ron Putt,2007).Therefore ,the makeup flow rate Q_m would be

$$Qm = (0.001\ \frac{\boldsymbol{m}}{\boldsymbol{d}})(5{,}000\ m^2) = 5\ \frac{\boldsymbol{m^3}}{\boldsymbol{d}} \qquad \text{eq. 26}$$

$$= (5\ \frac{m^3}{d})(\frac{980\ kg}{1m^3})(\frac{1d}{24\ hr}) = 204\ \text{kg/hr}$$

Nutrient balance

Each mass of algae contains 52% carbon,9% nitrogen and 1% phosphorus(Chisti,2007).Therefore for each pond to produce 208.5 kg algae per day needs

- 0.52 * 208.5 kg algae per day = 108.42 kg elemental carbon
- 0.09 * 208.5 kg algae per day = 18.77 kg elemental nitrogen
- 0.01 * 208.5 = 2.09 kg elemental phosphorus

All the available carbon obtained is used and converted to algae. Carbondioxide obtained from the cement flue gas is in excess and mass balance is not considered.

Therefore it is proposed to compute the nitrogen and phosphorus balance obtained from the chemical fertilizer DAP. Diammonium phosphate (DAP) is an excellent source of nitrogen and phosphorus.

Chemical formula – $(NH_4)_2HPO_4$

Molecular weight of DAP = 132.06 gm, N=28gm, P=31gm

i. Nitrogen mass balance

The daily need of nitrogen per pond

$$= \left(\frac{\mathbf{0.09\ kg\ Nitrogen}}{\mathbf{1\ kg\ Algae}}\right)\left(\frac{\mathbf{208.5\ kg\ algae}}{\mathbf{per\ pond\ per\ day}}\right) = 18.77 \text{ kg N} \qquad \text{eq. 27}$$

The amount of DAP to be used

$$\text{`} = \left(\frac{18.77\ kg\ N}{per\ pond\ per\ day}\right)\left(\frac{132.06\ kg\ DAP}{28\ kg\ N}\right) = 88.53 \text{ kg } \frac{DAP}{per\ pond\ perday} \qquad \text{eq. 28}$$

ii. Phosphorus mass balance

The daily need of phosphorus

$$= \left(\frac{\mathbf{0.01\ kg\ phosphorus}}{\mathbf{1\ kg\ Algae}}\right)\left(\frac{\mathbf{208.5\ kg\ algae}}{\mathbf{per\ pond\ per\ day}}\right) = 2.09 \text{ kg P} \qquad \text{eq. 29}$$

The amount of DAP to be used

$$\text{`} \qquad = \left(\frac{2.09\ kg\ P}{per\ pond\ per\ day}\right)\left(\frac{132.06\ kg\ DAP}{31\ kg\ N}\right) = 8.88 \text{ kg } \frac{DAP}{per\ pond\ perday}$$

Therefore the amounts DAP to be supplied for phosphorus is well below the amount needed to supply nitrogen.

Carbondioxide delivery

Cement plants are relatively large point sources of CO_2,because the CO_2 concentration in cement flue gas is relatively high(about 25 mol %,d.b) compared to about 14% for a coal fired power plant. According to the data obtained from the Dangote cement industry annual product quality review, the cement industry flue gas carbondioxide content is between 85% -95% w/w.for consistency the CO_2 capture rate has been conservatively assumed at 85%.

An individual pond of the envisaged project would produce 208.5 kg of algae per day,and this would require 108.4 kg of carbon. The carbon were to come from the cement flue gas and atmosphere. The carbondioxide concentration of atmospheric air is 385 ppm by volume and the concentration of cement flue gas composition is 25% mole.

Carbondioxide concentration in air

CO_2 content in air = 385 ppm by volume

Ideal gas law:PV=nRT eq. 30

$$n = \frac{PV}{RT} = \frac{(1\ atm)(1000L)}{(0.082\frac{Latm}{mol.k})(300k)} = 41 \text{ mole air}$$

Concentration of CO_2 in air

$$C = \left(\frac{\mathbf{41\ mol\ air}}{\mathbf{m^3}}\right)\left(\frac{\mathbf{0.000385\ L\ \ CO2}}{\mathbf{L\ \ \ Air}}\right) = 0.016 \text{ mol } CO_2/m^3 \quad \text{eq. 31}$$

$$= \left(\frac{0.016\ mol\ CO2}{m^3}\right)\left(\frac{44\ g\ CO2}{mol\ CO2}\right) = 0.7 \text{ g } CO_2/m^3$$

Carbondioxide concentration in flue gas

Carbondioxide content of flue gas = 25% by volume

Assuming purified flue gas obeying ideal gas law and gas being cooled to 300k.then concentration of carbondioxide in the flue gas is

$$C = \left(\frac{41\ mol\ air}{m^3}\right)\left(\frac{25\ L\ \ CO2}{75\ L\ \ \ Air}\right) = 13.67\ \text{mol } CO_2/m^3 \qquad \text{eq. 32}$$

$$= \left(\frac{13.67\ mol\ CO2}{m^3}\right)\left(\frac{44\ g\ CO2}{mol\ CO2}\right) = 601.3\ \text{g } CO_2/m^3$$

The carbondioxide in the air is less than 0.1% in comparison with the CO_2 concentration in the flue gas. Therefore CO_2 delivery from atmosphere is assumed negligible.

A 5000 m^2 pond of the envisaged raceway produce 208.5 kg algae (db) and thus would require 108.4 kg of carbon per day. All the carbon were assumed to come from the flue gas. Thus 375.3 kg carbondioxide would have to be transported from the flue gas stream to the pond, at 75% capture efficiency (Ron putt,2007).

The flow rate of flue gas required is

$$Q = \left(\frac{81.3\ kg\ CO2}{d}\right)\left(\frac{1m^3\ flue\ gas}{601.3\ g\ \ CO2}\right)\left(\frac{1000\ g}{1\ kg}\right)\left(\frac{1\ d}{24\ h}\right)\left(\frac{1\ h}{3600\ s}\right) \qquad \text{eq. 33}$$

$$= \frac{0.00156\ m^3 flue\ gas}{s}$$

According to Ron Putt,2007 to maintain small,distinct bubble with high interfacial area for gas liquid transport,the superficial gas phase velocity in the column should be less than 0.03m/s.Thus,the minimum column area would be

$$A = \left(\frac{0.00156\ m^3}{s}\right)\left(\frac{1\ s}{0.03\ m}\right) = 0.0522\ m^2 \qquad \text{eq. 34}$$

The minimum column diameter would be

$$D = \sqrt{\frac{4*0.0522\ m^2}{\pi}} = 0.145\ \text{m} \qquad \text{eq. 35}$$

5.2.2 Pond Energy requirement

The energy requirement for the raceway pond is mainly due to the paddle wheel.The proposed 5,000 sq. meters pond will have the following dimension.

- Pond length(Lp) = 120 meters

- Pond width(Wp) = 42 meters
- Depth(D) = 0.25 meters
- Flow channel width(Wc) = 21 meters

The hydraulic diameter (D_H) is

$$D_H = \frac{4A_{CS}}{U} = \frac{4W_C D}{W_C + 2D} = \frac{4(21m)(0.25m)}{21m + 2(0.25m)} = \frac{21}{21.5} = 0.98 \text{ m} \qquad \text{eq. 36}$$

Typically the density and viscosity of the diluted culture broth, is closely related to the property of water. Therefore the density of the culture is 1000 kg/m^3 and the viscosity of water is taken as 0.001kg/m^2/s. The selected average velocity is 0.15 m/sec(Putt,2007).

Therefore, Reynolds number is

$$\text{Re} = \frac{\rho . v . D_h}{\mu} = \frac{(1000\,\frac{kg}{m^3})(0.15\,\frac{m}{s})(0.98)}{0.001\,\frac{kg}{m.s}} = 147,000, \text{ Turbulent flow.}$$

According to Chisti, 2010 the flow in raceway conduit needs to be turbulent to keep the cells in suspension, enhance vertical mixing, prevent thermal stratification and facilitate removal of the oxygen generated by photosynthesis.

The power requirement p(W) for a paddle wheel to generate a flow of velocity u in the straight channel of a typical raceway is estimated using the aaumption given by Mikko et al,2015). Energy requirement assumption of 1 W/m^2 for circulation of algal culture in open race way ponds and 100 W/m^3 in closed photo bioreactors is taken based on the initial assumption given in the study on Energy analysis of algae to biofuel production chains integrated with a combined heat and power plant by Mikkho et al,2015.See table 19.

Table 19. Initial energy requirement assumptions for cultivation and post processing path ways

SN	Streams and unit operations	Assumed Energy requirement
1	Circulation in raceway ponds	1 W/m^2
2	Circulation in closed photo bioreactors(PBRs)	100 W/m^3
3	Belt filter press	3.2 KJ/kg
4	Drying(electricity)	0.3MJ/kg
5	Extraction and transesterfication	0.5 MJ/kg

Adapted from :- Mikko et al,2015

Electricity consumption in cultivation of raceway pond assumed 1 W/m^2 as representative value of achievable consumption in this study per pond per year intermittently at 75% of power supply is calculated as

$$= \frac{\mathbf{1W}}{\boldsymbol{m^2}} * \frac{\mathbf{0.0036MJ}}{\boldsymbol{hr}} * \frac{\mathbf{24\ hr}}{\boldsymbol{day}} * \frac{\mathbf{300\ day}}{\boldsymbol{year}} * \frac{\mathbf{5000\ m^2}}{\boldsymbol{pond}} * 0.75 = 972{,}000 \text{ MJ/pond.year} \qquad \text{eq. 37}$$

Like wise,for the closed Photobioreactors used as inoculant of the raceway ponds, assumed 100 W/m^3 and the achievable energy consumption by the PBr per year is calculated as

$$= \frac{\mathbf{100W}}{\boldsymbol{m^{23}}} * \frac{\mathbf{0.0036MJ}}{\boldsymbol{hr}} * \frac{\mathbf{24\ hr}}{\boldsymbol{day}} * \frac{\mathbf{300\ day}}{\boldsymbol{year}} * \frac{\mathbf{125\ m^3}}{\boldsymbol{pond}} * 0.75 = 243{,}000 \text{ MJ/pond.year} \qquad \text{eq. 38}$$

Table 20.Summary of pond material requirement

Description	Symb.	Unit	Value	reference
Individual Pond Area	A	m^2	5,000	
Pond length	l	m	120	
Pond depth	D	m	0.25	
Pond width	W	m	42	
Individual Pond volume	V	m^3	1250	
Culture density /PBR		Kg/m^3	0.44	Experiment
Culture density/Pond		Kg/m^3	0.0695	Assumed 10-15% of PBR
Algae produced(Kg drywt/day/pond)		kg	208.5	
Harvesting rate (kg algae/pond/day)		%	10	Experiment
CO_2 required /kg algae,o.d.b		kg	1.80	Chisti,2007
No of days per year		No	300	

Table 21. Summary of Pond energy requirement

Description	Unit	Value per unit	Value per pond.year
Assumed energy requirement for open raceway pond	W/m2	1	1,296,000MJ
Assumed energy for PBR	W/m3	100	324,000 MJ
Total energy required for cultivation	MJ	-	1,620,000 MJ
Total energy required for cultivation normalized with 75% intermittent supply	MJ	-	1,215,000 MJ

5.3 Harvesting

Harvesting system composed of three sub systems

1. Flocculation

2. Dewatering using gravity settling

3. Dewatering using belt filter press

5.3.1 Flocculation process

The flocculation process agglomerates individual micro-algae cells in to macroscopic materials which are easily dewatered through settling, filtration and pressing. The flocculation process starts with addition of alum, and produces a floc which makes easy for dewatering. The pond water flow rate to the harvesting system is

$$Q_H = \frac{\mathbf{1{,}200{,}000\ kg\ pond\ culture}}{\mathbf{day}} \text{ x } \frac{\mathbf{1\ day}}{\mathbf{24\ hr}} * \mathbf{0.1} = 5{,}000 \text{ kg/hr} \qquad \text{eq. 39}$$

The aluminium sulphate feed rate is

Basis:- 92 mg/lt(ppm) of alum in pond water with 5% aluminium sulphate solution, molecular weight of aluminium sulphate is 342.15 g/mole.

Thus, flow rate is:

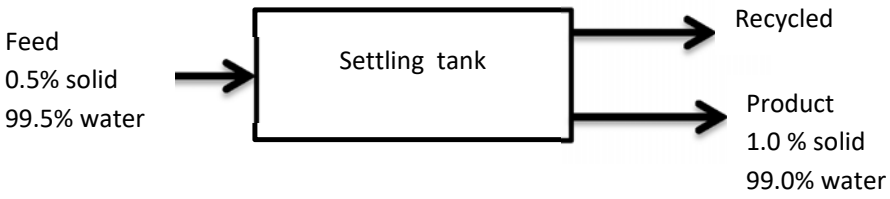
$$= \frac{\mathbf{5{,}000\ kg}}{\mathbf{hr}} * \frac{\mathbf{92\ g\ Al}}{\mathbf{1{,}000{,}000\ g\ pond\ water}} * \frac{\mathbf{342.15\ g\ alum}}{\mathbf{27\ g\ aluminium}} * \frac{\mathbf{100\ g\ alum}}{\mathbf{5\ g\ aluminium}} \qquad \text{eq. 40}$$

= 116.58 kg/hr.

The settling tank

The flocculated solids at a rate of 5,000 kg/hr is sent to the gravity settling tank,which was assumed with capture efficiency of 95%,and a nominal 0.5% solid algae mass concentration from the flocculation tank will enter to the settling tank and after a residence time of 1 to 2 hour,a final concentration of 1.0% solid mass will be transferred to the next dewatering unit(belt filter press).

2,500 kg/hr of the supernatant of the content of the settling tank will be recycled to the pond.The material balance around the settling tank is indicated below.



Algae balance

Solids in feed = solids in product

5,000 kg/hr x 0.005 = product MF x 0.01

Product mass flow = 2,500 kg/hr

The settling tank assumed to operate at 95% efficiency.thus

Product mass flow = 0.95 x 2,500 kg/hr = 2,375 kg/hr

Over all material balance

Feed flow = recycled flow + product flow

5,000 = Recycled flow + 2,375

Recycled flow = 2,625 kg/hr

Therefore

The feed composition is

- Solid mass(Algae) = 0.005 x 5,000 = 25.0 kg/hr
- Liquid mass(water) = 0.995 x 5,000 = 4,975 kg/hr

The product composition is

- Solid mass(Algae) = 0.01 x 2,375 = 23.75 kg/hr

- Liquid mass(water) = 0.99 x 2,375 = 2351.2 kg/hr

Table 22. Summary of material balance around settling tank

Stream	Input material- kg/hr	Out put material- kg/hr
Feed	5,000	-
• Algae • Water	25.0 4,975.0	- -
Product	-	2,375.0
• Algae • Water	- -	23.75 2,351.25
Recycle	-	2,625.00
• Algae • Water	- -	1.30 2,623.8
Total	5,000.00	5,000.00

Energy requirement of flocculation

According to Ron putt,2007 six element mixers for the flocculant which would provide the required mixing at a low pumping power.The puming power for this is estimated from the power gained by the fluid from a pump.thus

$$P = m * w \qquad \text{eq. 41}$$

Where P = power(w)

m = mass flow rate = 5,000 kg/hr = 1.389 kg/s

W = specific work(J/kg or Nm/Kg)

$$W = g * h \qquad \text{eq. 42}$$

Where g = acceleration of gravity = 9.8 m/s^2

h = 0.43m (as suggested by Ron putt,2007)

$$P = 1.389 * 9.8 * 0.43 = 5.853 \text{ W}$$

Therefore, the energy consumption during flocculation per pond per year is

$$= 5.853 * \frac{0.0036 MJ}{hr} * \frac{24\ hr}{day} * \frac{300\ day}{year.pond} = 151.71 \text{ MJ/pond /year}$$

5.3.2 Algae dewatering using belt press

The wet flocculated algae which are in the bottom of the settling tank would contain 1% solids. Using mechanical belt press filter,the water content of the algal biomass will be reduced to minimize the amount of energy required during drying.The smallest belt filter press can accommodate 0.6 tons/hr on a dry basis(Ron putt,2008).The number of ponds that a single belt filter press can accommodate is calculated as follows.

$$\left(\frac{5{,}000\ kg\ Algae\ solution}{pond.day}\right)\left(\frac{1\ ton}{1{,}000\ kg}\right)\left(\frac{1\ day}{24\ hr}\right) = \frac{0.208\ ton\ algae\ solution}{pond.hr}$$

and thus,

$$= \frac{0.6\ ton/hr}{0.208\ \frac{ton\ algae\ sol.}{pond.hr}} = 2.88 \approx 3.0$$

Therefore,one belt press can be sufficient for three ponds.

Material balance over belt press filter

Solid balance

Solids mass entering = solids mass leaving

2,500 kg/hr x 0.01 = product MF x 0.2

Product mass flow = 125.0 kg/hr

The efficiency of the belt press is assumed 98%(Ron putt,2008)

Hence, Product mass flow = 122.5 kg/hr

Over all material balance

Feed mass flow = product mass flow + Recycled mass flow

2,500 = 122.5 + Recycled mass flow

Recycled mass flow = 2,377.5 kg/hr

Composition of dewatered product

- Solid mass (Algae) = 0.2 x 122.5 = 24.5 kg
- Liquid mass (water) = 122.5 – 24.5 = 98.0 kg/hr

Table 23. Summary of material balance around belt filter press

Stream	Input material- kg/hr	Out put material- kg/hr
Feed	2,500.0	-
• Algae • Water	25.0 2,475.0	- -
Product	-	122.5
• Algae • Water	- -	24.5 98.0

Recycle	-	2,372.5
• Algae • Water	- -	0.5 2,377.0
Total	2,500.0	2,500.0

Energy requirement of filter press

Cultivated algae is dewatered in to appropriate mechanical filter press.The initial assumption for the filter press is 3.2 KJ/kg.Thus,the energy required for accommodating the filter press per pond per day is

$$E = \frac{3.2\ KJ}{Kg\ Algal\ culture} * \frac{2{,}500\ kg\ algal\ culture}{hr} * \frac{24\ hr}{day} * \frac{300\ day}{yr} * \frac{1\ MJ}{1000\ KJ} \qquad \text{eq. 43}$$

= 57,600MJ/pond. Year

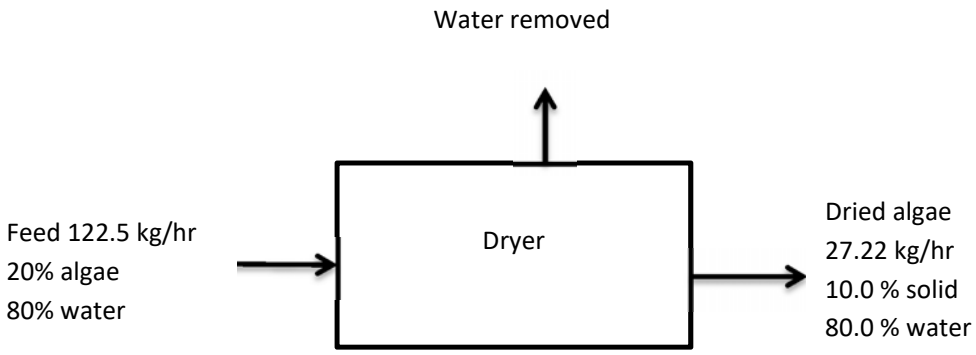
5.4 Drying

The final step in processing algae biomass is usually drying the dewatered slurry to a moisture content of 90%.By drying or dehydrating the algal biomass for better storage condition.

There are several main drying methods. Among which drum driers are selected for this algae biomass drying. Dehydrating algae mass with a thin layer drum dryier yield an excellent product(Shelef et al,1984).Drying the algae on the drum dryer has the dual advantages of sterilizing the samples and breaking the cell wall.

The material balance of the dryer

122.5 kg of wet algal biomass containing 20% solids by weight is fed to the drum dryer where it is dried by hot air.the product finally will contain 10% moisture by weight.



Algae balance

Algae in wet solids = Algae in dried product

122.5 kg/hr x 0.2 = dried product x 0.9

Dried product = 27.22 kg/hr

Efficiency of the drier is assumed to be 98%

Thus, Dried product = 26.68 kg/hr

Over all material balance

Amount Feed = Amount Dried product + Amount Water removed

122.5 kg/hr = 26.68 kg/hr + Amount water removed

Table 24. Summary of material balance around the dryer

Stream	Input material- kg/hr	Output material- kg/hr
Feed	122.5	-
• Algae • Water	24.5 98.0	- -
Dried Product	-	26.678

• Algae • Water	- -	24.0 2.67
Water removed	-	2,3725
• Algae • Water	- -	0.49 95.3
Total	122.5	122.5

The energy requirement of the drying process

The Energy required for drying algae to 10% water content is again taken from table 21.

For drying the micro algae 0.3 MJ/kg electrical energy needed.Thus the amount of energy required for the dryer per pond per year is calculated as

$$E = \frac{0.3\ MJ}{Kg\ dewatered\ algae} * \frac{122.5\ kg\ dewaered\ algae}{hr} * \frac{24\ hr}{day} * \frac{300\ day}{yr.pond} \qquad \text{eq. 44}$$

= 264,600 MJ/pond. Year

In this process of biodiesel production from microalgae, drying is the largest heat consumer in this study.

5.5 Algal oil Extraction

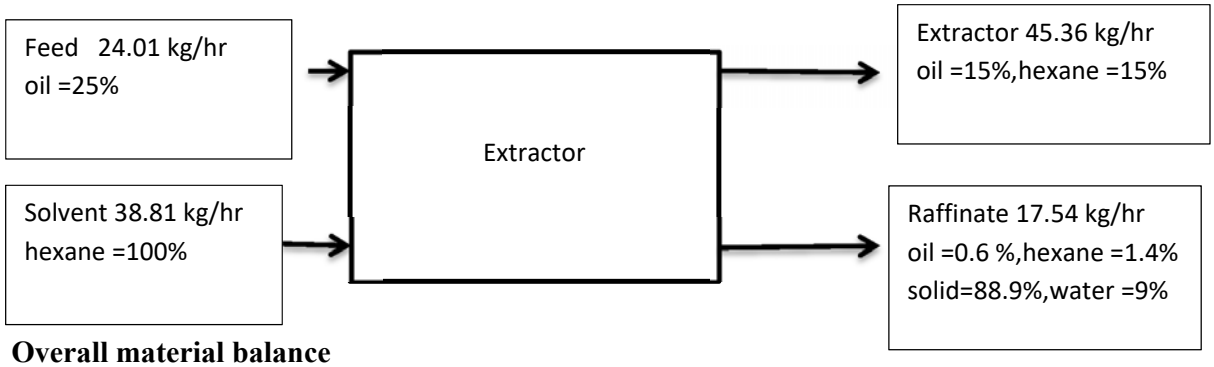
The overwhelming majority of oil extraction using solvent has the benefit of significantly higher oil yield than mechanical extraction, along with lower unit operating costs. The solvent used is commercial hexane, boiling in the temperature range of 65-69^{o}C.

The dried biomass is conveyed from the biomass silos to the solvent extraction process and enters the solvent extractor that operates in a continuous basis that uses hexane as solvent. The extractor unit contains heat recuperator that recovers the heat recover for other streams.

The extractor separate the lipid oil from the biomass with in a residence time 90 -120 minutes.After extraction ,a flash desolventizing system is needed to remove over 99.9% of the solvent from the algal oil and lipid extracted residual biomass operating at a temperature of 75^{o}C.

Hexane separated out is cooled and recycled back to the extractor.A portion of water is also separated out from residual biomass during the heating and cooling process and is recycled to the algae pond.Hexane solvent is lost due to the residual hexane contained in algal oil and residual biomass and fugitive emissions during the extraction and post extraction process.

5.5.1 Material balance over extractor



Overall material balance

$$\text{Feed (F)} + \text{Solvent(S)} = \text{Raffinate(R)} + \text{Extract (E)}$$

$$24.01 + S = R + E \qquad \text{eq.45}$$

Component balance for Oil

$$F * 0.25 + S * 0 = R * 0.006 + E * 0.15$$

$$6.002 = 0.006R + 0.15\,E \qquad \text{eq.46}$$

$$R = 17.54 \text{ kg}$$

Solving equation (5.5) by substitution

$$E = 39.31 \text{ kg}$$

Solving the equation 5.4i) by substituition

S = 29.84 kg

Therefore, the solvent to feed ratio is

S/F = 29.84/24.01 = 1.6

Table 25. Material balance around extractor

Stream	Stream flow Rate-kg/hr	Component	Input Mass flow Kg/hr	Out put Mass flow Kg/hr
Feed	240.1	• Oil • Algae • Water • Hexane	6.025 15.6 2.4 -	
Solvent	388.96	• Oil • Algae • Water • Hexane	- - - 38.89	
Extract	453.64	• Oil • Algae • Water • Hexane		6.8 - - 38.6
Raffinate	175.4	• Oil • Algae • Water • Hexane		0.1 15.6 1.6 0.25
Total			62.9	62.9

The residence time for extraction is 45 minutes. The theoretical amount of extracted oil per annum per pond is

$$\frac{6.8\ kg\ oil}{pond.hr} * \frac{24\ hr}{day} * \frac{300\ days}{Annum} * \frac{1\ ton\ oil}{1000\ kg\ oil} = 48.96 \text{ ton oil} \qquad \text{eq. 47}$$

5.5.2 The Energy requirement of the extractor

The assumption for energy required for lipid oil extraction and transesterfication is taken from table 21.

0.5 MJ/kg energy is assumed for both lipid oil extraction and transesterfication. Therefore, the amount of electrical energy required for extraction of the algal oil produced per pond per year is calculated as

$$E = \frac{0.5\ MJ}{Kg\ Algal\ oil} * \frac{6.8\ kg\ algal\ oil}{hr.pond} * \frac{24\ hr}{day} * \frac{300\ day}{yr} \qquad \text{eq. 48}$$

= 24,480 MJ/pond. Year

5.5.3 Energy requirement for hexane recovery

The energy required for solvent (hexane) recovery is given by Rogers et al, 2014.

$$E = \frac{C_p * w\ (Tb - 20)}{3600} \qquad \text{eq. 49}$$

Where,E = energy in kwh

Cp = specific heat of hexane = 2.26 kJ/Kg^{o}C

W = number of kg of hexane entering to the extractor every hour = 38.8 kg

Tb = Boiling point of hexane =69oC

20 is the starting temperature of hexane

3600 is the conversion factor for kJ to kwh

For a single pond per day under continuous operation,the solvent recovery system requires

$$E = \frac{2.6\frac{kJ}{kgoC} * 38.8\ kg * 49}{3600} = 1.373 \text{ kwh}$$

Therefore,the energy consumption for hexane recovery per pond per year is

$$= \frac{1.373\ kwh}{pond.day} * \frac{3.6\ MJ}{kwh} * \frac{300\ days}{pond.yr} = 1{,}482.84 \text{ MJ/pond /year}$$

5.6 Biodiesel production

In the transesterfication reaction system 3 mol of alcohol required for each mole of triglyceride to produce 1 mole of glycerol and 3 mole of methyl ester(Y.Chisti,2007).This is equivalent to mass ratio of methanol to oil should be 1:4.4.In addition 1 wt% of NaOH is added as catalyst(Y.Chisti,2007).No pre-treatment in order to neutralize free fatty acids(FFA).Because FFA content in microalgae is very low i.e. 0.88%.

If the FFA content is high (>1.0%) large soap is formed during transesterfication, which affects the yield of biodiesel. The conversion rate is assumed to be 99.7% and for every kg of biodiesel 0.1 kg of glycerol is formed.

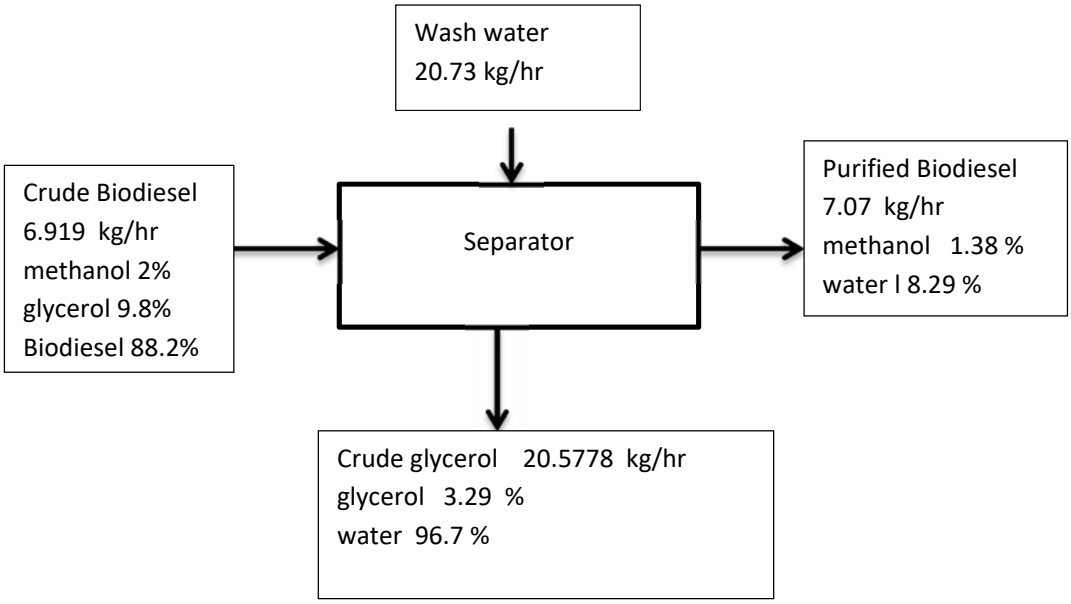
Alkali catalysed transesterfication is carried out approximately at 60^{o}C under atmospheric pressure, as methanol boils at 65^{o}C at atmospheric pressure. Under this condition reaction takes place about 90 minutes to complete.

The theoretical amount of biodiesel produced per annum per pond is

$$\frac{6.103\ kg\ biodiesel}{pond} * \frac{1}{90\ min} * \frac{1440\ min}{1\ day} * \frac{300\ day}{1\ yr} * \frac{1\ ton}{1000\ kg} = 29.3 \text{ ton/annum}$$

5.6.1 Biodiesel purification

Biodiesel is purified by repeated washing with water to remove glycerol and methanol as shown in the material balance on the separator.



The mixture of fatty acid methyl ester (FAME) obtained from the transesterfication reaction must be purified in order to comply with the established quality standard for biodiesel.Therefore FAME must be washed and neutralised and dried.As per the experimental result indicated in section 3 above,the biodiesel to water volume ratio shall be 1:3 to effective mass transfer from biodiesel to water phase(4.23% in biodiesel phase and 91.2% in water phase).

Material balance for the separation of biodiesel from glycerol and other components is shown in table 26.

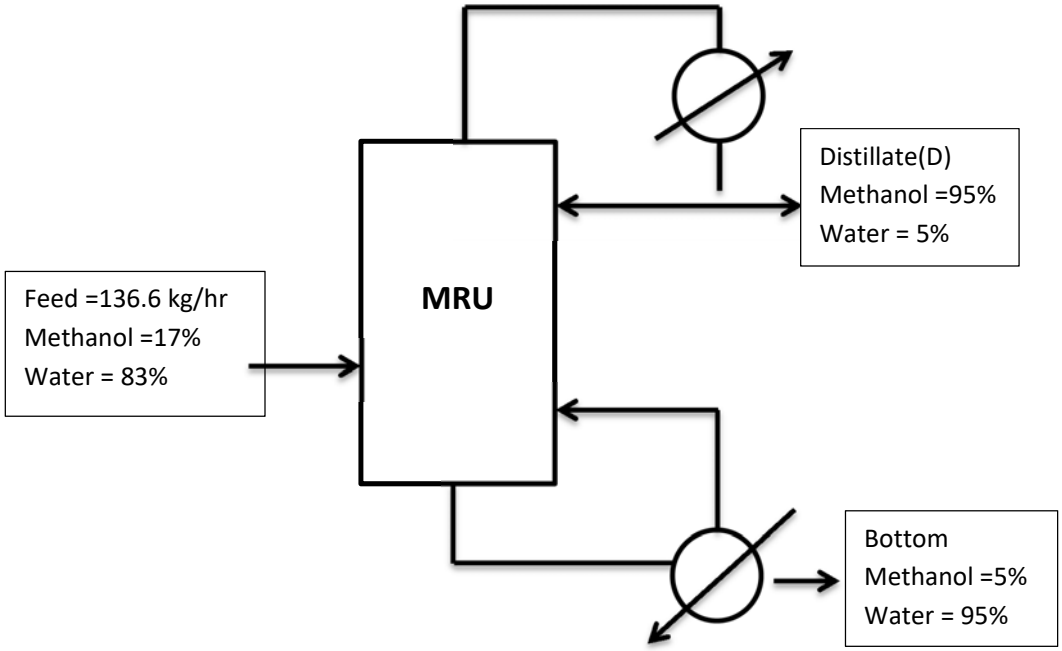
Table 26. Summary of material balance during biodiesel washing

Stream	Flow rate	Components	In put flow	Out put flow
Crude biodiesel	6.919	• Biodiesel • Methanol • Water • Glycerol	6.1 0.138 0 0.678	
Washing water	20.73	• Biodiesel • Methanol • Water • Glycerol	0 0 20.73 0	
Purified biodiesel	7.07	• Biodiesel • Methanol • Water • Glycerol		6.386 0.097 0.586 0.000
Crude glycerol	20.578	• Biodiesel • Methanol • Water • Glycerol		0 0.0408 19.9 0.677
		Total	27.649	27.649

5.6.2 Methanol recovery unit

After the completion of the transesterfication reaction, the excess methanol is distributed to the mixture of the products (biodiesel and glycerol).This mixture is separated in the separator. Methanol recovery unit (MRU) used after phase separation, in which biodiesel and glycerol still contain excess methanol. This MRU can be used to separate methanol from biodiesel and glycerol. This is a common approach of methanol recovery in most conventional biodiesel production processes.

136.6 kg/hr of feed supplied from the central biodiesel plant will be fed to the distiller in the middle of the distillation column. The feed contains 17% methanol and 83% water. The distillate is assumed to contain 95% methanol and the bottom product to contain 5% methanol. The material requirement for the MRU is indicated below.



Overall Material balance

$$\text{Feed (F)} = \text{Distillate(D)} + \text{Bottom product(W)}$$

$$136.6 = D + W \qquad \text{eq. 50}$$

Methanol (solvent) balance

$$136.6 \times 0.17 = 0.95 \times D + 0.05 \times W$$

$$23.222 = 0.95D + 0.05W \qquad \text{eq. 51}$$

Rearranging (5.7) and (5.8) and solving simultaneously

$$0.95D + 0.05\,W = 232.22$$

$$D + W = 136.6$$

Multiplying (i) by 0.05 gives

0.95D + 0.05 W = 23.22

0.05D + 0.05 W = 68.3

0.9D = 163.92

D = 182.13 kg/hr

Therefore , W = 136.6 – 18.213 = 118.39 kg/hr

5.6.3 The energy requirement of Methanol recovery unit

The energy required for methanol recovery, is again given by Rogers et al

$$E = \frac{C_p * w\,(Tb-20)}{3600} \qquad \text{eq. 52}$$

Where,E = energy in kwh

Cp = specific heat of methanol = 2.533 kJ/Kg^{o}C

W = number of kg of methanol entering to the MRU every hour = 136.6 kg

Tb = Boiling point of Methanol =64.6 ^{o}C

20 is the starting temperature of hexane

3600 is the conversion factor for kJ to kwh

under continuous operation the power requirement of the methanol recovery system is calculated as

$$E = \frac{2.533\frac{kJ}{kgoC} * 136.6\,kg * 44.6}{3600} = 4.286 \text{ kwh}$$

Therefore, the energy requirement in Mega joule of the methanol recovery unit per pond per year is

$$= \frac{4.286\ kwh}{pond.day} * \frac{3.6\ MJ}{kwh} * \frac{300\ days}{pond.yr} = 4,\ 6288.8\ \text{MJ/pond /year}$$

5.7 Preliminary equipment specification and sizing

The major unit operations material of construction and sizing is described below

5.7.1 Raceway pond material of construction and sizing

The raceway pond to be constructed is a closed loop flow channel with a typical culture depth of about 0.25 meter, length about 120 m and width 42m with resulting area of 5000 sq meter.

Volume of raceway pond

V = 120m*42m*0.25m = 1,260 cubic meter.

A compacted earth construction with 1 mm thick plastic membrane used is relatively cheap set up (Chisti 2007).therefore plastic lined surface is chosen.

5.7.2 Closed photobioreactor materials and sizing

Many configurations of closed photobioreactor have been revised and the material of construction that represent the PBR as micro algae inoculant for each raceway ponds chosen based on practical issues from costs and biological applications. The material characteristic for the construction of closed PBR selected having high transparency, high flexibility, durability,non toxicity and high resistance to chemical and metabolites produced by microorganisms.

The type of the closed PBR to propose for this purpose is A tubular Photobioreactors consisting of an array of straight transparent low density polyethylene (LPDE) tubes. The benefit of using LPDE include high visible light and near infrared transmission and low cost.

The closed PBR system is proposed to be designed with a bearing capacity of 125 m^3, which is connected with a gas exchange unit via air purge and the culture will be mechanically pumped to the respective raceway pond after inoculation.

5.7.3 Flocculation and settling tank materials and sizing

The tank is suggested to be made of non-reactive surface of concrete. In the design of rectangular sedimentation tank the following specification was given.

a. Surface area.

The surface area of the tanks calculated assuming the over flow rate to be 125 litre per day per square meter is proposed.

$$A = \frac{Volumetric\ flow\ rate}{Over\ flow\ rate} = \frac{Q}{OR} = \frac{5{,}000\ lt/day}{125\ \frac{Lt}{day.m2}} = 40\ m^2 \qquad \text{eq. 53}$$

b. Volume

The volume of the tank is calculated by multiplying the flow rate by the detention time. Detention time is here assumed 1 day for effective flocculation and settling.

$$V = \frac{volumetric\ flow}{detention\ time} = \frac{Q}{t} = \frac{125\ m3/day}{day} = 125\ m^3 \qquad \text{eq. 54}$$

c. Depth

The tank depth calculated from

$$d = \frac{Volume}{surface\ area} = \frac{V}{A} = \frac{125\ m3}{40\ m2} = 3.125\ m \qquad \text{eq. 55}$$

d. Width and length

volume = length * width * depth

V = L * W * d , where L = 3W eq. 56

Thus,V= 4W3D

$$W = \sqrt[3]{\frac{V}{4d}} = \sqrt[3]{\frac{125\ m3}{4*3}} = 2.795\ \text{m} \qquad \text{eq. 57}$$

Therefore, the length is

$$L = 4 * 2.795 = 11.18\ \text{m}$$

e. Flow through velocity

First let us calculate the cross sectional area of the tank.

$$Ax = W * D \qquad \text{eq. 58}$$

$$Ax = 2.795\ \text{m} * 4\ \text{m} = 11.18\ \text{m2}$$

Then,the flow through velocity of tank is calculated as

$$V = \frac{Q}{Ax} = \frac{0.0139\ m3/sec}{11.18\ m2} = 0.00124\ \text{m/sec} \qquad \text{eq. 59}$$

5.7.5 Belt filter press material and sizing

A belt filter press compresses the algae solution between two endless porous belts tensioned over a series of rollers to squeeze out the water. The basic operational steps of the process are illustrated in Fig. 5.4

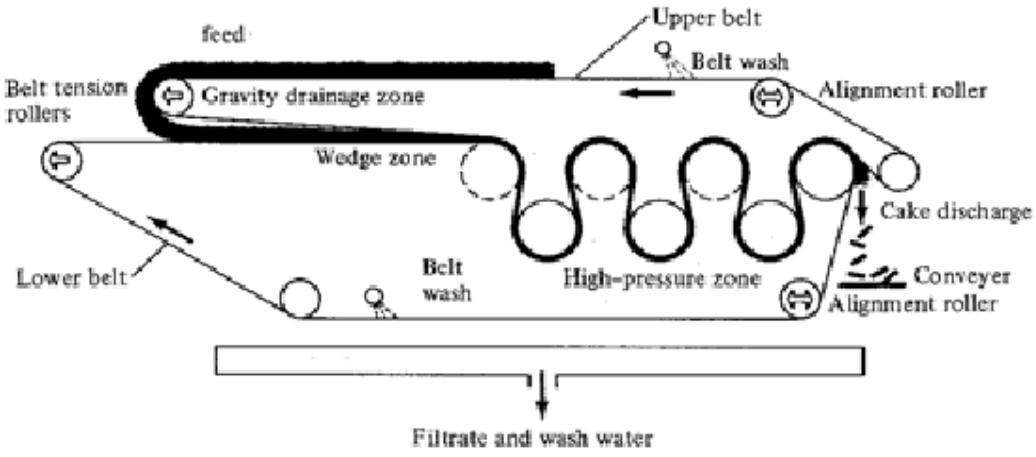


Figure 34.Schematic diagram of a belt filter (Courtesy of Ashbrook-Simon Hartley).

Sizing of Belt Filter Press

Belt widths of presses range from 0.5 to 3 m, with the size taken the upper limit 3.0m. The selection during design of a sludge dewatering facility depends based on the size of the plant, the desired flexibility of operations, anticipated conditions of dewatering, and economics.

The hydraulic rate calculated based on the belt filter press with an effective belt width of 3.0 m is used to dewater the algae suspension is

$$\text{Hydraulic rate} = \frac{2{,}500\frac{kg}{hr} * \frac{0.001m3}{kg}}{3.0} = 0.833\ m^3/m.h \qquad \text{eq. 60}$$

5.7.6 Oil extractor material of construction and sizing

The proper material used for the design of the hexane extraction system was chosen under the criteria that the material could not be corrosive when in contact with hexane. Given that the properties pertaining to stainless steel permitted contact with hexane without the possibility of corrosion. Stainless steel becomes the primary used for the design of the hexane extraction system.

Due to time and financial constraint, it was not possible to attempt completely to design the hexane extraction system. Therefore, the unit specification based on the material balance done on the extractor and the following specification proposed.

Extraction vessel

- Volume = 50 litres
- Batch capacity = 25 kg
- Direct steam = 0-7 kg/hr,0-3.5 bar

Miscella tank

- Volume = 50 litres
- Direct steam = 0-4 kg/hr,0-3.5 bar

Solvent pump

- Type = centrifugal
- Solvent flow = 7.45 litre /min

5.7.7 Transesterfication reactor and sizing

Based on the stoichiometric equations mentioned in the literature and results from the experiment, the design specifications are set as follows.

- 98% conversion shall be achieved
- Compatible construction of materials must be used
- Vessel capacity or reactor volume obtained by multiplying the entering flow rate with the residence time(1 .5 hours),and with the head space of 20% of liquid volume. Thus

Reactor volume = flow rate * residence time * head space eq. 61

$$= \frac{6.3\ kg}{hr} * 1.5\ \text{hr} * \frac{1\ lt}{kg} * 1.2 = 11.34\ \text{litres}$$

- Atmospheric operating pressure
- Steam is used for heat supply
- Ideal mixing in the continuous stirrer reactor vessel

The columns were assumed to be packed with 2 inches carbon steel ball rings.

Heat exchangers were designed as single pass shell and tube. Detail design of shell and tube heat exchangers omitted deliberately due time and financial constraint.

The pump type was chosen to minimize the cost and hence centrifugal or external gear pumps used.

5.8 Energy Analysis

When converting energy from one form to another, the second law of thermodynamics dictates that some energy will be lost.Net energy gain(NEG) i.e the difference between the total energy output and total energy input is one of the accepted indices for analysis of biofuels.

Net energy gain = Energy out put – Energy in put eq. 62

- Total energy required for cultivation

  = 1,215,000 MJ/pond/year

- Energy required for filter press

  = 57,600 MJ/pond/year

- Energy required for drying

  = 264,600 MJ/pod/year

- Energy required for algal oil extraction and transesterfication

  = 127,111.76 MJ/pond/year

- Energy required for hexane recovery

  = 1,482.84 MJ/pond/year

- Energy required for methanol recovery unit

  = 4,628.8 MJ/pond/year

The energy available in biodiesel produced is calculated as

=Qty of biodiesel $\frac{kg}{pond.year}$ * calorific value of biodiesel eq. 63

$= \frac{46{,}080\ kg\ biodesel}{pond.year} * \frac{37.8\ MJ}{kg\ biodiesel}$ = 1,741,824 MJ/pond/year

Therefore, the net energy assessment equals

$= E_{output} - E_{input}$

=1,741,824 - 1, 670,4291,

= 71,395 MJ/pond/year

5.9 Carbon assessment

Direct utilization of cement flue gas has been considered for CO_2 feed to the biomass production in algae pond and photobioreactor. Carbondioxide sequestration can be effectively carried out using algae to produce algal biomass and this can be converted to biodiesel and it can be used to reduce the greenhouse gases and there by global warming will be avoided.

However, considering the emission factors from electricity consumption in the biodiesel plant under study must be considered. Composite electricity/heat emission factor published by the international Energy agency (EIA, 2010) is used, which is the basis for the electricity factor for emissions from purchased electricity. The emission factor for grid electricity of Ethiopia in 2009 is 0.1189 kg CO_2 per kwh generated .

The carbon balance of each stream in the biodiesel manufacturing system is indicated below.

- CO_2 emission due to electricity for cultivation

$$= \frac{1{,}215{,}000\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{55{,}281.37\ kg\ CO2}{pond.yr}$$

- CO_2 emission due to energy for filter press

$$= \frac{57{,}600\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{1{,}965.56\ kg\ CO2}{pond.yr}$$

- CO_2 emission due to electricity for drying

$$= \frac{264{,}600\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{9{,}029.29\ kg\ CO2}{pond.yr}$$

- CO_2 emission due to electricity for algal oil extraction and transesterfication

$$= \frac{127{,}111.76\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{4{,}337.6\ kg\ CO2}{pond.yr}$$

- CO_2 emission due to electricity for hexane recovery

$$= \frac{1{,}482.8\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{50.6\ kg\ CO2}{pond.yr}$$

- CO_2 emission due to electricity for methanol recovery unit

$$= \frac{4{,}628.8\ MJ}{pond.year} * \frac{0.287\ kwh}{MJ} * \frac{0.1189\ kg\ CO2}{kwh} = \frac{157.96\ kg\ CO2}{pond.yr}$$

The carbon dioxide sequestration by microalgae is calculated from the assumption that 1 kilogram algal biomass consumes 1.83 kilogram of CO_2(Chisti,2007) equals

$$= \frac{208.5\ kg\ algae}{day.pond} * \frac{300\ day}{yr} * \frac{1.83\ kg\ CO2}{kg\ algae} = 114{,}466.5$$

The total emission for biodiesel extraction from microalgae equals

= - 144,466.5 + 55,281.37+1,965.56+9,029.29+4,337.6+50.6+157.96

= - 43,644.1 Kg CO2/year Pond

The negative result shows, carbondioxide is sequestered due to emission from the biodiesel plant.

5.10 Net Energy ratio (NER)

The energy efficiency of biofuels can be analysed by finding net energy ratio(NER).Net energy ratio is defined as the ratio of total energy outputs to total energy inputs.

$$\text{NER} = \frac{\sum \textbf{Energy out put or energy content of the fuel}}{\sum \textbf{primary energy input}} \qquad \text{eq. 64}$$

$$= \frac{1{,}741{,}824}{1{,}670{,}429.4}$$

= 1.03

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The first aim of this research was to produce biodiesel from microalgae as a way to help win our country in reducing or completely substituting the fossil oil import. The annual importation of gas oil (petroleum diesel) in Ethiopia in the year 2010/11 to 2011/12 was 1,175,156 Metric ton in average. Whereas, this preliminary study of the design of the microalgae biodiesel based on the carbondioxide released from cement industry(Dangote cement, Ethiopia) shows that ,the possible quantity of biodiesel that can be produced with the proposed algae farm area of about 100 hectar(200 ponds) is only about 5,860 Metric ton. This is about 0.5% of the imported fossil fuel.

The low level production of the biodiesel is due to the low yield of algal biomass and lipid oil productivity. The lipid oil yields is found to be 20%,whereas researches shows that the lipid oil content of algal oil can reach above 60%, if favourable condition of algal biomass can be kept. In this experiment, conditions were not properly monitored due to shortage of special instruments to control the growth parameters like pH, carbondioxide rate and light intensity.

To address this challenge continued research and development must be conducted with fulfilment of research facilities for algal biotechnology. Research based on innovative biological and engineering approach, could help develop new capabilities to make algal biofuel a viable substitute to the imported diesel in our country.

The second aim of this research was, initially to estimate the greenhouse gas (CO_2) emission associated with the cement industry, in particular the Dangote cement industry. Using the IPCC estimation method it was possible to estimate that, about 610,000 MT CO_2 per annum is released by Dangote cement plant to the atmosphere. Whereas the possible CO_2 sequestration capability by the algal biomass produced on the proposed algae farm is 22,893.3 ton CO_2 per annum. With this

quantity it was only possible to capture biologically 3.8% of the carbondioxide emission by the industry. The reason for the low level of carbondioxide sequestration by the proposed algae farm is due to low productivity of algal biomass.

The net energy ratio of 1.03 calculated based on the design and energy calculation of the biodiesel plant suggested that the process is energy wise sustainable, but needs more improvement for better result. Among the unit processes the main energy challenge is the energy consumption of paddle wheel and pumps to circulate the culture volume of the PBR and the open raceway pond.72.7% of the energy expenditure goes to this culture system. The other energy challenge is due to drying of microalgae. About 15.8% of the energy is consumed during drying stage. These energy bottlenecks can be addressed by the use of algal meal produced as input for energy to feed the boiler for steam energy.

In the evaluation to assess the carbon released by the biodiesel industry plant, due to the electrical energy consumption was found to be -71,395 kg CO_2/pond/annum.This showed that the process of making algal biodiesel is a carbon sink.

6.2 Recommendations

Identifying single species of microalgae having high biomass and lipid activity beside the optimum cultivation condition is desirable. As per the information obtained from the biodiversity institute of Ethiopia, a vast and diverse spectrum of algal species available in our country. The lakes near Debrezeit, Awassa, Bahirdar and others consist of a wide range of algal species, but the study on identification of strains and species of microalgae is lowest. Genomic analysis and physiological studies in our universities and related research areas should be done in future for identifying algal species with high lipid content and other valuable characteristics. From the process engineering prospective, further improvement to best technology for algae cultivation, dewatering, drying and extraction could reduce the material and energy requirement of algal biodiesel manufacturing.

Direct use of flue gas was necessary to study the real tolerance of microalgae for sulfur dioxide, nitrogen oxide and particulate matter present in the cement flue gas during cultivation. It would be more sensible to work with actual carbondioxide source of the cement industry for future research work.

References

Abbas Amin Umar.(2014).Feasibility Study of Algae Biodiesel Production in the Cambois Peninsular (UK), International Journal of Energy and Environmental Research,2(1),pp.21-54

Abraham M. Asmare, Berhanu A. Demessie, Ganti S. Murthy. (2013).Theoretical Estimation of Algal Biomass Potential and Lipid Productivity for Biofuel Production in Ethiopia International Journal of Science and Research (IJSR), India Online ISSN: 2319-7064, Volume 2 Issue 6

Amos Richmond. (2004).Handbook of Microalgal Culture: Biotechnology and Applied Phycology, Blackwell Science Ltd, a Blackwell Publishing company

André F. Young, Fernando L. P. Pessoa, Eduardo M. Queiroz. (2015). Comparison between Biodiesel Production from Soybean Oil and Palm Oil with Ethanol: Design and Economic Evaluation, chemical engineering transaction, VOL. 43

Ayhan Demirbas, M. Fatih Demirbas.(2010). Green energy and technology-Algae energy-Algae as a New Source of Biodiesel, Trabzon, Turkey, springer

Birhanu Andualem and Amare Gessesse.(2014).Impact of Petroleum on Developing Economies and Prospect of Liquid Biofuel Substitute: Scenario in Ethiopia, World Applied Sciences Journal 32 (8), 1652-1663

Biofuels - A Failure for Africa- A briefing by the African Biodiversity Network, the Ethiopian Society for Consumer Protection, and The Gaia Foundation.(December, 2010).Retrieved from **http://www.africanbiodiversity.org/sites/default/files/PDF**

Blander M., man sood,Charlotte wylie,Amy Haughton and Jessica Lowell.(2011).Electricity specific emission factors for grid electricity/technical paper,Retrived from http://www.emissionfactors.com

Borowitzka M.A. and Moheimani. N.R. (2014). Algae for Biofuels and Energy, Developments in Applied Phycology 5, 1 DOI 10.1007/978-94-007-5479-9

Bruce A. Babcock.(Summer 2008,vol 14 N0 3).Breaking the Link between Food and Biofuels. Retrieved from http://www.card.iastate.edu/iowa_ag_review/summer_08/article1.aspx

CRGE, 2011; Ethiopia's Climate-Resilient Green Economy, Green economy strategy; Federal Democratic Republic of Ethiopia, Ethiopia, Addis Ababa,

Dinabandhu Sahoo, Geetanjali Ellingham and Salam Sonia Devi.(2012). Using algae for carbon dioxide capture and bio-fuel production to combat climate change.Phycological Society, India,42(1),pp.32-38

Douglas C.Montegomery. (2001).Design and analysis of experiments; 8th edition, Arizon state university, John Wiley & sons.Inc

EPA. (2010). Available and emerging technologies for reducing greenhouse gas emissions from the Portland cement industry, U.S. Environmental Protection Agency Research Triangle Park, North Carolina

Ernest orlando Lawrence.(2013). Estimation of CO2 Emissions from China's Cement Production: Methodologies and Uncertainties; Reprint version of journal article published in "Energy Policy", Volume 57, pp. 172–181

Gabriel. Acién Fernandez & C. V. González-Lopez & J. M. Fernandez Sevilla & E. Molina Grima.(2012). Conversion of CO2 into biomass by microalgae: how realistic a contribution may it be to significant CO2 removal, Appl Microbial Biotechnology 96, pp.577–586

Farooq Ahmad, Amin U. Khan and Abdullah Yasar.(2013).Transesterfication of oil extracted from different species of algae for biodiesel production, African Journal of Environmental Science and Technology, Vol. 7(6), pp. 358-364, June 2013

Giuliano Dragone, Bruno Fernandez, Antonio A. Vicente, and José A. Teixeira.(2010). Third generation biofuels from microalgae; IBB - Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Hrvoje Mikulčića, Milan Vujanovića, Nataša Markovskab, Risto V. Filkoskic, Marko Bana, Neven Duić.(2013). CO_2 Emission Reduction in the Cement Industry. A publication of AIDIC, vol 35, DOI: 10.3303/CET1335117

Indhumathi P, Syed Shabudeen , Shoba.(2014).A Method for Production and Characterization of Biodiesel from Green Micro Algae ,International Journal of Bio-Science and Bio-Technology Vol.6, No.5,pp.111-122

Indhumathi Ponnuswamy, Soundararajan Madhavan and Syed Shabudeen.(2013).Isolation and Characterization of Green Microalgae for Carbon Sequestration, Waste Water Treatment and Bio-fuel Production, International Journal of Bio-Science and Bio-Technology Vol. 5, No. 2.

Intergovernmental panel on climate change (IPCC). (1996).Guide lines for national greenhouse gas inventories reference manual (revised), vol 3

ISBT. (2001).International society of beverage technologists(ISBT) carbondioxide guide line, Stefan M.Ringo,2001

Van Gerpen,J., B. Shanks, and R. Pruszko , D. Clements , G. Knothe.(2004). Biodiesel Production Technology; National Renewable Energy Laboratory 1617 Cole Boulevard, Golden, Colorado

Lundquist, J.J, Woertz, C..Quinn, andJ.R.Benemann.(2010).A Realistic Technology and Engineering Assessment Of Algae Biofuel Production , Energy Biosciences Institute University of California Berkeley, California

Jared Abodeely, Daniel Stevens, Allison Ray, Kastli Schaller, Deborah Newby. (2013). Algal Supply System Design –Harmonized Version , U.S. Department of Energy National Laboratory, Idaho National Laboratory, Idaho Falls, Idaho 83415

John R. Benemann and David M. Gillett.(1987).Effects of fluctuating environments on the selection of high yielding microalgae, Schools of Applied Biology and Chemical Engineering Georgia Institute of Technology Atlanta, Schools of Applied Biology and Chemical Engineering Georgia Institute of Technology , Atlanta

John Sheehan, Terri Dunahay, John Benemann, Paul Roessler.(1998).A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae.1617 Cole Boulevard Golden, Colorado. National Renewable Energy Laboratory

Jonathan N.Rogers,Julian N.Rosenberg,Bernardo J.Guzman,Voctor H.oh,Luz Elena Mimbela,Abbas,Ghassemi,Michael,J.Beterbaugh,George,A.Oyler,Marc,D.Donohue.(2014). A critical analysis of paddle wheel driven raceway ponds for algal biofuel production at commercial scale,Elselvier,Algal research 4,pp. 76-88

Jos G.J. Olivier (PBL), Greet Janssens-Maenhout (IES-JRC), Marilena Muntean (IES-JRC), Jeroen A.H.W. Peters (PBL).(2014).Trends in global CO2 emissions: 2014 Report.: Textcetera, The Hague,PBL publishers

Lee, Ju Nu.,.Jin Suk Lee,Chul seung shin, soon chulpark.(2011).Methods to enhance tolerance of chlorella to toxic compounds in flue gas, Applied Biochem & Biotech.

Lei Shen a, TianmingGao a,b, Jianan Zhao a, LimaoWang a, LanWang c, LitaoLiu a, Fengnan Chen a,b,n, JingjingXue.(2014).Factory-level measurements on CO2 emission factors of cement production in China; Renewable and Sustainable Energy Reviews. 34, pp.337–349

Liam Brennan a, Philip Owende. (2010).Biofuels from microalgae - A review of technologies for production, processing, and extractions of biofuels and co-products. Renewable and Sustainable Energy Reviews 14 (2010) ,pp.557–577

Manual on the Production and Use of Live Food for Aquaculture (2016).Retrived from http;//www.fao.org/fishery

Marc Veillette, Mostafa Chamoumi, Josiane Nikiema, Nathalie Faucheux and Michèle Heitz.Production of biodiesel from microalgae. Retrived from http://www.intechope.com

MayZaw H., Lim Yan Ling, Sek Hui Yun and Olaganathan Rajee. (2013). Biofuel from microalgae – a review on the current status and future trends. International journal of advanced biotechnology and research, 4(3), pp. 329-341

Michael Taylor, Cecilia Tam and Dolf Gielen. (2006).Energy Efficiency and CO_2 Emissions from the Global Cement Industry, International Energy Agency

Mikko Keuhia.Henik Holmberg, Matty sonk, Pekka Ahtila. (2015).Energy analysis of algae to biofuel production chains integrated with a combined heat and power plant.23rd European biomass conference and exhibition algae report.

Ministry of Industry. (2014).Ethiopian Cement Industry Development Strategy: First Draft (2015-2025).Adama science and Technology University.

Mukesh Kumar, Mahindra Pal Sharma.(2014).Potential assessment of micro algal oils for biodiesel production: A review.J. Mater. Environ. Sci. 5 (3) (2014) 757-766

Olaizola,M., T Bridges, S Flores, L Griswold, J Morency, T. Nakamura; Microalgal removal of CO_2 from flue gases: CO_2 capture from a coal combustor, Retrived from https://www.usea.org

Parsons Brinckerhoff.(2011).Accelerating the uptake of ccs: industrial use of captured carbon dioxide, Global CCS institute.Retrived from https://www.globalccsinstitute.com

Pooja. Himabindu.v.(2012).CO2 Removal from Industrial Flue Gas using Botryococcus braunii for Simultaneous Lipid production, International Journal of Science and Research (IJSR) ISSN: 2319-7064

Qian Zhu. (2011). CO_2 abatement in the cement industry; IEA Clean Coal Centre. Retrived from https://www.iea-coal.ork.uk

Rajiv Chandra Dev Goswami, Nitumani Kalita, Mohan Chandra Kalita.(2012).A study on growth and carbon dioxide mitigation by microalgae Selenastrum sp.: its growth behaviour under different nutrient environments and lipid production, Annals of Biological Research,3 (1),pp.499-510.Retrieved from https://www.scholarsresearchlibrary.com

Romano S. D. and P. A. Sorichetti. (2011). Dielectric Spectroscopy in Biodiesel Production and Characterization, Green Energy and Technology, DOI: 10.1007/978-1-84996-519-4_2, Springer-Verlag London Limited

Ron Putt. (2007).Algae as a Biodiesel Feedstock: A Feasibility Assessment, Centre for Micro fibrous Materials Manufacturing, Department of Chemical Engineering Auburn University, Alabama

Roy.M. Kundu, K. and Dahake, V.R. (2014).Microalgae – a potential energy source for decentralised power generation: a review, African Journal of Science and Research, 2014,(3)3:11-19

Saddam H. Al-lwayzy, Talal Yusaf and Raed A. Al-Juboori. (2014). Biofuels from the Fresh Water Microalgae Chlorella vulgaris (FWM-CV) for Diesel Engines; Energies 2014, 7, 1829-185

Saminu,A, A. UT Soho, G Harunaand, L Sagir.(2013). Design and Construction of a Model Sedimentation Tank Using Existing Slow Sand Filter For NDA Treatment Plant, international journal of engineering sciences & research technology, ISSN: 2277-9655

Sanet Janse van Vuuren, Jonathan Taylor, Carin van Ginkel, Annelise Gerber. (2006).Easy identification of the most common fresh water algae, A guide for the identification of microscopic algae in South African fresh waters, South Africa, North west university

Sharmila.K, Ramya.s, Babu Ponnusami.A. (2014).Carbon sequestration using microalgae-a Review, International Journal of ChemTech Research CODEN (USA): Vol.6, No.9, pp 4128-4133

Shelef, G., A. Sukenik,M, M, M, M. Green.(1984). Microalgae Harvesting and Processing: A Literature Review, Technion Research and Development Foundation ltd., Haifa, Israel

Surendhiran D. and Vijay M. (2012). Microalgal Biodiesel - A Comprehensive Review on the Potential and Alternative Biofuel, Research Journal of Chemical Sciences, Vol. 2(11), 71-82

Tadele Ferede, Zenebe Gebreegziabher, Alemu Mekonnen, Fantu Guta, Jorgen Levin, and Gunnar Kohl in; Biofuels.(2013). Economic Growth and the External Sector in Ethiopia-A computable general equilibrium analysis. Environment for development discussion paper series.EfD DP 13-08.

Udara S.P.R. Arachchige, Dinesh Kawan, Lars-André Tokheim, and Morten C. Melaaen.(2013). Model Development for CO2 Capture in the Cement Industry , International Journal of Modelling and Optimization, Vol. 3, No. 6

Viktor Anderson Sarah Broberg Roman Hackl.(2011).Integrated Algae Cultivation for Biofuels Production in Industrial Clusters; Arbetsnotat nr 47November 2011-11-15ISSN 1403-8307

Volker Hoeing; Helmut Hoppe, and Bernhard Emberger. (2007). Carbon Capture Technology - Options and Potentials for the Cement Industry, Tannenstrass, Duesseldorf, Germany European Cement Research Academy,

Xiaodong Deng Yajun Li1 and Xiaowen Fei.(2009). Microalgae: A promising feedstock for biodiesel, African Journal of Microbiology Research Vol. 3(13) pp. 1008-1014

Xing Zhang. (2015).Microalgae removal of CO2 from flue gas; IEA Clean Coal Centre, 14 Northfields London SW18 1DD ,United kingdom

Yusuf Chisti. (2007).Biodiesel from microalgae; Biotechnology Advances 25 (2007) 294–306

Yusuf Chisti. (2008).Biodiesel from microalgae beats bioethanol. School of Engineering, Massey University, Private Bag 11 222, Palmerstone North, New Zealand

Yusuf Chisti. (2016). Large-Scale Production of Algal Biomass: Raceway Ponds, Springer International Publishing Switzerland 2016, School of Engineering, Massey University, Private Bag 11 222, Palmerstone North, New Zealand

Zhang, Y. M.A. Dube , D.D. McLean , M. Kates.(2003). Biodiesel production from waste cooking oil. Process design and technological assessment, Bio resource Technology 89 (2003) 1–16

APPENDIX

Appendix I

Scanned absorbance measurement values of algal culture during growth phase

- Time – Day 18,Wave length interval – 475nm to 650 nm, Instrument :Perkin Elmer spectrophotometer,Winlab5.1.5,
- Venue :- AAU,AAit School of Chemical and Bioengineering lab
- Condition – temperature 25OC,atm pressure, light intensity -3000 lumen,Sample name – Culture vessel A

Wave length	Absor bance	Wave length	Absor bance	Wave length	Absorb ance	Wave length	Absor bance	Wave length	Absor bance	Wave length	Absor bance	Wave length	Absorba nce	Wave length	Absorba nce
650	0.0731	628	0.075	606	0.078	584	0.080	562	0.081	540	0.083	518	0.086	496	0.088
649	0.0731	627	0.076	605	0.078	583	0.080	561	0.082	539	0.084	517	0.086	495	0.089
648	0.0732	626	0.076	604	0.078	582	0.080	560	0.082	538	0.084	516	0.086	494	0.089
647	0.0730	625	0.076	603	0.078	581	0.080	559	0.082	537	0.084	515	0.086	493	0.089
646	0.0734	624	0.076	602	0.078	580	0.080	558	0.082	536	0.084	514	0.086	492	0.089
645	0.0737	623	0.076	601	0.078	579	0.080	557	0.082	535	0.084	513	0.087	491	0.089
644	0.0737	622	0.076	600	0.079	578	0.080	556	0.082	534	0.084	512	0.087	490	0.089
643	0.0739	621	0.076	599	0.078	577	0.080	555	0.082	533	0.084	511	0.086	489	0.090
642	0.0739	620	0.076	598	0.078	576	0.080	554	0.082	532	0.085	510	0.087	488	0.090
641	0.0739	619	0.077	597	0.079	575	0.080	553	0.082	531	0.085	509	0.087	487	0.090
640	0.0736	618	0.077	596	0.079	574	0.080	552	0.082	530	0.085	508	0.087	486	0.090
639	0.0743	617	0.077	595	0.079	573	0.080	551	0.082	529	0.084	507	0.087	485	0.090
638	0.0744	616	0.077	594	0.079	572	0.081	550	0.082	528	0.085	506	0.087	484	0.090
637	0.0746	615	0.077	593	0.079	571	0.081	549	0.082	527	0.085	505	0.087	483	0.090
636	0.0746	614	0.077	592	0.079	570	0.081	548	0.083	526	0.085	504	0.087	482	0.090
635	0.0746	613	0.077	591	0.079	569	0.081	547	0.083	525	0.085	503	0.088	481	0.090
634	0.0745	612	0.077	590	0.079	568	0.080	546	0.083	524	0.085	502	0.088	480	0.091
633	0.0750	611	0.077	589	0.079	567	0.081	545	0.083	523	0.085	501	0.088	479	0.091
632	0.0751	610	0.077	588	0.079	566	0.081	544	0.083	522	0.085	500	0.088	478	0.091
631	0.0754	609	0.078	587	0.079	565	0.081	543	0.083	521	0.086	499	0.088	477	0.091

Scanned absorbance measurement values of algal culture during growth phase

- Time – Day 18,Wave length interval – 475nm to 650 nm, Instrument :Perkin Elmer spectrophotometer,Winlab5.1.5,
- Venue :- AAU,AAit School of Chemical and Bioengineering lab
- Condition – temperature 25OC,atm pressure, light intensity -3000 lumen
- Sample name – Culture vessel B

Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance
650	1.042	628	1.06	606	1.084	584	1.091	562	1.089	540	1.098	518	1.117	496	1.134
649	1.04	627	1.063	605	1.083	583	1.092	561	1.092	539	1.101	517	1.117	495	1.137
648	1.039	626	1.065	604	1.082	582	1.092	560	1.092	538	1.102	516	1.121	494	1.137
647	1.036	625	1.064	603	1.085	581	1.09	559	1.092	537	1.102	515	1.122	493	1.134
646	1.042	624	1.066	602	1.087	580	1.088	558	1.089	536	1.101	514	1.123	492	1.136
645	1.041	623	1.065	601	1.087	579	1.092	557	1.092	535	1.102	513	1.125	491	1.138
644	1.042	622	1.066	600	1.09	578	1.093	556	1.093	534	1.104	512	1.125	490	1.137
643	1.044	621	1.069	599	1.087	577	1.093	555	1.094	533	1.106	511	1.125	489	1.137
642	1.044	620	1.07	598	1.086	576	1.092	554	1.094	532	1.107	510	1.125	488	1.138
641	1.041	619	1.071	597	1.09	575	1.087	553	1.092	531	1.109	509	1.127	487	1.139
640	1.045	618	1.072	596	1.09	574	1.09	552	1.092	530	1.109	508	1.128	486	1.138
639	1.048	617	1.071	595	1.092	573	1.092	551	1.095	529	1.106	507	1.127	485	1.139
638	1.05	616	1.073	594	1.089	572	1.092	550	1.095	528	1.107	506	1.129	484	1.14
637	1.054	615	1.074	593	1.087	571	1.092	549	1.095	527	1.11	505	1.129	483	1.14
636	1.053	614	1.074	592	1.092	570	1.092	548	1.097	526	1.113	504	1.129	482	1.14
635	1.053	613	1.074	591	1.09	569	1.088	547	1.095	525	1.113	503	1.133	481	1.139
634	1.051	612	1.076	590	1.09	568	1.088	546	1.095	524	1.114	502	1.134	480	1.14
633	1.056	611	1.077	589	1.089	567	1.092	545	1.096	523	1.113	501	1.134	479	1.142
632	1.059	610	1.074	588	1.091	566	1.092	544	1.096	522	1.114	500	1.134	478	1.142
631	1.06	609	1.08	587	1.089	565	1.092	543	1.097	521	1.117	499	1.131	477	1.142
630	1.063	608	1.081	586	1.089	564	1.092	542	1.099	520	1.118	498	1.133	476	1.141
629	1.06	607	1.082	585	1.093	563	1.091	541	1.098	519	1.118	497	1.134	475	1.141

Scanned absorbance measurement values of algal culture during growth phase

- Time – Day 18,Wave length interval – 475nm to 650 nm, Instrument :Perkin Elmer spectrophotometer,Winlab5.1.5,
- Venue :- AAU,AAit School of Chemical and Bioengineering lab
- Condition – temperature 25^{O}C,atm pressure, light intensity -3000 lumen
- Sample name – Culture vessel C

Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance
650	1.369	628	1.397	606	1.418	584	1.429	562	1.436	540	1.459	518	1.499	496	1.529
649	1.368	627	1.399	605	1.417	583	1.430	561	1.436	539	1.462	517	1.500	495	1.532
648	1.368	626	1.402	604	1.421	582	1.432	560	1.437	538	1.464	516	1.501	494	1.533
647	1.368	625	1.400	603	1.422	581	1.430	559	1.438	537	1.465	515	1.504	493	1.530
646	1.369	624	1.404	602	1.424	580	1.429	558	1.437	536	1.463	514	1.506	492	1.530
645	1.370	623	1.402	601	1.423	579	1.431	557	1.440	535	1.464	513	1.508	491	1.532
644	1.370	622	1.402	600	1.426	578	1.433	556	1.442	534	1.469	512	1.509	490	1.532
643	1.371	621	1.405	599	1.424	577	1.434	555	1.443	533	1.471	511	1.510	489	1.532
642	1.373	620	1.407	598	1.421	576	1.433	554	1.444	532	1.474	510	1.513	488	1.533
641	1.373	619	1.408	597	1.424	575	1.429	553	1.442	531	1.476	509	1.514	487	1.532
640	1.371	618	1.409	596	1.426	574	1.432	552	1.444	530	1.475	508	1.515	486	1.533
639	1.378	617	1.408	595	1.427	573	1.434	551	1.446	529	1.475	507	1.515	485	1.536
638	1.380	616	1.409	594	1.427	572	1.434	550	1.447	528	1.477	506	1.518	484	1.537
637	1.383	615	1.410	593	1.424	571	1.434	549	1.448	527	1.481	505	1.519	483	1.536
636	1.385	614	1.412	592	1.429	570	1.434	548	1.452	526	1.486	504	1.520	482	1.533
635	1.385	613	1.411	591	1.427	569	1.432	547	1.450	525	1.486	503	1.524	481	1.534
634	1.384	612	1.411	590	1.428	568	1.432	546	1.450	524	1.488	502	1.526	480	1.538
633	1.391	611	1.411	589	1.426	567	1.436	545	1.452	523	1.487	501	1.526	479	1.538
632	1.391	610	1.412	588	1.428	566	1.437	544	1.454	522	1.490	500	1.526	478	1.538
631	1.395	609	1.416	587	1.427	565	1.438	543	1.456	521	1.494	499	1.525	477	1.539
630	1.397	608	1.417	586	1.426	564	1.438	542	1.457	520	1.494	498	1.526	476	1.539
629	1.393	607	1.418	585	1.430	563	1.437	541	1.458	519	1.497	497	1.528	475	1.540

Scanned absorbance measurement values of algal culture during growth phase

- Time – Day 18,Wave length interval – 475nm to 650 nm, Instrument :Perkin Elmer spectrophotometer,Winlab5.1.5,
- Venue :- AAU,AAit School of Chemical and Bioengineering lab
- Condition – temperature 25OC,atm pressure, light intensity -3000 lumen
- Sample name – Culture vessel D

Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance
650	0.57782	628	0.58655	606	0.59932	584	0.6049	562	0.6004	540	0.60294	518	0.61459	496	0.63007
649	0.57634	627	0.58881	605	0.59868	583	0.60533	561	0.60023	539	0.60493	517	0.61304	495	0.63204
648	0.57656	626	0.5907	604	0.60039	582	0.60465	560	0.60204	538	0.60582	516	0.61621	494	0.6317
647	0.57318	625	0.59054	603	0.60229	581	0.60152	559	0.60184	537	0.60547	515	0.61685	493	0.63048
646	0.57975	624	0.59179	602	0.60238	580	0.60304	558	0.59876	536	0.60363	514	0.61768	492	0.63279
645	0.57961	623	0.59	601	0.60222	579	0.60515	557	0.6005	535	0.60395	513	0.61807	491	0.63495
644	0.57979	622	0.58955	600	0.60276	578	0.60708	556	0.60205	534	0.60601	512	0.6184	490	0.63589
643	0.58124	621	0.59125	599	0.60158	577	0.60655	555	0.60177	533	0.60796	511	0.61858	489	0.63692
642	0.58193	620	0.59401	598	0.59995	576	0.60475	554	0.60092	532	0.60906	510	0.61821	488	0.63908
641	0.57986	619	0.59315	597	0.60319	575	0.60202	553	0.59928	531	0.60955	509	0.6183	487	0.63879
640	0.57747	618	0.59465	596	0.60347	574	0.60046	552	0.59891	530	0.60897	508	0.62055	486	0.63884
639	0.58242	617	0.59327	595	0.60432	573	0.60386	551	0.60109	529	0.60659	507	0.62138	485	0.64237
638	0.58348	616	0.59405	594	0.60435	572	0.60451	550	0.60121	528	0.6068	506	0.62192	484	0.64451
637	0.58542	615	0.59312	593	0.60268	571	0.60411	549	0.6024	527	0.61008	505	0.62154	483	0.64432
636	0.58373	614	0.59616	592	0.60374	570	0.6052	548	0.60135	526	0.61181	504	0.62138	482	0.64351
635	0.58277	613	0.59498	591	0.60211	569	0.60213	547	0.59876	525	0.61182	503	0.6246	481	0.64399
634	0.58339	612	0.59471	590	0.60517	568	0.60035	546	0.60134	524	0.61165	502	0.627	480	0.64551
633	0.58629	611	0.59345	589	0.60263	567	0.60406	545	0.60207	523	0.61004	501	0.62688	479	0.64726
632	0.58806	610	0.59596	588	0.6049	566	0.60411	544	0.60152	522	0.61044	500	0.62535	478	0.64834
631	0.58869	609	0.59883	587	0.60326	565	0.60385	543	0.60162	521	0.61358	499	0.62417	477	0.6494
630	0.58808	608	0.59785	586	0.60121	564	0.60192	542	0.60228	520	0.61339	498	0.62733	476	0.64906
629	0.58631	607	0.59911	585	0.60591	563	0.60071	541	0.6013	519	0.6144	497	0.62971	475	0.64999

Scanned absorbance measurement values of algal culture during growth phase

- Time – Day 18,Wave length interval – 475nm to 650 nm, Instrument :Perkin Elmer spectrophotometer,Winlab5.1.5,
- Venue :- AAU,AAiT, School of Chemical and Bioengineering lab
- Condition – temperature 25OC,atm pressure, light intensity -3000 lumen
- Sample name – Culture vessel E

Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance	Wave length	Absorbance
650	0.95109	628	0.97972	606	0.01748	584	0.04122	562	0.05356	540	0.07217	518	0.11027	496	0.16085
649	0.94996	627	0.98308	605	0.01742	583	0.04357	561	0.05442	539	0.07722	517	0.11084	495	0.16583
648	0.9504	626	0.98609	604	0.01668	582	0.04595	560	0.05312	538	0.07787	516	0.11265	494	0.16889
647	0.9491	625	0.98587	603	0.01948	581	0.04302	559	0.054	537	0.07896	515	0.11629	493	0.16766
646	0.95473	624	0.98767	602	0.02298	580	0.04203	558	0.05547	536	0.07915	514	0.11888	492	0.17001
645	0.9582	623	0.98709	601	0.02463	579	0.04643	557	0.05744	535	0.07998	513	0.12103	491	0.17531
644	0.95687	622	0.99167	600	0.02853	578	0.05195	556	0.0588	534	0.08294	512	0.12182	490	0.17838
643	0.96066	621	0.99341	599	0.0242	577	0.05382	555	0.06036	533	0.08526	511	0.12361	489	0.18064
642	0.96077	620	0.9964	598	0.02607	576	0.04882	554	0.05936	532	0.08746	510	0.12596	488	0.1839
641	0.96055	619	0.99674	597	0.0293	575	0.04449	553	0.05646	531	0.08984	509	0.12798	487	0.18537
640	0.95787	618	0.99654	596	0.03139	574	0.0455	552	0.06115	530	0.09002	508	0.13056	486	0.18676
639	0.964	617	0.99678	595	0.03282	573	0.04948	551	0.06264	529	0.08843	507	0.1322	485	0.19107
638	0.96708	616	0.99987	594	0.03399	572	0.05099	550	0.0629	528	0.08997	506	0.13382	484	0.19451
637	0.96922	615	0.00034	593	0.03357	571	0.05233	549	0.06359	527	0.09412	505	0.13428	483	0.1957
636	0.96962	614	0.00285	592	0.03592	570	0.05242	548	0.06689	526	0.09691	504	0.13861	482	0.1965
635	0.97113	613	0.00311	591	0.03558	569	0.04702	547	0.06558	525	0.09751	503	0.1442	481	0.19884
634	0.96786	612	0.0054	590	0.03614	568	0.04929	546	0.06366	524	0.09837	502	0.14781	480	0.20321
633	0.97249	611	0.00577	589	0.03593	567	0.05397	545	0.06651	523	0.09823	501	0.14918	479	0.20624
632	0.97542	610	0.00319	588	0.03838	566	0.05464	544	0.06833	522	0.09995	500	0.14976	478	0.20853
631	0.97775	609	0.0106	587	0.03983	565	0.05469	543	0.07018	521	0.1047	499	0.15006	477	0.21162
630	0.98074	608	0.01343	586	0.03751	564	0.05504	542	0.07254	520	0.10636	498	0.15507	476	0.21229
629	0.97803	607	0.01391	585	0.04156	563	0.05386	541	0.07193	519	0.10824	497	0.15933	475	0.21454

Appendix II

Composition and preparation of Walne medium

Constituents	**Quantities**
Solution A (at 1 ml per litre of culture)	
Ferric chloride (FeCl3)	0.8 gm
Manganous chloride (MnCl2, 4H2O)	0.4 gm
Boric acid (H3BO3)	33.6 gm
EDTA(b), disodium salt	45.0 gm
Sodium dihydrogen orthophosphate (NaH2PO4, 2H2O)	20.0 gm
Sodium nitrate (NaNO3)	100.0 gm
Solution B	1.0 ml
Make up to 1 litre with fresh water(c)	Heat to dissolve
Solution B	
Zinc chloride (ZnCl2)	2.1 gm
Cobaltous chloride (CoCl2,6 H2O)	2.0 gm
Ammonium molybdate ((NH4)6Mo7O24, 4H2O)	0.9 gm
Cupric sulphate (CuSO4, 5H2O)	2.0 gm
Concentrated HCl	10.0 ml
Make up to 100 ml fresh water(c)	Heat to dissolve
Solution C (at 0.1 ml per liter of culture)	
Vitamin B1	0.2 gm
Solution E	25.0 ml
Make up to 200 ml with fresh water(c)	
Solution D (for culture of diatom sused in addition to solutions A and C, at 2 ml per liter of culture)	

Sodium metasilicate (Na2SiO3, 5H2O)	40.0 gm
Make up to 1 litre with fresh water(c)	Shake to dissolve
Solution E	
Vitamin B12	0.1gm
Make up to 250 ml with fresh water(c)	
Sodium nitrate (NaNO3)	200.0 gm
Make up to 1 litre with fresh water(c)	

Appendix III

Composition and preparation of Guillard's F/2 medium

Nutrients	**Final conc.(mg.l1 seawater)a**	**Stock solution preparations**
NaNO3	75	Nitrate/Phosphate Solution Working Stock: add 75 g NaNO3 + 5 g NaH2PO4 to 1 liter distilled water (DW)
NaH2PO4.H2O	5	
Na2SiO3.9H2O	30	Silicate Solution Working Stock: add 30 g Na2SiO3 to 1 liter DW
Na2C10H14O8N2.H2O (Na2EDTA)	4.36	Trace Metal/EDTA Solution Primary stocks: make 5 separate

CoCl2.6H2O	0.01	1liter stocks of (g.l1 DW) 10.0 g CoCl2, 9.8 g
CuSO4.5H2O	0.01	CuSO4, 180 g MnCl2, 6.3 g Na2MoO4, 22.0 g ZnSO4
FeCl3.6H2O	3.15	
MnCl2.4H2O	0.18	Working stock: add 1 ml of each primary stock solution + 4.35 g Na2C10H14O8N2 + 3.15 g FeCl3 to 1 liter DW
Na2MoO4.2H2O	0.006	
ZnSO4.7H2O	0.22	
Thiamin HCl	0.1	Vitamin Solution Primary stock: add 20 g thiamin HCl + 0.1 g biotin + 0.1 g B12 to 1 liter DW
Biotin	0.005	
B12	0.005	Working stock: add 5 ml primary stock to 1 liter DW

Appendix IV

Various combinations of fertilizers that can be used for mass culture of marine algae

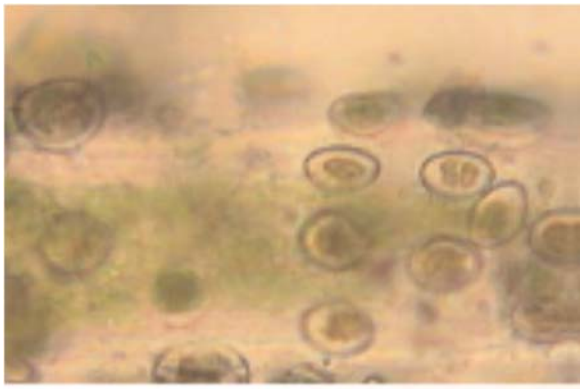
Fertilizer	Concentration in mg/lt					
	A	**B**	**C**	**D**	**E**	**F**
Ammonium sulfate	150	100	300	100	-	-
Urea	7.5	5	-	10-15	-	12-15
Calcium superphosphate	25	15	50	-	-	-
Clewat 32	-	5	-	-	-	-
N:P 16/20 Fertilizer	-	-	-	10-15	-	-
N:P:K 16-20-20	-	-	-	-	12-15	-
N:P:K 14-14-14	-	-	-	-	-	30

Excerpt from manual on production and use of live food for aquaculture:www.fao.org/fishery

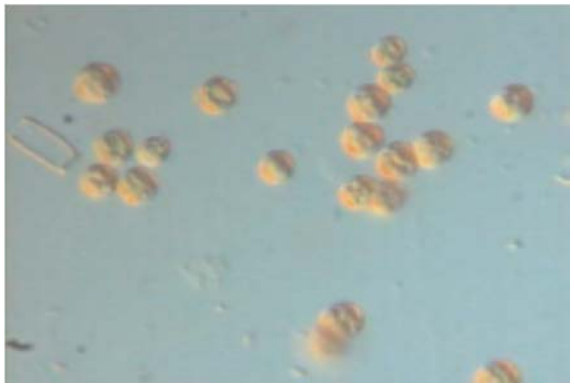
Appendix V

Observed view of microalgae type under microscope

(Image taken from S.janet et al)



Diatom



Chlorella

Appendix VII

Flue gas composition of Dangote cement plant

The actual composition (average) of the Dangote cement (Ethiopia) industry flue gas with reference to SOx and NOx tolerance limit of chlorella in flue gas.

SN	Emission description	unit	Actual value	tolerance limit	reference
1	Sulfur dioxide	ppm	150	250	Sharmila .k et al,2014
2	Nitrogen oxides	ppm	270	300	Sharmila .k et al,2014
3	Particulate matter	mg/Nm^3	30	-	-

Appendix VIII

Actual composition (Average) of the G global gas carbondioxide factory in reference to Acceptable limit of international society of beverage technology (ISBT) for carbondioxide Purity.

SN	**Emission description**	**unit**	**Actual value**	**Acceptable limit**	**Standard reference**
1	CO_2 purity	v/v	99.9%	>99.9%	ISBT,2001
2	Nitrogen oxides	ppm	2.5	$\geq$2.5	ISBT,2001
3	SO2	ppm	0.9	$\geq$1.0	ISBT,2001