# TECHNO-ECONOMIC ANALYSIS OF MICRO-ALGAE BIO-JET FUEL PRODUCTION PROCESSES

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# ABSTRACT

The production of bio-fuel from autotrophic micro-algae are being extensively studied and documented. However very few focuses specifically on the production of bio-jet fuel, with even fewer that assesses both the environmental and economic state of micro-algal bio-jet fuel production through modelling efforts.

In this research study, an integrated energy, techno-economic and lifecycle assessment deterministic model was successfully developed for the production of micro-algal bio-jet fuel. The developed model acts as a simple tool which can be used to assess the economic and environmental (Net energy ratio, greenhouse emission and water footprint) state of micro-algal bio-jet fuel production in Malaysia as well as for the identification of the key input parameters which influence these state. Prior to model construction, an initial economic investigation was carried out and compared some of the technologies/methods required for bio-jet fuel production. A base case process pathway was established based on this investigation, and formed the foundation of the process model.

The integrated model simulates the major steps involved in bio-jet fuel production, which are; micro-algal cultivation, harvesting and dewatering, cell disruption and lipid extraction, lipid purification and upgrading to bio-jet fuel and an additional anaerobic digestion of residual biomass.

Through the mass and energy balances and relevant equations, the material and net energy ratio (NER) are estimated with the aid of performance equations, Aspen plus, Matlab and reported data in literature. The economics of bio-jet fuel production process is evaluated by estimation of the capital and operating cost and discounted cash flow. Additionally, greenhouse (GHG) emissions and water resource consumption associated with the production of bio-jet fuel are assessed.

Process model results indicates the minimum fuel-selling price (MFSP) of algal derived jet fuel would be \$5.89/L, which is 14 times more than the market price of fossil derived jet fuel at \$0.43/L.

The NER of bio-jet fuel production was however positive, >1, more energy produced than used in the production process and $CO_2$ is abated at a rate of -7.49tonnes$CO_2$/L of bio-jet fuel produced. Results indicated that an additional membrane filtration process prior to centrifugation greatly reduces harvesting and dewatering energy consumption by 93%. Water usage is also estimated at 2702 tonnes/L of bio-jet fuel produced.

Sensitivity analysis results indicated that lipid recovery efficiency is one of the most influential parameter and significantly influences the NER, GHG, MFSP and water usage for micro-algal bio-jet fuel production. Case scenario studies in addition to the sensitivity analysis showed algal lipid content and algal productivity significantly influences the MFSP.

It was concluded that algal bio-jet fuel production plant would benefit from co-location with wastewater treatment plant and flue-gas producing sites in Kota Kinabalu, Malaysia. This includes exploitation of micro-algal species with high lipid fraction and productivity and cost effective technologies and combinations. The lowest possible MFSP achievable was $1.31/L based on an optimistic case scenario encompassing all the benefits aforementioned but still not sufficient in achieving an economically viable production process.

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## SYMBOL AND UNITS

| | |
|---|---|
| A | amp |
| d | Day |
| eq. | Equivalent |
| $CO_2$ | Carbon dioxide |
| cm | centimetre |
| $cm^2$ | Square centimetre |
| g | gram |
| H | Hydrogen |
| ha | Hectare |
| hr | Hour |
| K | Potassium |
| kWh | Kilowatt hour |
| kg | Kilogram |
| L | Litres |
| $m^3$ | Cubic metre |
| $m^2$ | Square metre |
| m | Metre |
| mm | millimetre |
| mg | Milligram |
| mL | Millilitres |
| MJ | Mega joule |
| N | Nitrogen |
| P | Phosphorus |
| S | Sulphur |
| sec | Seconds |
| W | Watt |
| wt. | Weight |
| yr | Year |
| V | Voltage |

| | |
|---|---|
| v | Liquid velocity |
| D | Tube diameter |
| V | Volume of PBR |
| ρ | Density of fluid |
| L | Tube length |
| μ | Viscosity of fluid |

## ABBREVIATION AND NOMENCLATURE

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| DW | Dry weight |
| GHG | Greenhouse gas |
| GREET | The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model |
| HP | High pressure |
| HHV | Higher heating value |
| HTL | Higher heating value |
| HTG | Hydrothermal gasification |
| HTC | Hydrothermal carbonisation |
| LCA | Life cycle assessment |
| LHV | Lower heating value |
| MFSP | Minimum fuel selling price |
| NAABB | National Alliance for Advanced Biofuels and Bioproducts |
| NER | Net energy ratio |
| PBR | Photo bioreactor |
| SEQHTL | Sequential Hydrothermal Liquifaction |
| TSS | Total suspended solid |
| USD | United States dollars |
| VDC | Volts direct current |
| VS | Volatile solids |

# 1 INTRODUCTION

## 1.1 Background

### 1.1.1 $CO_2$ emission and fossil derived fuel

Fossil derived fuels are fuels such as petroleum, natural gas, coal and oil shale derived from fossil. Ever since the industrial revolution began, fossil fuels have been the driving force behind the industrialized world and its economic expansion. Coal is the most abundant fossil fuel and produced largely in China, United States and Australia. According to a statistical review of world energy by BP in 2015, the global total reserves level by fossil fuel is 892 billion tonnes of coals, 186 trillion cubic meters of natural gas and 1688 billion barrels of crude oil. Unlike coal, oil resources are much less abundant and estimated to last for only about 60 years at present use rates. However, with enhanced oil recovery and the use of unconventional oils, the recoverable oil resources might be further prolonged. Alternatively, coal can be converted to gaseous or liquid fuels. In addition, natural gas can be catalytically reformed to produce liquids for transportation. Nevertheless, the continuing challenge is to develop efficient and economic processes for performing these chemical conversions.

In the 2011 and 2016 edition of the BP Energy Outlook, it is stated that currently about 80% of all primary energy in the world is derived from fossil fuels with oil accounting for 32.8%, coal for 27.2% and natural gas for 20.9%. Global energy demand between 2014 and 2035 is expected to rise 34%, an average of 1.4% per year. This increasing fuel demand is partly due to the increase in industrial growth and development particularly in Asia and has already resulted in higher crude oil prices.

The vast majority of scientists agree that the world climate is changing with the earth's average temperature increase by 1.5°F over the past century, and projected to rise another 0.5 to 8.6°F over the next hundred years (EPA, 2016). A phenomenon known as global warming may occur as a result of the release of carbon dioxide, methane, chlorofluorocarbons, nitrous oxide and trioxygen into the earth's atmosphere. These gases absorb heat energy (infra-red radiation) that would otherwise be radiated from the earth to space, resulting in a warming of the troposphere (lower atmosphere). Of these gases, $CO_2$ is the major gas that presently accounts for about one-half of the changing greenhouse phenomenon. In addition, global reliance on fossil energy brings about an associated emission problem. Roughly, 70% of all anthropogenic GHG emissions derived from the energy sector with fossil fuel combustion being the largest contributor of $CO_2$. In 2008, nearly 30 billion tons of $CO_2$ were emitted from fossil fuel consumption and this has doubled since 1970 (Höök and Tang 2013).

The continued combustion of fossil fuels created serious environmental concerns over global warming due to the increased release of greenhouse gases (GHG). This has resulted in a variety of legislation throughout the world, in order to reduce greenhouse gas (GHG) emissions, the most common being the Kyoto Protocol. The Kyoto Protocol is an international treaty that extends the 1992 United Nations Framework Convention on Climate Change (UNFCCC) that commits State Parties to reduce greenhouse gas emissions.

The need to reduce greenhouse gas emission is paramount; Malaysia, at Conference of the Parties (COP15) pledged to reduce its carbon intensity by 40% by 2020 from 2005 level subject to availability of technology and finance. In 2016, aviation was responsible for 12% of $CO_2$ emission from all transport sources (ATAG, 2016). In addition, the energy consumed by aviation is projected to increase to 13% of the global transportation energy by 2030 (Moavenzadeh et al., 2011).

### 1.1.2 Biomass derived fuel in the aviation sector

With the ever-growing demand for energy and the increasing concern of $CO_2$ emissions from fossil derived transport fuel, it is without doubt that a more renewable and economically sound alternative energy source would be indeed very attractive.

In Malaysia, the aviation industry is one of the highest energy consumers, accounting for 15% of the total fuel consumption in the transportation sector. According to the United Nations Energy Statistics Division database, aviation fuel (kerosene type) consumption by air transport sector in Malaysia is averaged at around 850 million Litres annually from 2010 to 2014. (UN database, 2016). Around 4 billion litres of kerosene-type aviation fuel was produced annually from 2010 to 2014.

According to the Malaysia Energy Statistics handbook, there was no primary production of fuel from biomass until 2012. This indicates progress of biomass-derived fuel production in Malaysia, a major agricultural commodity producer amongst the South-Eastern Asian countries.

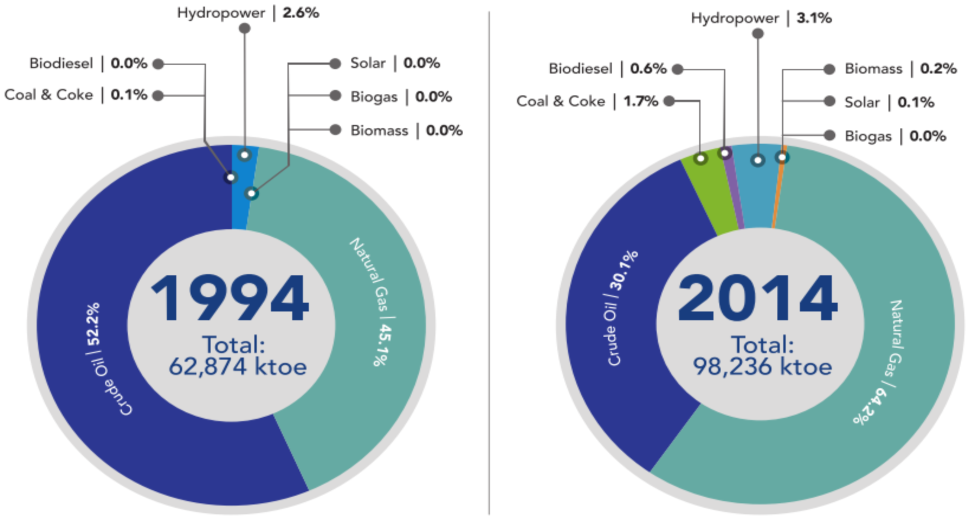


Figure 1: Primary production of energy by fuel type in 1994 and 2014 for Malaysia (Malaysia Energy Statistics handbook, 2016)

The future growth of air travel depends on the ability of the aviation industry to find solutions for three challenges: the global increase in mobility demand, the aviation’s impact on the environment and climate as well as the declining fossil resources for fuel production (Endres et al., 2012). Alternative fuels are considered promising options of tackling all these challenges. In addition to the concerns of global warming, is the problem of decreasing of fossil fuel reserves and increasing in fuel price and fuel consumption.

Renewable fuels are fuels derived from renewable non-petroleum sources such as crops, animal waste, or municipal solid waste. Whereas, alternative fuels are substitute fuels from the traditional gasoline and diesel fuels such as hydrogen, natural gas, and propane. New low-carbon biofuels could help reduce $CO_2$ emissions significantly and provide the aviation sector with enhanced energy and price security.

As of 2014, 27 major airlines; comprising of The Sustainable Aviation Fuel Users Group, pledged to use renewable fuels with lower carbon impact (Sustainable Aviation fuel, 2014). At least ten commercial airlines have approved flights using renewable jet fuel since the approval of hydro processed renewable jet fuel (HRJ) since July of 2011.

A big challenge facing the use of biofuels in aviation is the high quality standards fuel requirements. Safety and fuel quality specifications are of high importance in the aviation sector, nevertheless, these are not limiting the use of biofuels. The technical requirements for aviation biofuels are; a high performance fuel that can withstand a range of operational conditions, a fuel that does not compromise safety, a fuel that can directly substitute traditional jet fuel aviation and a fuel that meets strict performance targets (ATAG, 2009).

Testing of biofuels is crucial in determining suitability for use in the aviation sector. In the testing process, which aims to maintain the highest standards in safety, biofuels must undergo numerous of experiments in the laboratory, both on the ground and in the air (ATAG, 2009).

Table 1: Flight demonstrations with different biofuel feedstock (EBTP, 2016)

| **Year** | **Airline name** | **Bio-fuel type** |
|---|---|---|
| 2016 | LAN Colombia | Blend of jet fuel derived from Camelina |
| 2012 | Air Canada | Recycled cooking oil supplied by SkyNRG |
| 2012 | Azul Brazilian Airlines | Jet fuel produced from sugarcane using Amyris technology. |
| 2011 | Interjet and Airbus | Jatropha-based biofuel |
| 2010 | EADS | 100% algal biofuel |
| 2009 | Japan Airlines | 50:50 blend of Jet A fuel and 2nd generation synthetic kerosene, mainly produced from Camelina |
| 2008 | Virgin Atlantic | 20% blend of coconut and babassu oil |

Biomass sources for advanced bio-jet fuels include oil crops such as jatropha and camelina, waste fats and oils, biomass sugars, algae and halophytes (ATAG, 2009; IEA Bioenergy 2012; EBTP, 2016). Many major airlines and air forces have been involved in major test flights over the past years (shown in table 1) with biofuels and the number of these demonstration flights continues to grow indicating an increasing interest in biofuels for aviation.

### 1.1.3 Autotrophic microalgae for bio-jet fuel

In as early as the 1920s, algae has been collected and studied around various countries with an estimation of more than 50,000 known species. At the National Institute for Environmental Studies Collection (NIES), Japan, which was founded in 1983, there is a collection of 2451 different types of algal strains including cyanobacteria, eukaryotic microalgae, protozoa and endangered algae (NIES, 2014). In Malaysia, Algae Culture Collection, University of Malaya (UMACC) was established for the repository of micro-algal cultures. More than 150 micro-algal isolates holds by the UMACC and is one of the biggest microalgae culture collection in Malaysia.

Algae range from small unicellular single-celled forms to complex multicellular form. The variation in size allows for a simple division into two groups, the microalgae and the macro-algae (known as “sea-weed”). Microalgae are photosynthetic organisms that exist in most habitats due to their ability to live in different environments. Microalgae can either be prokaryotic or eukaryotic. Prokaryotic microalgae possess an outer plasma membrane enclosing protoplasm which contains photosynthetic thylakoids, ribosomes and DNA fibrils which are not enclosed in a separate membrane (Lee, 2008). However, eukaryotic microalgae have their DNA enclosed within a nuclear membrane.

Algal growth is divided into three main classes, autotrophic, heterotrophic and mixotrophic growth. This research project is focused on autotrophic microalgae as it has substantial amounts of available data as opposed to heterotrophic microalgae. Autotrophic microalgae directly consumes $CO_2$ (which can be supplied from a $CO_2$ emitting plant or other source) acting as an effective way of carbon capturing and $CO_2$ abatement. Although carbon recycle also occurs via the heterotrophic pathway, it is less efficient as it relies on terrestrial biomass growth, which shows the lower photosynthetic efficiency in comparison to autotrophic algae (Davis et al., 2011).

On the other hand, mixotrophic microalgae are capable of using either metabolism process (autotrophic or heterotrophic) for growth, meaning that they are able to photosynthesise as well as ingest prey or organic materials (Zhang et al., 1999).

$$[a]\ CO_2 + [b]\ \text{Nutrients} + \text{Sunlight} \rightarrow [c]\ O_2 + \text{Biomass} \qquad \text{(Equation 1)}$$

The efficiency of this process of photosynthesis is significant and influences the growth rate and biomass productivity. Algal biomass contains three main components; carbohydrates, protein and natural oil and one of the attractive properties of microalgae as a source of biofuel is its high lipid content (shown in table 2). The energy content of the micro-algal lipid is highly desirable at around 47MJ/kg in comparison to protein at 25MJ/kg and carbohydrate at 16MJ/kg (Amer et al., 2011).

Table 2: Oil content of various microalgae species (Gouveia et al., 2009; Phang et al., 2015; Sakthivel et al., 2011)

| **Microalgae species** | **Oil content (dry weight. %)** |
|---|---|
| *Chlorella sp.* | 28-43 |
| *Botryococcus braunii* | 25-75 |
| *Crypthecodinium cohnii* | 20 |
| *Nannochloropsis sp.* | 31-68 |
| *Dunaliella primolecta* | 23 |

Advantages of microalgae includes;

- High photon conversion efficiency (approximately 3–8% in comparison to 0.5% for terrestrial plants), resulting in higher biomass yields per hectare and higher growth rates.
- High $CO_2$ sequestration capacity; it is capable of growing in a liquid medium and can utilize nutrients from salt water and waste water (saline, brackish water,

seawater), hence less freshwater demand and offers the benefit of wastewater bioremediation.

- Micro-algae can be cultivated on marginal areas deemed unsuitable for agricultural purposes such as desert and seashore land and does not compete with arable land which are required for food production.
- The production of microalgae does not have to be seasonal, it can be harvested batch-wise all-year-round and cultures can be induced to produce a high concentration of feedstock (oil, starch, and biomass).
- The production systems of algal biomass can be easily adapted to various levels of operational and technological skills.
- Microalgae can be cultured without the use of fertilizers and pesticides, less waste and pollution is created.
- They have minimal environmental impact such as deforestation. Microalgae are a source of a wide range of fuel synthesis such as bioethanol, biodiesel, biomethane via biochemical, thermochemical, chemical and direct combustion processes (Campbell, 1997; Chisti, 2007; Gouveia, 2011; Huntley and Redalje, 2006; Khan et al., 2009; Li et al. 2008; Rodolfi et al., 2009)

The potential of algal bio-fuel seems promising and some companies in the US and other parts of the world are trying to commercialise algae fuel production processes with various cultivation, harvesting and processing technologies. Through commercial jet fuel flight demonstration, jet fuel derived from microalgae has been proven to meet the specifications for D7566; an 11 Annex A2 standard specification for aviation turbine fuel containing synthesized hydrocarbons, for renewable jet fuel (at 50% blend with Petroleum jet fuel)(Lupton et al., 2011).

### 1.1.4 Prior research and modelling work on bio-jet fuel production

There have been many reported research works over the years based on micro-algal fuel production. In some of the analyses reported, a developed process model exists which includes assumed process parameters. The final energy product for these modelling efforts differs, these includes biomass production, biodiesel, biogas and algal lipid. The process technology assumed in the process model also differs. Some of the reported analyses focus on the economics aspect of the energy product in question, whilst others focus on the greenhouse gases (GHG) emission (taking the form of an LCA study) and some on the energy aspects and water-foot print. However few studies exists which encompasses all four aspects mentioned for the production of micro-algal bio-jet fuel production. Past most relevant research approach are investigated and summarised in table 3.

Table 3: Past published modelling work on algal biofuel production.

| **Analysis type** | **Simulation Software used** | **Means of model development** | **Fuel produced** | **Reference** |
|---|---|---|---|---|
| Techno-economic | SuperPro Designer software, Aspen plus economiser. | Published data, reaction equation, reasonable assumptions, vendor quotation. | Aviation fuel | (Klein-marcuschamer, 2013) |
| Energy balance and techno-economic | None mentioned. | Developed using reaction equations, other pre-existing equations. Model implemented in Microsoft excel spread sheet. | Biogas | (Milledge, 2013) |
| Energy, economics and GHG | None mentioned. | Model developed using conservation laws and reaction equations. | Biodiesel | (Henson, 2013) |
| Process Design and Economics | Aspen plus, Icarus, Aspen Economic Evaluator. | Model developed using specified software, experimental data, assumptions, vendor quotation and published data. | Diesel blend stock | (Davis et al., 2014) |
| Economics, GHG, water footprint and GHG | ProSimPlus. | Model developed using monte carlo sampling method, specified software for energy estimation, assumptions, and published literature data. | Biodiesel | (Delrue et al., 2012) |

| | | | | |
|---|---|---|---|---|
| Economics | None mentioned. | Model developed using theoretical calculation, published literature data. | Biodiesel and Biogas | (Harun et al., 2011) |
| Techno-economic | None mentioned. | Model developed using experimental data, assumptions and literature data.<br>Model Implemented in spread sheet with macros and spread sheet. | Biodiesel | (Amer et al., 2011) |
| LCA and production cost | Ecoinvent v.2.0, Matlab | Data entries in Ecoinvent v.2.0 as the bases for life cycle inventory development. | Bio-jet fuel | (Agusdinata et al., 2011) |

As shown in table 3, there have been numerous reported modelling work for the production of biofuel from algae. Of all analyses mentioned, few use software to aid in model development whilst some do not. Works of model that do not use software might be criticised because of the non-dynamic nature of the model as opposed to dynamic models. A dynamic model runs in real time and mimics the behaviour of a real plant. Software like aspen plus and UNISIM are capable of producing dynamic mass and energy balance however, there are much data and unit operations required for micro-algal biofuel production which are yet not available (during the course of this research). Whilst some compounds that are not available in this software can be substituted with similar compound available in the software database; this initiative does not go without critic.

From prior studies, it is still yet unclear if algal bio-jet fuel production is a sustainable alternative to conventional jet fuel. Of the reported studies, bio-jet fuel was the energy product for only two out of the entire studies reported in table 3.

For bio-jet fuel production from microalgae, there is need for a detailed yet flexible model that can allow for prediction of the economic, energy and environmental state associated with the production process. There is also need for a model in which variation of assumptions and process parameter are possible to enable the main drivers of the system performance to be quickly identified and the sensitivities of key performance metrics to specific process inputs be established.

## 1.2 Description of research work

### 1.2.1 Research Motivation

A past techno-economic analysis by Klein-Marcuschamer et al. (2013) shows the production of algal bio-jet fuel to be at a disadvantage when the suggested minimum selling price is compared against that of fossil derived jet fuel. Whilst algal bio-jet fuel is not yet competitive; there are several technologies and methods that can significantly improve its economics as revealed by a cost analysis performed by (Davis et al. (2011) for an open pond and closed PBR cultivation system at a production capacity of 3.8 × $10^6$L/yr algal oil. Still, there is no generally accepted production process yet and no company is currently known to produce commercial scale quantities of algae bio-jet fuel at a competitive price with fossil derived jet fuel. There are several conflicting views about the near term economic practicality of algae bio-jet fuel as a result of uncertainties arising from variations in algae species, cultivation and harvesting methodologies, and technological variations, process scale-up assumptions and lack of validations.

In order to determine if microalgae derived bio-jet fuel is worthy of future investment; for its production and commercialisation, economic feasibility and environmental benefits, a techno-economic analysis together with analysis on its energy, GHG and water foot-print profile is necessary.

### 1.2.2 Research Aim and Objectives

The main aim of this research is to develop a process model to assess the techno-economic state for the commercial production of bio-jet fuel from autotrophic microalgae culture in Malaysia. This process model is to be adequately comprehensive that all of the major processing steps required to produce micro-algal bio-jet fuel is included. Whilst economics is emphasised as the research title suggests, the environmental aspect (GHG emission, NER and water footprint) are also investigated.

As with other past works, this research project seeks to make novel contribution in the area of algal bio-jet fuel production by analysing the production state of bio-jet fuel production from microalgae at commercial quantity whilst considering the economics aspects, GHG emission, water footprint and NER.

This aim is achievable by the following objectives:

1. To identify and gather information into the possible process routes and process technologies (both new and existing) for the production of bio-jet fuel from autotrophic microalgae.
2. To construct and develop a flexible process model as a rational basis for assessing GHG emission, energy balance (NER), MFSP and water usage associated with the production of algal bio-jet fuel in Malaysia.
3. To identify and evaluate the crucial parameters that influences GHG emission, energy consumption, MFSP and water requirement associated with the production of algal bio-jet fuel.
4. To conduct a case study into the further potential improvement of the algal bio-jet fuel production system in terms of GHG emission, energy consumption, and MFSP and water usage.

## 1.3 Structure of Thesis

This thesis consists of 7 chapters

The present chapter introduces key theories and concerns into renewable fuel production from micro-algae, discussing the challenges that exist and the novelty of the research. The aims and objectives of the work are also summed up.

Chapter 2; provides reviewed, analyzed and summarized information for the processes involved in micro-algal bio-jet production whilst identifying the gaps present in literature.

Chapter 3; describes initial work carried out to provide a starting point for the assessment of micro-algal bio-jet fuel production technologies .

Chapter 4; describes the work carried out during the construction of the model including the model equations used, assumptions made and validation of the model.

Chapter 5; documents all aspects of the process economics including the capital and operating costs.

Chapter 6; presents the model output results and discussion, sensitivity analysis results and case studied into the further potential improvement of the algal bio-jet fuel production system in terms of $CO_2$ emission, energy consumption, and production cost and water usage.

Chapter 7; concludes entire research work and suggestions for further future work

# 2 LITERATURE REVIEW ON ALGAE BIO-JET FUEL PRODUCTION PROCESSES AND TECHNOLOGIES

In this chapter, literature is reviewed, analyzed and summarized for the process methods and technologies involved in micro-algal bio-jet fuel production.

## 2.1 Microalgae to bio-jet fuel production pathway

There are different process technologies capable of converting algal biomass into bio-jet fuel substitutes. Some of these technologies exist at commercial scale level, pilot scale and some are still in the research and development phase. In this report, the different process pathways suitable for the production of bio-jet fuel from microalgae are discussed and evaluated.

Microalgae can be converted to liquid fuel by a range of different conversion technologies that includes thermochemical, physical, biochemical and biological treatments. There are several potentially viable liquid fuels such as bio-diesel, gasoline and diesel produced from algae, but the fuel of focus in this research is algal bio-jet fuel.

There are four major potential pathways for the conversion of algal biomass to a bio-jet fuel: (i.) Biomass-to-sugars to bio-jet fuel, (ii.) Biomass-to-alcohol to bio-jet fuel, (iii.) Biomass-to-oil to bio-jet fuel and iv.) Biomass-to-gas to bio-jet fuel.

The major process steps that all pathways have in common are cultivation, harvesting and dewatering process. The process pathways are shown in the figure 2.

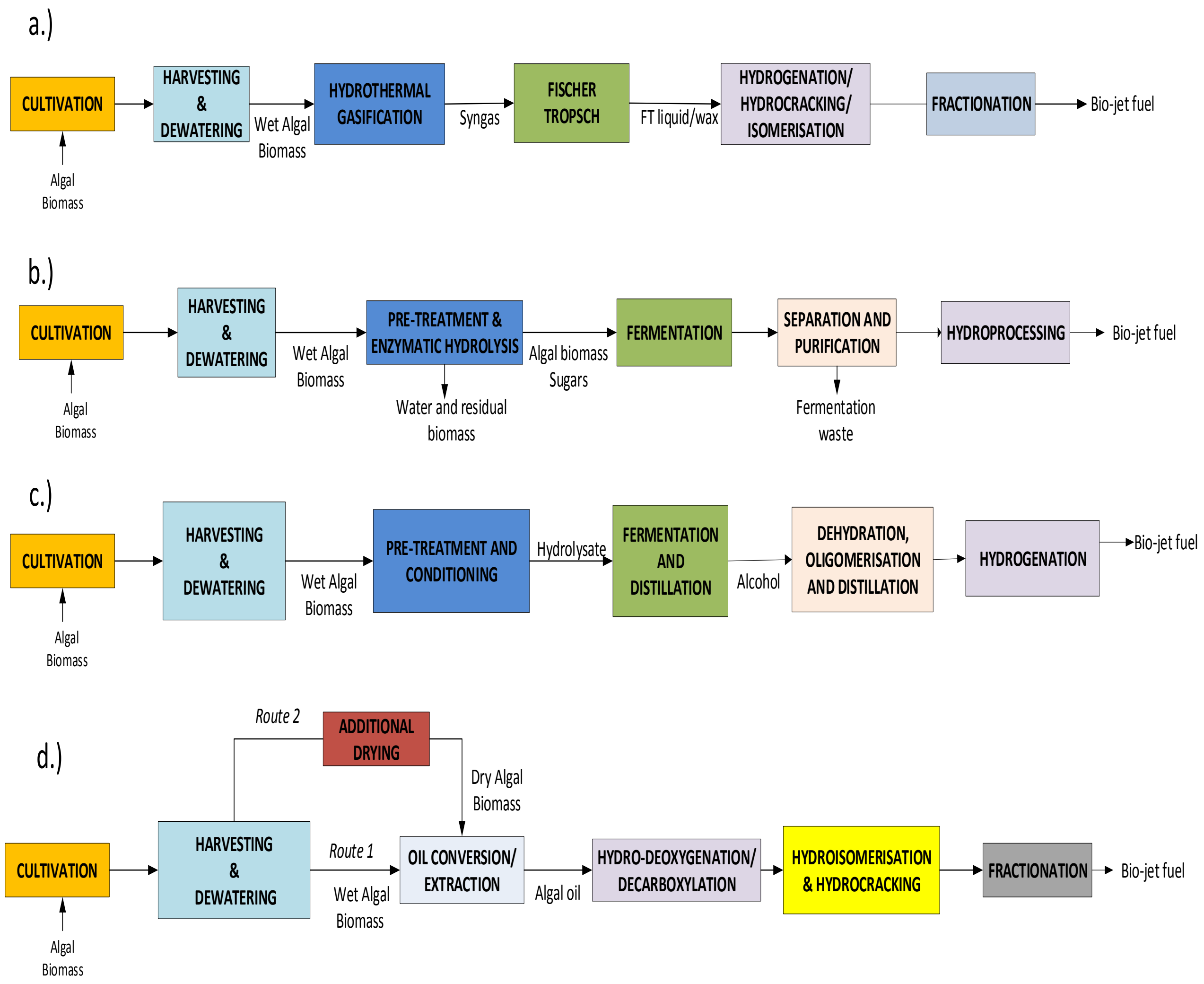


Figure 2: Algal biomass to bio-jet fuel process pathways: a.) Biomass-to-gas to bio-jet fuel, b.) Biomass-to-sugars to bio-jet fuel, c.) Biomass-to-alcohol to bio-jet fuel d.) Biomass-to-oil to bio-jet fuel.

### 2.1.1 Biomass-to-gas to bio-jet fuel

The biomass-to gas to bio-jet fuel pathway describes a process where algal biomass is converted to synthesis gas or methane by undergoing catalytic hydrothermal gasification at temperatures in the range of 350-500°C and pressure at 206-360 bar(Elliott et al., 2009; Onwudili et al., 2013; Stucki et al.,2009).

Syngas consist mainly of hydrogen, carbon monoxide and some carbon dioxide. Therefore, the methane rich gas will have to undergo a steam reforming process before syngas can be produced. After the production of the syngas it will require a further processing step in order to produce synthetic paraffinic kerosene (Freitas and Guirardello, 2013). There are few studies on the gasification of microalgae for the purpose of syngas production. Elliott et al. (2009) hydrothermally gasified *Spirulina* at temperature of 350°C and pressure at 206 bar.

A common process known as the Fischer Tropsch synthesis involves the reaction of syngas with carbon monoxide and hydrogen in the presence of catalysts to make long hydrocarbon chains. Conventional refinery processes such as hydrocracking, isomerization, hydrogenation and fractionation, is applied to upgrade the Fischer Tropsch (F-T) synthesis product to high quality, low-aromatic fuels. Hydrocracking/isomerization is used to convert the wax into lighter products with shorter chain length and lower boiling points. Products from the hydrocracking/isomerization reactor are then heated and distilled to produce jet fuel, diesel fuel and lubricants. Hydrogenation is applied to produce naphtha from the F-T liquid (Wang and Tao, 2016). Reliable literature quantifying the product yield of bio-jet fuel from algal biomass derived syngas is currently lacking.

### 2.1.2 Biomass-to-sugars to bio-jet fuel

In this pathway, the algal cell wall is hydrolyzed and the resulting sugars fermented to hydrocarbon intermediates. Fermentation process can occur either by fed-batch or continuous fermentation. The resulting hydrocarbon products are then phase separated to recover bio-jet fuel and other by-products after purification and downstream hydro-processing (Department of Energy, 2012). Companies such as LS9 and Amyris have successfully converted sugars to hydrocarbon fuel. The renewable jet fuel produced from sugarcane feedstock was used in an Embraer E195 jet operated by Azul Brazilian Airline (Amyris, 2012). Whilst biomass derived sugars has been shown to be a possible means of producing bio-jet fuel, available data which demonstrates that algal derived sugars can be converted to bio-jet fuel is currently lacking.

### 2.1.3 Biomass-to-alcohol to bio-jet fuel

Microalgae is able to accumulate significant amounts of carbohydrates hence there is the potential to convert the carbohydrate to alcohol (Harun et al., 2010). Microalgae such as *Chlorella vulgaris, Dunaliella, Chlamydomonas* are good sources of alcohol due to the high starch content( up to 53% of algal dry weight) for which up to 65% ethanol conversion efficiency has been documented (Brennan and Owende, 2010).

The extracted carbohydrates requires hydrolyses to convert to simple sugars. During fermentation, the yeast effectively convert the sugars to bioethanol (Pandey et al., 2014). In the pre-treatment process, the algal biomass is combined with steam and treated with dilute sulfuric acid catalyst at a high temperature for a short period of time to hydrolyze the glucan carbohydrates to monomeric sugars. Ammonia is then added to the pre-treated slurry to increase its pH to approximately 5 for the purpose of fermentation (Davis et al., 2014; Milbrandt & Mccormick, 2013).

Gevo and Cobalt are some of the companies exploring alcohol to jet fuel option. Gevo developed a trademarked integrated fermentation technology (GIFT) comprising of a yeast biocatalyst that converts sugars into iso-butanol. The alcohol is then converted into iso-paraffinic kerosene (IPK), a blendstock used in jet fuel, via additional reactions such as dehydration, oligomerization, hydrogenation, and distillation (Gevo, 2011). Cobalt also developed its own process for extracting sugars from biomass and converting them directly into bio n-butanol, a platform molecule for the production of a wide range of fuels and chemicals; including jet fuel (Cobalt, 2013).

### 2.1.4 Biomass-to-oil to bio-jet fuel

In this process pathway, there exist three potential routes: hydrothermal liquefaction(HTL), pyrolysis and cell disruption and lipid extraction.

### *2.1.4.1 Cell disruption and lipid extraction*

In the cell disruption and extraction route, the micro-algal lipid must first be liberated from within the cellular matrix of the algae cell (Halim et al., 2012). Microalgae comprises of protein, carbohydrate, lipid and nucleic acid. The percentage of lipid is dependent on the algal strains and the cultivation condition within the range of 7-75% of oil content (Demirbas, 2011).

The algal lipids produced from the cell disruption method will have to undergo further upgrading process. Based on experimental works of Hillen et al. (1982), the hydrocracking of algal lipids to produce fractions of aviation fuels (15%), diesel (15%), gasoline (67%) and residual oil (3%) was performed using the conventional cobalt–molybdenum catalysts at the temperatures between 400°C and 440°C (Tran et al., 2010). The fraction of jet fuel produced after upgrading is however variable. Another experimental study by Murata et al. (2014) showed that that algal oil can be upgraded to aviation fuel range hydrocarbons. Algal oil from Botryococcus braunii was hydrocracked using Pt-Re catalyst at temperatures between 310°C to 340°C to produce jet fuel ($C_{10}$–$C_{15}$) at yield of up to 50.2% with diesel-range hydrocarbons ($C_{16}$–$C_{20}$) of 16.7% yield (Murata et al., 2014).

### *2.1.4.2 HTL route*

In the HTL route, the wet algal biomass is liquefied hydrothermally to an oil product. Hydrothermal liquefaction requires high temperature ranging from 300-450°C, high pressure at 70-200 bar, catalyst and hydrogen. At such conditions, water is considered to be in a near critical state. The HTL of algae has in the past been performed in continuous flow reactors and either whole algae or lipid extracted algae biomass can undergo hydrothermal liquefaction (Elliott et al., 2013). There are several experimental studies for microalgae hydrothermal liquefaction. The highest yield was 64% dry wt. basis of oil with HHV of 45.9 MJ/kg.

The algal oil produced by the hydrothermal liquefaction of the algae requires further upgrading process. The purpose of this upgrading is to remove oxygen, nitrogen and sulphur.

#### *2.1.4.3 Pyrolysis of micro-algae*

In the pyrolysis route, the wet algal biomass undergoes a drying stage before being pyrolysed (Pandey et al., 2014). Pyrolysis is the conversion of biomass to bio-oil, syngas and charcoal at medium to high temperatures (350–700 °C) in the absence of air (Goyal et al.,2008).

Dry algal biomass is converted to bio-oil by undergoing pyrolysis at temperatures between 350°C and 800°C. Experimental studies conducted by Miao et al. (2004) showed that bio-oil yields of up to 24% (HHV of 29 MJ/kg) from fast pyrolysis of *C. prothothecoides* and Microcystis aeruginosa grown autotrophically is achievable.

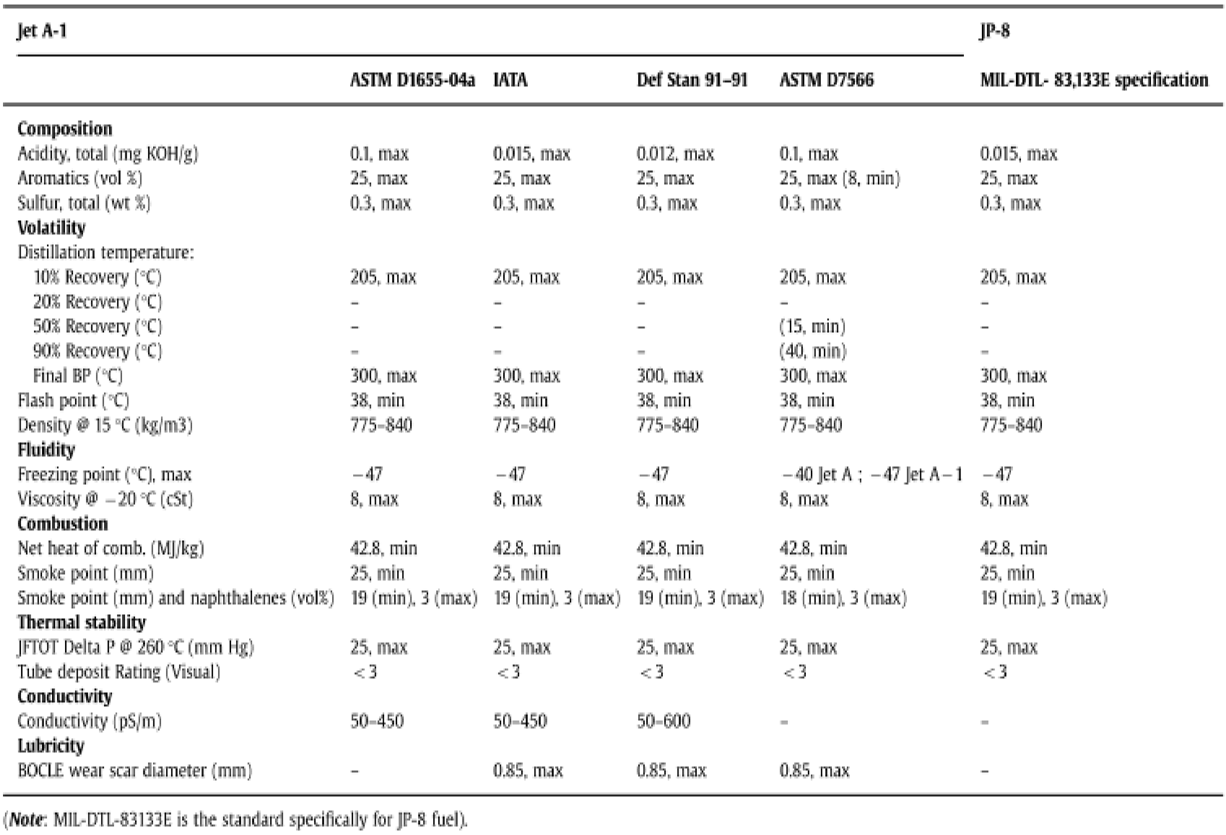
In addition, experimental works of Demirbas (2007) showed that for the microalgae *Chlorella protothecoides,* bio-oil yield increased with temperature up to a point and then decreased at higher temperature. For example, the bio-oil yield increased from 5.7% to 55.3% when temperature increased from 254 to 502°C, and afterwards decreased to 51.8% at 602°C.

The bio-oil produced by pyrolysis requires further upgrading to produce jet fuel fraction as the oil produced contains a large amounts of high molecular unsaturated compounds and oxygen containing compounds (Freitas & Guirardello, 2013). Algal lipid and algal oil are different in that the unlike the algal lipid, the oil derived from algae also contains protein and derivatives of algal biomass as the whole algae biomass is converted to yield the algal oil (Chen et al., 2012). The algal oil produced by pyrolysis and hydrothermal liquefaction have different oxygen composition, pyrolysis oil are more oxygenated and requires more severe upgrading conditions to obtain bio-jet fuel fraction (Huang et al., 2011).

### 2.1.5 Jet fuel specification

Whilst alcohol, sugars, synthesis gas and bio-oil can be further upgraded to produce bio-jet fuel, they have to meet the jet fuel specifications and requirements. These requirement includes aspects of fuel composition, volatility, fluidity, combustion, thermal stability conductivity and lubricity (see table 4).

Table 4: Jet fuel specification (Wang et al., 2016)



| Jet A-1 | | | | | JP-8 |
|---|---|---|---|---|---|
| | **ASTM D1655-04a** | **IATA** | **Def Stan 91–91** | **ASTM D7566** | **MIL-DTL- 83,133E specification** |
| **Composition** | | | | | |
| Acidity, total (mg KOH/g) | 0.1, max | 0.015, max | 0.012, max | 0.1, max | 0.015, max |
| Aromatics (vol %) | 25, max | 25, max | 25, max | 25, max (8, min) | 25, max |
| Sulfur, total (wt %) | 0.3, max | 0.3, max | 0.3, max | 0.3, max | 0.3, max |
| **Volatility** | | | | | |
| Distillation temperature: | | | | | |
| 10% Recovery (°C) | 205, max | 205, max | 205, max | 205, max | 205, max |
| 20% Recovery (°C) | – | – | – | – | – |
| 50% Recovery (°C) | – | – | – | (15, min) | – |
| 90% Recovery (°C) | – | – | – | (40, min) | – |
| Final BP (°C) | 300, max | 300, max | 300, max | 300, max | 300, max |
| Flash point (°C) | 38, min | 38, min | 38, min | 38, min | 38, min |
| Density @ 15 °C (kg/m3) | 775–840 | 775–840 | 775–840 | 775–840 | 775–840 |
| **Fluidity** | | | | | |
| Freezing point (°C), max | −47 | −47 | −47 | −40 Jet A ; −47 Jet A−1 | −47 |
| Viscosity @ −20 °C (cSt) | 8, max | 8, max | 8, max | 8, max | 8, max |
| **Combustion** | | | | | |
| Net heat of comb. (MJ/kg) | 42.8, min | 42.8, min | 42.8, min | 42.8, min | 42.8, min |
| Smoke point (mm) | 25, min | 25, min | 25, min | 25, min | 25, min |
| Smoke point (mm) and naphthalenes (vol%) | 19 (min), 3 (max) | 19 (min), 3 (max) | 19 (min), 3 (max) | 18 (min), 3 (max) | 19 (min), 3 (max) |
| **Thermal stability** | | | | | |
| JFTOT Delta P @ 260 °C (mm Hg) | 25, max | 25, max | 25, max | 25, max | 25, max |
| Tube deposit Rating (Visual) | < 3 | < 3 | < 3 | < 3 | < 3 |
| **Conductivity** | | | | | |
| Conductivity (pS/m) | 50–450 | 50–450 | 50–600 | – | – |
| **Lubricity** | | | | | |
| BOCLE wear scar diameter (mm) | – | 0.85, max | 0.85, max | 0.85, max | – |

(***Note***: MIL-DTL-83133E is the standard specifically for JP-8 fuel).

The American Society of Testing and Materials (ASTM) specification D1655 establishes the characteristics of Jet-A and Jet-A1, which are conventionally petroleum-based fuels with no addition of any non-petroleum component.

In 2009, ASTM released specification D7566 for jet fuel containing synthesized hydrocarbons. When released, D7566 covered blends of traditional jet fuel and hydrocarbons produced by FT synthesis and other new methods to produce alternative jet fuel. Another significant world authority on the characteristics of jet fuel is the British Ministry of Defence, whose Standard (DEF STAN) 91-91 covers jet fuel for military use and has also been widely implemented by civilian users of jet fuel.

### 2.1.6 Conclusive remark

The product intermediate and bio-jet fuel yields for the four different potential pathways discussed so far are summarized in table 5. Of all four pathways, the biomass-to-oil to bio-jet fuel pathway has the highest achievable yield of bio-jet fuel.

Table 5**:** Bio-jet fuel production yield from algal biomass of different process pathways.

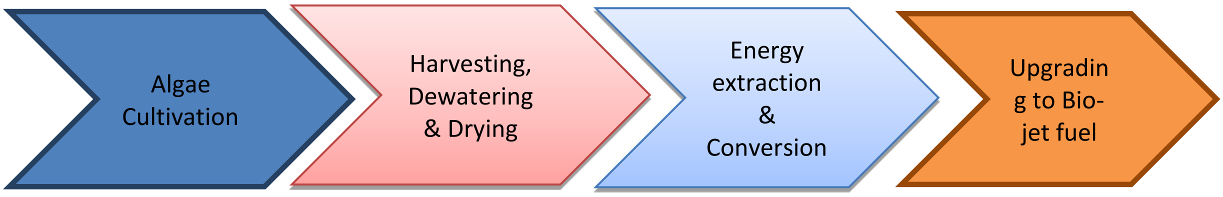
| **Pathway** | **Intermediates** | ***Intermediate yield (% dry weight basis)** | ***Bio-jet fuel yield (L/kg of dry algal biomass)** | **Technology approval by ASTM** | **Technology developer** |
|---|---|---|---|---|---|
| Biomass-to-oil to bio-jet fuel | Algal lipid | up to 75 | up to 0.41 | Approved in 2011 | Honeywell UOP, Neste Oil, Dynamic Fuels, EERC, Airbus |
| | HTL oil | up to 64 | up to 0.32 | | |
| | Pyrolysis oil | up to 55 | | | |
| Biomass-to-alcohol to bio-jet fuel | Ethanol or butanol | up to 65 | up to 0.17 | Approval in 2016 | Gevo, Cobalt |
| Biomass-to-sugars to bio-jet fuel | Sugars | - | - | Approval in 2014 | Amyris, LS9 |
| Biomass-to-gas to bio-jet fuel | Syngas | up to 69 | - | Approved in 2009 | Sasol, Shell, Syntroleum |

*refer to *Appendix A* for supplementary information about these estimates

Whilst the upgrading technology for the conversion of biomass intermediates to bio-jet fuel have met ASTM D7566 standards, there is still lack of experimental data on both the biomass-to-gas and biomass-to-sugar pathway that enables reasonable yields and cost estimate. Based on available information on yield of bio-jet fuel, the algal lipid route of the biomass-to-oil to bio-jet fuel pathway appears to be the most favourable pathway for bio-jet fuel production from microalgae, and thus is further reviewed in this study.

## 2.2 Algal bio-jet fuel production process overview

In order for the production of bio-jet fuel from microalgae, series of process steps are required. These process steps can essentially be grouped into four main levels: (i.) Cultivation, (ii.) Harvesting, Dewatering & Drying, (iii.) Energy extraction and conversion and (iv.) Upgrading. There are varieties of technological options to accomplish each of the processing steps; some examples are illustrated in figure 3 for each of the processing steps. The different aspects of each process steps are reviewed and discussed in detail.



- Open pond
- Closed photo-bioreactor
- Hybrid systems

- Flotation
- Flocculation
- Filtration
- Centrifugation
- Sedimentation
- Screening
- Solar drying
- Cross-flow air drying

- Solvent extraction
- Supercritical fluid
- Subcritical aqueous extraction
- Mechanical cell disruption
- Hydrothermal liquefaction

- Catalytic Hydrotreating / Hydro-processing

Figure 3: Algal bio-jet fuel production and processing steps with various technological options

### 2.2.1 Algal cultivation

The cultivation of autotrophic micro-algae requires water, a source of carbon and light as well as nutrients (nitrogen, phosphorus and sulphur). The type of algal strain is also essential information to consider for algal cultivation as it influences the technology selection process.

#### *2.2.1.1 Micro-algal strains in Malaysia*

Malaysia has an estimated 309 known species of marine algae, 279 of which consist of micro-algae and macro-algae (Mazlan et al., 2005). In recent years, there has been increased interest of lipid rich microalgae as feedstocks for biofuel production (Chisti 2007; Harun et al. 2010). Algal strains selection for prospective use as feedstock for biofuel production is significantly dependent upon high growth rate and high lipid and carbohydrate productivities.

In 2013, a collaborative initiative between the University of Malaya, Aerospace Malaysia Innovation Centre (AMIC) and AIRBUS Group focused on selecting suitable tropical strains that are suitable for aviation fuel production in Malaysia. Seventy-nine environmental samples were collected from 30 collection sites including from freshwater, brackish water and marine habitats. The freshwater sites included three hotsprings locations. Polluted sites included the vicinity of palm oil mills and the highly eutrophicated lake of the University of Malaya. Marine sites were from Port Dickson and Kelantan including mangroves and an estuary (Phang et al., 2015).

Table 6: Micro-algae strain of interest for high lipid productivity for the purpose of bio-jet fuel conversion (Phang et al., 2015)

| Habitat of study | Species | Biomass productivity(mg/L/day) | Lipid productivity (mg/L/day) | Lipid content (DW %) |
|---|---|---|---|---|
| Hotspring | *Chlorella* sp. | 34.43 ± 8.29 | 13.78 ± 4.33 | 40.08 ± 2.74 |
| Palm oil Mill effluent | *Chlorella* sp. | 76.27± 11.08 | 30.57 ± 6.63 | 40.38 ± 7.89 |
| Palm oil Mill effluent | *Chlamydomonas* sp. | 32.95 ± 7.23 | 14.03 ± 3.08 | 43.34 ± 2.44 |

| | | | | |
|---|---|---|---|---|
| Freshwater lake | *Chlorella* sp. | 49.43 ± 2.07 | 12.71 ± 3.14 | 26.72 ± 6.20 |
| Marine | *Chlorella* sp. | 44.90 ± 6.44 | 13.48 ± 2.80 | 30.48 ± 5.85 |
| Marine | *Chlorococcum* sp. | 57.93± 14.00 | 22.55 ± 5.70 | 39.28 ± 1.96 |

Of the 79 samples, six algal genera, the Cyanophyte *Cyanosarcina*, the Chlorophytes *Chlorella*, *Chlamydomonas*, *Chlorococcum*, *Scenedesmus* and the Euglenophyte *Euglena* were included. *Chlorella*, *Chlamydomonas and Chlorococcum* are shown to be suitable for bio-jet fuel production due to their high lipid and high biomass productivity as shown in table 6.

#### ***2.2.1.2 Algal cultivation technologies***

Recent LCA studies on the hypothetical large-scale algae-to-energy systems, reveals that cultivation impacts are somewhat the most environmentally significant components of the overall algae-to-fuel life cycle (Clarens et al., 2010). There currently exist three main systems in which microalgae can be grown, open, closed and hybrid systems.

##### 2.2.1.2.1 Open system for microalgae cultivation

Open systems for microalgae cultivation include raceway ponds, circular pond, shallow pond and inclined cascade system. Open systems usually have lower capital cost and relative easier to construct. There are however some drawbacks of open systems; large land space requirement, high contamination risk and evaporative losses (Ben-amotz, 2008; Borowitzka and Moheimani, 2013;Xu et al., 2009). The most commonly cultivated microalgae in open systems are *Chlorella* and *Spirulina* (Pandey et al., 2013) with *Chlorella* being a common aquatic green microalga in Malaysia.

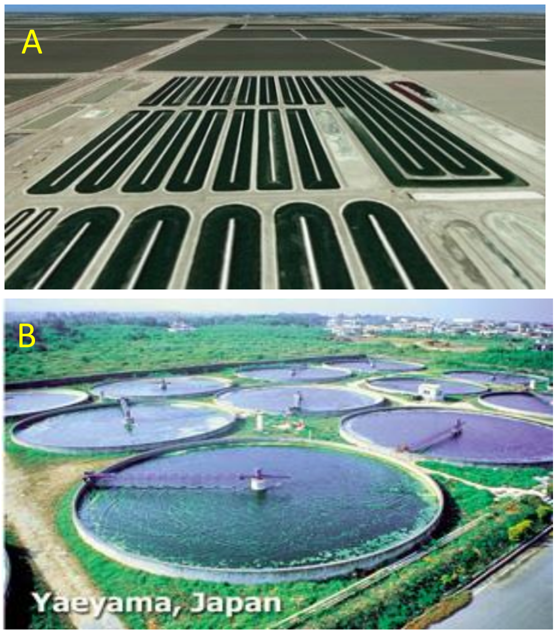


Figure 4: (A) Raceway pond (B) Circular pond (Andersen, 2005; Henrikson, 2014; White, 2011).

#### *2.2.1.2.1.1 Circular ponds*

Circular ponds have been used in countries such as South Africa, Taiwan and Japan for the production of *Chlorella* and *Scenedesmus sp.* (Borowitzka, 1999; Guldhe et al., 2014). They have centrally located rotating arm for mixing purpose and are normally 0.3 m to 0.7 m deep and up to 45 m in diameter (Shen et al., 2009). Productivities achieved by commercial circular ponds range from 8.5g/m$^2$/day to 21g/m$^2$/day (Benemann and Oswald, 1996; Suali and Sarbatly, 2012).

In comparison to other methods of microalgae cultivation, circular ponds are less attractive because they are expensive due to concrete construction, high energy consumption of stirring, and complexity of the central pivot mixing system(Chen et al., 2009). Other disadvantages of circular ponds include; low turbulence and mixing in the central part of the pond and supplying of $CO_2$ to the culture (Becker, 1994). While circular ponds are the oldest large-scale mixed algal growth system they are now currently only used to a limited extent and are difficult to scale up over 1000m$^2$ (Becker, 1994; Borowitzka, 2005).

###### *2.2.1.2.1.2 Raceway pond*

Raceway ponds are a modification of the much simpler conventional open ponds, having a difference in flow pattern. The flow direction of the water is controlled by the rotation speed of the paddlewheels where the water and nutrients are continuously circulated around the pond tracks in the direction of the paddlewheel.

Raceway ponds are about 15 to 35 cm deep and are usually lined with plastic and cement kept in continuous motion often by paddle wheels in order to increase the daily productivity. Raceway pond is typically used in commercial scale cultivation of microalgae *Dunaliella salina*, *Chlorella*, *Spirulina* and *Nannochlorpsis* (Borowitzka, 2012).

Table 7: Biomass productivities of open pond cultivation. Adapted from (Brennan and Owende, 2010).

| Algae species | Biomass conc. $X_{max}$(g/L) | Biomass areal productivity (g/m$^2$/day) | Photosynthetic efficiency (%) |
|---|---|---|---|
| *Chlorella* sp. | 10 | 25 | - |
| *Spirulina* | 1.25 | 69.16 | - |
| *Chlorella* sp. | 40 | 23.5 | 6.48 |
| *Chlorella* sp. | 40 | 11.1 | 5.98 |
| *Chlorella* sp. | 40 | 32.2 | 5.42 |
| *Chlorella* sp. | 40 | 18.1 | 6.07 |
| *Haematococcus pluvialis* | 0.202 | 15.1 | - |

Commercial pond have a size of up to 5,000m$^2$ with sizes of 1000m$^2$ also common (Acién Fernández et al., 2013). The largest raceway pond for biomass production has an area of 44ha and located in Calipatria, CA, USA (Acién Fernández et al., 2013) with algal areal productivity in open pond ranging from 3 – 38 g/m$^2$/day (Milledge, 2013).

Raceway pond in comparison to closed PBR requires more land for cultivation such that the land requirement for a raceway pond at a productivity of 10gm$^2$/day requires

400ha to produce 30Mg/ha/year.  For PBR at productivity of 20g/m$^2$/day, 10 ha are required to produce 60Mg/ha/year (Slade and Bauen, 2013).

#### 2.2.1.2.2 Closed systems for microalgae cultivation

Closed system, also referred to as photobioreactor (PBR) is another option for cultivating microalgae. In comparison to the open pond system, PBR systems are more expensive in terms of capital and operating cost. The high cost of PBR is justifiable based on the following factors; easy control of specific process condition, low risk of contamination, lower harvesting cost due to high biomass concentration, low water consumption due to less evaporative losses and higher biomass productivity in comparison to open pond .

PBR system includes flat panel/plate, vertical column and horizontal tubular reactor. Other types of reactor which do not fall strictly into these categories includes helix, helical bio-coil, waterbed, special flat panel, internally illuminated and thin film photobioreactor.

##### *2.2.1.2.2.1 Flat plate/panel photobioreactor*

Flat panel photobioreactors consist of transparent plate which are joined together and the culture illuminated from either one side or both sides. The culture is stirred by aeration and light is usually emitted evenly from a flat transparent screen or from lamps above the culture. In terms of dimension, the flat panels are varied but heights lower than 1.5m and width less than 0.10m is preferable to avoid using high mechanical resistance material (Acien et al., 2013). A new low cost design for vertical flat panel PBR consisting of transparent bags (can be replaced when needed) located between two iron frame was proposed (Rodolfi et al., 2009). Although, scaling up of flat panel system is still a rather challenging problem due to the requirement of extensive quantities of module and bag replacement. Also due to the increase of increased volume with scaling up, there is increasing hydrostatic pressure. The plate system structure is not capable of withstanding very high pressure (Pandey et al., 2014).

### *2.2.1.2.2.2 Tubular photobioreactor*

Tubular photo-bioreactors are more widely used for the outdoor production of microalgae as a result of their large illumination surface area. Most outdoor tubular photobioreactors are usually constructed with glass or plastic tubes. Their culture is re-circulated either with pumps or an airlift system. Tubular reactors can either be horizontal, vertical, near horizontal, conical and inclined (Molina et al., 2001; Ugwu et al., 2008).

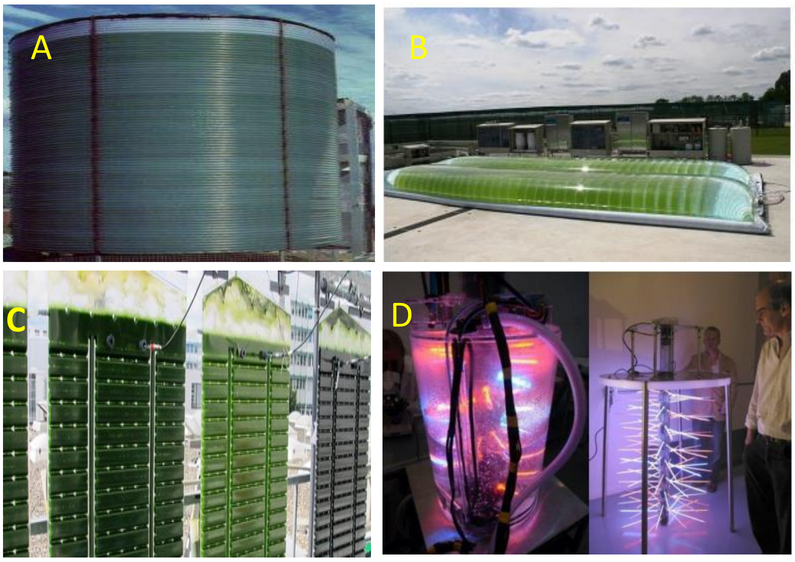


Figure 5: (A) Biocoil Helical Tubular reactor (B) Water bed AlgaeParc (C) Flat Panel Airlift reactor (D) Origin oil Helix photo bioreactor (Fishace, 2014; Qiu, 2013; Fraunhofer, 2014).

#### *2.2.1.2.2.2.1 Airlift tubular photobioreactors*

Airlift photobioreactors (ALPBR) consist of two interconnecting zone known as the riser where the gas mixture is sparged and the downcomer . Mixing is achieved by bubbling of the gas through a sparger in the riser tube without need for physical agitation. A riser is similar to the bubble column where the sparged gas moves upwards (Chisti, 1989; Miron et al., 2000)

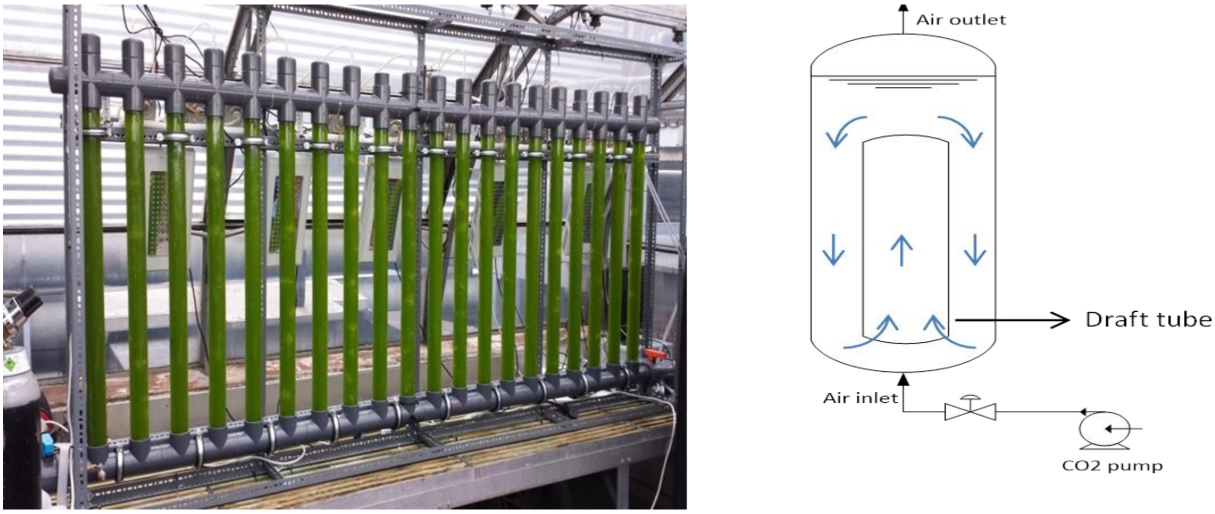


Figure 6: Picture (Variconaqua,2016) and schematic diagram of an airlift photo bioreactor

Several advantages of the ALPBR include good mixing, well-defined fluid flow pattern, relatively high gas–liquid mass transfer rate, and low capitals and operating costs. Mixing in the ALPBR can be achieved without causing too much shear force in the liquid phase, which could otherwise inhibit growth of the microalgae (Krichnavaruk et al., 2005). Experimental observations have shown that in terms of cell growth, the airlift photobioreactor provides better performance than the bubble column PBR's (Monkonsit et al., 2011).

Table 8: Algal biomass productivity and capacity for closed photobioreactors

| Species | PBR type | Volume (L) | Growth rate ($h^{-1}$) | Areal productivity ($g/m^2$/day ) | Volumetric productivity (g/L/day ) | PBR material | Reference |
|---|---|---|---|---|---|---|---|
| *Chlorella vulgaris* | Airlift tubular | | 0.049 | | | Clear acrylic | Sasi et al., 2011 |
| *Phaeodactylum tricornutum* | Airlift tubular | 200 | 0.048 | 32 | 1.90 | Plexiglas | Molina et al., 2001 |
| *Nannochloropsis gaditana* | Vertical bubble column | 340 | | 15.4 | 0.59 | | San Pedro et al., 2014 |
| *Chlorella pyrenoidosa* | Inclined tubular | 12 | | 72.5 | 2.90 | Polyvinyl chloride | Lee et al., 1995 |
| *Chlorella pyrenoidosa* | Inclined tubular | 10 | | 130.0 | 3.64 | Pyrex glass | Lee & Low, 1991 |
| *Spirulina platensis* | Helical tubular | 12 | | 5.44 | 0.51 | Transparent tubing | Watanabe et al., 1995 |
| *Haematococcus Pluvialis* | Parallel tubular | 25,000 | | 10.2 | | Plastic | Huntley and Redalje, 2006 |
| *Spirulina platensis* | Horizontal tubular | 8000 | | 27 | 1.60 | Transparent polycarbonate | Richmond et al., 1993 |
| *Nannochloropsis* sp. | Horizontal tubular | 10 | | 15.7 | 0.85 | | de Vree et al., 2015 |

In comparison to closed PBR's, biomass productivity of open pond systems are less efficient. Some influential factors that affects biomass productivity includes evaporation losses, temperature fluctuation in the growth media, $CO_2$ and nutrient deficiencies, inefficient mixing, and light limitation( Pulz, 2001). In open system, temperature fluctuation because of seasonal variation are more difficult to control. In addition, $CO_2$ deficiencies due to diffusion into the atmosphere may result in less efficient utilisation of $CO_2$.

For both open and closed system, poor mixing by inefficient stirring mechanisms may result in poor mass $CO_2$ transfer rates. Light limitation due to top layer thickness may also reduce biomass productivity. However, enhancing light supply is possible by reducing layer thickness; using thin layer inclined types of culture systems, and improved mixing can minimise impacts to enhance biomass productivity (Brennan and Owende, 2010).

#### 2.2.1.2.3 Hybrid system for microalgae cultivation

Hybrid algae cultivation systems are essentially an integration of open pond and PBR systems; a dual cultivation process. The first part of cultivation is usually in a photobioreactor where conditions are more controllable and contamination from other organisms is minimised hence favouring continuous cell division. The second cultivation stage aimed at exposing the cells to nutrient stresses, which enhances synthesis of the desired lipid product takes place in an open system (Huntley and Redalje, 2007; Rodolfi, et al., 2008).

A classic example of a hybrid system is the Alduo technology, which uses open ponds for batch cultivation and PBR for continuous cultivation. HR BioPetroleum developed and patented the Alduo technology and established a joint venture company called Cellana with Dutch Shell Plc to build and operate a 2.5-ha demonstration facility in Hawaii for growing marine algae for biodiesel (Andersen, 2005; Cellana, 2013).

#### *2.2.1.3 Algae cultivation requirement*

##### 2.2.1.3.1 Nutrients and water source

Microalgae requires a fixed source of nitrogen obtainable from ammonia or nitrate. Nitrogen fertilisers are commonly made using the Haber-Bosch process that uses methane and nitrogen to produce ammonia. The cost of ammonia is rather significant, having a market price of around $200/tonne.

A life cycle assessment of the production of micro-algal biodiesel showed that recycling of harvest water back to the growth system could reduce nutrient requirement by 55 % (Yang et al., 2011b). Efficient recycling of harvest water could minimise to need for fertilizer and in addition, anaerobic digestion of algal biomass with the digester effluent returned into the cultivation stage could allow recycling of up to 90 % of nutrients (Lundquist et al., 2010; Williams and Laurens, 2010).

Utilisation of wastewater can reduce both the need of nitrogen and fertiliser purchase, and thus provide a means for the removal of chemical and organic contaminants, heavy metals and pathogens from wastewater whilst producing biomass for biofuel production (Munoz and Guieysse, 2006). In addition, wastewater utilisation can minimise fresh water use for algal biomass cultivation.

In Malaysia, an enormous amount of palm oil mill effluent (POME) is continuously generated from 453 palm oil mills in operation (mpob.gov.my, 2017). POME is non-toxic wastewater with a pH ranging from 4.91 to 10.5.7, COD ranging from 225 to 96,666 mg/L, $NH_3N$ (0.8 to 124.0mg/L), $NO_3N$ (1.0 to 45.3 mg/L) and $PO_3$ (5.2 to 430 mg/L) (Phang et al., 2015). As shown in table 6, relatively high biomass productivity is attainable when the microalgae *Chlorella* is grown in POME. In addition, *Chlorella vulgaris* has been cultivated successfully in wastewater discharge from a steel plant and achieved an ammonia bioremediation rate of 0.022 g $NH_3$/L/ day (Yun et al., 1997).

##### 2.2.1.3.2 $CO_2$ supply

Carbon is also an important nutrient and supply in the form of $CO_2$ is required for autotrophic micro-algae. Microalgae require 1.7kg – 2.8 kg of $CO_2$ to produce 1 kg of algae, the $CO_2$ is injected in a controlled manner into the system to optimize growth ( Dorpel., 2009, Pandey et al., 2014). The supply of atmospheric $CO_2$ for the purpose of algal biofuel production is not economically viable as the potential yield from the atmosphere is limited to low $CO_2$ concentration in the air (360 ppm) (Stephan et al., 2002).

Flue gases from power plants contributes more than 7% of the total world $CO_2$ emissions from energy use (Kadam et al., 2001). For this reason, the use of flue gas emission from an industrial process unit as a source of $CO_2$ for microalgae growth has great potential to mitigate $CO_2$. Flue gas normally has a $CO_2$ content of up to 20% with concentrations from gas-fired stations usually lower at 7.4 to 7.7%, than that from coal-powered stations at 12.5 to 12.8 % ( Brune et al., 2009, Douskova et al., 2009; Xu et al., 2003)

Studies have also shown that microalgae can efficiently utilize the $CO_2$ in flue gases. Growth rates for *Chlorella* were shown to be higher when cultivated using flue gases with a $CO_2$ content of 11-13 % than air enriched to 12 % $CO_2$ (Douskova et al., 2009). Chiu et al. (2011) recorded that the average efficiency of $CO_2$ removal from the flue gas could reach up to 60% using *Chlorella.* A comparative study by Yoo et al. (2009) of *Botryococcus braunii*, *Chlorella vulgaris*, and *Scenedesmus sp*. under flue gas conditions showed *Scenedesmus sp.* to be the most suitable for $CO_2$ mitigation due to its high biomass productivity (0.218 g/L per day). B. braunii and Scenedesmus sp. are reported to grow better using flue gas as in comparison to air enhanced with $CO_2$. Utilization of $CO_2$ from flue gas by microalgae provides an opportunity of cost reduction when the flue gas is obtainable at a lower cost than air enriched with $CO_2$.

#### 2.2.1.3.3 Light energy

Light intensity is a significant factor that influences the growth rate of microalgae. Light can either be artificial (i.e. fluorescent light) or natural sunlight. Depending on the light source, the light intensity on the reactor wall is recorded in literature within the range of 23-8000µmol$m^{-2}s^{-1}$( Andrade et al. 2007; Carvalho et al. 2011; Farooq et al. 2013; Gordon et al. 2007; Qiang et al., 1998; Matos et al., 2014; Pickett et al. 1996; Wang et al., 1999). The light intensity when sunlight is the light source recorded to be in the range of 200-1300μmol$m^{-2}s^{-1}$(Qiang et al., 1998; Sanchez et al., 2000). Light intensity is often expressed as the photon flux density (PFD), which the number of photons impinging on a flat surface per unit of time, micromole/$m^2$/s.

In Malaysia, the average annual daily solar radiation is 4.21 kWh/$m^2$ to 5.6 kWh/$m^2$ The Northern region and a few places in East Malaysia have the highest potential for solar energy application due to its high solar radiation throughout the year. In most microalgae, photosynthesis is saturated at about 30% of the total terrestrial solar radiation (Pulz, 2001).

A study by Fabregas et al. (2004) showed the increase growth rate at low irradiances of 40 and 60μmol quanta $m^{-2}$ $s^{-1}$. Although further increase over 220 μmol quanta $m^{-2}s^{-1}$ in the incident irradiance had no effect on the growth rate which shows the point of light-saturated and limited conditions. In addition, another study by Khoeyi et al. (2012) shows that light regime had an effect on growth rate for biomass production of *Chlorella vulgaris.*

### 2.2.2 Harvesting, dewatering and drying technologies

Harvesting and dewatering is the subsequent stage of the cultivation of algae and is necessary to achieve a higher biomass concentration for the processing of micro-algal to up to 30% TSS concentration (Brennan and Owende, 2010). By harvesting alone, up to 15% TSS concentration of algal biomass is achievable (Shelef, 1984).

Separating the algae from external water is a major challenge to the industrial scale processing of algae largely due to the small size of the algal cells, with unicellular eukaryotic algae typically measuring at 2–30μm (Kleivdal et al., 2013).

The cost effectiveness for the harvesting and dewatering of microalgae is considered as a key factor which limits the commercial use of microalgae (Olguı, 2003). The costs of harvesting and dewatering are also a major component of production between 20 to 30 % of the total biomass production cost (Mata et al., 2010). But estimate as high as up to 50 % of the total biomass production cost has been recorded (Greenwell et al., 2010).

The desired moisture content of the harvested algal biomass is an important criterion for selecting the appropriate harvesting method. The desired moisture content of the harvested microalgae will significantly influence the costs and the subsequent method for further processing the microalgae (Molina Grima et al., 2003). A typical microalgae culture contains less than 0.7 % algae cells and the process of harvesting alone achieves less than 10% of total suspended solid (TSS) concentration of algae.

Several harvesting and dewatering technologies include:

- Flocculation (includes chemical flocculation, bio-flocculation, auto-flocculation and electrolytic flocculation
- Gravity settling/sedimentation
- Flotation(includes electro-flotation, dispersed and dispersed-air flotation, auto-flotation, froth flotation and micro-flotation
- Filtration ( includes pressure filtration, vacuum filtration, deep bed, cross-flow ultra-filtration and magnetic)
- Centrifugation( includes hydrocylone, solid decanter, nozzle-type)
- Screening (includes micro-straining and vibrating screens)
- Ultrasonic method

#### *2.2.2.1 Flocculation*

Flocculation is usually used for harvesting microalgae, as part of a two-step harvesting process. A wide range of flocculating microalgae have been explored both from traditional flocculation methods; widely used in other fields of industry (e.g., chemical flocculation), to novel methods (e.g., bio-flocculation and co-pelletisation) and electrical methods (e.g. electrolytic flocculation) (Vandamme et al., 2013).

#### *2.2.2.2 Chemical flocculation*

In chemical flocculation, inorganic or long chain organic coagulants are used and cause the algal cells to form large lumps making them more easily filtered and settle more quickly to ease harvesting. Aluminium sulphate and chitosan are common coagulants used for water treatment and for algae harvesting (Moraine et al., 1980). Flocculation experiment using chitosan has been carried out and effectively separated three freshwater algae *Spirulina*, *Oscillatoria* and *Chlorella* (Divakaran and Pillai, 2002).

#### *2.2.2.3 Bio-flocculation*

Bio-flocculants produced from bacteria have been shown to be effective in the flocculation of *Chlorella sp.*, *Pediastrum sp.*, *Phormidium sp.* and *Scenedesmus sp.* (Van Den Hende et al., 2011; Molina Grima et al., 2003).

Bio-flocculation enables the harvesting of microalgae without addition of chemical flocculants and allows for re-use of the cultivation medium without any additional treatment. Bio-flocculation of microalgae with bacteria requires additional substrate as well as an extra energy source for bacterial growth likely to cause bacterial contamination during harvesting. Naturally flocculating diatom *Skeletonema*, have been used to form flocs of *Nannochloropsis.* As diatoms have a silica-based cell wall, they require medium composition different from that used for biofuel production which incurs additional cultivation costs (Salim et al., 2011).

#### *2.2.2.4 Autoflocullation*

Autoflocculation in comparison to chemical flocculation uses carbon dioxide supply to interrupt the algal system causing them to flocculate. The elevated pH as a result of photosynthetic carbon dioxide consumption corresponds to precipitation of inorganic precipitate (mainly calcium sulphate) which causes flocculation (Shelef and Sukenik, 1984).

#### *2.2.2.5 Electrolytic flocculation*

Electrolytic flocculation does not require flocculants but rather non-sacrificial anodes are used in which negatively charged algae move towards the anode enabling flocs to be formed (Poelman et al., 1996) Although it is an advantage that electrolytic flocculation does not require flocculants, it requires electrodes which are prone to fouling (Uduman et al., 2010). Electrolytic flocculation has been demonstrated to be effective at a bench scale, removing 95% of the original micro-algae in suspension with an energy consumption of 0.3kWh/m$^3$(Poelman et al., 1996).

#### *2.2.2.6 Filtration*

Filtration of algal culture works by forcing the culture to flow through a filter medium (using a suction pump) which retains the algal biomass for harvesting. There are several types of filtration as stated earlier and depending on the properties of the algae and the desired downstream processing certain methods of filtration are suitable. Filtration is mainly a dewatering means and it is normally applied following coagulation/flocculation to improve harvesting efficiency. Pressure drop across the system needs to be maintained in order to force fluid flow through the membrane. In this process, micro-algal deposits on the filtration membrane usually grow thicker throughout the process, increasing resistance and decreasing filtration flux upon a constant pressure drop (Barros et al., 2015).

Comparisons of different pressure filter for the harvesting of *Coelastrum* investigation by Mohn(1980) showed that harvested solid concentration in the range of 5-27% is achievable and recommends chamber filter press, cylindrical sieve and filter basket for algae filtration.

In the harvesting experiments conducted by Sim et al. (1988), mixed algae cultures containing smaller species such as *Chlorella sp*. and *Oocytis sp.* were used for waste water treatment. The pump energy input for filtration of the micro-algae and to back-flush the drum filter was between 0.3 and 0.5 kWh per cubic meter of algal suspension.

#### *2.2.2.7 Flotation*

Flotation is an alternative harvesting method to sedimentation which works better for very thin algal suspension. Unless coagulant is used in optimal doses to assist flotation, only limited algae can be harvested. In flotation, small bubbles are created by electrolysis or pressure relief and introduced into the suspension, adhering to the surface of the alga cells and transporting the algae to the surface of the water where they can be skimmed off (Petrick et al., 2013). Solids concentration of harvested slurry (up to 6%) from dissolved air flotation can be further increased by a second downstream stage flotation(Pandey et al., 2014).

A study by Sim et al. (1988) on algal harvesting method showed that 1.6 kWh of power was consumed to obtain an algal suspension with an average 4 % total solid content (dry mass) from a culture medium with just under 0.1 % algal biomass per kilogram of dry algae. A power consumption rate of 0.1 kWh/m$^3$ specified for micro-flotation is essentially less energy intensive in comparison to that in Sim et al. (1988) study. The lower pressure in the pressure saturator and the special design of the pressure-relief valves is notably responsible for the low energy consumption in comparison to conventional pressure-relief flotation technique (Petrick et al., 2013).

#### *2.2.2.8 Ultrasonic method*

Ultrasound has been used to successfully harvest microalgae at laboratory scale and has also been used to support flocculation and cell decomposition in order to improve the harvest efficiency (Bosma et al., 2003;  Zhang et al., 2009).

A pilot-scale ultrasonic harvester which was assembled and tested outdoors with *Nannochloropsis oculata* feedstock achieved a typical concentration factor of 6 times averaged over trial periods and a peak concentration factor of 18 times above the feedstock concentration. The scaled-up unit operated at 45–225 L/hr and Solix Biosystems provided the ultrasonic harvester from their Coyote Gulch, Colorado algae cultivation facility (NAABB, 2014).

#### *2.2.2.9 Centrifugation*

In centrifugation, the suspended particle is accelerated by centrifugal force which reduces greatly the separation time. Almost all types of micro-algae can be separated by centrifugation, with some of them being considered as very efficient as a one-step separation process (Mohn, 1988).

Centrifugation is considered as the fastest harvesting method, but also the most expensive due to its high energy consumption, which limits its application. Centrifuges are able to harvest majority of microalgae strains and are efficient as a one-step separation process. There are however, evidence that shows that the exposure of micro-algal cells to high gravitational and shear forces results in cell structure damage (Barros et al., 2015).

Many different designs of centrifuge exist such as nozzle type, solid ejecting disc, disc-stack centrifuge and hydrocyclone.  Disc stack centrifuge are used in widely in commercial plants for the production of high value algal products algal biofuel (Molina Grima et al., 2003). A disc-stack centrifuge consists of a moderately shallow cylindrical bowl containing a number (stack) of closely spaced metal cones (discs) that rotate with the bowl. They are suitable for separating particles of the size (3 -30 µm) and concentration (0.02 to 0.05 %) of algal cells in a growth medium (Milledge, 2013).

### *2.2.2.10 Novel harvesting and dewatering technologies*

2.2.2.10.1 Evodos dynamic settler

Evodos developed three types of dynamic settlers suitable for the harvesting of algae. This includes the Evodos type 10 and type 25 which has a high separation efficiency of up to 95% and capable of achieving high total solid concentration of up to 30 %. Evodos dynamic settler uses a spiral plate technology which enhances the gravitational forces in a manner similar to traditional centrifuges, but minimizes the distance particles must travel before settling (Evodos, 2016).

Table 9: Basic information on Evodus 25 (Evodus, 2016).

| | |
|---|---|
| Separation energy requirement | 0.95 kWh per $m^3$ |
| Pump energy requirement | 0.25 kWh per $m^3$ |
| Discharge energy requirement | 0.2 kWh with a maximum of 5 discharges per hour |
| Pressurized air requirement | 6 bar |
| Air consumption | < 5 litres / hour |
| Pump discharge pressure | Max. 0.2 bar |
| The discharge time | 3.5 minutes |
| The separation efficiency | >95% |
| Dry solid percentage | Up to 30%, |

2.2.2.10.2 OriginClear electro water separator (EWS)

OriginClear's electro water separator (EWS) harvester is an algae harvesting technology which complements existing harvesting, drying and extraction systems. It operates as a stand-alone system for continuous harvesting of viable algae cells using very small amounts of electric power capable of achieving a 99.5% removal of suspended solids and organics. It is also easily integrated into existing commercial algae extraction systems for the purpose of improving overall productivity significantly and reducing operating cost (OriginClear, 2016)

### 2.2.2.10.3 AlgaeVenture System Harvesting, dewatering and drying

AlgaeVenture System harvesting, dewatering and drying (AVS hdd) is a belt type harvest system based on advanced membrane (figure 7). The system removes water and dries algae up to 5% moisture content in a continuous manner and reduces energy consumption by 95% in comparison with traditional centrifuge method (Chen et al., 2009).

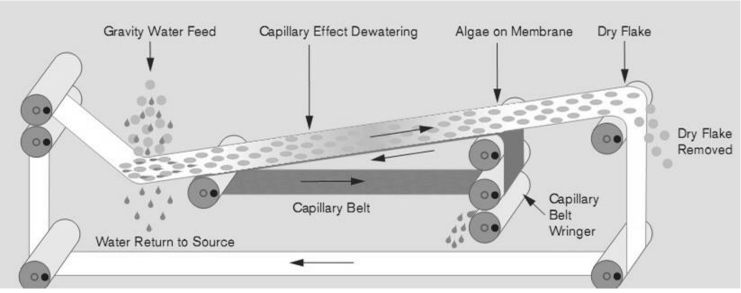


Figure 7: AlgaeVenture System harvesting, dewatering and drying (AVS hdd)

Table 10: Harvesting and dewatering technology comparison

| Technology | Advantages | Disadvantages | Total solid outputs concentration (%) | Energy consumption | References |
|---|---|---|---|---|---|
| Micro-straining | Low capital cost. | Low harvesting efficiency and difficulty in handling particles. Build-up of bacteria and alga biofilm slime on mesh. Not suitable for chlorella harvesting. | 1.5 | 0.25kWh/$m^3$ for thickening *Coelastrum proboscideum* to 1.5%TSS | (Griffiths et al. 2010; Pandey et al., 2014; Shelef et al., 1984) |
| Vibrating screens | High removal efficiency up to 95%. | Build-up of bacteria and alga biofilm slime on mesh. | 5-10 | 0.4kWh/$m^3$ | (Pandey et al., 2014; Van Den Hende et al.,2011) |
| Centrifugation | Suitable for most algal strains. Efficient harvesting method. | High capital and operational cost. | 10-30 | 0.3 kWh/$m^3$<br>up to 20 kWh/$m^3$ | (Molina et al 2003; Milledge, 2013) |
| Vacuum filtration | Low operating expenditures. | Problems with fouling particularly to smaller algal strains like *Chlorella.* | 5-18 | 5.9 kWh/$m^3$ | (Dodd, 1980;Pandey et al.,2014;Singh et al 2013) |
| Membrane ultrafiltration | Can handle delicate cells. | High capital costs. Membranes may require replacement. | 1.5-9 | 0.04 to 3kWh/$m^3$ | (Davis et al., 2016; Milledge,2013) |

| | | | | | |
|---|---|---|---|---|---|
| Chemical Flocculation | Wide range of flocculants available, price varies, flocculants can be low cost. Expensive for large scale. | Necessary removal of flocculants. Chemical contamination. | 3-8 | | (Benemann et al 1980;<br>Salim et al., 2011;<br>Singh et al., 2013) |
| Flotation | More rapid than sedimentation. | Algal strains specific. High capital and operational cost. | <7 | | (Pandey et al., 2014) |
| Sedimentation | Low operating cost. | Slow process not suitable for large scale. | 2-7 | 0.1kWh/$m^3$ | (Singh et al., 2013) |
| Electrolytic flocculation | No flocculants required | Requires an extra method to be efficient | <10 | 0.17-0.33kWh/$m^3$ | (Schlesinger et al., 2012; Singh et al.,2013) |

Suitability of harvesting and dewatering technology is dependent on the algae species, size, density, extent of dewatering and value of the target products. *Chlorella*, *Chlamydomonas and Chlorococcum* are micro-algal species shown to be suitable for bio-jet fuel production, however harvesting and dewatering data for *Chlamydomonas and Chlorococcum* are rather sparse. Harvesting and dewatering technologies like vacuum filtration, centrifugation, magnetic filtration, electrolytic coagulation, microfiltration, auto-flocculation and bio-flocculation are all suitable for *Chlorella* sp.

Centrifugation is capable of achieving the highest total solids output algal biomass concentration but requiring more energy (0.3 kWh/m$^3$ up to 20 kWh/m$^3$) to achieve this. In the case where the downstream process (post energy extraction conversion technique) requires the total output algal biomass concentration to be >20% TSS, the centrifugation techniques whilst being energy intensive is the most suited method. Centrifugation can be combined with other less energy intensive methods like flocculation or membrane ulltrafiltration to reduce overall energy consumption.

#### ***2.2.2.11 Drying***

Drying is an additional process step after the harvesting and dewatering step in order to achieve a higher percentage of algal total suspended solids(>30% -88%TSS). Drying is only an essential process step if the conversion technology after the harvesting and dewatering stage requires the algal biomass concentration with a TSS greater than 30%. It is preferable to choose energy extraction methods that do not require the need for drying the micro-algae biomass (Milledge and Heaven, 2012). The main consideration in the selection of the drying technology depends on the production scale the purpose for which the dried biomass is intended (Shelef and Sukenik,1998). Earlier in section 2.1, it was discussed that the algal lipid to bio-jet fuel was the pathway for further review. Some cell disruption methods however may require additional drying and thus discussed in chapter 3. Example of drying method includes solar drying, rotary dryer, spray dryer, freeze dryer and flash dryer. Only drying technologies that have been used to dry microalgae in the past are discussed.

#### 2.2.2.11.1 Rotary drying

Rotary drying involves the use of a sloped rotating cylinder to move the algae from one end to the other by gravity to achieve drying ( Shelef and Sukenik,1984). *Scenedesmus* algae using a thin layer drum dryer was dried successfully (Soeder and Pabst, 1975). A pilot electric drum-dryer was also tested for drying wet slurry containing 30% solids of *Scenedesmus* algae at 120°C for about 10s at an energy consumption rate of 52 kWh (Show et al., 2015). Processing cost could be reduced by 6.8 times by replacement of the electrically heated drum dryer by a steam heated dryer.

In an assessment on energy requirement for drying algae with a water content of 4%, heat energy of up to 18.23kWh was consumed for evaporating 18.2 kg of water for every kg of dry algae product. Additionally, a supplementary electric energy input of 1.4 kWh was needed to run the dryer (Show et al., 2015). Energy requirement largely depends on the water content of the final dried algal. Energy conversion method with acceptable higher algal biomass water content before processing are desirable to lower energy cost.

#### 2.2.2.11.2 Solar drying

Drying of micro-algal biomass is achievable by either direct solar radiation or by solar water heating. Drying by direct sun radiation causes algal chlorophyll to dehydrate and disintegrate thus altering the texture and color of the final algal product. In solar water heating system, solar thermal energy is derived by specially designed glass panels or tubes used to heat up the water. Experimental works of Prakash et al. (1996) showed that *Spirulina* and *Scenedesmus* algal species was successfully dried to less than 10% moisture content in 3-5 hours. Whilst solar drying is an economical method, it is highly unreliable and weather dependent. In addition it is unsutaible to large scale drying as it is a time consuming process (3-6 hours) ( Shelef and Sukenik,1984).

#### 2.2.2.11.3 Cross-flow air drying

*Spirulina* algal biomass containing 55–66% moisture was successfully dried using cross-flow air drying for 14h at 62°C in a compartment dryer producing dried algal product 2–3mm thick with 4–8% moisture contents (Becker and Venkataraman, 1982). In addition, this method of drying keeps the cell wall of *Chlorell*a and *Scenedesmus* intact after drying. Further assessment reveals that this method of drying is cheaper than drum drying and faster than solar heat drying (Show et al., 2015).

### 2.2.3 Energy extraction and conversion technologies

#### ***2.2.3.1 Cell disruption and lipid extraction methods***

Microalgae comprises of protein, carbohydrate, lipid and nucleic acid. The key constituents of algae for the production of biofuel are lipids. The percentage of lipid is dependent on the algal strains and the cultivation condition within the range of 1-75% of oil content (Demirbas, 2011). In order to recover this lipid, it must first be liberated from within the cellular matrix of the algae cell (Halim et al., 2012). There are various technologies available for the disruption and extraction of lipid which can be classified into four categories; biological, chemical and mechanical and non-mechanical. Apart from the chemical route, the other categories are only suitable for cell disruption which aids in further extraction of lipid.

Figure 8: Algae cell disruption and Lipid Extraction Technologies

#### 2.2.3.1.1 Supercritical fluid extraction

Supercritical fluid extraction works by utilizing the solvating power of fluids above their critical point. The majority of supercritical fluid applications uses $CO_2$ because of its ideal critical properties (i.e., moderate critical temperature of 31.1˚C and pressure of 73.9 bar), low toxicity, and chemical inertness (Luque De Castro et al., 1999). Supercritical fluid extraction has been applied for the extraction of essential oils from plants as well as for lipid extraction from microalgae (Mendes et al., 1994; Metzger and Largeau 2005). Nevertheless, economical production of biofuels from microalgae via supercritical processing is challenged by the energy-intensive nature of the process.

#### 2.2.3.1.2 Solvent extraction

Because of its high percentage of oil recovery, solvent extraction has become a very popular method of oil extraction. Solvent extraction method have been used in the past to successfully extract lipid from are green algae obtained from open pond system and recovers almost all the oils leaving behind only 0.5% to 0.7% residual oil (Topare et al., 2011). The use of organic solvents for extracting lipids uses energy intensive distillation after extraction for separating lipid from the solvents (Mubarak et al., 2015).

The extraction of lipids from algae biomass use non-polar solvents such as hexane, benzene, toluene, diethyl ether, chloroform and polar solvents such as methanol, acetone, ethyl acetate, and ethanol. The non-polar solvents disrupt the hydrophobic interactions between non-polar and neutral lipids available in the algae biomass. The solvents used for extracting lipid from microalgae biomass are n-hexane, ethanol, 1-butanol, dimethyl ether, and mixtures of chloroform/methanol, n-hexane/ethanol, n-hexane/ isopropanol, n-hexane/2-propanol, methanol/1-ethyl-3-methyl imidazolium methyl sulfate, methylene chloride/methanol, dichloroethane/methanol, dichloroethane/ethanol, and acetone/dichloromethane (Mubarak et al.,2015).

Lipids from *Chlorella* was extracted using methylene chloride and methanol solvent systems and greater amounts of neutral lipid was recovered similar to a modified Bligh and Dyer's method, which used phosphate buffer in addition to the chloroform, methanol and water mixture (Guckert et al.,1988).

D'Oca et al. (2011) used different methods like Soxhlet extraction, magnetic stirring, and ultrasonic bath with five solvent systems such as mixtures of chloroform and methanol (2:1 v/v), methanol, chloroform, ethanol, and hexane for lipid extraction from the dry biomass of *Chlorella pyrenoidosa*. They reported that a mixture of chloroform/ methanol used as a solvent for extraction yields more lipids from microalgae than other solvents.

#### 2.2.3.1.3 Expeller method

Pressing/Expeller press involves subjecting the micro-algal biomass to high-pressure, which ruptures cell walls and releases oil. In an expeller press, as the raw material is pressed, friction causes it to heat up; in some cases, the temperatures may exceed 120$^{o}$F (Chavan et al., 2011).

As different strains of algae vary widely in their physical characteristics, various press configurations (screw, expeller, piston, etc.) better suited for specific algae types. Often, mechanical pressing is used in combination with chemical solvents. Many commercial manufacturers of vegetable oil use a combination of mechanical pressing and chemical solvents in extracting oil. Although simple in design, pressing can be highly energy intensive and low extraction efficiency (can extract between 70- 75% of the oils out of microalgae) in comparison to solvent extraction (Popoola and Yangomodou, 2006).

#### 2.2.3.1.4 Bead beating /milling

Bead beating (also Ball milling) is a mechanical cell disruption method, which aggressively grinds cell suspension together with solid beads. A ball mill comprises a tubular vessel made of metal or thick glass containing the cellular suspension as well as small metal or glass balls. By rotating around their axis, the balls roll in the opposite direction to the direction of rotation of the vessel. The cell disruption occurs as a result of the grinding motion at high velocities due to the variously rolling and dropping balls (Petrick et al., 2013).

Cells of *Chlorella vulgaris, Scenedesmus obliquus and Spirulina* sp. have been disrupted using the ball mill (Hedenskog and Ebbinghaus 1972; Hedenskog and Enebo 1969). The energy input needed to disrupt the cells depends greatly on the cell concentration and the thickness of the cell wall. Cell disruption is most effective when the concentration is high and when the cell debris can be easily separated (Greenwell et al., 2010).

#### 2.2.3.1.5 Ultrasound

Ultrasound is another method used for cell disruption using a sonotrode, which generates the ultrasound waves when placed in the biomass suspension. Usually 25 kHz is used for cell disruption but the frequency selection also depends on the types of cell. The generated sound wave in turn generates high-pressure cycles and low-pressure cycles which forms small vacuum bubbles or cavities in the liquid. When a certain volume is reached the bubbles cannot absorb any more energy and burst during a high-pressure cycle. As a result, mechanical energy is released in the form of shock waves which destroys the surrounding cells (Petrick et al.,2013).

Over 90 % of the fatty acids and pigments in the micro-alga *Scenedesmus obliquus* were extracted by means of ultrasound (Wiltshire et al., 2000). Although extraction of fatty acids and TAGs by means of ultrasound is implemented on a laboratory scale, there is still a lack of adequate information on the subject of its practicability and cost of its application on a commercial scale (Harun et al., 2010).

#### 2.2.3.1.6 OriginOil's single step extraction

The OriginOil Corporation developed a process that combines ultrasound with electromagnetic pulses in order to decompose alga cells. $CO_2$ introduced into the algal suspension in order to lower the pH value. The OriginOil single step extraction harvests, concentrates and extracts oil from algae, and separates oil, water and biomass in one step without the use of chemicals or heavy machineries. The single step process requires no initial dewatering and separates the oil, water and biomass in a short period of time (<1hr). The cell walls are broken down by means of OriginOil's quantum fracturing technology which combines electromagnetic pulses and pH modification to release oil from the algae cells (OriginClear, 2014). Up to 97% efficiency of algae oil is achievable with yields of 19.4 % to 72% dry weight of oil (Amer et al., 2011).

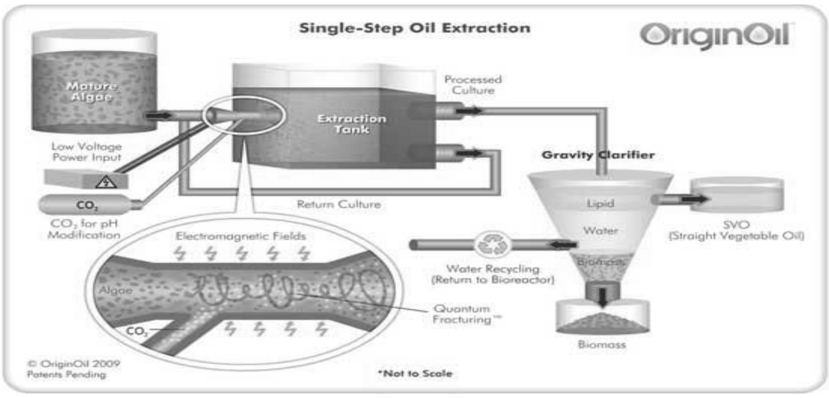


Figure 9: OriginOil single step extraction process diagram (Dejoye et al., 2013).

Table 11: Algal cell disruption and extraction technology comparison

| Cell disruption and extraction Technology | Notes | Advantages | Disadvantages | Oil recovery from microalgae (%) | Energy consumption | References |
|---|---|---|---|---|---|---|
| Expeller Press | Uses high mechanical pressure and used friction from the screw drive to compress the filamentous algae. | No solvent required. Easy operation. | Mechanical methods are energy intensive. | Up to 75% of oil from the algae cell is recoverable.<br>Yield can be less than 15% up to 56% dry weight of oil. | Mechanical process which is energy intensive installed power ranges: 1.1-15 kW ( based on various types) | (Amer et al., 2011;Chavan et al., 2011;Pandey et al., 2014; Sharma et al., 2011) |
| Bead-beating /mill | Uses beads for the disruption of the algae cell wall. | No solvent required. | Mechanical methods are energy intensive. | 53.36%-88% of oil from the algae cell is recoverable.<br>Yield can be between 10.67 % to 66% dry weight of oil. | Bead mill installed power ranges: 1.1-4 kW ( based on various types) | (Gouveia, 2011; J.-Y. Lee; Pandey et al., 2014;Zheng et al.,2011) |
| Solvent extraction | Uses solvent, usually two different types. Algal biomass may be dried prior to extraction. | Solvent use is relatively inexpensive. | Energy intensive distillation for separating lipid from the solvents. Toxic solvent. | Up to 98% of purified fatty acids is obtainable.<br>Expeller press & hexane solvent together can derive more than 95% of the total oil in the algae. | High drying cost | (J.-Y. Lee et al., 2010; Munir et al., 2013) |
| Soxhet extraction | Uses chemical solvents such as hexane under reflux. | Solvent used is relatively inexpensive. | Time consuming and requires large amount of solvent and time consuming not suitable for large scale. | 10% of neutral lipids | High drying cost | (Ryckebosch et al., 2011) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ultrasonic extraction | Uses high pressure cycles of the ultrasonic waves to support the diffusion of solvents into the algal cell structure. | Reduces the time needed for the chemical conversion in solvent extraction by up to 90% | Still requires solvent to enhance lipid recovery. | Yield of approximately 19.6% neutral lipids is achievable. | Based on 20 – $100m^3/hr$ flowrate , 62 x 16KW of power is required | (Halim et al., 2012; Lee et al., 2010; Pandey et al., 2014; Zheng et al.,2011) |
| Supercritical carbon dioxide extraction (SC-$CO_2$) | Uses a supercritical fluid usually $CO_2$ as the solvent for extraction | Uses less toxic solvents for extracting lipids. | High power consumption and difficulty in scaling up. | Yield of approximately 5% algal lipids. | | (Oilgae, 2008; Pandey et al., 2014) |
| Osmotic shock | There is a sudden reduction in osmotic pressure, which can cause cells in a solution to rupture releasing the cellular components such as oil. | Eliminates costly multi-steps and solvent in comparison to conventional methods. | Requires a longer treatment time in comparison to bead mill. | | | (Pandey et al., 2014, Lee et al., 2010) |

The chemical methods of lipid extraction are solvent and soxhet extraction, and supercritical fluid extraction; and the mechanical methods are expeller press, microwave assisted extraction, and ultrasonic assisted extraction and bead beating.

In reported experimental literature, organic solvents such as n-hexane, chloroform, methanol, ethanol, isopropanol are used for extracting oil from microalgae biomass, which are relatively cheaper due to lower initial capital investment. The solvent extraction process is shown to be the most efficient method however, adopting just a single method is inefficient for obtaining the maximum yield. A combination of both mechanical and chemical methods in necessary to obtain higher yield such as solvent extraction with ultrasonication employed as a pre-rupturing stage.

The use of toxic solvents like hexane and chloroform can cause adverse health and environmental hazards and is the major disadvantage of solvent extraction method of algae oil. Whilst methods like supercritical fluid extraction uses less toxic solvents for extracting lipids the downside is the associated high capital investment.

#### *2.2.3.2 Upgrading algal oil to bio-jet fuel*

As with the other types of conversion methods, the algal lipids produced from the cell disruption method will have to undergo a further upgrading process. Algal lipid derived from autotrophic microalgae has successfully been upgraded to naphtha, synthetic paraffinic kerosene (jet fuel) and diesel hydrocarbon fuels after undergoing deoxygenation and hydrogenation. The algal lipid was obtained by extraction after harvesting.

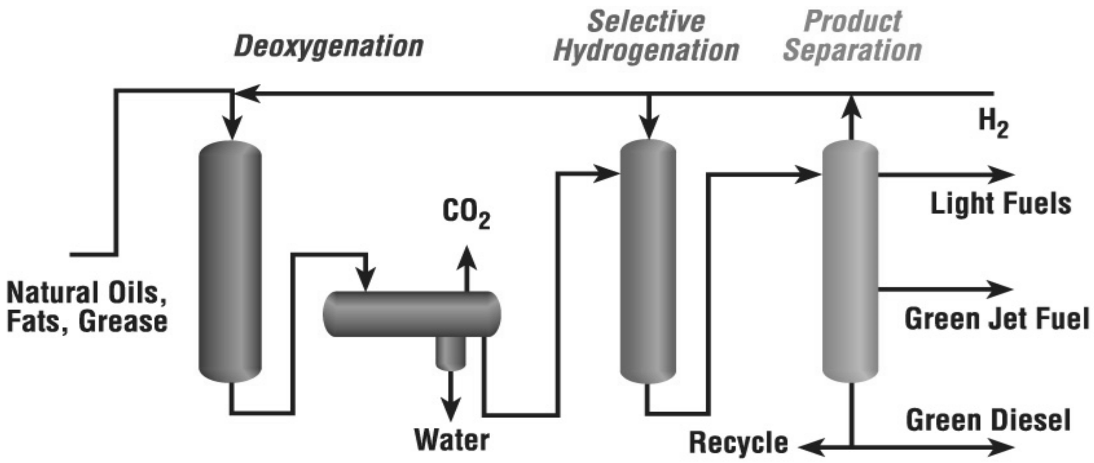


Figure 10: Process diagram of green Jet fuel production from algal oil by deoxygenation, selective hydrocracking and product separation (Lupton et al.,2011).

Extracted algal oil of approximately 1325L produced by Sapphire energy have been utilised for the production of synthetic paraffinic kerosene (jet fuel) via the Honeywell UOP green jet fuel production process shown in figure 10. The jet fuel was tested during Boeing's commercial jet fuel flight demonstration and appeared to meet the specifications for D7566; an 11 Annex A2 Standard Specification for aviation turbine fuel containing synthesized hydrocarbons, for renewable jet fuel at 50% blend with Petroleum jet (Chen et al., 2012).

### 2.2.4 Conclusion

By the extensive review of several literatures it is revealed that a vast number of methods for the growth, harvesting and dewatering and energy extraction and conversion unit operations exist for the production of algal oil for bio-jet fuel production. Of the four main pathways for production of bio-jet from microalgae, the algal lipid route of the biomass-to-oil pathway was chosen for further review based on high yield. Local Malaysian microalgae species *Chlorella*, *Chlamydomonas and Chlorococcum* are shown to be suitable for bio-jet fuel production due to their high lipid and high biomass productivity. The species *Chlorella* has been shown to grow successfully in POME medium and efficiently utilize the $CO_2$ in flue gases. Adopting these options is argued to reduce operating cost but the extent of cost reduction is yet unknown. Cost of cultivation for an open pond is indicated to be cheaper than PBR systems although with certain drawbacks, such as lower biomass productivity, difficulty of temperature control and contamination, and larger land requirement. There is need to determine if the lower capital cost of open pond compensates for its lower productivity level and high land requirement which may affect overall production cost of algal bio-jet fuel, NER and GHG emission and water footprint.

Suitability of harvesting and dewatering technology is dependent on the algae species and extent of dewatering.  Centrifugation is indicated to be the most energy intense for of harvesting and dewatering but also capable of achieving a high water removal percentage. Harvesting and dewatering technologies like vacuum filtration, centrifugation, magnetic filtration, electrolytic coagulation, microfiltration, auto-flocculation and bio-flocculation are all suitable for *Chlorella* sp. Harvesting and dewatering literature for *Chlamydomonas and Chlorococcum* microalge are rather sparse. There is a need to explore the combination of more than one harvesting and dewatering method to reduce operating cost and the exclusion of drying and its impacts on overall MFSP of algal bio-jet fuel, NER and GHG emission.

Energy extraction and conversion methods were reviewed. For the lipid extraction route, methods included solvent extraction, ultrasonication and bead beating. A combination of both mechanical and chemical methods is necessary to obtain higher yield. There is a need to explore these combinations and the overall impact on MFSP of algal bio-jet fuel, NER and GHG emission. This review shows Honeywell UOP green jet fuel production process to be the only method so far for upgrading of algal oil to bio-jet fuel.

# 3 INITIAL INVESTIGATION: TECHNOLOGY ASSESSMENT

This section of the thesis documents preliminary work carried out to assess and determine the most suited technologies for the development of a base case algal bio-jet production pathway. Suitability is defined based on economics and species suitability. Cost analysis is an important evaluation criterion for considering feasibility and viability of large-scale microalgae based bio-fuel production. Energy requirement and efficiency/yield are reflected in the cost criterion. Species suitability criterion is also equally significant and assesses the suitability of the technology for the processing of the micro-algal strain of focus *Chlorella* sp.

## 3.1 Process technologies

The technologies presented for the assessment is representative of promising technologies, avoiding an exhaustive approach. Figure 11 shows the process steps and process technologies considered for assessment.

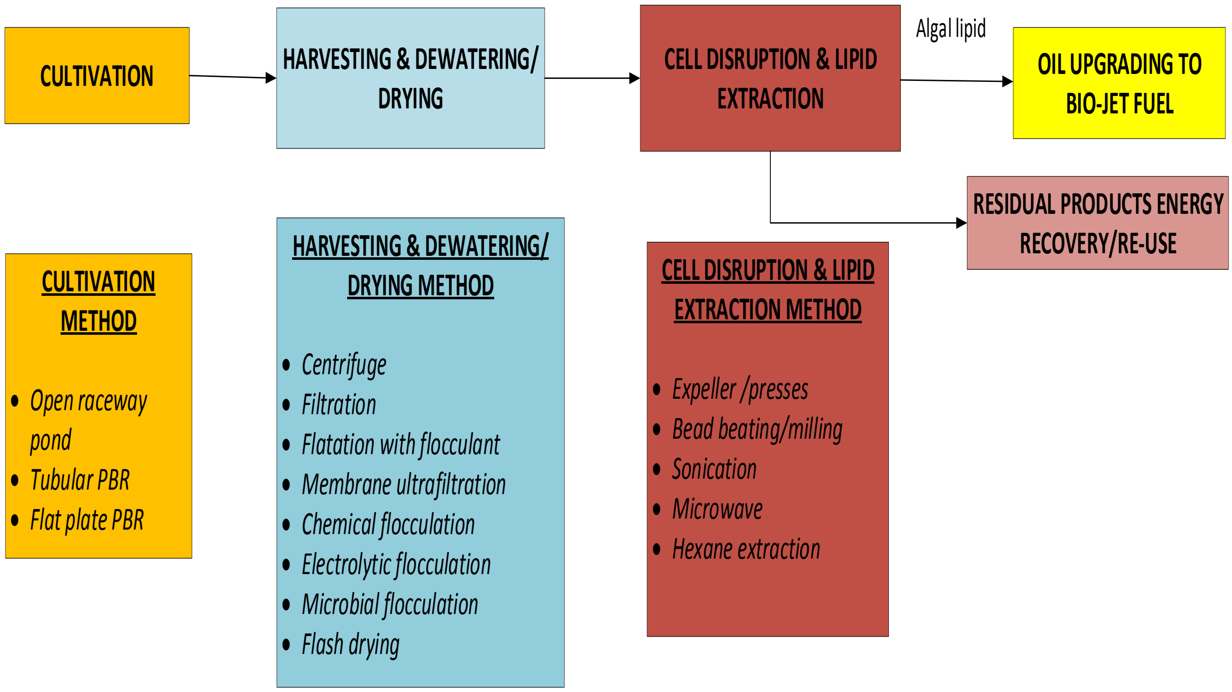


Figure 11: Process stages for the production of bio-jet fuel from microalgae including all technologies considered.

### 3.1.1 Weighted decision matrix

The technology assessment method is based on the principle of a weighted decision matrix for the criteria; cost and species suitability. The weighting factor (W) of a specific criterion represents its importance comparative to the other criteria and ranges from 0 (neglecting the criterion) to 10 (highly important). Each considered technology is assigned a score with respect to each criterion ranging from 0 (least desirable) to 10 (most desirable).

For the assessment in the weighted decision matrix this score is then multiplied by the weighting factor (0-10) to give a weighted score.

$$S_w = S_i \text{ x } W_i$$

(Equation 2)

Where: $S_w$ =Weighted score weight, $S_i$ = Score with respect to i criterion, $W_{i=}$ weighting factor for i criterion.

Species suitability and cost have a weighting factor ($W_i$) of 10 and are considered as equally influential criteria because economics is a significant aspect of this research and algal species highly influences technology selection, thus both have the same weighting factor.

Table 12: Scoring for each criteria

| **Criteria** | **Scoring** |
|---|---|
| Cost | $P>P_0$; S=0<br>$P_0 \geq P \geq P_{10}$; $S=10*\frac{P-P_0}{P_{10}-P_0}$<br>$P \geq P_{10}$; S=10<br>$P_{10}$ and $P_0$ are the upper and lower cost limits respectively |
| Species suitability | *Chlorella* sp.; S=10<br>Not *Chlorella* sp.; S=0 |

The upper limit of the cost criterion for the cultivation stage is defined as \$0.3/kg DW algal biomass for a score of 10 and the lower limit at \$10.0/kg DW algal biomass for a score of 0. Values ranges are taken from literature and estimated to the nearest 10 (Acién et al., 2012). The upper limit of the cost criterion for the harvesting, dewatering and drying stage is defined as \$0.1/m$^3$ of water removed algal biomass for a score of 10 and the lower limit at \$5/m$^3$ of water removed for a score of 0. Value ranges are taken from literature and estimated to the nearest 10 (Lee et al., 2013). The upper limit of the cost criterion for the energy extraction and conversion technologies stage is defined as \$0.1/litre of oil for a score of 10 and the lower limit at \$10/litres of oil for a score of 0.

### 3.1.2 Technology assessment result

A comparative analysis is presented as weighted scores based on costing calculations and species suitability for the different process technologies. The higher the total score the more desirable the technology.

Table 13: Weighted score of the production technologies for bio-jet fuel production.

| | **Cost** | **Species suitability** | **Total score** |
|---|---|---|---|
| **Cultivation** | | | |
| Open raceway | 58 | 100 | 158 |
| Tubular PBR | 60 | 100 | 160 |
| Flat panel | 28 | 100 | 128 |
| **Harvesting, dewatering & drying** | | | |
| Centrifugation | 93 | 100 | 193 |
| Chemical flocculation with settler | 97 | 100 | 197 |
| Membrane Ultrafiltration | 98 | 100 | 198 |
| Filtration | 97 | 100 | 197 |
| Flotation with flocculants with settler | 97 | 100 | 197 |
| Microbial flocculation with settler | 96 | 100 | 196 |

| | | | |
|---|---|---|---|
| Electrolytic flocculation with settler | 96 | 100 | 196 |
| Flash drying | 73 | 100 | 173 |
| **Energy extraction and conversion** | | | |
| Mechanical Press + pre-drying | 71 | 100 | 171 |
| Bead beating/ wet milling | 99 | 100 | 199 |
| Ultrasonication + pre-drying | 9 | 100 | 109 |
| Microwave + pre-drying | 42 | 100 | 142 |
| Solvent extraction(wet) and recovery | 99 | 100 | 199 |

### 3.1.3 Technology assessment discussion

The production cost is defined as the sum of capital and operating costs minus the credits resulting from all co-products. The capital and operating cost can be further broken down into categories; elements of these categories include land, labour, maintenance, electricity and equipment costs.

$$C_{Production}=\sum C_{Operating} + \sum C_{capital} - \sum C_{co-products}$$

(Equation 3)

Where:

$C_{Production}$= Total production cost,

$C_{Operating}$= Operating cost,

$C_{capital}$ = Capital cost

$C_{co-products}$ = Co-products cost.

The capital and operating costs for the different technologies are obtained from various referenced sources and depending on the scenario from these sources, the cost breakdown may or may not be broken down into subcategory. The credits derived from the coproducts are not considered at this preliminary stage of technology assessment. Some of the categories of cost are calculated as a percentage of the major equipment cost as shown in table 14.

Table 14: General cost estimation for some elements of the capital and operating cost (Sinnott, 2005).

| **Cost elements** | **Estimated percentage** |
|---|---|
| Maintenance | 2-10 % of Major equipment cost |
| General plant overheads | 55% Labour and maintenance cost |
| Installations costs | 15 % Major equipment cost |
| Instrumentation | 10 % Major equipment cost |
| Piping | 30 % Major equipment cost |

Obtained cost data from literature or otherwise is converted to 2015 dollars using the Chemical Engineering Plant Cost Index, US consumer price index and exchange rate (documented in the *Appendix B*). Whenever an original document did not include information about the time for which the inflation of the currency is calculated, the year of publishing is taken instead.

#### *3.1.3.1 Cultivation*

Based on the literature review in chapter 2, *Chlorella* sp. has successfully been cultivated in the open raceway, PBR and flat panel PBR cultivation system.

Capital and operating cost estimate for open raceway pond, PBR and flat panel PBR is shown in table 15. The operating cost is the sum of the cost, which includes utilities, labour and other variable cost. Economic data from Norsker et al. (2011) and Richardson et al. (2012), were majorly used to evaluate the capital and operating cost recorded in the table 15. Supplementary data by Norsker et al. (2011) provided a detailed economic analysis of a 1ha and 100 ha biomass production facility in the Netherlands for 3 different types of cultivation methods. Whilst the study by Richardson et al. (2012) gives a cost analysis for the production of 50,000 tonnes per year of algal lipid for raceway pond and PBR cultivation methods which used data from Davis et al. (2011) study. Capital costs exclusive to tubular PBRs are: PBR tubes, culture and circulation pump and air blowers. For open ponds the only exclusive cost is paddlewheels. Capital cost conversion from \$/ha to \$/DW biomass is done assuming a plant life of 20 years and operation per year of 340 days. All costing values obtained from cited sources are adjusted and updated to 2015-dollar basis.

Table 15**:** Capital and operating cost estimate for microalgae cultivation method (updated to 2015 dollars)**.**

| | Open raceway pond | Tubular PBR | Flat panel PBR |
|---|---|---|---|
| Biomass areal productivity ($g/m^2$/day) | 11 | 25 | 27 |
| **Capital cost ($/ha)** | | | |
| Major equipment, pumping and mixing system | 575,962.03 | 792,644.45 | 1,025,817.39 |
| Installations costs | 98,592.93 | 135,684.54 | 175,598.98 |
| Piping | 197,185.87 | 271,369.07 | 351,197.96 |
| Instrumentation and control | 54,842.49 | 75,474.76 | 97,677.24 |
| Buildings | 196,594.07 | 270,554.65 | 350,143.95 |
| Land cost of plant | 7,621.81 | 7,621.81 | 7,621.81 |
| Total cost | 1,130,799.20 | 1,553,349.28 | 2,008,057.33 |
| Total cost ($/ kg DW biomass) | 1.51 | 0.91 | 1.09 |
| **Operating cost ($/kg DW biomass)** | | | |
| Pumping power | 0.26 | 0.06 | 0.04 |
| Medium preparation pump power | 0.06 | 0.01 | 0.01 |
| Culture circulation pump power | | 0.74 | |
| Blower/ paddle wheel power | 0.05 | 0.05 | 3.77 |
| Carbon dioxide | 0.53 | 0.53 | 0.53 |
| Culture medium | 0.69 | 0.69 | 0.69 |
| Maintenance | 0.72 | 0.83 | 0.77 |
| Labour | 0.17 | 0.09 | 0.06 |
| Salary overhead | 0.04 | 0.02 | 0.01 |
| Plant overheads | 0.34 | 0.29 | 0.32 |
| Total cost | 2.86 | 3.31 | 6.2 |
| Total capital and operating cost($/kg of DW biomass) | 4.37 | 4.22 | 7.29 |

In terms of capital cost, the raceway pond is shown to be cheaper, however when the biomass productivity of the raceway pond is compared with that of the raceway pond and flat panel it is at a disadvantage. The tubular PBR is a cheaper option because it is capable of producing more quantities of biomass with the same area as the raceway pond, table 16 shows a range of biomass areal productivities. In terms of operating cost, the flat panel PBR is the most expensive, almost twice the amount necessary for cultivation in a raceway pond or tubular PBR.

Table 16: Biomass areal productivity of different cultivation methods

| | **Biomass areal productivity ($g/m^2/day$)** | **References** |
|---|---|---|
| Open raceway pond | 3-35 | (Goldman, 1979;Jonker and Faaij, 2013; Reijnders, 2009) |
| Tubular PBR | 5-48 | (Borowitzka, 1992; Benemann, 2008; Watanabe et al.,1995) |
| Flat panel PBR | 21-27 | (Jorquera, 2010, Norsker et al., 2011) |

The sum of the capital cost and operating for tubular PBR is lowest at $4.22/ kg of DW biomass in comparison to $7.29/ kg of DW biomass and $4.37/ kg of DW biomass for flat panel and raceway pond respectively. These cost values are used to establish weighted scores. Production cost of micro-algal biomass has been estimated to be as high as about $10/kg for a 10ha plant (Benemann and Oswald, 1996).

#### *3.1.3.2 Harvesting, dewatering and drying*

Based on the review documented in chapter 2, harvesting and dewatering technologies like vacuum filtration, centrifugation, dispersed air flotation, cross-flow filtration, electrolytic flocculation, microfiltration, chemical flocculation, auto-flocculation and bio-flocculation are all suitable for the harvesting and dewatering of *Chlorella* sp.

Whilst these technologies are suitable, not all of them are capable of achieving a minimum concentration of 15% TSS of micro-algal biomass required for downstream processing. Harvesting, dewatering and drying technologies cost estimates are shown in table 17. The harvesting and dewatering technology with the lowest capital and operating cost is the membrane ultrafiltration method. Flash drying is shown to be the most expensive method followed by centrifugation, which are capable of achieving higher solid outputs concentration in comparison to the other technologies. A comparative analysis of harvesting and dewatering methods showed centrifugation to be among the least economical and membrane ultrafiltration method amongst the most economical (Al hattab et al., 2015).

Table 17: Cost estimate for harvesting and dewatering methods in 2015 dollar basis.

| | **Centrifugation** | **Chemical flocculation with settler** | **Membrane ultrafiltration** | **Filtration** | **Flotation with flocculants** | **Microbial flocculation with settler** | **Electrolytic flocculation** | **Flash dryer** |
|---|---|---|---|---|---|---|---|---|
| Extent of dewatering (TSS %) | up to 30 | **up to 8** | **up to 9** | **up to 18** | **up to 7** | **up to 8** | **up to 10** | **up to 95** |
| **Capital cost** ($/m$^3$) | | | | | | | | |
| Equipment cost | 0.12 | 0.05 | 0.03 | 0.08 | 0.06 | 0.05 | 0.06 | 0.25 |
| Installations cost | 0.02 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | * |
| Piping cost | 0.04 | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.02 | * |
| Instrumentation and control | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | * |
| Total capital cost | 0.19 | 0.07 | 0.05 | 0.11 | 0.10 | 0.07 | 0.09 | |
| **Operating cost** ($/m$^3$) | | | | | | | | |
| Operating power | 0.23 | * | 0.03 | 0.03 | * | * | * | 0.3 |
| Raw material | | 0.11 | | | 0.11 | 0.16 | * | |
| Maintenance | 0.005 | * | 0.003 | 0.003 | 0.003 | * | * | 0.010 |
| Total capital and operating cost | 0.43 | 0.18 | 0.08 | 0.14 | 0.21 | 0.23 | 0.09 | 0.56 |

*included in total cost obtained from literature

For centrifugation technology, the capital cost range is estimated to be the average value of 0.5–1.5 €/ $m^3$ of water removed (TWR)/year and the energy required for disc stack centrifuge ranges from 0.53–5.55 kWh/$m^3$ (taking the average at 3.04 kWh/$m^3$) and converted to 2015 US dollars (Dresser and McKee, 1995). The chemical flocculation method requires flocculants; there are inorganic and organic flocculants. A large number of chemicals (ferric sulphate, ferric chloride, aluminum chloride, aluminum sulfate) are used for inorganic flocculation. Inorganic flocculants are cheaper than the organic types like chitosan and praestol. Alum sulphate is chosen as the inorganic flocculants, which is more effective in flocculating *Chlorella* species than ferric salts (Shelef et al., 1984). Cost of alum sulphate is taken as the average of 0.1-0.13€/kg, converted to 2015 US dollars, flocculants dosage concentration as the average of 50-300mg/L, and cost range of 0.02-0.13€/kg of DW biomass (Petrick et al., 2013).

Cost estimate for a belt filter press for the filtration method is estimated to be 0.25–0.75€/TWR/year, an average of 0.5 €/TWR/year is taken as the capital cost. Energy requirement is taken as 0.37 kWh/TWR based on the range 0.18–0.55kWh/TWR (EPA, 2000; Mohn, 1980; Putt, 2007). For microbial flocculation, an organic carbon flocculants is taken as glycerine, which is available at about $0.72/kg. Approximately 0.2 kg of glycerine/ kg dry biomass flocculated is required. Capital and operating cost is taken at $0.13/m$^3$ and converted to 2015-dollar basis (Lee et al., 2010). Membrane ultrafiltration capital cost is estimated by assuming cultivation occurs in an open pond. The unit cost for an ultrafiltration is taken as $73,552,695. Removing 738,400 $m^3$/day of water from microalgae cultivated in an open raceway pond requires four units, 20 years of machine life and 89% efficiency is assumed. Energy is required in the range of 0.04-3.06 kWh/$m^3$ of water removed (et al., 2009; GAI, 2016).

The capital and energy cost for electrolytic flocculation is estimated at $0.17/m$^3$ of water removed and is converted to 2015-dollar basis (Lee et al., 2010). The capital and energy cost for air flotation with flocculation is estimated at $0.70/m$^3$ of water removed and is converted to 2015-dollar basis (Lee et al., 2010). Overall, all cost estimates are converted to $2015/m$^3$ by assuming an average micro-algal biomass concentration of 0.3g/L.

Additional drying when needed by the chosen energy extraction method is achievable by flash dryer. The water content of the wet algal biomass is assumed 70% and the residual moisture of 5 % is assumed after drying. The energy consumption of a flash dryer is taken as 1,380kWh/m$^3$ of water evaporated (heat demand of 1200kWh/m$^3$ and electric demand of 180kWh/m$^3$) (Petrick et al., 2013). The capital cost range of a flash dryer is estimated at 0.75–3.6€/TWR/year (Transparent Technologies Private Ltd., 2015). Overall, an equipment lifetime of 10 years is assumed.

#### *3.1.3.3 Energy extraction and conversion*

The capital and operating cost estimates for the different cell disruption, lipid and whole conversion technologies are shown in table 18. Of all the methods, the solvent extraction and bead beating/wet milling has the lowest production cost whilst the ultrasonication methods has the highest cost of production.

Ultrasonication of microalgae currently occurs on an experimental scale, it is also highly energy intensive and requires additional pre-drying which is a contributing factor to its high capital and operating cost. To eliminate the additional energy consumption required for drying, wet processing methods are explored to produce biofuels (Reddy et al., 2014). Whilst having a high cost, advantages of ultrasonication is its fast extraction rate as well as it suitability for all algal cell type (Byreddy et al., 2015). Solvent extraction and bead beating/ wet milling are examples of methods that do not require drying.

Table 18: Cost estimates for cell disruption, lipid and whole biomass conversion methods.

| **Capital and operating ($2015/litres of oil)** | **Mechanical Pressing method + drying** | **Bead beating/ wet milling** | **Ultrasonication + drying** | **Microwave + drying** | **Solvent extraction (wet) and recovery** |
|---|---|---|---|---|---|
| *Capital cost* | 0.003 | 0.010 | 0.130 | 0.010 | 0.050 |
| Additional capital cost if drying required | 0.672 | | 0.854 | 0.752 | |
| *Operating cost* | 0.090 | 0.120 | 5.410 | 2.650 | 0.120 |
| Additional operating cost if drying required | 2.160 | | 2.730 | 2.420 | |
| Total capital and operating cost | 2.93 | 0.13 | 9.12 | 5.83 | 0.17 |

The equipment cost for the expeller press method is estimated at $2,170-10,000 for a production capacity of 150-250kg/hr based on vendor's quotation. By assuming 20% oil content, 75% efficiency, equipment lifetime of 10 years and 340 days a year operation, 266,920 litre of oil/year and 444,880 litres of oil/year is produced. Taking the average of the two gives $6085 for 355,900 litres of oil/year. Energy requirement is estimated at 0.1-0.3kWh/kg of dry weight algal biomass (Nebraska Screw Press, 2016). Additional drying is required and the cost for flash drying is included.

For the bead-beater/wet milling method, the equipment cost is estimated at $2,000-8,000 for 100-500L/hr capacity based on vendor's quotation. By assuming 20% algal oil content, 62% efficiency, equipment lifetime of 10 years and 340 day a year of operation, the average of the given range gives an estimate of $5,000 for 61,200 litres of oil (Halim et al., 2013). Energy requirement is estimated at 0.1-2kWh/kg of dry weight algal biomass (Vma-Getzmann, 2016).

The equipment cost of the ultrasonication method is estimated at $1,555 - $5,970 for a production capacity of 19 L/hr based on vendor's quotation. By assuming 20% algal oil content, 60% efficiency (Halim et al., 2013), equipment lifetime of 10 years and 340 day a year of operation, cost $3,763 for 4,651.2 litres of oil. Energy requirement is estimated at 10-12kWh/kg of dry weight algal biomass (Byreddy et al., 2015; Petrick et al., 2013). Additional drying is required and the cost for flash drying is included in this method.

The equipment cost for the microwave method is estimated at $1,895-$2440 for a production capacity of 100L/hr based on vendor's quotation. By assuming 20% algal oil content, 67% efficiency (Guldhe et al., 2014), equipment lifetime of 10 years and 340 day a year of operation, the average of the given range gives an estimate of $2,168 for 21,869 litres of oil. Energy requirement is estimated at 5-7kWh/kg of dry weight algal biomass (Byreddy et al., 2015; Guldhe et al., 2014 ). Additional drying is required and the cost for flash drying is included in this method.

The range of variation for the capital cost for solvent extraction is 40-120€/TDWB/year. According to a report by Davis et al. (2014), the capital cost of $71.5M for solvent extraction method with solvent recovery. The production input capacity is 1,215 tonnes/day. Assuming a 340 days per year of operation, 20% oil content and 98% recovery efficiency the capital cost is calculated.

### 3.1.4 Base case establishment

The base case pathway based on the selected technologies is shown in figure 12. A process model based on this base case pathway is constructed and simulated. This is further discussed in Chapter 4. The results of the technology assessment using the weighted decision matrix method is used to determine the "most desirable" technologies. The higher the total score, the more desirable the process technology. Based on the highest score for the cultivation process stage, tubular PBR has the highest score.

Membrane ultrafiltration has the highest score for harvesting and dewatering process stage but only capable of concentrating the algal biomass to up to 13% TSS. Of the two technologies capable of concentrating algal biomass to up to 30% TSS, the centrifugation technology is the most desirable.

The solvent extraction and bead beating/wet milling method has the highest weighted score for energy extraction and conversion process stage. Based on the review documented in chapter 2, it was established that adopting a single method of extraction might be insufficient in obtaining the maximum oil yield from the micro-algal biomass. Overall, one or more combinations of methods may be required for the harvesting and dewatering process as well as the energy extraction process which impacts the capital cost as well as operating cost. The extent of this impact is discussed in Chapter 6.

The base case pathway for the selected technologies with the highest weighted score is shown in figure 12. For the cultivation process, tubular PBR is selected, membrane ultrafiltration is selected for concentrating the algal biomass to up to 13% TSS and centrifugation for concentrating algal biomass to up to 20% TSS for the harvesting and dewatering process. In addition, the solvent extraction and bead beating/wet milling which had the same total score is selected for the energy extraction and conversion process. Technology assessment was not carried out for the algal oil upgrading process because Honeywell UOP green jet fuel production process is so far the only method for upgrading algal oil to bio-jet fuel.

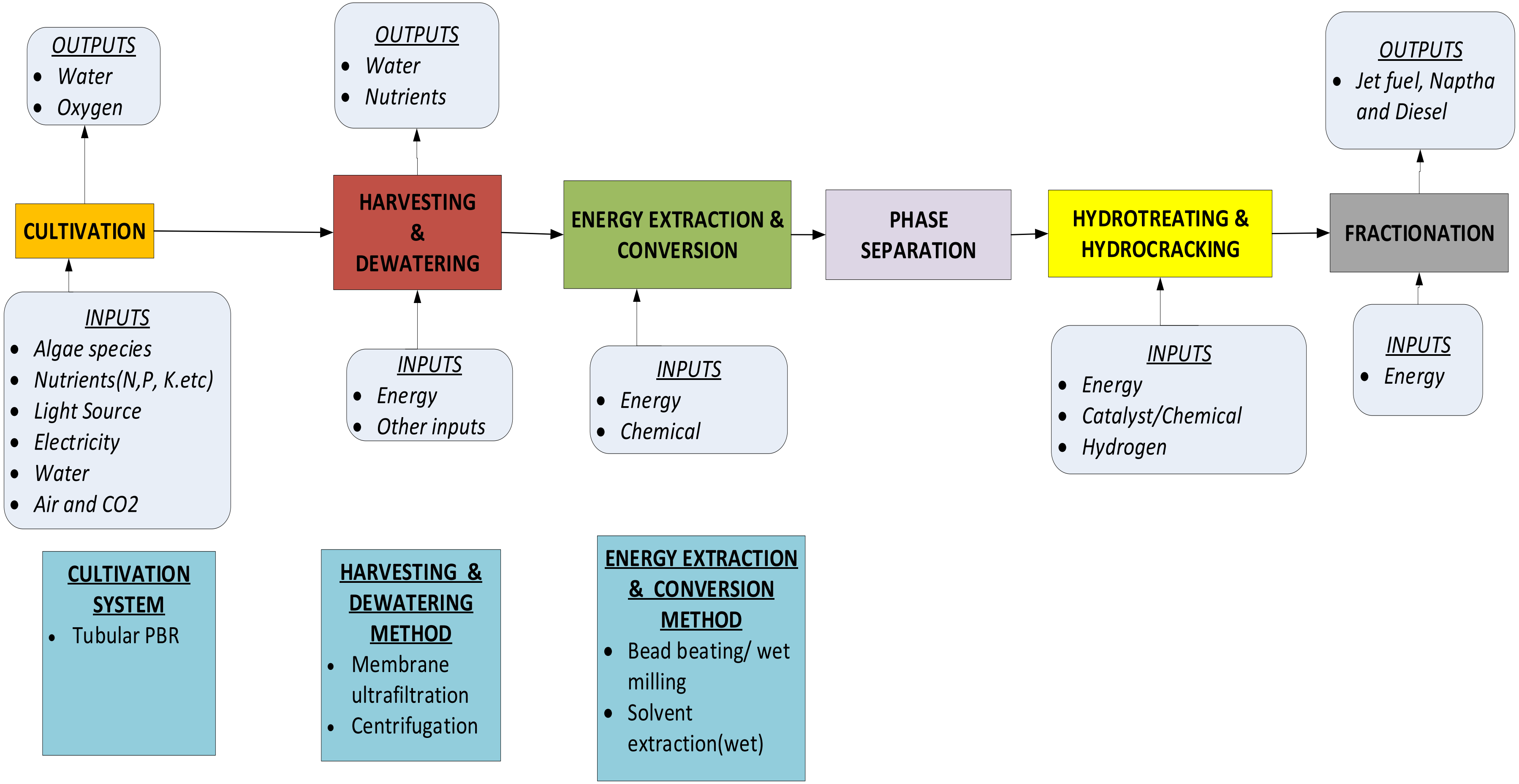


Figure 12: Simplified block diagram of the base case pathway

# 4 PROCESS MODEL CONSTRUCTION

This section of the thesis describes the model construction process including studies associated with this construction process, mass and energy balance calculations, NER, GHG and water usage calculation and assumptions made. Elements of the process economics are discussed at a later stage in chapter 5.

## 4.1 Techno-economic approach

The technology assessment stage discussed earlier, allows for the selection of the "best choice" technologies for each process step for the establishment of a production pathway termed the "base case production pathway". A process and then an economic model is developed to determine the environmental and economic viability of algal bio-jet fuel production at a large scale.

Table 19: Baseline model specification

| | |
|---|---|
| Production quantity of algal bio-jet fuel (L/year) | 8,500,000 |
| Operating days per year (days) | 340 |
| Algae strain | *Chlorella* sp. |
| Algal lipid content (wt.%) | 30 |

The conceptual algal bio-jet fuel plant is assumed to be located in Malaysia and producing 8.5 million litres of bio-jet fuel per year at 340 days per year of plant operation. This production quantity is introduced if approximately 1% of the aviation fuel consumed annually (at 850 million litres) in Malaysia by the air transport sector, is produced from algal derived aviation fuel. In Malaysia, biomass derived fuel accounts for 0.2% of the primary production of energy (Malaysia Energy Statistics handbook, 2016). The estimated production capacity of algal derived bio-jet is deemed reasonable since the production biomass-derived fuel production in Malaysia is still recent.

The plant operation is assumed to occur all year round with approximately one month per year allocated to facility shut-down, either as a result of maintenance, upstream upsets or other interruptive factors. The microalgae strain of focus is also taken to be

*Chlorella* sp., which are very commonly cultivated in Malaysia and promising for aviation fuel production. The lipid content of the micro-algal biomass is assumed as 30wt.% based on a reported range of 20-48% as shown in table 6.

The process model consists of these process stages; the initial is the growth rate prediction, cultivation, harvesting and dewatering, energy extraction/conversion, oil upgrading to bio-jet fuel and an additional anaerobic digestion stage. The resulting process information from the process model is then used as inputs to the economic model to estimate capital and operating costs for the system, in order for the yearly cash flows and product selling prices to be established. All process stages are linked and presented in an excel spreadsheet. Excel allows a substantial amount of supporting information to be entered directly into the working spreadsheets and allows easy navigation by the user.

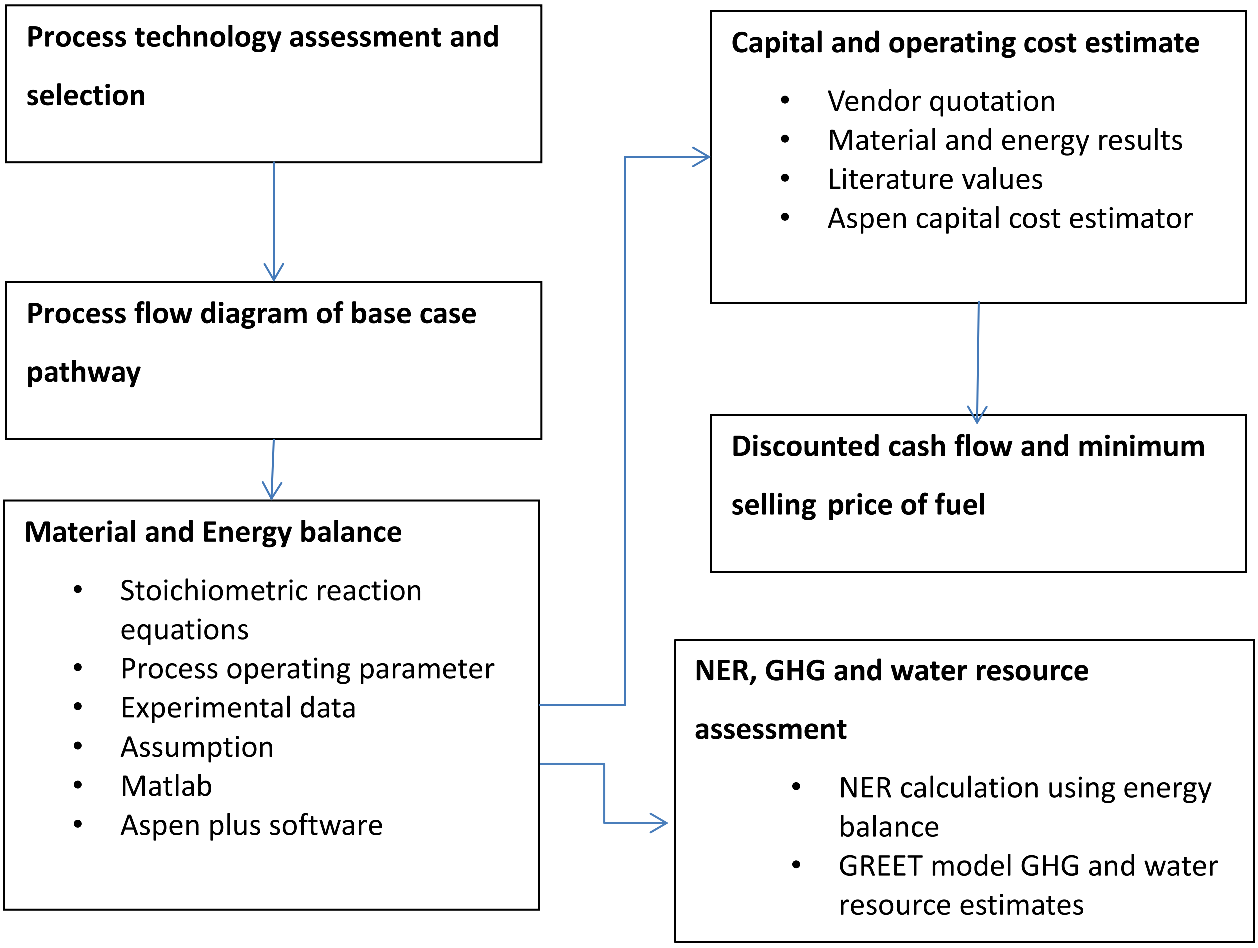


Figure 13: Techno-economic analysis of micro-algal bio-jet fuel production approach.

## 4.2 Process model aspects

### 4.2.1 Cultivation stage

Based on the base case pathway in chapter 3, the PBR system is considered for the cultivation process. This stage of the process model is intended to predict the growth rate of the algal biomass after cultivation as well the quantities of nutrient, carbon dioxide and water that must be supplied, the occupied surface area required for the PBR, the energy used, and how much carbon dioxide and nutrient is converted into micro-algal biomass.

#### *4.2.1.1 Growth rate prediction*

The growth rate prediction of the microalgae is necessary in the calculation of the algal biomass productivity which influences the prediction of the amount of water, nutrient, carbon dioxide converted into the biomass. Several existing growth equations were reviewed to determine which was best for the prediction of micro-algae growth (Carvalho and Malcata, 2003; Concas and Coa,2013; Filali and Dumur,2011;Hueseman et al., 2016; Legović and Cruzado,1997; Suh et al.,2012; Yanga et al.,2012).

A growth rate equation which takes into consideration the photosynthetic rate, respiration rate and specific uptake of nitrogen was considered suitable. A growth equation that allowed experimental data input, was also considered suitable. A growth rate equation developed by Quinn et al. (2011) is adapted for the growth rate prediction. The main output of the model is to predict the growth rate of the microalgae during cultivation expressed in day$^{-1}$ and shown in equation 4.

$$\mu = P_c - rR_c - \xi . rN \qquad \text{(Equation 4)}$$

Where:

$P_c$ : *Carbon specific rate of reaction*

$rR_c$: Maintenance respiration rate

$rN$: Specific uptake of nitrogen

$\xi$: Biosynthetic efficiency

The value for the specific growth rate of the microalgae is calculated using the specific growth rate equation. The four variables in the equation however need to be obtained from experimental observation recorded in literature or otherwise. The growth rate input variables are shown in *Appendix C*. Two input variables were identified in which the type of micro-algal strain influences significantly, these are; maximum growth rate and maximum cell quota of nitrogen in biomass.

Using the predicted growth rate, the output concentration of the micro-algal is calculated. The dry weight of the algal biomass at different growth times in the photo bioreactor ($cX_{dw}$) over time can be calculated using the equation 5:

$$cX_{dw}= 2*cC,X_0*e^{\mu*t}$$

(Equation 5)

Where;

$cC,X_0$ : Carbon content of biomass at initial time before growth in the reactor (kg/m$^3$)

$CX_{dw}$: Biomass concentration in the reactor (kg/m$^3$)

$\mu$: Specific growth rate (day$^{-1}$)

t: time (day)

The above equation enables calculation of the final algal biomass concentration in the reactor before harvesting and assumes that the algal biomass is 50% carbon and the specific growth rate is constant for the duration of the specified time.

#### 4.2.1.2 *Cultivation mass inputs and outputs balance*

In order for the model to predict how much nutrients, carbon dioxide and water is necessary for the growth of the microalgae, the amount of carbon dioxide to be converted to biomass, the empirical formula of the microalga, and of each of the nutrient (nitrate, phosphate and sulphate) that will be used to the grow the microalgae is required.

*Nutrients, water, $CO_2$ consumption and $O_2$ production*

Some assumptions are made to simplify the equation:

- The chemical $MgSO_4$ is the main source of the nutrient sulphate.
- The chemical $K_2HPO_4$ is the main source of the nutrient phosphate. Although based on the basal mode, there are more than one chemical, which can supplement phosphorus for algal growth.
- The chemical $NaNO_3$ is main source of the nutrient nitrate.
- Carbon dioxide is the only source of carbon fixed during the growth of microalga
- It is assumed that no $CO_2$ is lost to the atmosphere as the growth medium is being circulated around the PBR. This assumption cannot be justified for open pond system however.

There are very few empirical formulas for microalgae which contains sulphur, phosphorus. Mostly contains carbon, hydrogen, oxygen and nitrogen with the exception of sulphur and phosphorus. From documented literature, the elemental composition of *Chlorella* in table 20 is assumed and used to calculate the empirical formula, $CH_{1.671}O_{0.342}N_{0.121}S_{0.0047}P_{0.0082}$.

Table 20: Elemental composition of microalgae (Zhao et al., 2014 and Experimental result for *Chlorella vulgaris* (obtained with permission from University of Malaya, Malaysia).

| | ***Chlorella*** | **Used in the model ( adjusted to close mass balance)** |
|---|---|---|
| Component | wt.% | wt.% ash free |
| C | 48.7- 50.2 | 56.43 |
| H | 6.8 - 8.3 | 7.91 |
| O | 24.3 - 36.5 | 25.77 |
| N | 2.2 - 9.8 | 7.98 |
| S | 0.4 - 0.6 | 0.71 |
| P | 0.1- 1.1 | 1.20 |
| Ash | 2.8 - 8.1 | |
| Total | | 100 |

Based on the mentioned assumptions and the empirical formula for the micro algal, the stoichiometric equation is derived and balanced using matlab (see *Appendix D)* for calculations). The equation is used to estimate the mass flow rate of the nutrients, carbon dioxide and water before and after algal growth. As some level of nutrient loss is expected through system losses, 20% excess nutrient levels beyond stoichiometric biomass compositional demands is specified.

The consumed nutrients are calculated using the equation 6 below.

$$CO_2 + 0.121NO_{3^-} + 0.0047SO_4^{2-} + 0.0082PO_4^{2-} + 0.9093H_2O \rightarrow CH_{1.68}O_{0.342}N_{0.121}S_{0.0047}P_{0.0082} + 1.4176O_2 + 0.1468OH^-$$

(Equation 6)

Consumed mass of $NO_3$= (mass of micro-algal produced - Inlet micro-algal mass)/MW of microalgae *no. of mols*(MW of $NO_3$*no. mols).

(Equation 7)

*Water input requirement*

From equation 8 and 9, it is noted that water is a reactant in the photosynthesis reactions and the amount of water consumed was calculated in the stoichiometric analysis described in the prior section.

Generally, a closed cultivation system requires less refill of water than an open system because it has a lower rate of evaporation. The net amount of water lost due to evaporation depends on cultivation system design, the climate, particularly temperature, humidity, precipitation, and wind velocity (Murphy & Allen, 2011).

In order to calculate how much water refill is required to make up for evaporation loses, the water evaporation rate is required. Based on data from the Malaysian meteorological department, annual average evaporation rate is taken as 0.05cm/day. An additional water blowdown loss of 5% is assumed and must be replaced by the makeup fresh water.

An additional cooling mechanism for temperature control may be necessary to avoid the negative effect of high temperature on the growth of the microalgae. The average temperature in Malaysia is 28°C with average daily sunshine hours between 6-8 hours. The optimum temperature for algal growth ranges from 25 to 30°C for *Chlorella* sp,. Chinnasamy et al. (2009). Based on observations recorded in literature it is shown that without temperature control in the PBR, the temperature can reach a level 10-30°C higher than the ambient temperature (Wang et al., 2012).

Water balance equation:

$$W_{fresh} + W_{waste} = W_{evap} + W_{react} + W_{blowdown} + W_{eff} \quad \text{(Equation 8)}$$

$$W_{fresh} = W_{evap} + W_{react} + W_{blowdown} \quad \text{(Equation 9)}$$

$W_{fresh}$ = mass flow rate of fresh water make-up refilling the PBR [kg/day];

$W_{waste}$ = mass flow rate of treated wastewater entering PBR [kg/day];

$W_{evap}$ = mass flow rate of water evaporated from PBR [kg/day];

$W_{blowdown}$ = mass flowrate of blowdown water loss [kg/day];

$W_{eff}$ = mass flow rate aqueous medium leaving the PBR for dewatering [kg/day].

#### *4.2.1.3 Biomass productivity, areal and volumetric productivity*

Biomass productivity is the measure of the amount of biomass produced by the microalgae over a given time period. It is the most significant factor necessary to adequately analyze the techno-economic state of the cultivation stage for the overall production of bio-jet fuel. Biomass productivity is represented either as areal or volumetric productivity. The areal productivity of micro-algal biomass is a measure of how much biomass is produced over a certain time period over a given land area. The volume to area ratio is taken as 44.8L/m$^2$, representative of a tubular PBR (Norsker et al., 2011).

The areal productivity is calculated by:

$$P_{\text{areal productivity}}\ (\text{g/m}^2/\text{day}) = \frac{(\boldsymbol{P_{volumetric}}\ \textbf{productivity} \times \boldsymbol{V_R})}{\boldsymbol{A_{ground}}}$$

(Equation 10)

Where;

$P_{\text{volumetric productivity}}$ : Volumetric productivity; $A_{\text{ground}}$: occupied ground area photobioreactor (m$^2$); $V_R$ : Photobioreactor volume (L).

The volumetric productivity is calculated by:

$$P_{\text{volumetric productivity}}\ (\text{g/L/day}) = (C_{xi} - C_{xf}) \times (t)$$

(Equation 11)

Where:

$C_{xi}$ : initial dry weight algal concentration(g/L); $C_{xf}$: final harvest dry weight algal concentration(g/L); t: length of algal growth period(days).

### *4.1.1.1 Photosynthetic efficiency*

In autotrophic micro-algae, energy from solar radiation is converted into stored biomass by means of photosynthesis. Although not all of the solar energy reaching the cell can be used during photosynthesis. The photosynthetic efficiency (PE) therefore, is the percentage fraction of total light energy (solar insolation) converted into chemical energy (higher heating value of biomass) during photosynthesis by microalgae (Milledge, 2013). The annual average solar insolation in Kuala lumpur, Malaysia is 1746kWh between 2005-2009 (MET, 2013). Only approximately 45 % of total solar energy can be utilised by plants within the wavelength of range of 400 to 700 nm (Weyer et al., 2010). This spectrum region is called “Photosynthetic Active Radiation” (PAR). Microalgae can conserve a maximum of 9–10% of photosynthetic efficiency but micro-algal outdoor production systems hardly ever exceeds 6% (Carvalho, et al., 2006).

The photosynthetic efficiency can be calculated with equation 12 (de Vree et al., 2015).

$$PE_{sunlight} = (P_{x,ground} \times \Delta H^{o}_{c})/((I_{ground,daily} \times (0.43 \times E_{PAR}))/10^{3})$$

(Equation 12)

Where:

$PE_{sunlight}$: Photosynthetic efficiency (% sunlight)

$P_{x,ground}$: Average ground areal productivity (g $m^{-2}$ $day^{-1}$)

$\Delta H^{o}_{c}$: Standard enthalpy of combustion (22.5 kJ $g^{-1}$)

$I_{ground,daily}$: Average daily areal photon flux density (mol $m^{-2}$ $day^{-1}$ [PAR, photosynthetic active radiation])

$E_{PAR}$: energetic content of the PAR fraction of sunlight (4.76 $Jmol^{-1}$)

0.43 is the conversion factor from sunlight to PAR light on an energy basis (J $J^{-1}$).

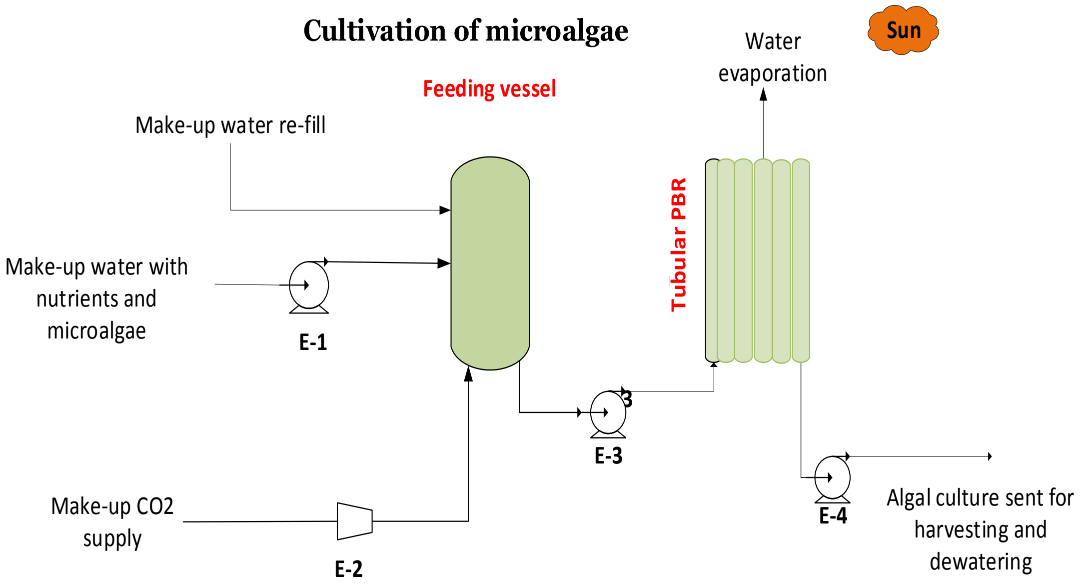


Figure 14: Simplified process diagram for the cultivation system

#### *4.2.1.4 Pumping and mixing energy*

##### 4.2.1.4.1 Pumping energy for liquid circulation in PBR

The power requirement for circulation of the culture in the tubular photobioreactor is calculated by equations 13-18. The design of the PBR is that of a horizontal configuration with airlift driven mixing which serves to circulate the culture through the PBR tubes.

The tubular photobioreactor construction is based on that reported by Norsker et al. (2013) which is constructed as a manifold system with 50 m tubes, with pressure drops consequently originating from friction loss from 100 m straight tube and from 2 manifold T-junction entries and 2 T- junction exits. Pressure drop arising from components in the system, such as valves and bends are considered negligible.

$$P = \frac{\boldsymbol{\Delta P Q}}{\boldsymbol{\eta}} \quad \text{(Equation 13)}$$

$$\Delta P = \Delta P_t + \Delta P_m \quad \text{(Equation 14)}$$

$$\Delta P_t = 8 f \frac{L}{d} \frac{\rho v^2}{2} \quad \text{(Equation 15)}$$

$$\Delta P_m = \Delta h_m \rho g \quad \text{(Equation 16)}$$

$$\Delta h_m = h_m 2\Delta v f \quad \text{(Equation 17)}$$

$$h_m = \frac{v^2}{2g} \quad \text{(Equation 18)}$$

Where:

$P$ = Power requirement (W)

$\Delta P$ = Pressure drop (kg/m.s$^2$)

$Q$ = Volumetric flowrate (m$^3$/s)

$\eta$ = Pump efficiency (no unit)

$\Delta P_t$ = pressure drop for straight tube PBR (kg/m.s$^2$)

$\Delta P_m$ = additional pressure drop due to manifold elements (kg/m.s$^2$)

$\Delta h_m$ = velocity head loss due to manifold element (m)

$g$ = gravitational acceleration (m/s$^2$)

$\rho$ = density of liquid (kg/m$^3$)

v = velocity of liquid flow (m/s)

L = Length of tube (m)

d = diameter of tube (m)

f = friction factor ( no unit)

$\Delta$vf= velocity head loss factor due to manifold component (no unit)

The general Darcy-Weisbach equation for head loss due to friction is used to calculate the pressure drop for the straight tube PBR assuming smooth tubes and estimating the friction factor using Moody chart (1994), Reynolds number and a default value of 0.000046m for average roughness (Coulson and Richardson, 1999). Velocity head loss factors is taken as 1.2 for 2 T-junctions upon entry and 1.8 for 2 T-junctions upon exit and a pump efficiency of 0.7 (Coulson and Richardson, 1999).

Liquid flow velocity in the solar tubular loop must be sufficiently high to ensure a turbulent low so that cells do not stagnate in the darker interior of the tube for long. However, excessive turbulence can damage cells and this poses an upper limit on the culture velocity (Acien Fernandez et al., 2001). The liquid flow velocity ranges from 0.17-0.5m/s in PBR (Acien Fernandez et al., 2001; Stephenson et al., 2010; Molina et al., 2000).

Density of microalgae is taken as 1100kg/m$^3$ based on the range of between 1040 and 1140 kg /m$^3$ for freshwater green micro-algae such as *Chlorella* sp. (Van Lerland and Peperzak, 1984). The density of the algal residual sludge is taken as 1000kg/m$^3$ (Schlagermann et al., 2012).

The physical properties of the micro-algal suspension vary with concentration which may influence subsequent treatment and handling process. For algae suspensions with concentration >8% the suspensions are non-Newtonian and exhibit shear thinning (Adesanya et al., 2012, Wileman et al., 2012). The viscosity for such concentration is in a reported range of 0.001-0.0035 kg/s/m (Bolhouse, 2010).

4.2.1.4.2 $CO_2$ compressing energy requirement

For $CO_2$ compressing, the use of large industrial cyclo (screw) blowers are assumed and capable of producing 55m$^3$/ hr per kW at 0.34 bar for the tubular reactors (Norsker et al., 2013). It is assumed that gaseous $CO_2$ is supplied from biogas production and flue gas from waste source, the associated embodied energy is assumed negligible. Also assumed, is the supply of $CO_2$ for an average of 12 hours per day during sunlight hours.

$$\boldsymbol{T_{out} = T_{in}\left(\frac{P_{out}}{P_{in}}\right)^{((z-1)/z)}}$$

(Equation 19)

Where z is the ratio of specific heat at constant pressure to specific heat at constant volume and is assumed to be 1.4 for air (Rogers and Mayhew, 1992). $T_{in}$ and $T_{out}$ are temperatures (degree K) in and out of the compressor and $p_{in}$ and $p_{out}$ are pressures (Pa) in and out of the compressor.

$$\boldsymbol{Adiabatic\ Power(Ideal\ gas) = MC_p(T_{out} - T_{in})}$$

(Equation 20)

Where P is Power (W), M is mass flow (kg/s) and $C_p$ is specific heat capacity at constant pressure taken as 1.005KJ/kg/K for air (Rogers and Mayhew, 1992). Adiabatic power requirements are calculated by equations 19 and 20. The mass flow requirement is determined from the $CO_2$ requirement for algal growth at 20% excess.

### 4.2.2 Harvesting and dewatering stage

The harvesting and dewatering section of the model is developed to allow the variability of the concentration factor and the harvest algal biomass separation efficiency in order to predict both the composition and flow rate of the harvested algal biomass stream and the energy required for dewatering.

Harvesting and dewatering process collects algal cells from dilute suspension culture and characterized by the solid content and recovery efficiency. Based on the base case pathway in chapter 3, membrane filtration was the most suitable for concentrating algal biomass up to 9% TSS. Whilst centrifugation technology is the most desirable for concentrating algal biomass to up to 30% TSS. For wet lipid extraction route, the desired moisture content of the wet algal biomass can range from 20-35wt.% TSS whereas for dry extraction, the moisture content is in the range of >80%TSS (Delrue et al. 2012, Jonker and Faaij, 2013). The energy conversion and extraction method selected for the base case requires no additional pre-drying process.

#### *4.2.2.1 Mass inputs and outputs balance*

The output concentration upon primary dewatering is assumed as 9wt.%TSS and 27wt.% TSS upon secondary dewatering. The solid content is the mass ratio of microalgae to water after harvesting has occurred. The mass balance for micro-algal biomass is written as:

$M_{Fh} = M_{Ch} + M_{Dh}$ (Equation 21)

$M_{Ch} = r_m M_{Fh}$ (Equation 22)

$M_{Ch} = M_{Fh+1}$ (Equation 23)

$M_{Fh+1} = M_{Ch+1} + M_{Dh+1}$ (Equation 24)

$M_{Ch+1} = r_c M_{Fh+1}$ (Equation 25)

**Where:**

$M_{Fh(Fh+1)}$ = Mass flowrate of dry weight algal biomass in the feed to the primary or (secondary) dewatering step (kg/h);

$M_{Ch(Ch+1)}$ = Mass flowrate of dry weight algal biomass in the concentrate stream exiting the primary or (secondary) dewatering step (kg/h);

$M_{Dh(Dh+1)}$ = Mass flowrate of dry weight algal biomass in the dilute stream exiting the primary or (secondary) dewatering stage (kg/h);

$r_{m(c)}$ = Algal biomass separation efficiency of primary or (secondary) dewatering step (%);

The amount of water removed to achieve the desired concentration is calculated by a calculator block in the model using equations 25 and 26. In the case where by the algal broth concentration is 27wt. % TSS or greater the calculator block ensures the model is set not to remove any water as the desired water content is already achieved. The model allows user to specify the extent of dewatering up to a maximum of 30wt. % TSS.

The mass balance for water is written as:

$W_{Fh} = W_{Ch} + W_{Dh}$ (Equation 26)

$W_{Dh} = W_{Fh} - \frac{(M_{Ch} * 100)}{P_m}$ (Equation 27)

$W_{Ch} = W_{Fh+1}$ (Equation 28)

$W_{Fh+1} = W_{Ch+1} + W_{Dh+1}$ (Equation 29)

$W_{Dh+1} = W_{Fh+1} - \frac{(M_{Ch+1} * 100)}{P_c}$ (Equation 30)

**Where:**

$W_{Fh(Fh+1)} =$ Mass flowrate of water in the feed to the primary or (secondary) dewatering stage (kg/h);

$W_{Ch(Ch+1)} =$ Mass flowrate of water in the concentrate stream exiting the primary or (secondary) dewatering stage (kg/h);

$W_{Dh(Dh+1)} =$ Mass flowrate of water in the dilute stream exiting the primary or (secondary) dewatering stage (kg/h);

$P_{m(c)} =$ Desired TSS conc. after primary or (secondary) dewatering (wt.%).

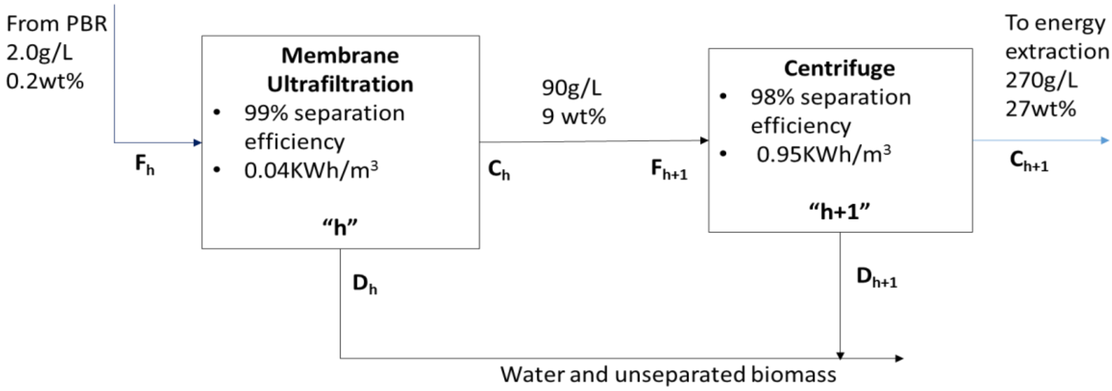


Figure 15: Simplified block diagram for the harvesting and dewatering system

4.2.2.1.1 Energy requirement for harvesting and dewatering

The separation energy requirement for centrifugation is taken as 0.95kWh/m$^3$ of water removed with a separation efficiency of 98% and is representative of the energy requirement for the Evodos 25 centrifuge technology discussed in chapter 2. The separation energy requirement for membrane ultrafiltration system is taken as 0.04KWh/m$^3$ and is representative of the energy requirement estimated for Global Algae Innovative harvesting membrane technology (Davis et al., 2016).

### 4.2.3 Energy extraction and conversion stage

Based on the base case pathway established in chapter 4, the chosen energy extraction and conversion method was solvent extraction and prior bead beating/ milling. The purpose of this extraction step is to separate lipids from the micro-algal biomass which consists of components such as polar lipids, hydrophobic proteins, and pigments. The percentage of algal lipid available for extraction as initially specified is 30wt.% of the dry weight algal biomass.

Solvent extraction can occur without prior drying and has been demonstrated at large scale via Valicor's process achieving >90% of lipid extraction (NAAB, 2014). Whilst hexane was the only solvent used and is considered a non-polar solvent and thus not efficient in extracting polar lipid fractions, the Valicor process includes an additional pre-conditioning (high temperature acid treatment) step which hydrolyses polar lipids (glycolipids and phospholipids) to lysolipids (diglycerides).

It is understood that hexane is not sufficient alone to recovery all algal lipid fractions (polar and non-polar), hexane and methanol are considered suitable solvents. Hexane is a non-polar solvent and methanol a polar solvent, the mixture of these solvent (1:1 vol.%) coupled with prior cell disruption are considered sufficient for a model target of 95% lipid recovery (Laurens et al., 2012; Mubarak et al., 2015).

Table 21: Cell disruption, lipid extraction and solvent recovery model assumptions.

| | |
|---|---|
| Algal biomass lipid yield (wt.%) | 30 |
| Overall lipid extraction efficiency (%) | 95 |
| Energy consumption of prior bead beating (KWh/kg of dry weight algal biomass) | 0.1 |
| Solvent input rate (kg/kg of dry weight algal biomass) | 5 |
| Hexane to methanol ratio | 1:1 |
| Hexane and methanol recovery (%) | 99 |

Using Aspen Plus V8.6, the lipid extraction and solvent recovery process is simulated to determine its mass and energy balance. The algal lipid is represented as the triolein and oleic acid, which are components of algal lipid and components on the Aspen database. Although in actuality algal lipid constitutes a large range of triacylglyceride, phosolipids, lysolipid and glycolipids but some of their physical properties are still unknown to allow addition as a non-conventional component in Aspen.

The algal biomass is represented as a solid termed “ALG” and the residual lipid extracted algal is termed “LEALG”. Properties used to define this solid are its molecular weight, solid heat of formation and heat capacity values (see *Appendix F*). The solid heat capacity and solid molar volume data used for representing LEALG and ALG is taken from Wooley and Putsche (1996), for the compound biomass and *Zymo* shown in table 22 and using the Aspen equation 31.

$$\boldsymbol{C_{p,i}^{*,S}(T)= C_{1i} + C_{2i}T + C_{3i}T^2+\frac{C_{4i}}{T}+\frac{C_{5i}}{T^2}+\frac{C_{6i}}{\sqrt{T}}} \text{ for } \boldsymbol{C_{7i} \le T \le C_{8i}} \quad \text{Equation 31}$$

Where $C_{1i\ldots\ldots 8i}$ corresponds to CPSPO1/1…8 shown in table 22

Table 22**:** Solid heat capacity and solid molar volume values used for ALG and LEALG

| **Aspen property** | **ALG values (J/Kmole.K)** | **LEALG values ( J/Kmole.K)** |
|---|---|---|
| CPSP01/1 | 38401 | 35910 |
| CPSP01/2 | 0 | 0 |
| CPSP01/3 | 0 | 0 |
| CPSP01/4 | 0 | 0 |
| CPSP01/5 | 0 | 0 |
| CPSP01/6 | 0 | 0 |
| CPSP01/7 | 298.15 | 298.15 |
| CPSP01/8 | 1000 | 1000 |
|  | ALG values (cum/Kmole) | LEALG values (cum/Kmole) |
| VSPOLY/1 | 0.0164 | 0.01549 |
| VSPOLY/2 | 0 | 0 |
| VSPOLY/3 | 0 | 0 |
| VSPOLY/4 | 0 | 0 |
| VSPOLY/5 | 0 | 0 |
| VSPOLY/6 | 298.15 | 298.15 |
| VSPOLY/7 | 1000 | 1000 |

The property method and NRTL (non- random two liquid) is used for the extraction column and solvent recovery columns in Aspen. This method includes NRTL liquid activity coefficient model, Henry's law for the dissolved gases, and R.KS (Redlich-Kwong-Soave) equation of state for the vapor phase, and is used to calculate properties for components in the liquid and vapor phases.

The cell disruption method by bead beating is modelled as a crusher (type ball mill) using Rosin Rammler sperling Bennet distribution function and a RYield reactor. The ball mill diameter is specified as 1mm and the energy requirement specified as 0.1kWh/kg of algal biomass (Shen et al., 2009; Vma-Getzmann, 2016). The RYield reactor is used to specify the fraction of the residual lipid extracted algal biomass and the lipid (30%wt.). The property method SOLIDS is chosen for the crusher and the bond equation in the form of equation 32 is used to determine the bond work index where the mean particle size is taken as 5μm for *Chlorella vulgaris*.

$$\boldsymbol{w} = \frac{\sqrt{100}.w_i}{\sqrt{P}} - \frac{\sqrt{100}.w_i}{\sqrt{F}} \quad \text{(Equation 32)}$$

Where;

W= Predicted mill energy consumption (kWh/ton)

Wi = Work index (kWh/ton)

P, F = 80% passing sizes in µm of feed (F) and Product (P)

After cell disruption, the algal stream is sent to an extraction system, which consists of a liquid-liquid extraction column and hexane and methanol recovery column. An additional solvent recovery column was deemed necessary to recover large quantity of solvent required for the extraction process for the purpose of re-use. A liquid-liquid multi-stage counter-current extraction column is used for the extraction stage and is modelled as an extract column with two stages, determined by sensitivity analysis.

Hexane, methanol and harvested algal sludge is fed into the extraction column through a mixer block and is initially preheated to 60°C at 5 bar , if the feed is introduced to the extractor too hot it will cause a great deal of boiling off of solvent and water and reduce extraction drainage and reduce extraction efficiency. The extracted light oil phase containing solvent, lipids and water is routed to a flash separator at 80°C, 10 bar to recover the solvent, leaving a high purity lipid stream (99%) that is sent for upgrading. The aqueous product (residual lipid extracted biomass) is sent for anaerobic digestion.

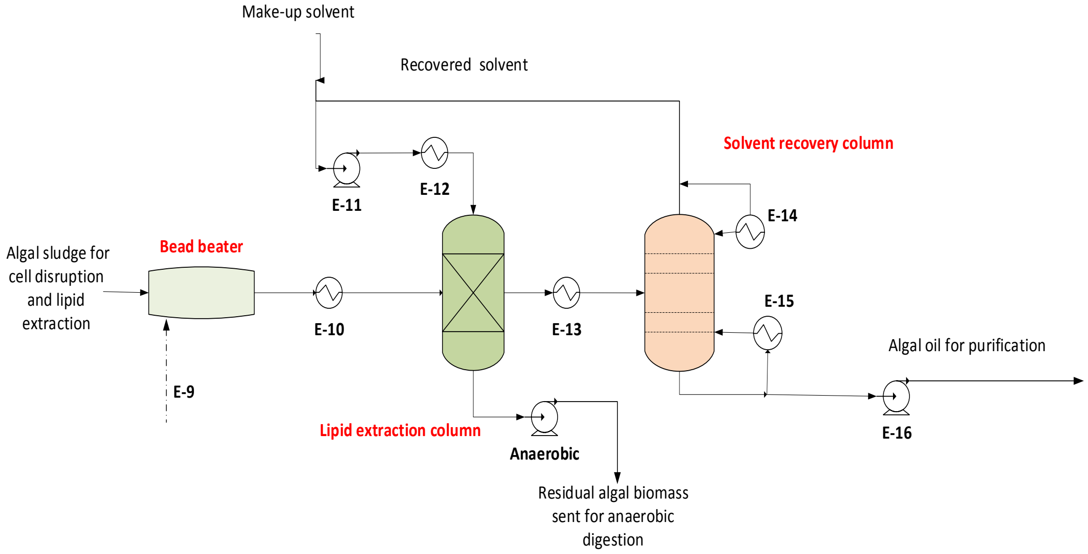


Figure 16: Simplified process diagram for the cell disruption and lipid extraction process

### 4.2.4 Lipid upgrading stage

An additional lipid purification stage is included in the model prior to upgrading to remove lipid impurities which would be problematic for the upgrading stage. Micro-algal lipid contains phosphorus in the form of phospholipids. The phospholipid content differs depending on which algal strain and have the tendency to form gums and deactivate catalysts (Bovornseripatai et al., 2012; Lu et al., 2013).

Lipid purification consists of degumming, demetallization, and bleaching steps to remove 1.7% lipid impurities and 0.3% of solvent from the lipid stream at 98% lipid purity with the use of phosphoric acid, wash water, silica, and clay (Ringers and Segers, 1977). These operations are similar to those utilized in the biodiesel industry.

The lipid purification stage is also modelled in Aspen plus. The lipid from the extraction stage is heated to 70°C and sent to a mixer in which phosphoric acid (0.19 wt. % of lipid) and wash water(10% wt. of lipid) is added (Davis et al., 2014). The mixer is modelled as a mixer block and routed to a reactor block (RYield) to specify the quantity of gums (which includes lipid impurities) removed. The reactor exit stream is routed to a separator block in which silica (0.1wt. % of lipid) and clay is added (0.2 wt. % of lipid) for the removal of gum with the residual solvent carry over from the prior lipid extraction and solvent recovery process(Davis et al., 2014). The high purity lipid is routed to a dryer for water removal.  The phospholipid (lipid impurity) content in the product oil is expected to be less than 10 ppm after purification.

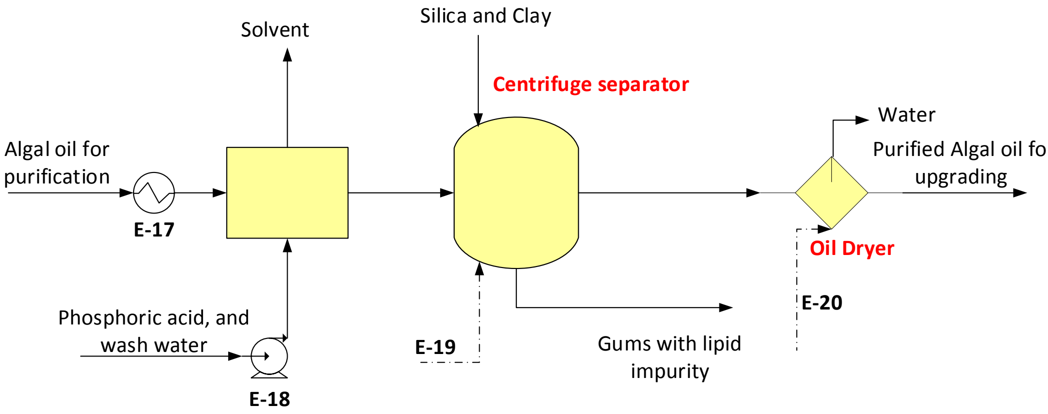


Figure 17: Simplified process diagram for the algal lipid purification process.

After the purification process, the next process is the lipid upgrading stage to bio-jet fuel. The Honeywell UOP green jet fuel production process (mentioned in chapter 2) is followed for the upgrading stage as it is certified for producing aviation fuel from renewable feedstock. The process unit consists of a deoxygenation reactor, flash separator, hydrogen stripper, isomerisation/hydrocracking reactor and product separation column modelled in Aspen plus. The Aspen property method RK-SOAVE is used based on its suitability for this upgrading process.  The purified algal lipid is still represented as the compound triolein and is sent to a deoxygenation reactor in addition to hydrogen. In total, there are three deoxygenation reactors but two is represented for simplification purpose. The process conditions and fraction assumptions of the product yield are shown in table 1.

The deoxygenation reactors is modelled as a RYield reactors in which 55% of the the algal oil is fed into the first reactor and 45% into the second reactor using a splitter block. The hydrogen gas is compressed and heated before entry into the reactor supplied at 20% excess of the overall hydrogen consumption rate for both hydrodeoxygenation and isomerisation/hydrocracking.

After undergoing hydrodeoxygenation it is expected that the hydrocarbons ranging from C1 to C22 will be present in the product, based on the fatty acid chain length of algal lipid ranging from C14-C24 (Sarpal et al., 2016). There is currently no freely available experimental data showing the fractions of the individual fatty chain length after each deoxygenation stage, collective data for the fraction of C1-C4 (light gases), $H_2O$, $CO_2$ and normal paraffinic hydrocarbons (C5-C22) after hydrodeoxygenation is available and shown in table 23. The compositions of the C5-C22 parrafinic hydrocarbon are determined using the component percentage of each fuel range Naphtha (C5-C8), Jet fuel (C9-C13), Diesel (C14-C19) and VGO (C20>) in addition to the component fractions of the grouped hydrocarbon range shown in table 23. The Aspen database compound used to represent the C1-C24 hydrocarbons are also shown in the *Appendix F*.

Simply deoxygenating the algal lipids typically results in straight chain paraffins having chain-lengths similar to, or slightly shorter than, the fatty acid composition of the algal lipids. The fuel produced by deoxygenation meets the general specification for a diesel fuel, but not for an aviation fuel hence further processing by isomerisation and selective hydrocracking is necessary(McCall et al., 2007).

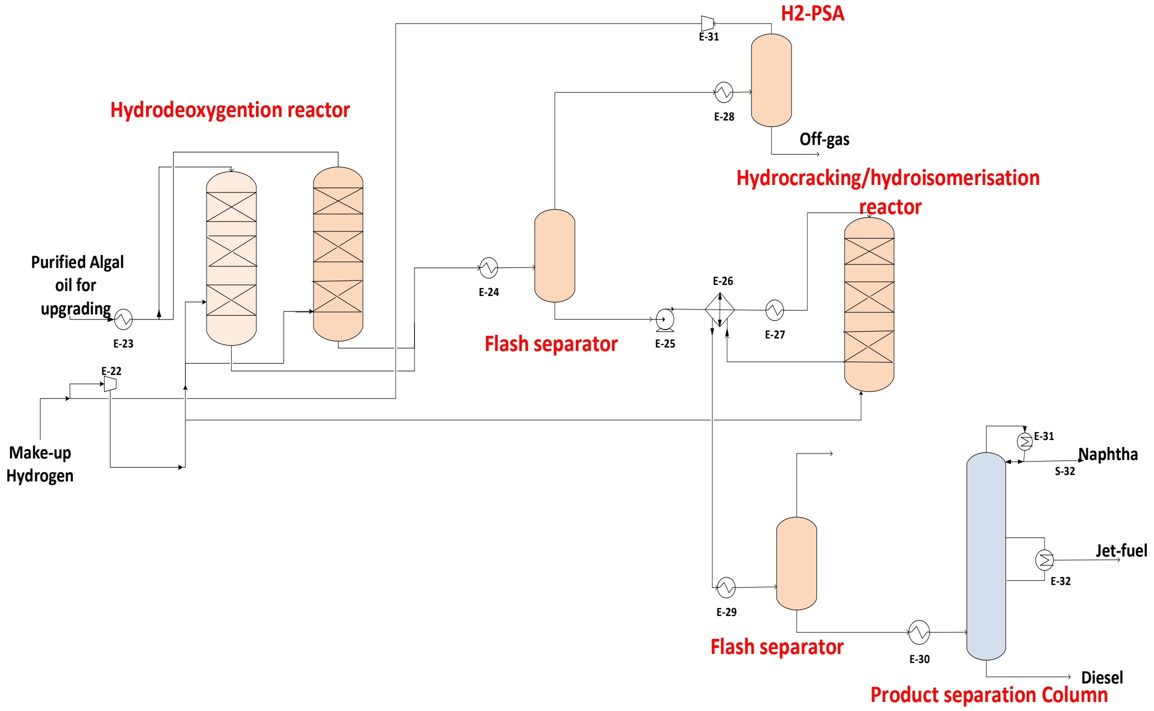


Figure 18: Simplified process diagram for the algal lipid upgrading process.

Table 23: Hydrodeoxygenation stage assumptions

| | **Model target based on reported range** | **UOP patent and experimental result of hydro-treated algal oil** |
|---|---|---|
| Hydrogen consumption rate, kg/hr per kg/hr of oil | 0.04 | 0.02-0.09 |
| Temperature, °C | 320 | 288-425 |
| Pressure, bar | 80 | 34-136 |
| Catalyst | Sulfided CoMo | zeolite Y or amorphous silica alumina and Sulfided CoMo/NiMo |
| LHSV, vol./hr per vol. catalyst | 0.2 | 0.15-0.6 |
| Product yield | | |
| $H_2O + CO_2$ ,wt.% | 10 | 10-20 |
| Algal oil conversion to paraffinic hydrocarbon, wt.% | 90 | 80-90 |
| C1 | 1.0 | 1.0 |
| C2 | 0.4 | 0.4 |
| C3 | 7.0 | 7.0 |
| iC4 | 2.0 | 2.0 |
| C4 | 1.6 | 1.6 |
| C5-C8 | 13.4 | 13.4 |
| C8-C13 | 35.0 | 9-40 |
| C14-C20 | 10.0 | 11-14 |
| >C20 | 19.6 | 5-42 |
| Sources | | Biller et al., 2015; Elliot et al., 2013; Jones et al., 2014; Kokayeff et al., 2010; Mccall et al., 2007; Mccall et al., 2009 |

After hydro-deoxygenation reaction, by-product gas are separated off using a model block flash separator and then routed to a further separation block to recover hydrogen at 40 bar. The liquid product is sent to an isomerisation and hydrocracking reactor represented as a RYield reactor prior to heating to 350°C. During the isomerisation and selective hydrocracking process, normal paraffinic hydrocarbons are converted to branched paraffins and the higher carbon number paraffins are selectively cracked to form paraffins in the desired jet fuel range (Mccall et al., 2009; Sajkowski et al., 2011). Assumptions made are shown in table 24, for simplification purpose it was assumed that the 100% of parrafins with carbon number greater than 20 are converted to jet fuel.

Table 24: Model assumption for hydrocracking and composition of the effluent of the Hydrocracking–hydroisomerizing reactor

| | **Model assumption** | **UOP patent and literature reported range** |
|---|---|---|
| Hydrogen consumption rate, kg/hr per kg/hr of oil | 0.03 | 0.02 |
| PSA $H_2$ recovery rate, % | 90 | |
| Temperature, °C | 350 | 150-375 |
| Pressure, bar | 35 | 17-200 |
| Catalyst | zeolite Y or amorphous silica alumina | zeolite Y or amorphous silica alumina |
| LHSV, vol./hr per vol. | 0.54 | $\geq$0.5 |
| C21> to jet fuel conversion, wt.% | 94 | |
| C8-C13 ( Jet fuel range) | 35.0 | |
| Source | | Jones et al., 2014; Mccall et al., 2009; Murata et al., 2014; Sajkowski et al., 2011 |

### *4.2.4.1 Product separation column*

The liquid product exiting the isomerisation and hydrocracking reactor is sent to a preflash tower prior to undergoing cooling via a cooler and flash separated at 200°C, 15 bar to remove the light gases before being sent for fractional distillation.

A PetroFrac block with 15 number of stages and a total condenser is used to model the distillation column. In Aspen, three different oils (jet fuel, diesel and naphtha) are defined and identified as assays. The assay data used in defining these cuts are their API gravity value, boiling point data and the hydrocarbon component fractions (*Appendix F*). A blend of the three different oils in the fraction specified in table 24 is used to define the oil blend that represents the isomerised and hydrocracked algal oil.

The property method Braun K-10 is selected for the column, as it is suitable for most refining application involving low pressure. The selected PetroFrac unit simulates the furnace and the atmospheric distillation column simultaneously, as a single unit.

The distillation feed is fed to a furnace block at stage 13 and the steam at stage 15. The condenser pressure is set to operate at 1.1 bar and the furnace at 1.7 bar. The distillation column separates off the pre-flash bottom to three cuts; naphtha, diesel and jet fuel. The desired jet fuel fraction of 54 wt. % of the upgraded algal oil is achieved by design specification to achieve ASTM 95% temperature of 270°C for the jet fuel stream. The simulated ASTM D86 jet fuel stream are shown in figure 19 and is within the reasonable distillation temperature of jet fuel A shown in table 2 in Chapter 2.

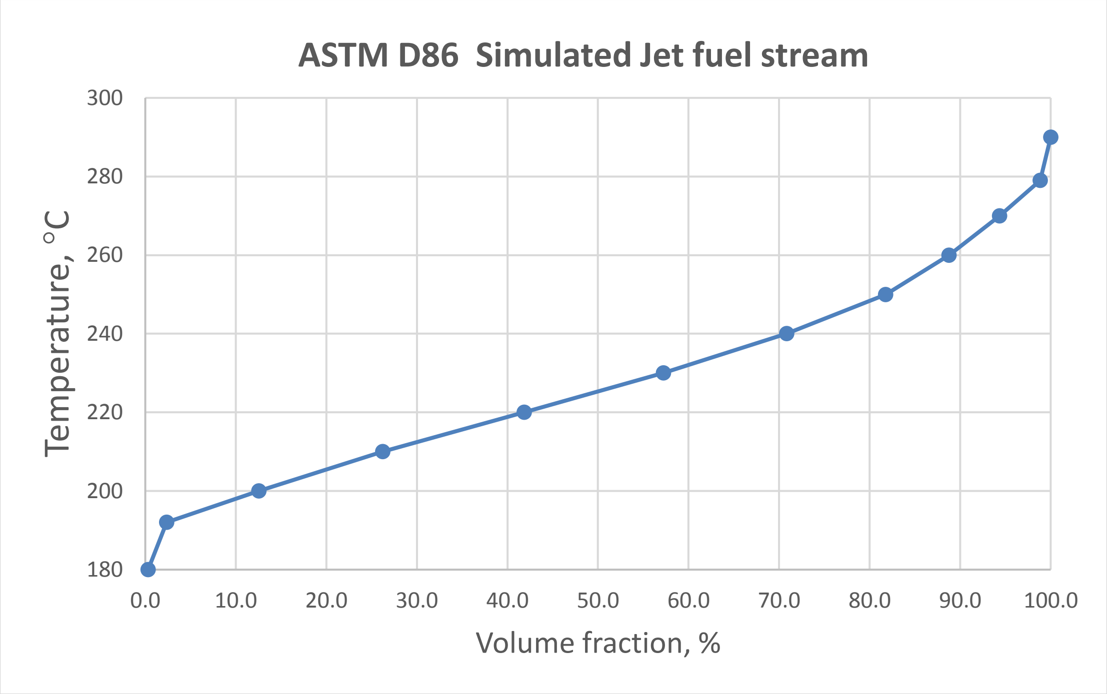


Figure 19: Graph of ASTM D86 Simulated Jet fuel results stream

### 4.2.5 Anaerobic digestion and biogas production

As a means of reclaiming carbon from the residual algal biomass after lipid extraction, anaerobic digestion is employed in the model. Anaerobic digestion (AD) is used in breaking down of biomaterials to produce biogas; which is a valuable by-product. As well as biogas production AD is used also as a means to recover nutrients (primarily nitrogen and phosphorus) for recycle to the cultivation step (Davis et al., 2014; Resurreccion et al., 2012).

Some of the first reports on the anaerobic digestion of micro-algal biomass includes the work of Golueke et al. (1957) in which the anaerobic digestion of *Chlorella vulgaris* and *Scenedesmus* microalgae was investigated. The anaerobic digestion of micro-algal biomass for the production of biogas after extraction of its lipid for the production of biodiesel has been suggested for the reduction of production cost by more than a quarter due to the use of biogas to power parts of the micro-algal biofuel process (Harun et al., 2011a).

#### *4.2.5.1 Biogas and methane yield*

The theoretical methane yield and nutrients from the lipid extracted algal biomass is calculated using the modified Buswell formula in equation 33 (Buswell and Mueller, 1952).

$$C_cH_hO_oN_nS_s + y(H_2O) \rightarrow x(CH_4) + (c-x)CO_2 + n(NH_3) + s(H_2S)$$

(Equation 33)

Where c, h, o, n and s are determined from the algal biomass elemental composition and stoichiometric coefficients x and y are calculated as: $x = (4c + h - 2o - 3n - 2s)/8$ and $y = (4c - h - 2o + 3n + 2s)/4$. In this equation, the lipid extracted algal biomass is stoichiometrically converted to methane, carbon dioxide, hydrogen sulphide and ammonia. Whilst this equation helps in estimating the methane yield, the downside is that it does not take into account needs for cell maintenance and anabolism.

Table 25: Elemental composition of whole algal cell and lipid extracted algae

| | ***Chlorella vulgaris*** | | Whole cell range | Lipid extracted range |
|---|---|---|---|---|
| | Whole cell | Lipid extracted | | |
| C | 52.81 | 44.90 | 27.45– 56.20 | 20.19–47.80 |
| H | 6.13 | 5.03 | 4.23–8.76 | 2.93–6.90 |
| N | 7.77 | 8.15 | 2.90–7.77 | 1.93–8.15 |

| | | | | |
|---|---|---|---|---|
| O | 29.33 | 27.82 | 23.41–29.33 | 27.82–34.00 |
| S | 0.72 | 0.79 | 0.55–1.29 | 0.76–1.29 |
| C/N ratio | 6.8 | 5.51 | 6.8–14.7 | 5.51–8.46 |

Source: Zhao et al., 2014

The residual algal sludge which is the lipid extracted algal sludge is sent to the anaerobic digester. AD organisms break down algal carbon into biogas (mainly methane and $CO_2$), as well as ammonia and sulphur. Upon anaerobic digestion, the residual digestate sludge is routed to a centrifuge to achieve a sludge solid content of 27wt.%. A gas turbine is used to generate power by combustion of the produced biogas. The gas turbine is part of a combined heat and power (CHP) unit which is more efficient than conventional combustion method alone. CHP units have been widely used for heat and power generation from biogas. The biogas burned in a CHP unit requires minimal or no gas scrubbing to remove hydrogen sulphide ($H_2S$) and other impurities (Salter and Banks, 2008).

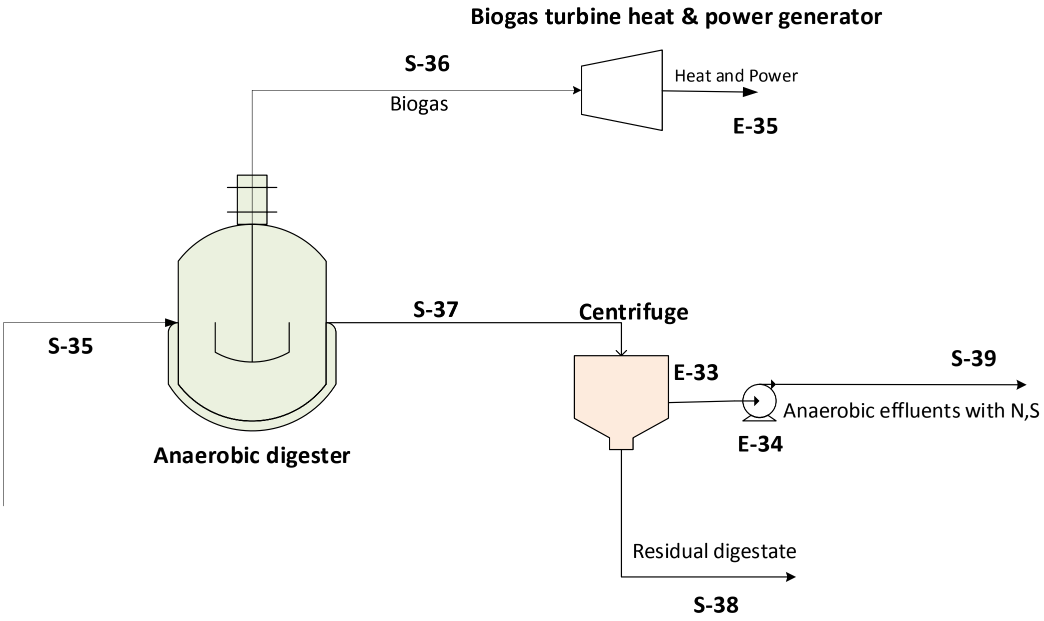


Figure 20: Biogas production from anaerobic digestion of residual lipid extraction algal biomass.

In order to estimate how much power is generated the higher heating value of methane is taken as 55.7 KJ/g and CHP efficiency is assumed as 65% (up to 75% is possible). Some other assumptions are made regarding the percentage recovery of nutrient in the anaerobic effluents and the percentage of the residual biomass digested in the digester. The AD effluent stream can be recycled back to the algal cultivation stage, in order to reduce the amount of make-up nutrients required for algal growth. The residual digestate sludge which has bioavailable nutrients can be further dried to cake form and be used as a fertiliser product.

Table 26: Assumptions for the anaerobic digestion stage

| | **Assumptions** | **Literature reported values (*Chlorella* and *Nannochloropsis*)** | **Sources** |
|---|---|---|---|
| Operating temperature of the anaerobic digester | 35°C | 35°C | Davis et al., 2014 |
| Hydraulic retention time | 20 days | 13-40 | Bohutskyi et al., 2015; Ward et al., 2014 |
| AD power demand for mixing | 0.085 KWh/kg total solids | | Davis et al., 2014 |
| Percentage of the residual biomass digested | 70% | | |
| Efficiency of the CHP unit | 65% | | |
| Ratio of electrical to heat energy produced from a CHP unit | 0.67 | | |
| Volatile solids of the total solid(TS) feed | 90% of TS | 90-93% of TS | Davis et al., 2014; Ras et al.,2011;Schwede et al., 2013; Ward et al., 2014 |

## 4.3 NER, GHG and water usage assessment

The environmental impact and resource consumption of the bio-jet fuel production system is assessed and quantified by lifecycle assessment (LCA). LCA is a systematic environmental management tool used for quantifying the input to output record of a product system throughout its life cycle stages, and projecting the environmental performance based on a selected functional value (a functional unit of the product) (Khoo et al., 2011).

LCA are commonly used as useful means to analyse and compare various biofuel production technologies/pathways from a life cycle outlook (Clarens et al., 2010; Khoo et al., 2011; Lardon et al., 2009). In some of these LCA investigations, focus is on the energy demands (Jorquera et al., 2010) and $CO_2$ emissions of the process chain (Stephenson et al., 2010).

The LCA covers the fundamental process of cultivation, harvesting & dewatering, cell disruption and lipid extraction, lipid purification and upgrading and anaerobic digestion. The emissions from the inputs into all stages of production such as nutrients and solvent are considered in the LCA. Emissions from wastes and other types of air pollutants are not covered in this LCA; neither is upstream transportation and end use of fuel. The GHG emissions from the raw material manufacture and consumption are calculated by multiplication factors obtained from GREET. Some of the most common approach and calculation tools for which LCA's are performed includes Greenhouse gasses Regulated Emissions and Energy use in Transportation (GREET), BioGrace, Gabi and GHGenius. In this assessment, the GREET model (GREET.net v1.3.0.12844, database version 12384) is utilized as it allows for the analysis of emissions and water resource use when liquid fuels are manufactured from algae.

### *4.3.1.1 GHG analysis*

The total emissions from fossil energy and resource depletion emitted during bio-jet production and the $CO_2$ intake by the microalgae (during cultivation) are considered in the $CO_2$ analysis. The net $CO_2$ is therefore the sum of intake $CO_2$ subtracted by the sum of emitted $CO_2$. Depending on different microalgae species, the resulting net greenhouse gas emissions may turn out to be $CO_2$ deficit (due to large amounts of $CO_2$

absorbed via photosynthesis) or surplus (more $CO_2$ emitted than absorbed). The GHG emissions is represented in gCO2eq and the GHG emissions considered were $CO_2$, $CH_4$, $SO_x$ and $N_2O$ using their 100-year global warming potential in agreement with the United Nations Framework Convention on Climate Change reporting guidelines (UNFCCC,2014). Global warming potential(GWP) is a measure of how much energy the emissions of 1 ton of gas will absorb over a given period of time, relative to the emissions of 1 ton of carbon dioxide. The larger the GWP, the more that a given gas warms the Earth compared to $CO_2$ over that time period. In additional, the emission factor of 0.73kg of $CO_2$ / kWh (IEA, 2010 data) and is taken in estimating the $CO_2$ emission value from fossil derived electricity use. In the case whereby natural gas is the source of energy the emission value is obtained using GREET.

#### *4.3.1.2 Water usage analysis*

The water usage for base case model is quantified by the total water footprint for the production of bio-jet fuel from micro-algae. This includes the water usage for the cultivation stage, harvesting and dewatering stage, cell disruption lipid extraction, upgrading of lipid to bio-jet fuel and the additional anaerobic digestion stage. The water resources used for production of the inputs are also included in the water analysis. The GREET model (GREET.net v1.3.0.12844, database version 12384) is also utilized.

#### *4.3.1.3 Energy analysis*

The energy performances of microalgae bio-jet fuel production process is evaluated by the net energy ratio (NER). This determines if the energy created by the proposed system is more than the energy it uses. The NER is defined as the ratio of produced energy and consumed energy and focuses on the system technologies (Pandey et al., 2014).

$$\text{NER} = \text{energy produced} \div \text{energy consumed} \tag{Equation 34}$$

The energy output from of the algal bio-jet fuel is calculated by multiplying the calorific value of jet fuel by the quantity produced based on the model results. The calorific value of jet fuel is taken as 43MJ/kg and for co-product diesel and naphtha, their calorific values is taken as 44MJ/kg and 44MJ/kg respectively. The process model calculates the energy inputs for the different process stages.

#### *4.3.1.4 LCA methods for co-product*

GHG emissions as well as energy and water balance can be allocated to co-products according to their energy, mass and economic value. In cases with particularly high yield of co-products in comparison to the main product, co-product allocation method in an LCA can have a significant impact on the GHG emission as well as energy and water performance of a product (Cherubini et al., 2009; Wang et al., 2011).

The use of the displacement method is deemed the most appropriate method according to the International Standards Organisation (ISO) for addressing multiple products. In the displacement method, the products to be displaced by the non-fuel products are determined first. The energy use and emissions burdens of producing the displaced products are then estimated. The estimated energy use and emissions burdens are added as credits to the total energy use and emission burdens of the bio-jet fuel production cycle and shown in equation 35 (Wang et al., 2011).

The GHG emission of bio-jet fuel production is estimated by the equation:

$$GHG_{fuel} = (GHG_{total} - GHG_{convproduct} \times R \times Output_{nonfuel})/Output_{fuel}$$

(Equation 35)

In the above equation, the outputs are represented as Output fuel and Output nonfuel, and the total GHG emissions are represented as $GHG_{total}$. Additionally, the non-fuel product displaces a conventional product (indicated by the subscript ‘’convproduct’’) with a displacement ratio of R (i.e., R units of convproduct to be displaced by one unit of the non-fuel product). The GHG emissions per unit of the convproduct on an LCA basis are represented as $GHG_{convproduct}$. In using the displacement method, the GHG emissions per unit of the fuel product are determined.

# 5 PROCESS ECONOMICS

This section of the thesis documents the process economic aspects of the process model described in chapter 4. The ultimate purpose for process modeling, design and cost estimates is to determine the economics of algal bio-jet fuel production. This information is used either as an absolute cost to assess the potential of algal bio-jet fuel in the market or as a relative cost to give future research a sense of direction and to guide, through examination of the change in production cost as a result of process modification.

## 5.1. Total Capital investment

The process economics of a process plant includes feedstock cost, capital and operating costs associated with construction and operation. These costs are combined in a discounted cash flow analysis to estimate the minimum fuel price needed to meet a specified internal rate of return when the net present value is equal to zero. The process economics model estimates the capital cost of a micro-algal bio-jet fuel manufacturing plant of the specified production capacity in the process model. The capital cost of each major process step is estimated by scaling the capital costs of a basis plant to match the production capacity of the micro-algal bio-jet fuel plant modeled. Most variable operating costs are calculated by multiplying a mass or energy usage rate by a specified unit price. Some fixed operating costs are estimated as percentages of certain capital or variable costs, while others are entered directly.

First, the total equipment cost and then the variable and fixed operating costs are determined. By means of a discounted cash flow analysis, the minimum fuel selling price (MFSP) of micro-algal bio-jet fuel is obtained at which the net present value (NPV) at a set internal rate of return is zero. During this cost analysis, policy factor such as carbon credits, subsidies have not been taken into account as they would be very hypothetical.

The total equipment cost is computed to estimate the capital investment. The equipment costs are obtained from different cost years ranging from 2005-2015 and differing currencies. These obtained costs are adjusted using the Chemical Engineering Plant Cost Index (CEPCI) obtained from the Chemical Engineering Magazine to a 2015 basis. The equipment costs table are documented in the *Appendix H*. The currency US dollars is used in this cost estimate as opposed to MYR to allow for ease during comparison with information from sources commonly reported in US dollars.

For some equipment, the equipment size required may be different from the originally designed size and in such cases; an exponential scaling expression is used:

$$\text{New cost} = \text{Base Cost} \left(\text{New size}/\text{Base size}\right)^{n}$$

(Equation 36)

Where n is a characteristic scaling exponent based upon some characteristic of the equipment related to production rate, such as flow or heat duty. The value n is typically in the range of 0.6 to 0.7 taken from the exponent range proposed in the 1994 Chem Systems report, and shown in Table 27.

Table 27: Scaling exponents for equipment cost.

| **Equipment** | **Exponent** |
|---|---|
| Agitators | 0.5 |
| Compressors, motor driven | 0.6 |
| Distillation column | 0.6 |
| Heat exchangers | 0.7 |
| Inline mixers | 0.5 |
| Package quotes / Skidded equipment | 0.6 |
| Pressure vessels | 0.7 |
| Pumps | 0.8 |
| Tanks, atmospheric | 0.7 |
| Solids handling equipment | 0.8 |

### 5.1.1 Equipment cost estimates

The maximum volume of each PBR is taken as 3000L similar to an existing algal production plant located in Spain with a total volume of 30,000L; each PBR with a capacity of 3000L (Acien Fernandez et al., 2013). The cost of the PBR is estimated at \$111/$m^3$ based on vendors quotation and is made of polyethylene and having a diameter of 0.05m. The cost of other equipment such as pumps, blowers and culture preparations column are obtained from referenced literature and vendor estimates and documented in *Appendix H*.

The cost of the centrifuge for the centrifugation process is represented for that of a westfalia centrifuge separator AG which is costed at 500,000€ per unit (2007€) capable of accommodating a flow of up to 72m$^3$/h. Membrane filtration costed at 50€ per m$^2$ based on estimates from citied literature (Judd and Judd, 2010). Harvest pumps are also included in the equipment cost estimate and costed at 1,600€ per unit (2007€) capable of accommodating a flow of up to 20m$^3$/h.

The equipment cost estimate for the cell disruption and lipid extraction stage consist of extraction columns, beat beaters, solvent recovery reboiler, solvent recovery column preheater exchanger, solvent recovery column and pumps. The extraction column is costed at $1,980,000($2013) per column. Each extraction column is capable of accommodating a total lipid feed rate of 5,894 kg/hr and has an overall height of 60 ft. The solvent recovery column is costed at $714,000($2009) per unit with each unit consisting of 3 columns each with is a packed tower with dimensions of 10-ft-diameter x 20-ft-height. The reboiler is also costed at $150,000($2009) per unit with each unit consisting of 3 reboilers.

The additional lipid purification stage equipment costing is taken from a 2014 NREL Algal biomass to biofuel design report. It is estimated at $6,400,000($2013). This is further adjusted using the scaling ratio and exponent to match the required production rate. The lipid upgrading unit cost includes hydrotreating unit, hydrocracking unit and separation vessels. The hydrotreater unit cost consists of hydrotreater reactors, feed and product pump, fired heater, heat exchanger, hydrogen compressor, flash drum and air cooler. The hydrocraking unit costs incudes cost of hydrocracker reactor, fired heater feed and product exchanger, air cooler, HP flash and LP flash. It is costed at $30,000,000($2005) accommodating a capacity of 10,727 kg/hr. In addition, storage cost for 7 days of product is estimated based on vendors quote.

The cost estimates for the anaerobic digestion stage includes anaerobic digesters, recycle pumps, mixers, centrifuge separator. Each AD vessel has a maximum capacity of 10,000 tonnes and this value is used to determine the number of AD unit required.

The biogas heat and power generator is also costed at $1000/kW generated ($2008) based on vendor estimates.

### 5.1.2 Other direct and indirect cost

Other direct and indirect costs are added to the total equipment cost in order to determine the total capital investment. For other direct cost, site development and warehouse costs are represented as 9% and 4% of installed equipment cost respectively (Davis et al., 2014). Warehouse costs accounts for cost for onsite equipment and supply storage, whereas the site development cost includes associated cost for fencing, roads, well drainage, rail system, soil borings, and general paving. The cost of installation for the equipment is taken as 15% of the equipment cost whilst instrumentation cost is taken as 10% of the equipment cost (Sinnot, 2005).

To represent piping cost 10% of the installed equipment cost is used based on estimates from Beal et al. (2015) costing analysis for the cultivation stage. The indirect cost includes project contingency (10% of total direct cost), field expenses (10% of total direct cost), home-office engineering and construction activities (20% of total direct cost), and other costs related to construction (10% of total direct cost). Working capital is taken as 5% of the fixed capital cost (Phillips et al., 2007). The fixed capital investment cost is the sum of the direct and indirect cost.

Table 28: Estimation percentages for additional costs

| **Associated Cost** | **Estimation percentage** |
|---|---|
| Piping | 10% of installed equipment cost for cultivation stage and 4.5% otherwise (excluding storage, AD equipment cost). |
| Installed equipment cost | 15% of purchase equipment cost |
| Instrumentation cost | 10% of purchase equipment cost |
| Site development | 9% of installed equipment cost( excluding storage, AD equipment cost) |
| Warehouse costs | 4% of installed equipment cost( excluding storage, AD equipment cost) |
| Project contingency | 10% of total direct cost |
| Field expenses | 10% of total direct cost |
| Home-office engineering and construction activities | 20% of total direct cost |

| | |
|---|---|
| Other costs related to construction | 10% of total direct cost |
| Working capital | 5 % of the fixed capital cost |
| Property insurance and taxes | 3% of installed equipment cost ( excluding storage, AD equipment cost) |
| Maintenance capital | 0.7% of fixed capital cost |

## 5.2 Operating cost

Operating cost consists of both variable and fixed. Variable cost includes cost of feedstock, raw materials and co-product credits which are incurred during process operation.

### 5.2.1 Variable operating cost

Quantities of raw materials used and co-products produced are determined using the material balance. Table 29 documents the costs and sources of chemicals used in the process.

Table 29**:** Raw material and resource cost including co-product credits

| **Components** | **Cost (2015$)** | **Source** |
|---|---|---|
| $CO_2$ | $0.0442/kg | Davis et al., 2016 converted to $2015 |
| Sodium nitrate | $0.290/kg | Suppliers quote |
| Magnesium sulfate | $0.3970/kg | ICIS, 2015 |
| Dipotassium phoshate | $1.1000/kg | Suppliers quote |
| Fresh water | $0.00003/kg | Suppliers quote |
| Hexane | $1.5000/kg | Suppliers quote |
| Methanol | $1.1000/kg | Suppliers quote |
| Silica | $1.0000/kg | Suppliers quote |
| Clay | $0.6600/kg | Davis et al., 2014 converted to $2015 |
| Phosphoric acid | $0.8000/kg | Suppliers quote |

| | | |
|---|---|---|
| Hydrogen | $1.4762/kg | Davis et al., 2014 converted to $2015 |
| Hydrotreater catalyst | $33.7553/kg | Jones et al., 2009 converted to $2015 |
| Hydrocracking catalyst | $33.7553/kg | Jones et al., 2009 converted to $2015 |
| Power | $0.0800/kWh (2015$) | Supplier TNB,2015 |
| Cooling water | $0.00005/kg | Intratec, 2015 |
| Steam | $0.015/kg | Intratec, 2015 |
| *Coproduct* | | |
| Anaerobic digestate sludge | $0.290/kg of N available | Davis et al., 2013 converted to $2015 |
| Power co-product | $0.0800/kWh | As previously mentioned |
| Anaerobic digestate effluent | $0.5957/kg | Average of nutrients cost |
| Naphtha | $0.8198/kg | Naphtha price in Malaysia, 2015 |
| Diesel | $0.9652/kg | Diesel price in Malaysia, 2015 |

The material costs for the cultivation process consist of carbon dioxide, nutrients (N, P, S), process water and power. Sodium nitrate, magnesium sulfate and dipotassuim phosphate prices were obtained from ICIS and other chemical pricing databank and suppliers quote for large-scale purchase; $285/ tonne for sodium nitrate, $397/tonne for magnesium sulfate, and $1100/tonne for dipotassium. The material cost for the rest of the downstream processes consists of hexane, silica, clay, phosphoric acid and hydrogen. The cost for power is estimated at $0.0800/kWh assuming power is supplied by Tenaga Nasional Berhad; one of the largest power company in southeastern Asia. Hydrogen is assumed to be purchased as a product from standard natural gas-derived steam methane reforming and costed at $1504/tonne. For the hydrotreater and hydrocracking catalyst cost, it is assumed that the catalyst lifetime is 2 years and 5 years respectively. Petroleum hydrotreater catalyst life is normally several years and future work is still required for more accurate determination of catalyst lifetime (Jones et al., 2014).

From the anaerobic digestion stage, potential co-products are the anaerobic digestate sludge (which contains bioavailable nutrient), AD effluents (consisting of nitrogen phosphorus and sulfur nutrients), power (generated from the produced biogas), gasoline and diesel. Cost for the anaerobic digestate sludge is valued at $290/tonne whilst the AD effluents is valued at $596/tonne; taken as the average cost for all three nutrients source (N,P,S).

Diesel, gasoline and light hydrocarbon range fuel is included with the co-product although there is much likelihood that it may not be readily appropriate for direct use as a fuel or blendstock and may therefore require further processing. Nonetheless, the prices for readily available fuels on the market are used to represent the potential prices for coproduct fuels. The naphtha coproduct value is taken as $0.82/L whilst the diesel as $0.97/L.

### 5.2.1 Fixed operating cost

The fixed operating cost generally represents cost incurred for a plant to run and disregards whether or not the full production capacity of the plant is reached. These costs include labour, land rental, supervision cost and other overheads, which includes maintenance, loan repayment and insurance. Labour and supervision cost is the total cost to be paid for the staff required for plant operation.

Using Peters and Timmerhau's (2003) chart, the operating labour requirement for a 1000 ton of product/day capacity is approximately 80 employee hours per day/processing step. The algal bio-jet fuel plant has a daily production capacity of 180 ton/day and an initial 37 ton/day of algal biomass with process steps of heat transfer, distillation, evaporation, drying and reaction. Thus, for 340 days annual operation, operating labour required = (5x35x340) = 59,500 employee-hours/year (~22 workers). Also using fixed operating cost data from past algal biomass related NREL reports (Davis et al., 2016; Jones et al., 2009; Jones et al., 2014) between 50-100 workers was estimated for production capacities of ~560-1340 tons/day. An additional 20 operators (to account for the large number of photo bioreactors) is added due to give a total of 42 workers using initiative based on works of Davis et al. (2016). The salaries for the labour and supervision are based on reported salary ranges in Malaysia and differ with years of experience.

Table 30**:** Fixed operating cost for plant labour and supervision

| **Labour and supervision** | | | |
|---|---|---|---|
| **Position** | **Salary** | **No. required** | **Cost $/yr** |
| Plant manager | 46,528 | 1 | 46,528 |
| Plant engineer | 22,333 | 2 | 44,666 |
| Maintenance supervisor | 18,611 | 1 | 18,611 |
| Maintenance technician | 11,632 | 6 | 69,792 |
| Lab manager | 18,146 | 1 | 18,146 |
| Lab technician | 10,375 | 1 | 10,375 |
| Shift supervisor | 16,750 | 4 | 67,000 |
| Shift operator | 11,632 | 20 | 232,640 |
| Yard employees | 6,281 | 4 | 25,124 |
| Clerks and secretaries | 9,499 | 2 | 18,998 |
| Total salaries | | 42 | 551,880 |
| Labour burden (90% of salaries) | | | 496,692 |
| **Other overhead** | | | |
| Property insurance and taxes | 3% of installed equipment cost | | 720,379 |
| Maintenance capital | 0.7% of fixed capital cost | | 360,484 |
| Land rental | Calculated from land requirement | | 3,465,713 |
| Total fixed operating cost | | | 5,595,148 |

Labour burden is calculated as 90% of the total salary cost to account for items such as general plant maintenance, payroll overhead (including benefits), plant security, janitorial and similar services, phone, light, heat, and plant communications and safety. This 90% estimate is the same with the median value for the general overhead range recommended in the 2008 PEP Yearbook produced by SRI Consulting. Additionally, the annual maintenance materials is estimated as 3% of the installed capital cost whilst property insurance and local property tax is estimated as 0.7% of the fixed capital investment. These estimates are established from the 1994 Chem Systems report described in NREL's 2011 ethanol report (Davis et al., 2014). Additionally land rental per year is included as part of the fixed operating cost at land rental cost of \$0.32/m$^2$ (Invest in Penang, 2015).

## 5.3 Discounted Cash Flow analysis and the Minimum Selling Price of fuel

It is without doubt that the purpose of investing money in biofuel plant is to earn money; hence some means of comparing economic performance is necessary. The discounted cash flow analysis is a standard and most common method used for the financial assessment of projects by most professional practitioners of techno-economic assessment. It is used to calculate the present worth of future remunerations from the production plant and is sensitive to the interest rate assumed.

By calculation of the net present value (NPV) for various interest rates, an interest rate at which the cumulative net present value at the end of the project is zero can be found. This particular rate is called the "discounted cash-flow rate of return" (DCFRR) and is a measure of the maximum rate that the project could pay and still break even by the end of the project life (Sinnott, 2005). The more profitable the project, the higher the DCFRR that it can afford to pay. The minimum fuel product-selling price (MFSP) for algal bio-jet fuel was determined using a discounted cash flow rate of return analysis. The MFSP is the selling price of the fuel that makes the net present value of the process equal to zero with a specified percentage discounted cash flow rate of return over a said plant life and specified percentage equity with the remainder debt financed at specified percentage interest for a period of term.

### 5.3.1 Discount rate

The discount rate represents the decrease in value of payment because it is not paid at the time of the capital outlay but a number of years. Capital investment is outlaid at the start of a project, but returns are not received until later, by which stage their value, in real terms has reduced. This is accounted for by the introduction of a discount rate in order that the overall economic result of a project realization is expressed in present money (Lauer et al., 2008).

The discount rate is set at 10% with a plant lifetime of 30 years. A discount rate of 10% is used, as it is the standard rate used in the past for biofuels design projects, which in turn was established from an economic evaluation, energy efficiency and renewable energy technologies manual by Short et al. (1995).

### 5.3.2 Net present value

The net present value (NPV) of a project is the sum of the present values of the future cash flow. The net present value is always less than the total future worth of the project because of the discounting of future cash flows. Net present value is easily calculated using the formula (Towler and Sinnott, 2008);

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n}$$

(Equation 37)

Where:

$CF_n$ is cash flow in year n;

t is project life in years;

i is the interest rate

### 5.3.3 Depreciation and Taxes

For the capital depreciation amount for the calculation of taxes to be paid, the General Depreciation System (GDS) within the IRS Modified Accelerated Cost Recovery System (MACRS) is used. A 7 year recovery period is also chosen and based on past discounted cash flow analysis for biofuel prospective plants (Davis et al., 2014; Davis et al., 2016; Jones 2009). In recent years, corporation (profits) tax has been running at around 30 per cent (Sinnott, 2005). In Malaysia this figure is around 25% and used in this analysis to make an estimate of the cash flow after tax. In actuality, the amount of income tax to be paid by a potential fuel producer varies annually due to changes in the volume of product produced and the allowable depreciation deduction. No income tax is usually paid in the first nine years of operation because the depreciation and loan interest deductions are greater than the net income.

### 5.3.4 Construction Time

During the construction time, no income is earned but rather large sums of money are expended. According to Perry and Green (1997) small projects with less than $10 million investment can be built in fewer than 18 months and larger projects can take up to 42 months. For larger projects (in the context of petroleum refining) with greater than 1 billion investments construction can occur in 24 months (Gary, 1994). A construction time of 24 months fits within these references with an additional twelve months are added before construction for planning and engineering. 8% percentage of total project cost is assigned for the initial 12months project plan period, 60% for the next 12 month construction period and 32% for final 12 months period.

### 5.3.5 Equity Financing

It is assumed that the plant would be 40% equity financed. The terms of the loan to be taken is assigned an interest rate of 8% interest for 10 years. The principal is borrowed in stages over the 3 year construction period. The Interest on the loan is paid during this period, but principal is not paid back (based on nth-plant assumption, in which cash flow comes from the parent company after plant starts up). The assumptions are in line with past works (Davis et al., 2014; Davis et al., 2016; Jones 2009). If the plant is 40% equity financed, the rest of the capital (60%) is to be borrowed and then repaid each year with interest. Repayment is calculated using the annual capital charge formula (ACC);

$$\text{Annual capital charge (ACC)} = \text{ACCR x total capital cost}$$

(Equation 38)

$$\text{ACCR}=\frac{A}{P}=\frac{\lfloor i(1+i)^n \rfloor}{[(1+i)^n-1]}$$

(Equation 39)

Where:

i = interest rate;

n = years of compound interest;

A = annual payments;

P = Principal (money borrowed)

### 5.3.6 Start-up time

The start-up time is taken as 6 month based on recommendations by Perry and Green (1997) which indicates that for a moderately complex plant, start-up should be about 25% of the construction time. It is assumed that an average of 50% production is achievable during the start-up period while incurring 75% of variable expenses and 100% of fixed expenses.

### 5.3.7 Working Capital

According to Peters and Timmerhaus (2003), the working capital is defined as money available; to cover cost of raw materials and supplies in inventory, finished product in storage, accounts receivable, cash on hand for monthly payments such as wages and maintenance supplies, accounts payable, and taxes payable. As stated in the capital cost estimation, the working capital as was used in prior work is 5% of fixed capital investment.

Table 31: Discounted cash flow analysis parameters

| | |
|---|---|
| Plant life | 30 years |
| Discount rate | 10% |
| General plant depreciation | 150% |
| General plant recovery period | 7 years |
| Federal tax rate | 30% |
| Equity Financing | 40% |
| Loan terms | 10 years loan at 8% APR |
| Construction period | 36 months |
| First 12 months' expenditures | 8% |
| Next 12 months' expenditures | 60% |
| Last 12 months' expenditures | 32% |
| Working capital | 5% of fixed capital investment |
| Start-up time | 6 months |
| Revenues during start-up | 50% |
| Variable costs incurred during start-up | 75% |
| Fixed costs incurred during start-up | 100% |

# 6 RESULTS, ANALYSIS AND DISCUSSION

This section of the thesis documents all the output results from the process model constructed in chapter 4. In addition to the model results, this section also discusses and analyses these results whilst validating key aspects of it. The most crucial parameters which affects the process economics, NER, water foot print and GHG emission are also identified via sensitivity analyses. A number of case scenarios are also explored for the potential positive improvement on the process economics, NER, water footprint and GHG emission results.

## 6.1 Model Testing

The main purpose of model testing is to demonstrate the model functionality. The overall aim of the model is to shed light on the expected technical, economic, and environmental status of micro-algal bio-jet fuel production on a commercial scale in Malaysia. Output data from the model simulation are examined, analyzed and discussed

### 6.1.1 Model inputs and output results and discussion

The most significant model input and output results are shown in the table 31 and 32. The conceptual plant produces 8,500,000 L/year of bio-jet fuel from microalgae.

Table 32**:** Model test inputs

| | **Input value** | **Units** |
|---|---:|---|
| **PROCESS OVERVIEW** | | |
| Desired quantity of Jet fuel to be produced | 8,500,000 | L/year |
| Federal tax rate | 30 | % |
| Equity Financing | 40 | % |
| Discount rate | 10% | % |
| Minimum selling price of diesel | 0.97 | $/L |
| Minimum selling price gasoline | 0.82 | $/L |
| Plant life | 30 | years |
| Cost year | 2015 | |

|  |  |  |
|---|---|---|
| **CULTIVATION** |  |  |
| Light intensity | 646 | µmolm$^{-2}$s$^{-1}$ |
| Initial biomass concentration of algae in the reactor | 0.50 | g/L |
| Water evaporation rate | 0.005 | m/day |
| Volume/land area ratio | 44.8 | L/m$^2$ |
| Pump efficiency | 70 | % |
| Blower efficiency | 60 | % |
| Calorific value of algal biomass | 20 | MJ/kg |
| **HARVESTING AND DEWATERING** |  |  |
| Concentration of algal broth after harvesting and dewatering (membrane ultrafiltration) | 9 | wt.% |
| Algal biomass separation efficiency (membrane ultrafiltration) | 99 | % |
| Algal biomass separation efficiency (centrifuge) | 98 | % |
| Concentration of algal broth after harvesting and dewatering (centrifuge) | 27 | wt.% |
| **CELL DISRUPTION AND LIPID EXTRACTION** |  |  |
| Algal biomass lipid content | 30 | % |
| Lipid recovery efficiency | 95 | % |
| Solvent recovery efficiency | 95 | % |
| Calorific value of algal lipid | 38 | MJ/kg |
| Calorific value of lipid extracted residual algal biomass | 13.5 | MJ/kg |
| **ADDITIONAL LIPID PURIFICATION AND UPGRADING** |  |  |
| Total hydrogen feed rate | 0.07 | kg/kg of recovered lipid |
| Hydrogen consumption rate for hydrotreating | 0.04 | kg/kg of recovered lipid |
| Hydrogen consumption rate for hydrocracking | 0.03 | kg/kg of recovered lipid |
| Hydrotreating catalyst, weight hourly space velocity | 0.24 | wt./hr per wt. catalyst |
| Hydrotreating catalyst, weight hourly space velocity | 0.54 | wt./hr per wt. catalyst |
| Hydrotreating catalyst lifetime | 2 | Years |

| | | |
|---|---:|---|
| Hydrocracking catalyst lifetime | 5 | Years |
| Calorific value of Jet fuel | 43 | MJ/kg |
| Calorific value of Diesel | 44 | MJ/kg |
| Calorific value of Naphtha | 44 | MJ/kg |
| **ANAEROBIC DIGESTION** | | |
| Percentage residual algal biomass digested | 70 | % |
| Desired concentration of residual digestate after dewatering | 270 | g/L |
| CHP unit efficiency | 65 | % |
| Ratio of electrical to heat energy produced from a CHP unit | 0.67 | |

Table 33: Model test results

| | **Output value** | **Units** |
|---|---:|---|
| **PROCESS OVERVIEW** | | |
| Bio-Jet fuel produced | 8,500,000 | L/year |
| Diesel fuel produced | 1,514,192 | L/year |
| Naphtha fuel produced | 2,233,294 | L/year |
| Total Capital cost | 85,353,450 | $ |
| Total Operating cost | 22,605,785 | $/year |
| Bio-jet fuel production cost | 2.98 | $/L |
| Total GHG emissions | -63,641.81 | tonne$CO_2$/ year |
| Net Energy Ratio (NER) | 3.87 | |
| Total water usage (freshwater and resource) | 22,969,477 | tonne/year |
| Payback time | 8.4 | year |
| Minimum selling price of bio-jet fuel | 5.89 | $/L |
| **CULTIVATION** | | |
| Specific growth rate | 0.31 | day$^{-1}$ |
| Areal productivity | 28.75 | g/m2/day |
| Volumetric productivity | 0.64 | g/L/day |

| | | |
|---|---:|---|
| Photosynthetic efficiency | 3.9 | % |
| Final mass of dry weight micro-algal cultivated | 53,566 | tonne/year |
| Initial mass of dry weight micro-algal feed | 11,424 | tonne/year |
| Sulphur nutrient requirement | 421 | tonne/year |
| Nitrogen nutrient requirement | 10,535 | tonne/year |
| Phosphorus nutrient requirement | 632 | tonne/year |
| Carbon dioxide requirement | 88,497 | tonne/year |
| Fresh water requirement incl. refill | 22,862,469 | tonne/year |
| Total cultivation energy requirement | 13,547,751 | MJ/year |
| Capital cost (installed equipment) | 10,886,027 | $ |
| Operating cost (variable) | 14,981,316 | $/year |
| CO2 fixation rate | 86,246 | tonneCO$_2$/ year |
| Total GHG emission rate | -76,352 | tonneCO$_2$/ year |
| Total water (resource) rate | 51,130 | tonne/year |
| **HARVESTING AND DEWATERING** | | |
| Concentration of algal broth before harvesting and dewatering | 2.35 | g/L |
| Concentration of algal sludge after harvesting and dewatering | 270.00 | g/L |
| Total harvesting and dewatering energy requirement | 4,667,409 | MJ/year |
| Capital cost (installed equipment) | 17,706,572 | $ |
| Operating cost (variable) | 103,720 | $/year |
| Total GHG emission | 946 | tonneCO$_2$/ year |
| Total water (resource) | 117 | tonne/year |
| **CELL DISRUPTION AND LIPID EXTRACTION** | | |
| Solvent requirement | 145,846 | tonne/year |
| Extracted algal lipid | 14,560 | tonne/year |
| Lipid extracted residual algal biomass | 36,379 | tonne/year |
| Total cell disruption and lipid extraction energy requirement | 60,925,453 | MJ/year |

| | | |
|---|---:|---|
| Capital cost (installed equipment) | 4,712,337 | $ |
| Operating cost (variable) | 3,961,537 | $/year |
| Total GHG emission | 6,296 | tonne$CO_2$/ year |
| Total water (resource) | 21,047 | tonne/year |
| **ADDITIONAL LIPID PURIFICATION AND UPGRADING** | | |
| Phosphoric acid requirement | 28 | tonne/year |
| Wash water requirement | 1,456 | tonne/year |
| Silica requirement | 15 | tonne/year |
| Clay requirement | 29 | tonne/year |
| Hydrogen requirement | 1,019 | tonne/year |
| Hydrotreating catalyst requirement | 7 | tonne/2 years |
| Hydrocracking catalyst requirement | 3 | tonne/5 years |
| Jet fuel produced | 8,500 | tonne/year |
| Diesel produced | 1,514 | tonne/year |
| Naphtha produced | 2,233 | tonne/year |
| Light gases produced | 1,817 | tonne/year |
| Total additional lipid purification and upgrading energy requirement | 64,117,636 | MJ/year |
| Capital cost (installed equipment) | 7,135,006 | $ |
| Operating cost (variable) | 1,801,885 | $/year |
| Total GHG emission | 6,227 | tonne$CO_2$/ year |
| Total (water resource) | 34,799 | tonne/year |
| **ANAEROBIC DIGESTION** | | |
| Residual algal sludge into digester | 229,866 | tonne/year |
| Residual digestate exiting digester | 54,805 | tonne/year |
| Anaerobic effluent exiting digester | 136,005 | tonne/year |
| Biogas produced | 41,616 | tonne/year |
| Power generated from biogas | 6,522,562 | MJ/year |
| Total anaerobic digestion energy requirement | 454,413 | MJ/year |
| Energy generated (Biogas credit) | 6,522,562 | MJ/year |

| | | |
|---|---|---|
| Capital cost (installed equipment) | 1,514,486 | $ |
| Total GHG emission | -759 | tonne$CO_2$/ year |
| Total (water resource) | 77 | tonne/year |

#### ***6.1.1.1 Cost results discussion and validation***

The results shows the total capital for micro-algal bio-jet fuel production is estimated at $85.3 million (RM332.67 million) and a fixed operating annual cost of $22.6 million (RM88.14 million).

A breakdown of the capital cost contribution in figure 21 shows the equipment cost investment by major production stages, the harvesting and dewatering equipment cost is largest cost contributor whilst the anaerobic digestion equipment cost is the least at 4%. A similar techno-economic study by Klein-marcuschamer et al. (2013) showed the harvesting and dewatering equipment cost accounts for more than 50% of the total equipment cost and the cultivation process was the second largest cost contributor. In another cost estimate by Davis et al. (2016), the harvesting and dewatering equipment cost was almost twice that of the cultivation cost.

The reason for the high equipment cost is due to the large quantity of water removed during dewatering and the high cost of the equipment required to do so at a large scale.

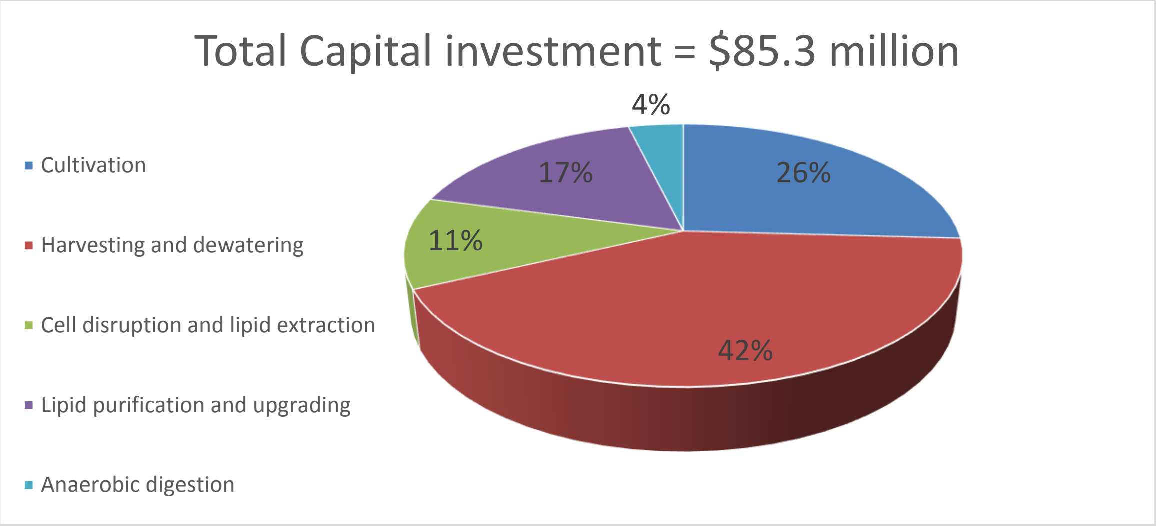


Figure 21: Plant equipment cost investment by major production stages expressed in percentages.

The total production cost is calculated as the sum of the depreciation plus the operating costs. The cost of micro-algal bio-jet fuel production is estimated at $2.98/L, production cost of biofuel from previous studies range from $2.2-12.2/L (Davis et al., 2012; Delrue et al., 2012; Richardson et al., 2014). Figure 22 reveals the cost of raw material as the major production cost contributor and the cost of labor as the least.

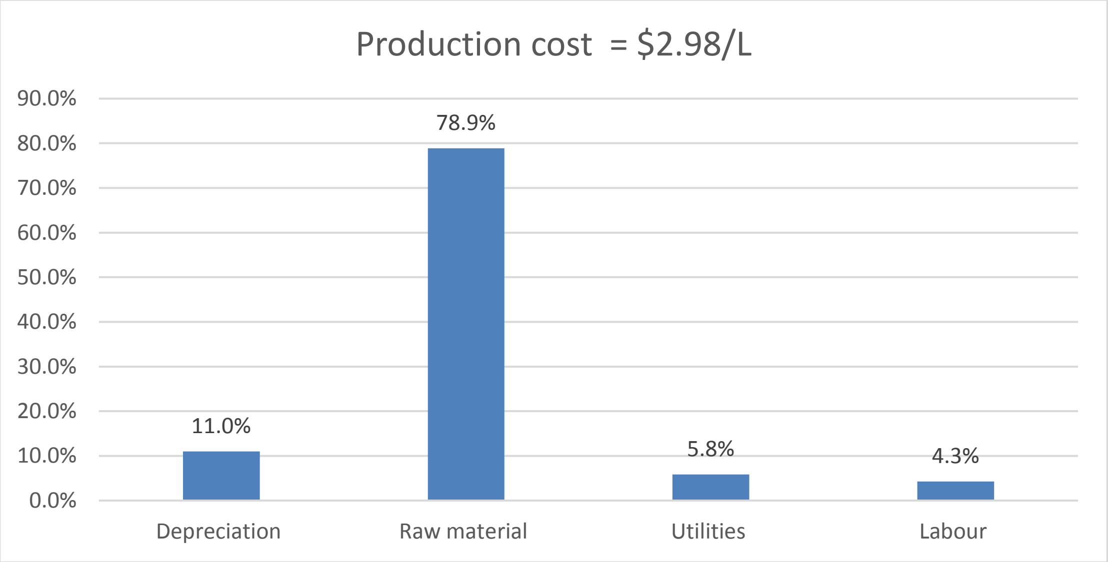


Figure 22: Major production cost of micro-algal bio-jet expressed in percentages.

A closer look at the operating cost contribution for each production stage in figure 22 shows the cultivation process to be a major contributor to the total operating cost. The high operating cost of the cultivation process is because of the large quantities of raw material purchase necessary for algal growth; this includes fresh water cost at \$6.9 million/year (without recycle), carbon dioxide purchase cost at 3.9 million/year and nitrate nutrient purchase cost \$3.1 million/year. A cost analysis on micro-algal cultivation carried out by Acien et al. (2012) also shows the cost of $CO_2$ to be a major operating cost contributor. The impact of water recycle and supply of freely available $CO_2$ on the overall production cost is discussed in section 5.4. The harvesting process is one of the least cost contributor to the variable operating cost; it is expected, since there are no cost of raw materials required for this process except for utility cost. In addition, the anaerobic digestion stage that is shown in figure 22 to be at a negative generates power thus reducing overall utility cost.

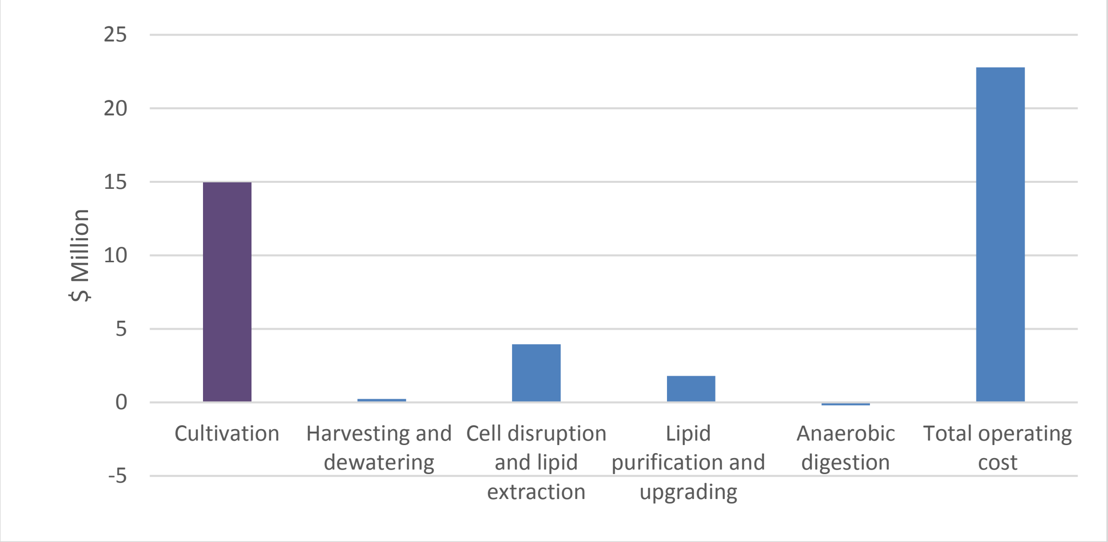


Figure 23: Plant variable operating cost by major production stages and overall total expressed in \$ Million.

The results from the economic analysis in table 33 shows the MFSP of bio-jet fuel which makes the net present value to equal to zero at a discounted rate of 10%, is \$5.89/L. When compared with the price of jet fuel on the market (\$0.43/L) based on 2015 average price, the model estimated price is more than 13 times greater. Whilst it is shown to be greater than market price, it is shown to be much less, than the estimated MFSP of micro-algal bio-jet fuel of \$8.45/L based on a techno-economic study by Klein-Marcuschamer et al. (2013). In comparison to the aforementioned techno-economic study, a lower MFSP is expected in this study due to cost reduction arising from reduced labor cost influenced by country of plant location and cost effective cultivation, harvesting, and dewatering methods. Sensitivity analyses of the major cost driver is carried out in section 5.3 to suggest how the MFSP of bio-jet fuel can be reduced.

#### 6.1.1.2 *Energy consumptions discussion and validation*

The Net energy ratio for bio-jet fuel production from microalgae based on the model result shown in table 33 is 3.87, which is higher than the minimum threshold for long-term sustainability. When the NER is greater than 1, it means the production plant will be able to produce its own energy on site thus reducing its demand on fossil derived electricity and its associated GHG emission. The total energy required for the production of bio-jet fuel from microalgae is 22.1MJ/kg of bio-jet fuel produced whilst the total energy consumption per year is 0.14 x $10^6$GJ. When compared with the energy requirement of 6.5-199.5MJ/kg of fuel reported for the production of biodiesel from micro-algae from past energy analysis, the model value is within reasonable range (Khoo et al., 2011; Lardon et al.,2009; Stephenson  et al., 2010).

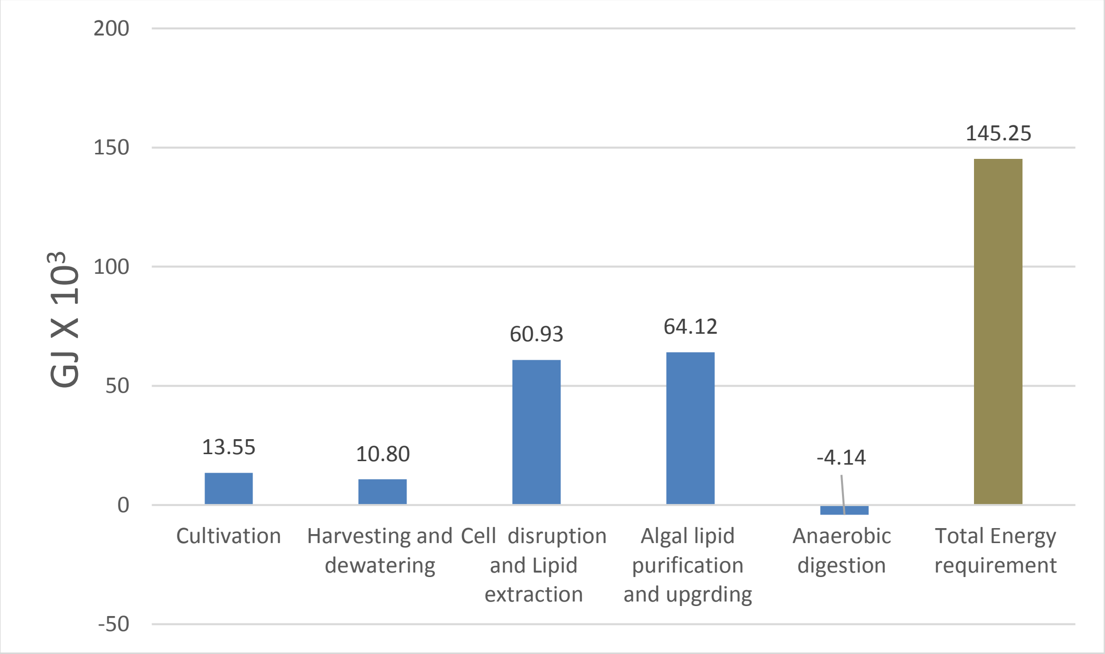


Figure 24: Energy use by major production stages including overall total expressed in GJ x $10^3$/year.

The energy requirement for the lipid purification and upgrading process as shown in figure 24, dominates the energy requirement of the bio-jet fuel production plant. In addition, the cell disruption and lipid extraction process also contributes a large percentage of the overall energy requirement. The anaerobic digestion step reduces the overall energy requirement by 4.2% when the energy credits from the biogas are added. The harvesting and dewatering process is the lowest contributor to the overall energy requirement due to the combination of the harvesting and dewatering technology, membrane ultrafiltration and centrifugation. The impact of this combination is further discussed in section 5.4.

#### *6.1.1.3 GHG discussion and validation*

The model results documented in table 33 reveals the intake rate of $CO_2$ is greater than the emission rate associated with the production of bio-jet fuel from micro-algae. Figure 25 shows the GHG emission profile of the major manufacturing steps, an estimated -63,556 tonnes$CO_2$ ($1.65 \times 10^{-4}$ kg$CO_2$/L of fuel produced) are captured per year. Overall, the intake of $CO_2$ during algal cultivation is enough to offset the $CO_2$ emission for the other stages of production. GHG emission emitted during the raw material production used in the manufacturing process (catalyst, fertilizer, hydrogen etc.) is included in the GHG emission profile.

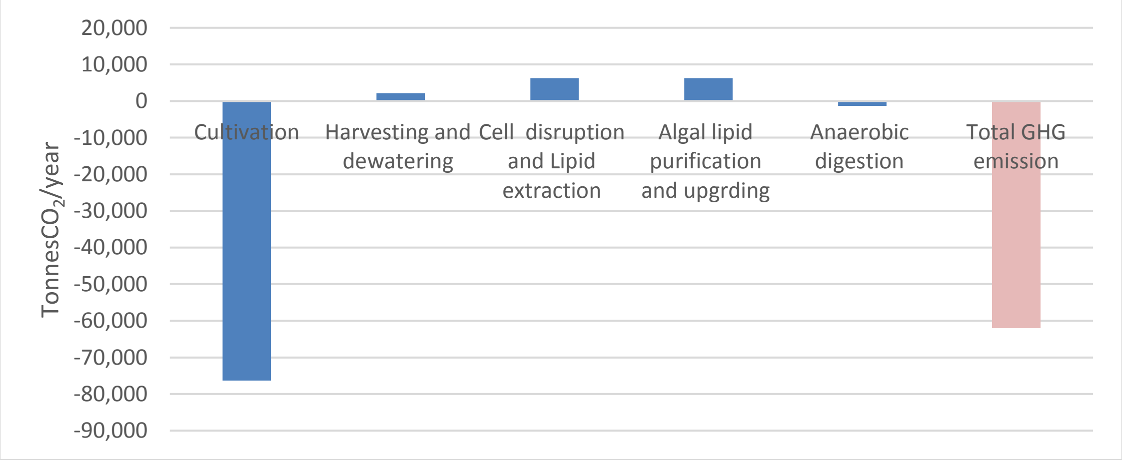


Figure 25: GHG emission rate by major production stages and overall total expressed in tonnes$CO_2$/year.

For the cultivation and anaerobic digestion process, $CO_2$ is taken up during the algal growth and the energy produced from biogas reduces demand on fossil derived energy. Of all the production stages, the cell disruption and lipid extraction stage has the highest GHG emission rate. Overall, the bio-jet fuel production from microalgae takes in more GHG than is emitted. One of the motivations of algal biofuel development is the potential to mitigate GHG's, as demonstrated from the results. The GHG emission rate of $-1.65 \times 10^{-4}$ $kgCO_2$/L of fuel is within the reported range for algal biofuels production (biodiesel) of -1.1- 8.7$kgCO_2$/L of fuel (Clarens et al., 2010; Lardon et al., 2009; Sander and Murthy, 2010; Stephenson et al., 2010).

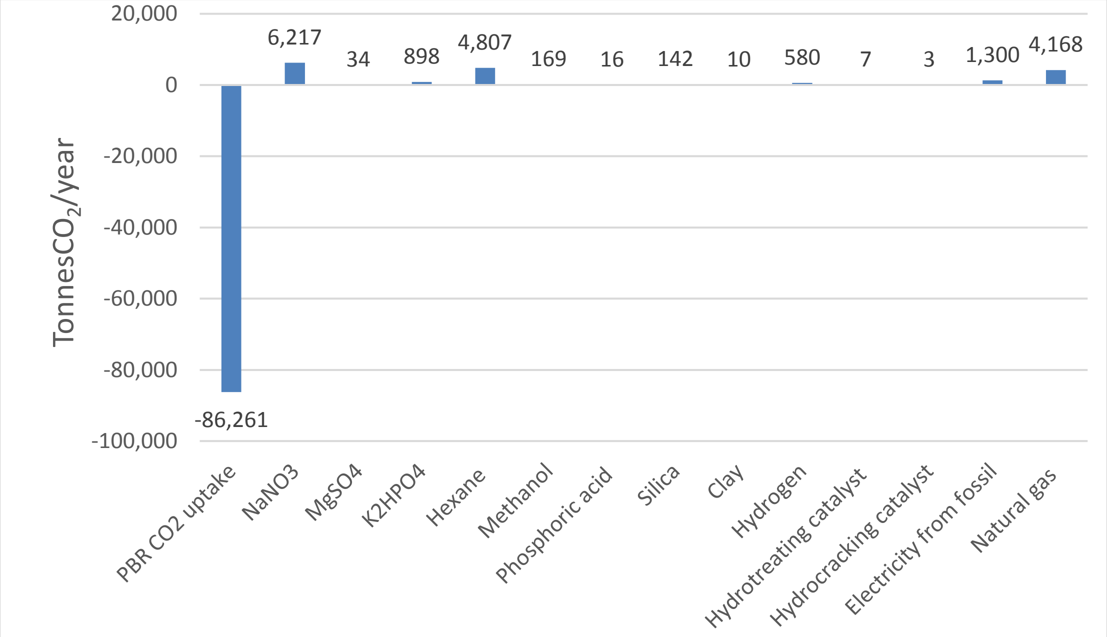


Figure 26: Associated GHG emission rate of raw material and utilities production expressed in $tonnesCO_2$/year

Upon further analysis, figure 26 shows the raw material hexane, which is required for the cell disruption and extraction stage, has the highest GHG contribution. To produce 1 kg of hexane 3.7$kgCO_2$ is emitted coupled with the large quantities of hexane required causing the GHG emission rate to be higher. Possible options for the reduction of GHG emission are discussed further in the section 5.4.

### *6.1.1.4 Water usage discussion and validation*

Figure 27 shows the water usage for the production of bio-jet fuel, the water usage includes fresh water consumption and resource water utilized during the production of the raw materials. The total water usage of 22.9 million tonne/year is required for the production of bio-jet fuel from micro-algae, whilst fresh water required for cultivation accounts for 92% of the overall water usage. Algae requires considerable amounts of water in order to grow and thrive and in addition, approximately 18,000 tonnes per year is lost due to evaporation and requires replacement.

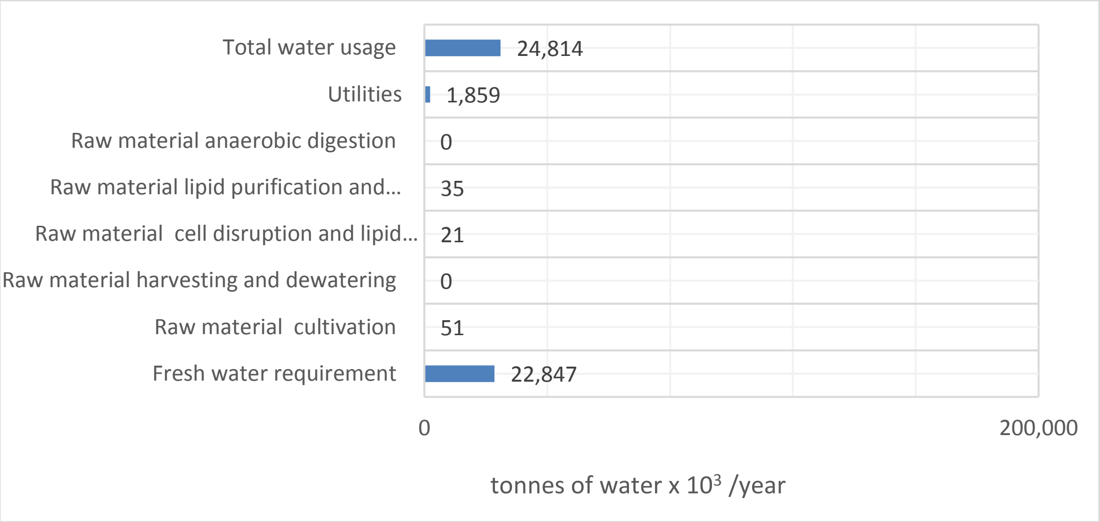


Figure 27: Water Usage by major production stages and overall total expressed in tonnes x $10^3$ /year

Lifecycle water usage for microalgae-to-biofuel process is reported to vary between -291 - 80 $m^3$/GJ of biofuel (Batan et al., 2013), when compared to an estimated total water usage of 60 $m^3$/GJ of biofuel from the model results it is within the reported range.

### 6.2 Seasonality and site analysis

The following analysis intends to determine to what extent seasonal variations in solar radiation and site location affects areal productivity and economics of algal bio-jet fuel production.

In the base case scenario, the annual average solar radiation value at 1792kWh/$m^2$, representative of the Kuala Lumpur region in Malaysia (2005-2009) was used as the input parameter to determine the areal productivity. The annual average daily solar irradiations in Malaysia varies with location, Kota Kinabalu records the highest solar radiation of 1900kWh/$m^2$ followed by Bayan Lepas with annual solar radiation of 1896 kWh/$m^2$(Haris, 2008).

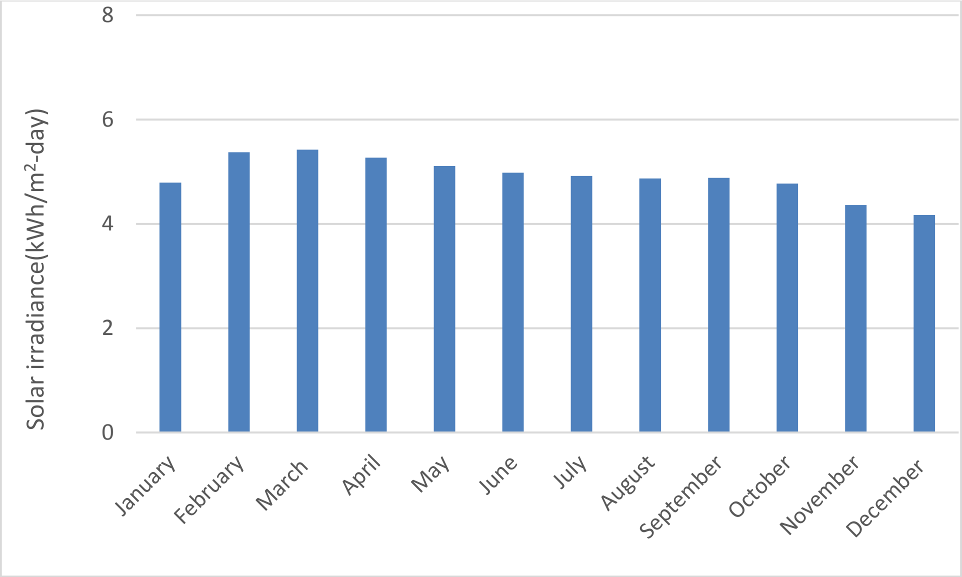


Figure 28: Average solar irradiance for Kuala Lumpur, Malaysia. Data obtained from the NASA database for the time period between 2005-2009. Annual average of 4.9kWh/$m^2$day over this time period.

It becomes clear that solar radiation differs over the course of a year and location thus affecting the areal productivity predicted by the process model. The extent of this difference is determined by running 12 simulations on the excel model using the goal seek function based on daily average solar irradiance data. The algal productivity from all 12 simulations are added, averaged and compared with the base case result (which was calculated using yearly average solar irradiation) shown in table 34.

Table 34**:** Impact of seasonality and site data on MFSP, NER and GHG associated with algal bio-jet fuel production.

| | **Base case yearly average solar irradiance in Kuala Lumpur** | **Base case monthly average solar irradiance in Kuala Lumpur** | **Min. solar irradiance, monthly average in Kuala Lumpur** | **Max. solar irradiance monthly, average in Kuala Lumpur** | **Solar irradiance @ 1900 kWh/m$^2$ yearly average in Kota Kinabalu** |
|---|---|---|---|---|---|
| Algal biomass areal productivity, g/m$^2$/day | 28.75 | 28.73 | 26.11 | 30.07 | 29.55 |
| Production cost, \$/L of bio-jet fuel | 2.98 | 2.98 | 3.06 | 2.94 | 2.96 |
| MFSP of bio-jet fuel,\$/L of bio-jet fuel | 5.89 | 5.89 | 6.05 | 5.81 | 5.84 |
| GHG emission, tonnes$CO_2$/L of bio-jet fuel | -7.49 | -7.49 | -7.35 | -7.55 | -7.53 |
| NER | 3.87 | 3.87 | 3.87 | 3.87 | 3.87 |

The results in table 34 shows that using the yearly average solar irradiance instead of the monthly average data has no significant impact on the areal productivity and therefore MFSP. The production cost, NER and GHG emission rate remains this same as the base case value. Further simulations using the maximum and minimum irradiance data in the month of March and December respectively. Using the monthly average solar irradiance for the month of March gives a higher algal areal productivity in comparison to the base case value. The MFSP in the maximum case is \$0.09/L cheaper than the base case. The algal areal productivity result for the month of December is lower than the base case value; the MFSP is \$0.06/L is more expensive.

A further simulation was performed using the process model for the region Kota Kinabalu where the solar irradiance is higher than in Kuala Lumpur. The areal productivity using the data for the location Kota Kinabalu is higher than the base case value. The MFSP is less by \$0.05/L when compared the base case MFSP, although not so significant, it is still a more economical option. Overall, the areal productivity values reported in table 34 lies within reasonable range of 3-50g/m$^2$/day for areal productivity reported in several literature ( Pienkos,2008; Reijnders, 2009; Singh and Olsen, 2011).

## 6.3 Sensitivity analyses

The model results so far has demonstrated that the model is capable of yielding results, which measures the economics, technical and environmental performance of bio-jet fuel manufacturing process. Model results are generated based on several interlinked input values and it will be a useful thing to be knowledgeable of which input parameters have the most significant influences on the economics (MSP), GHG emission, and energy and water usage of the bio-jet fuel production process. Sensitivity analyses are carried out in order to identify these parameters by running several simulations and varying one input parameter each time, and tracking the effect of this variation.

### 6.3.1 Sensitivity variable and tornado plots

The sensitivity analysis was performed using reasonable maximum and minimum limits for each variable, represented as the “Best case” and “Worst case “as shown in table 35.

Table 35: Variables represented in the sensitivity analysis

| **Process area** | **Variables** | **Best case** | **Base case** | **Worst case** |
|---|---|---|---|---|
| Algal biomass cultivation | Nitrate nutrient cost, \$/kg | 0.150 | 0.290 | 0.350 |
| | Phosphate cost, \$/kg | 0.5 | 1.1 | 1.5 |
| | $CO_2$ cost, \$/kg | 0 | 0.045 | 0.10 |
| | Process water cost, \$/kg | 0 | 0.0003 | 0.0008 |
| | Average evaporation rate, m/day | 0.004 | 0.005 | 0.008 |
| Harvesting and dewatering | Centrifuge power, kWh/m$^3$ | 0.70 | 0.95 | 5.00 |
| Cell disruption and lipid extraction | Solvent cost, \$/kg | 1.00 | 1.30 | 2.00 |
| | Lipid recovery efficiency, % | 98 | 95 | 80 |
| | Solvent recovery efficiency, % | 99.9 | 99 | 90 |
| | Hydrogen cost, \$/kg | 1.20 | 1.51 | 2.20 |

|  |  |  |  |  |
|---|---|---|---|---|
| Purification and Upgrading | Lipid purification and upgrading Capex | -50% | 0% | +50% |
|  | Additional lipid purification | Not included | Included | +25% capex |
|  | Catalyst cost, $/kg | 24.4 | 34.40 | 40.20 |
| Anaerobic digestion | AD sludge selling price, $/kg | 0.350 | 0.290 | 0.100 |
|  | AD effluent selling price, $/kg | 0.620 | 0.596 | 0.100 |
| Others | Power cost, $/kg | 0.050 | 0.080 | 0.120 |
|  | Project contingency cost | -50% | 0% | +50% |
|  | Fixed Capital investment | -25% | 0% | +25% |
|  | Discount rate, % | 8 | 10 | 20 |

By finding the most influential variables, the modeler is more aware of ensuring the accuracy of the input values, which significantly affects the model output results. It allows for strategic focus during research and development studies within the field of bio-jet fuel production from micro-algae. Tornado plots are plotted as a useful means of presenting sensitivity analyses results and are shown is figure 29 to 32. The average algal productivity and lipid content are not included in the sensitivity analysis but considered in the case scenario section 5.4.

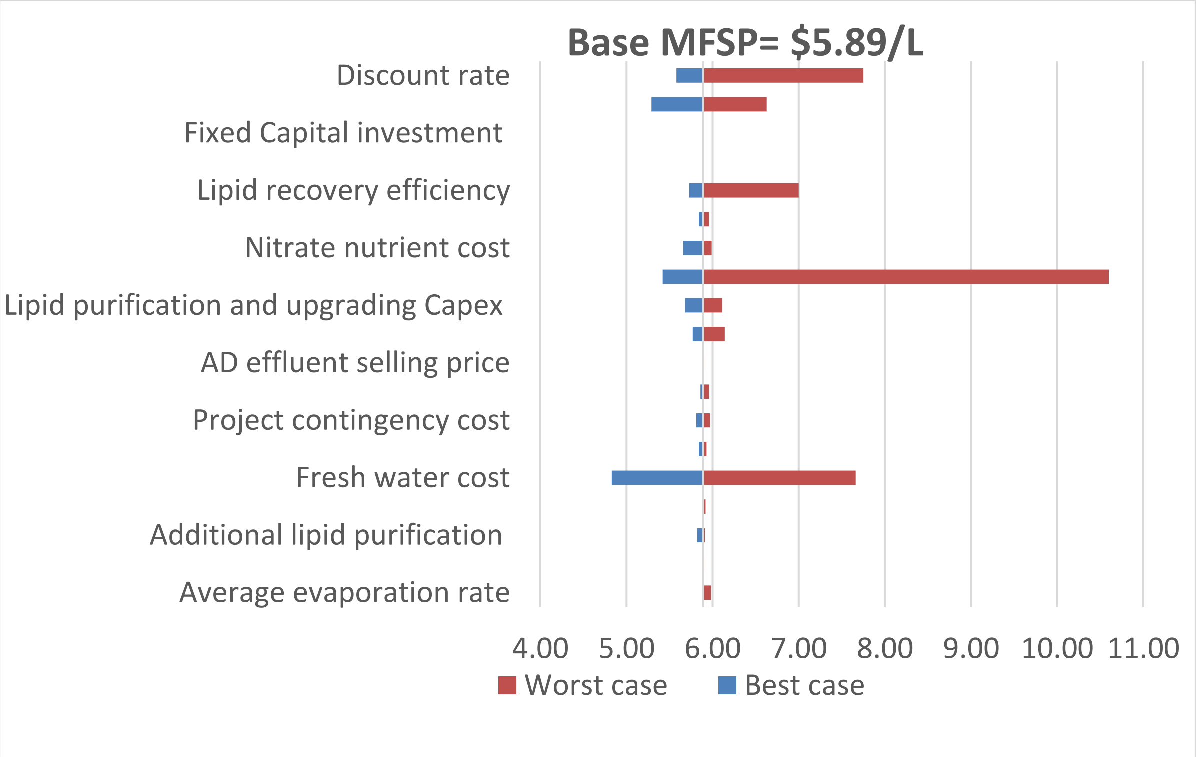


Figure 29: Tornado plot showing sensitivity of MFSP based on several input variable. The horizontal axis values indicates the deviation from the base value.

Figure 29 shows that amongst all the input variables, the top four variables having the greatest impact on MFSP of bio-jet fuel are lipid recovery efficiency, discount rate, solvent recovery efficiency and fresh water cost. Lipid recovery efficiency at 80% increases the MFSP of algal bio-jet fuel by $1.11/L relative to the base case whilst at a lipid recovery efficiency of 98%, the MFSP decreases by $0.16/L. The solvent recovery efficiency at 98% decreases the MFSP of algal bio-jet fuel by $ 0.47/L relative to the base case and at 90% increases the MFSP by $4.71/L. Solvent recovery efficiency determines how much less solvent will be purchased, solvent cost is rather high in comparison to other raw material cost at an average cost of $1.3/kg. The higher the solvent recovery efficiency, the higher the solvent recovery for recycling.

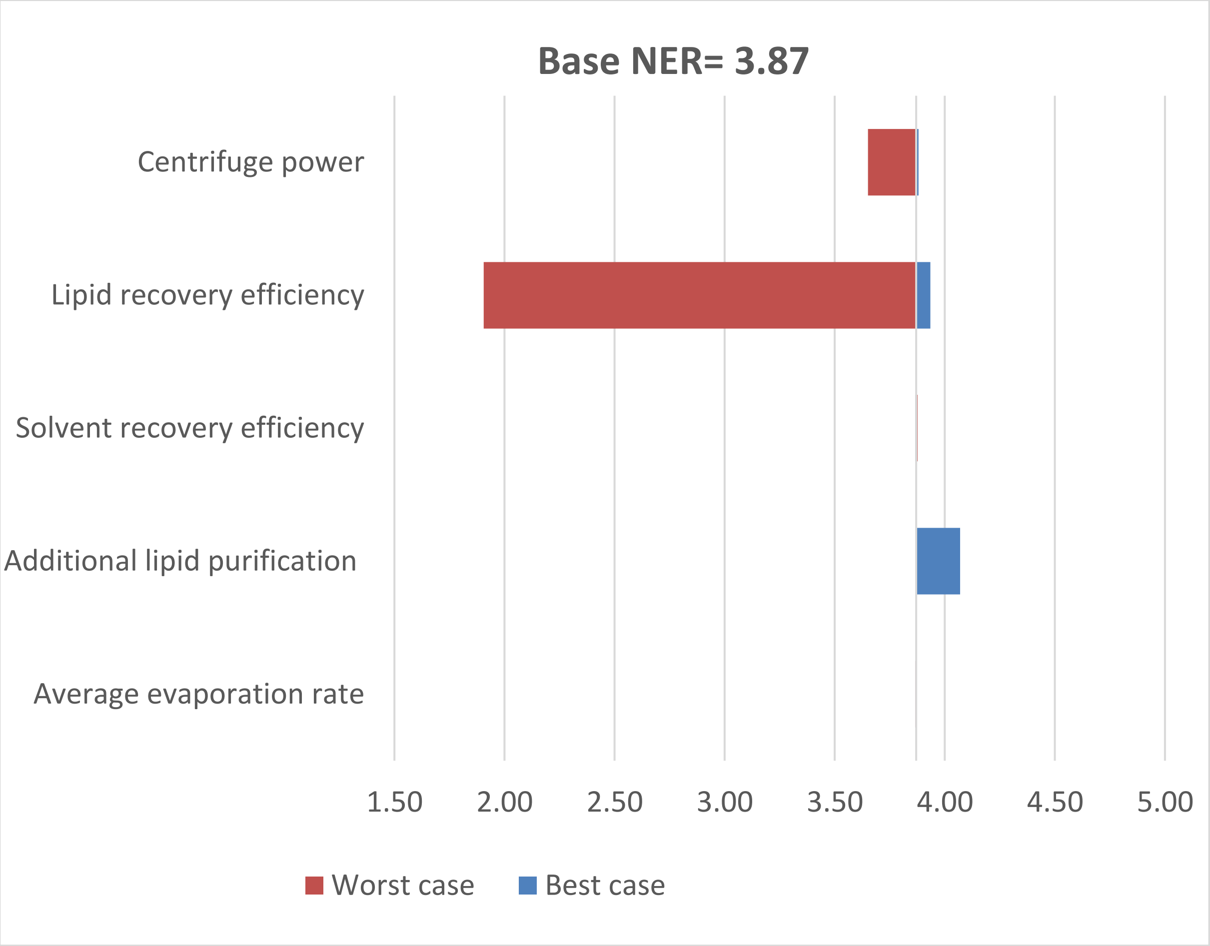


Figure 30**:** Tornado plot showing sensitivity on NER of algal bio-jet fuel production on several input variable. The horizontal axis values indicates the deviation from the base value.

Figure 30 shows that amongst all the input variables, the only three variables that majorly affects the NER of algal bio-jet fuel production are, additional lipid purification process, centrifuge power and lipid recover efficiency. The inclusion of a lipid purification step prior to upgrading increases the NER of algal bio-jet fuel production by 0.2 relative to the base case. As the NER is calculated from the energy usage, it is not unexpected that the centrifuge power consumption and lipid recovery efficiency rate influences the NER ratio. Lipid recovery efficiency has the greatest impacts on the NER such that at 80% lipid recovery efficiency, the NER decreases by 51%.

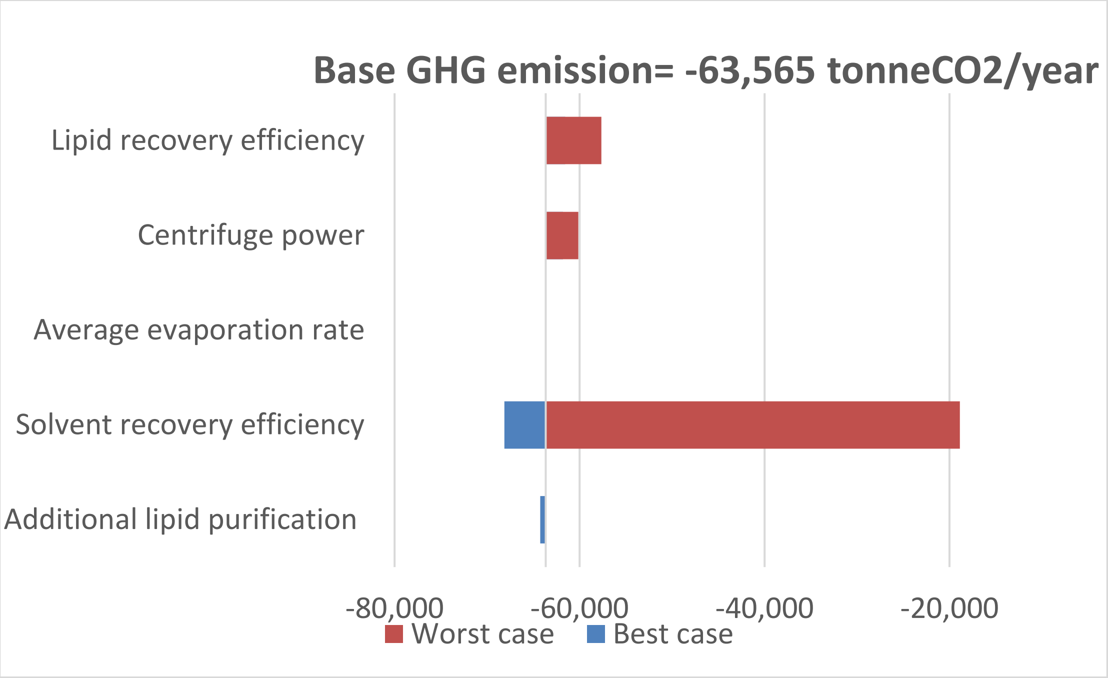


Figure 31: Tornado plot showing sensitivity on GHG emission associated with algal bio-jet fuel production on several input variable. The horizontal axis values indicates the deviation from the base value.

Figure 31 shows that amongst all the input variables, three variable majorly affects the GHG emission rate associated with algal bio-jet fuel production; solvent recovery efficiency, lipid recovery efficiency and centrifuge power. At a lower solvent recovery efficiency, more solvent purchase is necessary to make-up the required quantity, this increase in purchased solvent necessary for lipid extraction means the GHG emission rate associated with the production of solvent increases. Pumping of the solvent also contributes to the energy consumption rate, which in turn influences the GHG emission rate. Furthermore, since the GHG emission rate includes that associated with the raw material required throughout the algal bio-jet fuel production stage, it is expected that raw materials emitting higher GHG during their production have a negative impact on overall GHG emission rate when their quantity is increased in the production stage.

On the other hand, a lower lipid recovery efficiency positively affects the GHG emission rate in comparison to a higher recovery efficiency rate at 98%. A reason for this is that at a lower recovery efficiency, more algal biomass is required to meet the bio-jet fuel target quantity thus the pumping energy increases. Although, this increase of GHG because of increasing energy requirement is not significant to counter the GHG credit arising from the anaerobic digestion and the cultivation growth process, which increases with algal biomass quantity.

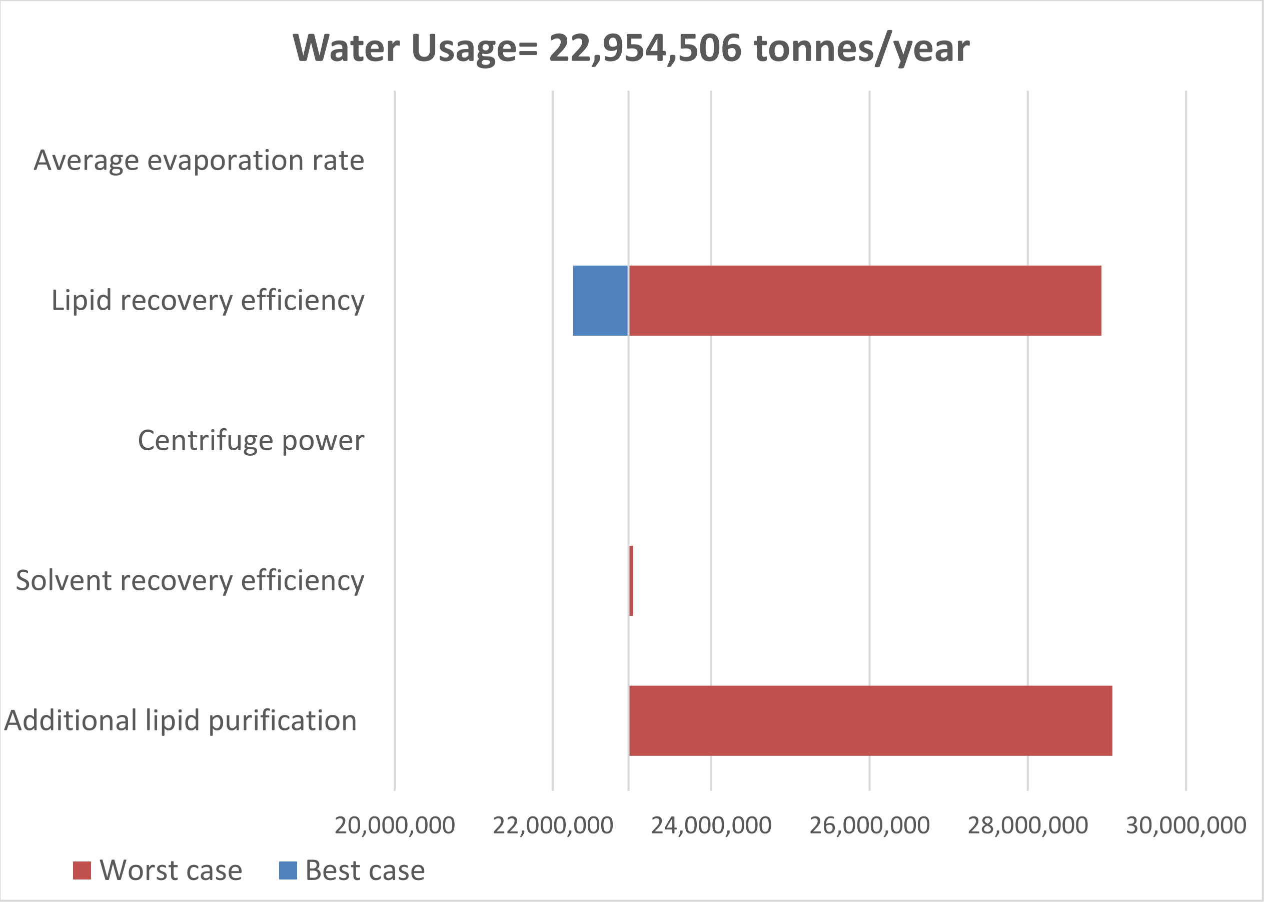


Figure 32: Tornado plot showing sensitivity on water usage associated with algal bio-jet fuel production on several input variable. The horizontal axis values indicates the deviation from the base value.

Figure 32 shows that amongst all the input variables only lipid recovery efficiency and additional lipid purification majorly affects the water usage rate associated with algal bio-jet fuel production. A lower lipid recovery efficiency negatively affects the water usage rate in comparison to a higher recovery efficiency rate at 98%. A reason for this is that at a lower recovery efficiency, more algal biomass is required to meet the bio-jet fuel target quantity thus more fresh water is required. At a lower lipid recovery efficiency of 80% in comparison to the base case percentage, an additional 5.97 million tonnes of water/year is required.

From all the tornado plot results, lipid recovery efficiency is shown to be the most influential variable on MFSP, NER, GHG emission and water usage rate. Based on these finding, careful consideration is necessary to ensure that as much of the algal lipid as possible is extracted; this is where technology plays an influential role as discussed in chapter 3.

## 6.4 Case Scenarios

In addition to the sensitivity analysis, a number of alternative case scenarios were also evaluated. There are three major different cases scenarios; fresh water reduction case, NER and GHG emission reduction case and MFSP reduction case. The purpose of the case scenarios is to identify and evaluate potential ways in which the algal bio-jet fuel production process can be more attractive both economically and environmentally.

### 6.4.1 Fresh water reduction case

In this section, scenario(s) for potential water usage/requirement reduction are investigated. Some influential variables were discovered by the sensitivity analysis; other possible scenarios are investigated outside that already reported in the sensitivity analysis to establish the extent of fresh water usage reduction.

#### *6.4.1.1 Wastewater usage and water recycle*

Based on the model results, the cultivation stage was identified earlier as the major water user in comparison to other downstream processes. Even in biodiesel production microalgae cultivation still poses to be the most water intensive process

(Farooq et al., 2015). The idea of water recycling and wastewater as a means to reduce water demand is not a new idea albeit it is not without disadvantages.

Water recycle occurs by continuous re-use of culture medium, although 100% water recycling is almost impossible even under highly optimised operation. Water is lost due to evaporation and also during harvesting and dewatering, in addition, a large quantity of unused nutrient is lost in the absence of water recycle.  It is expected that water recycling after biomass harvesting is necessary to reduce water and nutrients demand, which is vital for long-term sustainability of algal bio-jet fuel.

An example of a disadvantage that may result from water and nutrient recycling is that recycling can concentrate toxic contaminants such as metals or unidentified metabolic as well as particulate matter and increase in salinity over time (Borowitzka, 2005). Studies on reuse/recycling of culture medium following the cultivation of microalgae shows that recycling can influence both the quantity and quality of biomass. On one hand, the growth of marine microalgae *Nannochloropsis sp*. has been reported to decrease during the reuse of recycled water (Rodolfi et al., 2003) whilst on the other, the growth of microalgae, *Chlorella vulgaris* was not inhibited even after 63 days of water recycling (Hadj-Romdhane et al., 2013).

Based on the seasonality and location analysis, it is concluded that Kota Kinabalu is a more suitable locations for algal cultivation. Kota Kinabalu is the capital of Sabah, which is one of the largest palm oil producing state within Malaysia, and thus palm oil mill effluent (POME) is produced in abundance. In addition, Sabah has several power plants producing flue gas. As discussed in Chapter 2, several studies revealed that microalgae cultivation can be integrated with wastewater and industrial sources of carbon dioxide.

The results for which wastewater was used in replacement of fresh water and the nutrient N and P are shown in table 36. It is assumed that wastewater use does not influence or affect the productivity of both algal biomass and lipid and is obtained at no additional purchase cost. The wastewater source, POME, is assumed and subjected to primary and secondary clarification and incurs additional capital cost. Clarifier cost is estimated at $59,500($2010) for a 1000m$^3$ capacity for which a 62 million liter/day rate requires 5190 m$^3$ clarifier (Lundquist et al., 2010).

Table 36**:** Effect of water recycle and wastewater on water usage and MFSP of algal bio-jet fuel.

| | **Base case** | **Water recycle (90%)** | **Wastewater + pre-treatment + 90% recycle** |
|---|---|---|---|
| Total water Usage, L of water/L of bio-jet fuel | 2,701 | 276.71 | 276.71 |
| MFSP, $/L | 5.89 | 4.94 | 4.29 |

As shown in Table 36, it is evident that reclaiming and reuse of water at a ratio of 0.9 decreases water usage greatly by more than 75%. This extent of water usage reduction is within the same range of 3.81-149L of water/L of biofuel as documented by Yang et al. (2015) and Lardon et al. (2009).

In addition to water usage reduction, water recycling and wastewater use also positively influences the MFSP. In the case of water recycle alone, the MFSP decreases slightly by $0.95/L whilst with wastewater use and recycle the MFSP decreases by $1.60/L. The case with wastewater not only saves cost from fresh water purchase but also on nutrient, nitrates and phosphorus but also based solely on the assumptions that wastewater if freely obtainable. Also the additional cost for pre-treatment does not discourage the use of the reclaimed growth medium for new cultures and encourages pre-treatment for water recycle to avoid environmental issues that arise with discharging large volumes of nutrient rich water.

### 6.4.2 GHG and NER emission reduction case

In this section, scenario(s) for the potential reduction of GHG emission rate and NER are investigated. Some influential variables were revealed by the sensitivity analysis; in this section, other possible scenarios outside that already reported from the sensitivity analysis is investigated.

#### *6.4.2.1 Anaerobic digestion*

This section presents a more detailed analysis into the inclusion of an anaerobic digestion stage in the algal bio-jet fuel production stage and if its inclusion is justifiable. Anaerobic digestion is not essential to the manufacture of algal bio-jet but was included in the proposed bio-jet fuel manufacturing process as a means to recover the energy from the residual algal biomass. Here it is shown the economic implication as well as the GHG and energy profile of having an anaerobic digestion stage compared with the absence of it. A new scenario to represent the "No Anaerobic Digestion stage" is introduced in which several input parameters are adjusted or annulled. The input parameters for the capital and operating cost for anaerobic digestion were set at zero; findings are reported in table 37.

Table 37: Impact of anaerobic digestion step on the economics, NER, GHG emission associated with the production of algal bio-jet fuel.

| | **Anaerobic digestion (Base case)** | **No Anaerobic digestion with residual biomass sale** | **No Anaerobic digestion without residual biomass sale** |
|---|---|---|---|
| MFSP of bio-jet fuel,$/L | 5.87 | 5.34 | 5.83 |
| GHG emission, tonnes$CO_2$/yr | -63,656 | -62,896 | -62,896 |
| NER | 3.87 | 3.70 | 3.70 |

Based on findings in table 37, it appears that the anaerobic stage inclusion in the algal bio-jet fuel process is not economically justifiable. There is a 0.04$/L reduction on the MFSP for the case without sale of the residual lipid extracted biomass when compared to the base case value. Whilst the inclusion of an anaerobic digestion stage favors a higher NER and more capture of $CO_2$, the difference is not substantial enough to justify the capital investment required for anaerobic digestion.

It is important to note that for the base case, the residual algal lipid extracted biomass is converted into biogas to produce heat and power. The cost credits from the energy generated are added and the model is run to determine the MFSP. Whilst for the cases without anaerobic digestion, no biogas is produced instead the residual algal lipid extracted biomass is assumed to be saleable as a co-product.

### *6.4.2.2 Membrane filtration*

This section presents a more detailed analysis into the inclusion of membrane filters prior to centrifugation in the harvesting and dewatering stage of algal bio-jet fuel production and if its inclusion is justifiable.

Table 38**:** Impact of prior membrane filtration on the economics, NER, GHG emission associated with the production of algal bio-jet fuel.

| | **Base case** | **Centrifugation @ 0.95kWh/m$^3$ without prior membrane filtration** | **Centrifugation @ 2.5kWh/m$^3$ without prior membrane filtration** | **Centrifugation @ 5kWh/m$^3$ without prior membrane filtration** |
|---|---|---|---|---|
| Harvesting and dewatering energy input MJ/year | 4,665,252 | 77,494,018 | 203,896,329 | 407,771,024 |
| NER | 3.87 | 2.54 | 1.58 | 0.99 |
| GHG emission, tonnes$CO_2$/yr | -63,656 | -48,769 | -22,986 | 18,599 |
| MFSP of bio-jet fuel,$/L | 5.89 | 7.18 | 7.61 | 8.31 |

The results in table 38 shows the inclusion of membrane filtration process prior to centrifugation greatly affects NER, MSFP and GHG emission positively. Without prior membrane filtration (to remove majority of the water), the centrifugation process is left to remove all the water required to achieve a desired concentration of 27wt.% TSS which is rather energy intensive. Inclusion of membrane filtration reduces energy requirement by 93% and is expected, since the harvesting and dewatering stage accounts for majority of the energy requirement required for algal bio-jet fuel production (without prior membrane filtration). The energy consumption of centrifuge varies greatly as discussed in the Chapter 2; the energy consumption of 0.95kWh/m$^3$ of water removed was used as the base case value. At a centrifuge power consumption at 5kWh/m$^3$ of water removed (without prior membrane filtration), the

NER is shown to be below the minimum threshold for long-term sustainability of 1.0 whereby more $CO_2$ is released than taken up. The GHG emission rate remains negative without prior membrane filtration but at a lesser abatement rate of 14,887 tonnes $CO_2$ per year. Centrifuges are more expensive than membrane filters processing the same capacity, in the absence of membrane filters, which removes majority of the water during dewatering, there will be more purchase of centrifuge thus leading to a higher capital cost. In addition to the high capital cost is the operating cost, which increases with increasing energy consumption. Without prior membrane filtration, the MFSP increases by 1.29$/L, a significant increase.

### 6.4.3 Competitive MFSP of bio-jet fuel

In this section, scenario(s) with potential of decreasing the MFSP of algal bio-jet fuel from the base case value of $5.89/L ($22.29/gallon) are examined. The competitive market price of jet fuel is $1.64/gallon (based on 2015 average price) which is almost 14 times cheaper than the based case value. Four potential cases are investigated and compared with the base case value. Whilst economics is the main focus in this section, the other factors (GHG emission rate, energy and water usage) are also included.

The most influential variable from the sensitivity analysis in addition to two other variable, algal lipid fraction and average algal lipid productivity are also investigated in Figure 33 and 34 to determine the extent of their impact on MFSP.

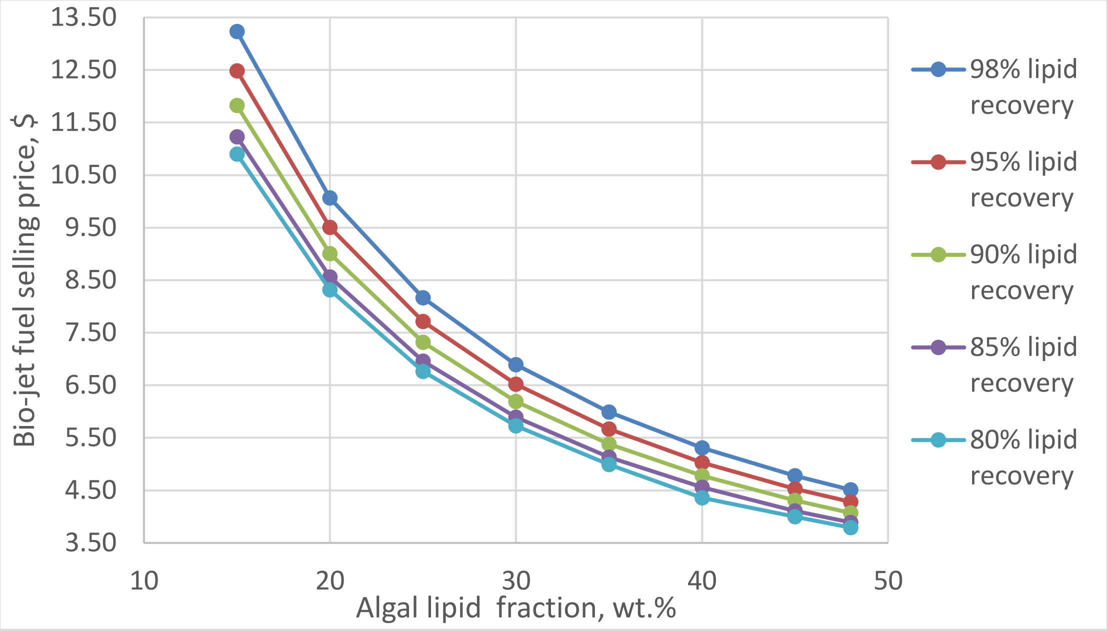


Figure 33: Bio-jet fuel selling price as a function of algal lipid fraction at varying lipid recovery efficiency.

Based on the sensitivity analyses results, the lipid recovery efficiency was the most influential variable. The lipid fraction of the algal biomass was assumed as 30wt.% based on the literature reported range for *Chlorella* cultivated in Malaysia. The lipid fraction of the algal biomass is varied from 15wt.% to a maximum reported value of 48wt.% to determine its impacts on the MFSP. Figure 33 shows the impact of MFSP at varying algal lipid fraction and lipid recovery efficiencies, the MFSP is lowest at $3.79/L when algal lipid fraction is 48wt.% and lipid recovery efficiency at 98%. Whilst the MFSP is highest at $13.23/L when the algal lipid fraction is 15wt.% and lipid recovery efficiency at 80%. Algal lipid fraction and lipid recovery efficiency both defines the yield of bio-jet fuel, the higher the algal fraction the higher the potential yield of bio-jet which greatly influences the MFSP.

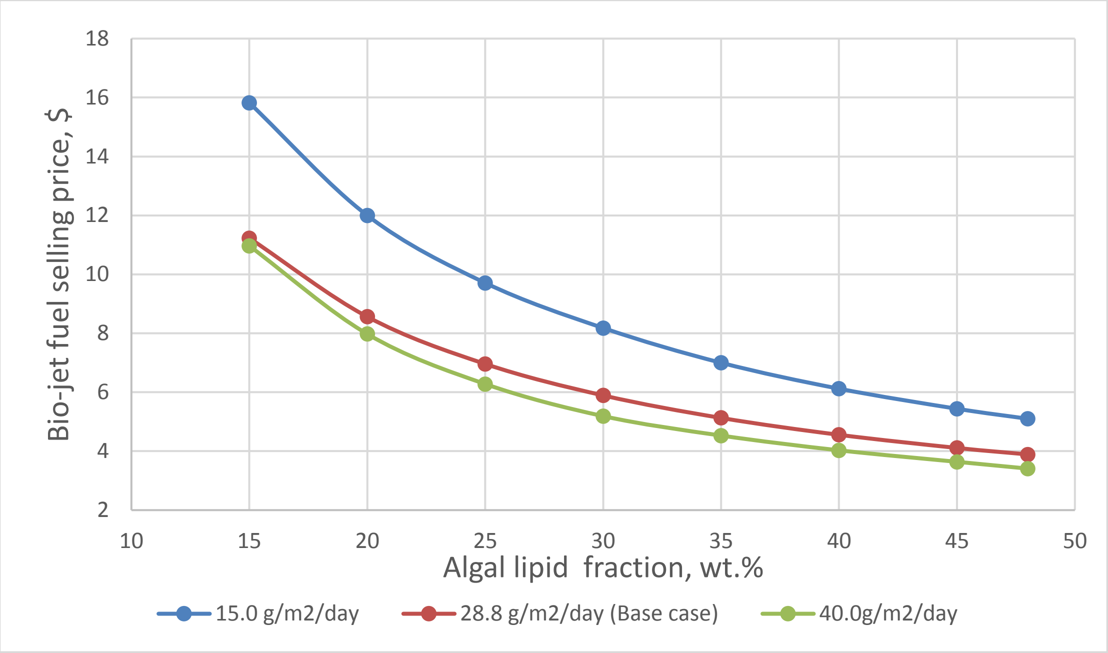


Figure 34: Bio-jet fuel selling price as a function of algal lipid fraction at varying average algal biomass productivity at fixed lipid recovery efficiency at 95%.

Figure 34 shows the impact of MFSP at varying algal lipid fraction and average algal biomass productivity, the MFSP is lowest at \$3.41/L when algal lipid fraction is 48wt.% and average algal biomass productivity at 40g/m$^2$/day. The MFSP is highest at \$15.82/L when the algal lipid fraction is 15wt.% and average algal biomass productivity is 15g/m$^2$/day. The lowest MFSP is achieved at 40g/m$^2$/day productivity when lipid recovery efficiency is 95% and algal lipid fraction is 48wt.%.

Table 39: Case scenario to achieve target MFSP at \$0.43/L (\$1.64/gallon)

|  | **Production cost, \$/L** | **MFSP of bio-jet fuel, \$/L** | **GHG emission, kgCO$_2$/L of bio-jet fuel** | ***Water Usage, kg/ L of bio-jet fuel** | **NER** |
|---|---|---|---|---|---|
| Case 1 (Base case)<br>- 30% algal lipid content , 95% recovery<br>- Anaerobic digestion included<br>- Purchase of water, No recycle<br>- Purchase of nutrient; N and P<br>- Purchase of CO$_2$<br>- Model calculated productivity @ 28.8 g/m$^2$/day | 2.98 | 5.89 | -7.49 | 2701.53 | 3.87 |
| Case 2<br>- 30% algal lipid content, 95% recovery<br>- Anaerobic digestion included<br>- Purchase of water and 90% recycle<br>- Purchase of nutrient; N and P<br>- Purchase of CO$_2$<br>- Model calculated productivity @ 28.8 g/m$^2$/day | 2.25 | 4.94 | -7.49 | 270.05 | 3.87 |

| | | | | | |
|---|---|---|---|---|---|
| Case 3<br>- 48% algal lipid content, 98 % lipid recovery<br>- Wastewater used<br>- No purchase of nutrient; N and P<br>- Purchase of $CO_2$<br>- Anaerobic digestion included<br>- Model calculated productivity @ 28.8 $g/m^2/day$ | 1.56 | 3.45 | -4.28 | 9.24 | 4.98 |
| Case 4<br>- 48% algal lipid content, 98 % lipid recovery<br>- Wastewater used<br>- No purchase of nutrient; N and P<br>- No purchase of $CO_2$<br>- Anaerobic digestion included<br>- Model calculated productivity @ 28.8 $g/m^2/day$ | 1.28 | 3.08 | -4.28 | 9.24 | 4.98 |
| Case 5<br>- "Best case" value in table 35<br>- 48% algal lipid content, 98 % lipid recovery<br>- Wastewater used<br>- No purchase of nutrient; N and P<br>- No purchase of $CO_2$<br>- No anaerobic digestion process<br>- Assumed productivity @40$g/m^2/day$ | 0.57(0.41) | 2.09(1.31) | -4.51(-5.04) | 8.83(9) | 5 |

*excluding wastewater

The base case is represented as case 1 in table 39, characteristics of the base case and other cases investigated are briefly highlighted in the table. For cases 3, 4 and 5, freely obtainable wastewater is assumed as the source of water supply for the cultivation process, which undergoes clarification prior to distribution. From case 1 to 5, variables (based on the sensitivity analysis and the results from graph 37 and 38) that improves the MFSP are adjusted which leads to a gradual decrease in MFSP from case 1 to 5 such that MFSP in case 5 is the lowest achievable.

Comparing case 1 and 2, the MFSP differs by \$0.95/L. A lower MFSP in case 2 is achieved by recycling 90% of the water, whilst this results in a lower MFSP it is still much larger than the competitive MFSP rate of \$0.43/L. By adjusting the algal lipid fraction, lipid recovery efficiency and by introduction of freely obtainable wastewater and nutrient N and P in case 3, a lower MFSP at \$3.45/L is achievable but still not low enough to be competitive. An assessment by Lundquist et al. (2010) on different scenarios of algae based wastewater treatment integrated with biofuel production, concluded that the near-term outcome for large scale algae biofuels production is not promising without wastewater treatment integration. Another review by Pittman et al. (2011) on the potential of algal biofuel production concluded that, based on current technologies, algae cultivation for biofuels without the use of wastewater is unlikely to be economically viable or provide a positive energy return. The results presented in table 39 provides tangible values that supports these concluding statements, as shown from the result, the use of wastewater greatly decreases the MFSP.

In case 4, the $CO_2$ is assumed to be freely obtainable from flue gas from a nearby facility, detailed information about flue gas distribution, layout $CO_2$ source location and pipeline economics are however not emphasized in this assumption. Even with such an optimistic assumption of obtaining wastewater and flue gas at no purchase cost, the MFSP reduction rate is still not low enough to the target value.

In case 5, the most optimistic values for the variables are inputted into the process model to determine the lowest possible MFSP achievable, are representative of case 5. The lowest MFSP was \$1.31/L, which is \$0.88/L higher than the market price and \$4.58/L lower than the base case value. Whilst even for the most optimistic case, bio-jet fuel produced from micro-algal biomass cannot compete with fossil derived jet fuel; several factors were identified to significantly improve the MFSP. Lipid recovery efficiency, algal productivity and algal lipid fraction are the top three most influential factors on the MFSP based on the sensitivity analysis and case scenario results. All three variables each affects the quantity of available lipid required for conversion to bio-jet fuel. Lipid recovery efficiency is highly determined by the technology used in the extraction process whilst the algal lipid fraction and biomass productivity is determined by cell biology, cultivation technology and climatic conditions.

## 6.5 Conclusion

Some of the result from the constructed process model are shown to be within reasonable range reported in literature, therefore validating certain aspects of the process model. The results showed the model estimate for the base case MFSP is more than 13 times greater than the market-selling price of fossil derived jet fuel. The GHG emission rate associated with the production process is at a negative; more $CO_2$ taken in than emitted. The NER is estimated to be $> 1$ and showed more potential energy is produced than utilized. The fresh water requirement was however very high. The sensitivity analyses performed identified algal lipid recovery efficiency as the most influential parameter on the MFSP, GHG emission rate, water usage and NER. In addition, further analysis showed biomass productivity and algal lipid content significantly influences the MFSP.

An additional membrane filtration process prior to centrifugation greatly reduces energy consumption and thus overall economics in comparison to centrifugation alone. Fresh water demand is reduced greatly by use of wastewater and by water recycling. Kota Kinabalu was shown to be a more suitable location for micro-algal production due to it higher solar irradiance, which improves algal areal productivity. Based on the results from the case scenarios it is established that even with great improvements on the economics; utilization of freely available $CO_2$ and wastewater, cheaper purchase cost of raw material, maximum algal lipid content and high productivity, the algal derived jet fuel cannot yet be offered at a competitive price when compared with fossil derived jet fuel. Overall, the production of micro-algal bio-jet fuel is environmentally sustainable but not yet economical, in terms of profitability.

# 7 CONCLUSION AND FUTURE WORK

This section of the thesis concludes the entire research work and makes suggestions for further future work.

## 7.1 Overview

The main purpose of this research work was to assess the economic as well as the environmental state (GHG, NER and water footprint) of micro-algal bio-jet fuel production in Malaysia. For the analysis and evaluation of the techno-economic state of micro-algal bio-jet fuel production, the following performance metrics, NER, MFSP, GHG emission and water usage are used.

The NER was defined as the ratio of outside energy required to release useable energy from microalgae. It determines if the energy created by the proposed system is more than the energy it uses. As $CO_2$ emission reduction is one the main catalyst for alternative biofuels exploration, information on the carbon dioxide emission associated with the production of microalga bio-jet was necessary. If biofuel production is not economically viable it will have a lesser chance of investment in comparison to an economically viable alternative, fossil derived fuel. Cost was therefore another factor which was included as a performance metrics. Cost track by means of the MFSP of bio-jet fuel allowed for comparison with market price alternative.

A process model was constructed and allowed for the energy consumption, associated GHG emission, water usage, operating and capital cost of the major process stages (i.e. cultivation, harvesting and dewatering). Prior to model construction an initial investigation, which compared some of the technologies/methods required for bio-jet fuel production was carried out. A base case scenario was established based on this investigation and formed the foundation of the process model.

## 7.2 Research findings, contributions and limitations

The work done in this research allows for the methodically evaluation of the effects of process technologies/methods, substitute micro-algal strain, location condition and raw material and resource on the economic and environmental performance of micro-algal bio-jet fuel production on a commercial scale. This was achievable by means of process modelling.

Based on the economic results from the model base case, production of bio-jet fuel from microalgae in Malaysia is not yet economically viable and cannot produce fuel at a competitive market price. Large-scale production of algal biofuel at 8.5 million litres per year requires huge initial investments, estimated at \$85.3 million (RM332.67 million) based on current technologies.

In terms of environmental sustainability, GHG emission associated with the production process is favorable, there is more $CO_2$ taken up than emitted. The Net energy ratio of bio-jet fuel production was also promising and greater than the sustainability threshold of 1, without co-product credits included.

By further analysis of detailed contributions breakdown, main drivers of NER, GHG, cost and water usage was identified. An additional membrane filtration process prior to centrifugation greatly reduces energy consumption and thus production cost. Solvent, particularly hexane used in the cell disruption and extraction stage contributed significantly to the high GHG emission rate. In addition, raw materials cost such as solvent, $CO_2$ and fresh water contributed majorly to the operating cost whilst the harvesting and dewatering process contributed most to the capital cost.

Sensitivity analysis indicated that lipid recovery efficiency is one of the most influential parameter and significantly influences the NER, GHG, cost and water usage for micro-algal bio-jet fuel production. Further case scenario studies in addition to the sensitivity analysis showed algal lipid content and algal productivity significantly influences the MFSP. Lipid recovery efficiency is highly determined by the technology used in the extraction process and is seen as an example of how technology influences process economics. Cell biology, cultivation technology and climatic conditions also influences algal lipid fraction and biomass productivity, which in turn influences the process economics.

An optimistic case scenario that assumes optimistic alternatives including utilization of free $CO_2$ and wastewater, revealed the lowest possible MFSP achievable was

$1.31/L, which is $0.88/L higher than the competitive market price and $4.58/L lower than the “base case” value in this study. There are currently no published studies, which reports a minimum selling price (MFSP) of algal bio-jet fuel at a competitive rate with conventional jet fuel at $0.43/L. The lowest achievable MFSP recorded in literature for algal bio-jet fuel based on an “optimistic case” is $2.42/L and $8.45/L based on the “base case” (Klein-Marcuschamer et al., 2013).

Some of the reasons that attributed to a lower MFSP in comparison to that reported in literature includes the algal strain of study, location, and choice of process technology. This study reveals how algal strain choice is an important aspect to consider when attempting cutting cost because each algal strain has different characteristic such as high lipid content and high growth rate, which from the models results significantly influences the MFSP. In addition, it showed how location is also a factor that influences algal biomass areal productivity that in turn influences the MFSP. Location also influences labor cost, which is shown from the model results to constitute 4.3% of the overall production cost. Model results from the case scenario also showed how choice of technology impacts process economics, for example centrifugation with prior membrane ultrafiltration is established to be more cost effective than centrifugation alone.

In addition, the case scenario results suggests that algal bio-jet fuel production plant will benefit from co-location with wastewater treatment plant and flue gas producing sites in Kota Kinabalu, Malaysia, although evidence to back up the assumption of obtaining wastewater and flue gas at no additional cost is required.

Whilst the analysis and results revealed important trends and sensitivities, the numerical values predicted by means of modelling and simulation are not without limitations. The scarcity of significant data on large-scale cultivation and processing of algal biomass as well as conversion to bio-jet fuel resulted in several assumptions during model construction and cost estimates that affects the degree of accuracy of the numerical results presented, particularly the MFSP. When a process plant is much closer to construction an estimate of +5%/-5% accuracy is required, this study however has an estimate of +20%/-15% accuracy.

## 7.3 Future work

The economic and environmental assessment reported in this research was achieved by means of deterministic modelling in which the output of the model is fully determined by the parameter values and the initial inputs. The modelling method does not allow for estimation of inherently random or uncertain input values.

Most input values was selected based on reported literature and experimental range value. But in reality the input values are random by nature. Several assumptions was also made to allow possible progression during modelling. To tackle the uncertainty nature of the model, Monte Carlo sampling method can be employed in addition to developed mathematical models that are able to predict relationships between key input parameters.

Some relationships includes:

- Effect of nutrients limitation or otherwise( N,P,K) on lipid content
- Effect of light intensity on lipid content
- Effect of cell wall properties on cell disruption and extraction extent
- Effect of wastewater nutrients on algal growth rate and lipid content

All of which will require extensive experimental data at a larger scale. Additionally, experimental works on algal lipid upgrading to bio-jet fuel conversion are also necessary for the development of solid mathematical models to predict bio-jet fuel yields from algal lipid. Another additional work that can be done is to enhance the model to allow the economics, GHG emission and water usage of other alternative technologies and algal strains to be evaluated too. This will be a complex task to undertake and requires yet more data which is yet unavailable. In this study, only the base case technologies discussed in the initial investigation documented in chapter 3 was included in the process model.

Micro-algal lipid content, areal productivity and lipid recovery efficiency based on the results in this study are highly influential variables. Biological advancement particularly in the area of high lipid induction and productivity are necessary and capable of influencing both the environmental and economic aspects of micro-algal bio-jet fuel production as demonstrated from the results in this study. Experimental data that characterises the fraction of lipid suitable for conversion to bio-jet fuel are also necessary to update the yield fraction assumption made in this study.

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# 9 APPENDICES

## 9.1 Appendix A: Literature review yields estimate

For the biomass-oil to bio-jet fuel pathway, the oil content of the algal oil is up to 75% where the intermediate product is algal lipid, up to 64% for the HTL oil and up to for pyrolysis oil(Demirbas, 2011; Ross et al., 2010). In the algal lipid case, It is assumed that 92% of this oil is usable triglyceride for biofuel production and 95% yield of oil is obtainable after extraction from the algal biomass (Abhari et al., 2011; Sheehan et al., 1998). After hydro-isomerization and hydrocracking reaction, it is assumed up to 50 wt.% jet fuel ($C_9$-$C_{15}$) is produced (Murata et al., 2014). In the HTL case, it is assumed that 80% yield of the hydrotreated HTL oil and up to 50wt.% jet fuel ($C_9$-$C_{15}$) is obtainable. In the pyrolysis case, it is assumed that 44 wt% of the pyrolysis oil is convertible to stable oil and that up to 50 wt% of the stable oil is converted into jet fuel (Elliot, 2012; Olarte et al., 2011). In the biomass-alcohol to bio-jet fuel pathway, the starch content is up to 53% of dry algal biomass of which up to 65% is converted to alcohol. It is assumed that 65% of the alcohol is converted to hydrocarbon and 80% conversion of the hydrocarbon to bio-jet fuel (Gevo,2016).

## 9.2 Appendix B: Indices, exchange rate and factors

Table 40: Producer price cost indices (Source: Bureau of Labor Statistics)

| Year | Index |
|---|---|
| 2011 | 107.78 |
| 2012 | 110.16 |
| 2013 | 110.51 |
| 2014 | 111.41 |
| 2015 | 105.76 |

Table 41**:** Capital cost indices (Source: Chemical Engineering Magazine, annual index)

| Year | Index |
|---|---|
| 2004 | 444.2 |
| 2005 | 468.2 |
| 2006 | 499.6 |
| 2007 | 525.4 |
| 2008 | 575.4 |
| 2009 | 521.9 |
| 2010 | 550.8 |
| 2011 | 585.7 |
| 2012 | 585.7 |
| 2013 | 567.3 |
| 2014 | 576.1 |
| 2015 | 543.0 |

Table 42**:** Exchange rate euro to dollars (Source: XE currency converter)

| Year | Rate (euro to USD) |
|---|---|
| 2015 | 1.15 |
| 2011 | 1.34 |
| 2007 | 1.37 |

## 9.3 APPENDIX C: Specific growth parameters

Table 43: Specific growth equation variables with input values

| **Specific growth rate Parameters** | **Symbol** | **Input values** | **Unit** | **Formula** |
|---|---|---|---|---|
| Specific growth rate | $\mu$ | calculated | day$^{-1}$ | $\mu=Pc-rRc-\xi*rN$ |
| Carbon specific rate of reaction | Pc | calculated | h$^{-1}$ | $Pc= Pc\_calc*(1-exp[(-\alpha*\Phi m*Eav/Pc\_calc)])$ |
| Maintenance respiration rate | rRc | 0.0004-0.025 | h$^{-1}$ | |
| Specific uptake of nitrogen | rN | calculated | h$^{-1}$ | $rN= (rN\_calc/qN,X)-rRN$ |
| Calculated specific uptake of nitrogen | rN_calc | calculated | h$^{-1}$ | $rN\_calc=rNmax *\Phi qN,Xint *\Phi qNext *\Phi T$ |
| Biosynthetic efficiency | $\xi$ | 4 | g/g of biomass | |
| Calculated maximum photosynthetic rate(carbon) | Pc_calc | calculated | h$^{-1}$ | $Pc\_calc= Pc\_max* \Phi_T*\Phi qNX_{int}$ |
| Maximum photosynthetic rate(carbon) | Pc_max | calculated | h$^{-1}$ | $Pc\_max= (\mu max + Rc)/(1-\xi*qNXmax)$ |
| Absorption coefficient | $\alpha$ | 0.0752 | m$^2$/g | |
| Photon efficiency | $\phi_m$ | calculated | g(µmolphotons)$^{-1}$ | $\Phi m=(Pc\_max)/(\alpha*E_k)$ |
| Light saturation level | $E_k$ | 274 | µmolm$^{-2}$s$^{-1}$ | |
| Average light intensity in the photo bioreactor | $E_{av}$ | calculated | µmolm$^{-2}$s$^{-1}$ | $Eav= (Ein (1-e^\wedge(\alpha*cXdw*B)))/(\alpha*cXdw*B)$ |
| Reactor thickness | B | 0.05 | m | |
| Light intensity entering the photobioreactor | $E_{in}$ | 240-650 | µmolm$^{-2}$s$^{-1}$ | |
| Initial biomass concentration of algae in the reactor | cXdw | 1 | g/L | |
| Temperature efficiency factor | $\phi T$ | 1 | | |

| | | | | |
|---|---|---|---|---|
| Uptake of internal nitrogen concentration efficiency | ϕqN,Xint | calculated | - | ΦqN,Xint =(1- qN,Xmin)/(qN,X) |
| Maximum growth rate | $\mu_{max}$ | See table 45 | $h^{-1}$ | |
| Respiration rate | $R_c$ | 0.0004-0.0.025 | $gg^{-1}h^{-1}$ | |
| Maximum cell quota of nitrogen in biomass | $q_{N,Xmax}$ | See table 32 | g/g of biomass | |
| Minimum cell quota of nitrogen in biomass | $q_{N,Xmin}$ | 0.0092-0.01 | g/g of biomass | |
| Cell quota of nitrogen in biomass | $q_{N,X}$ | calculated | g/g of biomass | qN,X= qN,$X_0$* e^(rN*t) |
| The cell quota of nitrogen inocula | $q_{N,X0}$ | 0.06 | g/g of biomass | |
| Maximum specific uptake rate of nitrogen | $r_{Nmax}$ | calculated | $gg^{-1}h^{-1}$ | rNmax=Pcmax * qNXmax |
| Uptake of external nitrogen concentration efficiency | $\Phi_{qNext}$ | calculated | - | ΦqNext = (cNmedium)/( cNmedium+$K_N$ ) |
| Nitrogen concentration in medium | $cN_{medium}$ | 0-0.07 | g/L | |
| Half saturation constant for nitrogen uptake | $K_N$ | 0.005 | g/L | |
| Respiration constant of nitrogen | $rR_N$ | 0 | $h^{-1}$ | |

Table 44: Composition of some microalgae strain

| **Strain type** | **Lipid (% by dry cell weight)** | **Prote*in* (% by dry cell weight)** | **Carbohydrate (% by dry cell weight)** |
|---|---|---|---|
| Chlorella vulgaris, | 11-63 | 7-38 | 11-55 |
| Spirulina | 4-7 | 46-71 | 8-16 |
| Scenedesmus dimorphus, | 16-40 | 8-18 | 21-52 |
| Nannochloropsis | 9-62 | 23-59 | 5-17 |

Sources: Sakthivel et al., 2011; Frank et al., 2011; Hu and Gao, 2006

Table 45**:** Maximum growth range and maximum cell quota of nitrogen for Chlorella and Nannochloropsis based on table 44

| **Strain type** | Maximum growth rate, $\mu_{max}$(day$^{-1}$) | Maximum cell quota of nitrogen, $qNX_{max}$(g/g of biomass) |
|---|---|---|
| *Nannochloropsis* | 0.34-0.56 | 0.05-0.12 |
| *Chlorella* | 0.13-3 | 0.01-0.08 |

Below explains each growth parameter used in the growth rate prediction shown in table 60.

1. $\mu$ is the specific growth rate, the rate at which the microalgae grows over a time period.
2. $P_c$ is the carbon specific rate of the reaction and is dependent on the light intensity, light absorption and the efficiency of the using photons.
3. $rR_c$ is the maintenance respiration rate and is defined as the respiration needed to provide the energy for all plant processes that do not result in a net increase in plant dry matter, (Chiariello et al., 1989). In models, it is normally

assumed that maintenance respiration rate is proportional to the dry weight of the biomass (Chiariello et al., 1989). It has been documented in literature that the respiration rate of microalgae can vary between 0.01-0.6/day( Geider et al., 1989).

4. $rN$ is the specific uptake of nitrogen that yields the total nitrogen in the biomass
5. rNcalc is the calculated specific rate of nitrogen
6. $\xi$ is the biosynthetic efficiency and accounts for the energy required for the reduction of nitrate to ammonium, assimilation of ammonium into amino acids and polymerisation of amino acid into protein (Geider et al., 1998). The biosynthetic efficiency is taken at 4 g biomass per g nitrogen assimilated based on literature data of 2g of carbon per g of nitrogen and the assumption that the biomass is 50% of carbon (Geider et al., 1998).

   It is noted that the biosynthetic efficiency is expected to depend on the nitrogen source: it will be greater for oxidized forms of nitrogen such as nitrate than for reduced forms such as ammonium or urea.
7. Pc_calc is the calculated carbon specific rate of the reaction.
8. Pc_max is the maximum carbon specific rate of the reaction.
9. $\alpha$ is the absorption coefficient. The absorption coefficient for *Chlorella* strain was determined experimentally at wavelength of 680 nm, 0.0752 $m^2 g^{-1}$ (Sirisansaneeyakul et al, 2011). It is assumed that the variation of the absorption coefficient over the course of a batch is not significant (Quinn et al., 2011).
10. $\Phi_m$ is the Photon efficiency and is assumed for now as 6.5 x $10^{-7}$gCH2O(µmol photons)$^{-1}$.
11. $E_k$ is the light saturation of green microalgae typically occurs at 10% of full sunlight (Fabregas et al., 2004). A light saturation of 274µmol$m^{-2}s^{-1}$ is therefore estimated using 10% of the light intensity at 2742µmol$m^{-2}s^{-1}$. It is assumed that the main source of light is direct sunlight. The average solar radiation in Malaysia is 7192 Wh/$m^2$ with average solar hours of 12hrs (ECOTECT 5.2v - weather) calculated to have a light intensity of 2742µmol$m^{-2}s^{-1}$.

12. $E_{av}$ is the average light intensity in the photobioreactor. Initially, the light strikes the reactor with a constant intensity but when the light is inside the reactor it is converted into photonic energy fuelling the algae concentration to grow. As the light continues to move through the reactor the intensity decreases and when the light passes fully through the photo bioreactor less light exits the photo bioreactor than initially entered ( Jean., 2011).
13. B is the reactor thickness taken as 0.05m.
14. $E_{In}$ is the light intensity entering the photo bioreactor varied at 240-650 µmol$m^{-2}s^{-1}$
15. cXdw is the initial concentration of algae in the photobioreactor.
16. $\Phi_T$ is the temperature efficiency factor which is a dimensionless number between 0-1. Whereby at the optimum growth temperature $\Phi_T$ = 1, and for temperatures higher or lower than the optimum temperature, 0 <$\Phi_T$< 1. (J. Quinn et al).The value of $\Phi_T$ is assumed to be 1.
17. $\Phi_{qN.X_{int}}$ is the uptake of internal nitrogen concentration efficiency and is a dimensionless efficiency factor for the intracellular nitrogen.
18. $\mu_{max}$ is the maximum growth rate obtainable from experimental data recorded in literature. It is a representation of the highest growth rate in the exponential growth phase. (Flynn et al., 1993, Gentile et al., 2001). Values of $\mu_{max}$ as obtained from literature data for chlorella vulgaris.
19. $R_c$ is the respiration rate and is defined as a percentage of the maximum photosynthetic rate. It has been documented in literature that the respiration rate of microalgae can vary between 0.01-0.6/d(0.0004-0.0.025/h) (Geider et al., 1989).Carbon accumulation is the primary process for plant biomass production, and depends both on photosynthesis and respiration (Iersel.,2000).
20. $qNX_{max}$ is the maximum cell quota of nitrogen which is the maximum amount of nitrogen that can be contained in the cell. It can be obtained experimentally and varies with time. Based on the protein content of the chlorella vulgaris it is possible to convert the protein content to a maximum cell quota of nitrogen. In literature, the protein content was divided by a factor of 4.8 this same logic is employed and the maximum cell quota

converts to 0.01- 0.08g nitrogen per g of biomass based on the protein content of *Chlorella vulgaris*. For comparison maximum cell quota recorded in literature are in the ranges of 0.07-0.2g of nitrogen per g of biomass.( Flynn et al.,1993, Quinn et al., 2011, Hu & Gao.,2003).

21. $qNX_{min}$ is the minimum cell quota of nitrogen which is the internal nitrogen level where the cells ceases to grow. The value is assumed to be 0.0092g of nitrogen per g of biomass which falls within the range of the values recorded in literature for the minimum cell quota of nitrogen. (Ambrose et al., 2006, Flynn et al., 1993).
22. The cell quota (qN,X) is defined as the mass of internal nitrogen per total mass of biomass. This quota can be experimentally measured and is time varying. The value for the qN.X will be taken from the ranges between $qNX_{max}$ and $qNX_{min}$.
23. $qN, X_0$ is the cell inocula which are obtainable from a sample of mature harvested culture. The nitrogen content for the inocula is estimated; using the nitrogen to protein conversion factor of 4.8 and the protein content of 30%, to be 0.06.
24. $rN_{max}$ is the maximum specific uptake rate of nitrogen.
25. $\Phi_{qNext}$ is the of external nitrogen concentration efficiency (Gieder et al., 1998, Legovic and Cruzado., 1997).
26. $cN_{medium}$ is the nitrogen concentration in the growth medium.
27. $K_N$ is the half saturation constant for nitrogen uptake. This is the available substrate needed in order for the organism to achieve half its maximum specific growth rate (Cormier., 2010).
28. $rR_N$ is the nitrogen respiration rate and is assigned a value of zero.

## 9.4 APPENDIX D: Stoichiometric equation derivation in Chapter 4

Table 46: Elemental composition of microalgae

| | *Nannochloropsis* | | *Chlorella* | | Used in the model (avg.) |
|---|---|---|---|---|---|
| **Component** | **Wt.%** | **Wt.% ash free** | **Wt.%** | **Wt.% ash free** | **Wt.% ash free** |
| C | 51.9 | 59.10 | 50.2 | 53.76 | 56.43 |
| H | 7.5 | 8.54 | 6.8 | 7.28 | 7.91 |
| O | 22.4 | 25.51 | 24.3 | 26.02 | 25.77 |
| N | 4.8 | 5.47 | 9.8 | 10.49 | 7.98 |
| S | 0.61 | 0.69 | 0.68 | 0.73 | 0.71 |
| P | 0.6 | 0.68 | 1.6 | 1.71 | 1.20 |
| ash | 12.8 | | 8.13 | | |
| Total | 100 | 100 | | 100 | 100 |

Calculating the empirical formula using the new adjusted elemental composition average of both micro-algal strain gives $CH_{1.68}O_{0.342}N_{0.121}S_{0.0047}P_{0.0082}$.

Empirical formula calculation:

(56.4g C ) x ( 1mol C/12.01g C) = 4.7 mol C

(7.9g H ) x ( 1 mol H/1.0g H) = 7.9 mol H

(25.77g O) x (1 mol O/ 16g O) = 1.6 mol O

(8.0g N) x ( 1 mol N/ 14g N) = 0.57 mol N

(0.71g S) x ( 1 mol S/ 32.07 S) = 0.022 mol S

( 1.2g P) x ( 1 mol P/ 30.97 P) = 0.039 mol P

Starting with the equation below with 8 unknowns the equation is balanced using matlab after conversion to a matrix form. The empirical formula for algae is represented as AlgNew

$aCO_2 + bNO_{3-} + cSO_4^{2-} + dHPO_4^{2-} + eH_2O \rightarrow f\, CH_{1.68}O_{0.342}N_{0.121}S_{0.0047}P_{0.0082} + gO_2 + hOH-$

**Table 47:** Reactants and products for equation to be balanced.

| | Reactant | | | | | Product | | |
|---|---|---|---|---|---|---|---|---|
| | $CO_2$ | $NO_{3-}$ | $SO_{4-}^{2-}$ | $HPO_4^{2-}$ | $H_2O$ | AlgNew | $O_2$ | OH- |
| C | 1*a | 0*b | 0*c | 0*d | 0*e | 1*f | 0*g | 0*h |
| H | 0*a | 0*b | 0*c | 1*d | 2*e | 1.68*f | 0*g | 1*h |
| O | 2*a | 3*b | 4*c | 4*d | 1*e | 0.342*f | 2*g | 1*h |
| N | 0*a | 1*b | 0*c | 0*d | 0*e | 0.121*f | 0*g | 0*h |
| P | 0*a | 0*b | 0*c | 1*d | 0*e | 0.0082*f | 0*g | 0*h |
| S | 0*a | 0*b | 1*c | 0*d | 0*e | 0.0047*f | 0*g | 0*h |
| Charge | 0*a | -1*b | -2*c | -2*d | 0*e | 0*f | 0*g | 1*h |

$1a=1f$

$1d+2e=1.8f+ 1h$

$2a+3b+4c+4d+1e=0.4f+2g+1h$

$1b=0.083f$

$1d=0.002f$

$1c=0.0017f$

$3a+4b+5c+5d+3e=3.2867f+2g$

$-1b-2c-2d=-1h$

$h=1$

There are 9 equations including the defined auxiliary equation which was assigned a value of 1 (h=1). The complete system of equations can be written in matrix form as A =X\b, where:

A=

$$\begin{matrix} 1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 2 & -1.68 & 0 & -1 \\ 2 & 3 & 4 & 4 & 1 & -0.342 & -2 & -1 \\ 0 & 1 & 0 & 0 & 0 & -0.121 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & -0.0082 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & -0.0047 & 0 & 0 \\ 0 & -1 & -2 & -2 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{matrix}$$

X =

$$\begin{matrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \end{matrix}$$

b =

0

0

0

0

0

0

0

1

The solution for X is found and shown below

X =

1.0000

0.1210

0.0047

0.0082

0.9093

1.0000

1.4176

0.1468

The balance equation is:

$CO_2 + 0.121NO_{3^-} + 0.0047SO_4^{2-} + 0.0082HPO_4^{2-} + 0.9093H_2O \rightarrow$

$CH_{1.68}O_{0.342}N_{0.121}S_{0.0047}P_{0.0082} + 1.4176O_2 + 0.1468OH-$

Table 48**:** Calculated mass of nutrient components using the relative molecular mass and no. of mols of each component in the balance equation.

| | **$CO_2$** | **$H_2O$** | **OH** | **$NO_3$** | **$SO_4$** | **$HPO_4$** | **Algae Produced** | **$O_2$** | Total (g) |
|---|---|---|---|---|---|---|---|---|---|
| Inlet(g) | 44.01 | 16.38 | | 7.50 | 0.45 | 0.79 | | | 69.13 |
| Outlet(g) | | | 2.50 | | | | 21.28 | 45.36 | 69.13 |

## 9.5 APPENDIX E: Experimental result for *Chlorella vulgaris* (obtained with permission from University of Malaya, Malaysia)

Table 49**:** Biomass and biochemical productivities for outdoor cultivation of *Chlorella vulgaris* UMACC001

|  | Day | Condition | Mean DW (mg/L) | STDEV | Mean Chl-a (mg/L) | STDEV | Biomass Productivity (mg/L/day) | SGR (µ) |  | Mean CHO (%DW) | STDEV | CHO Productivity (mg/L/day) | Mean Protein (%DW) | STDEV | PROTEIN Productivity (mg/L/day) | Mean Lipid (% DW) | STDEV | LIPID Productivity (mg/L/day) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EXPT 1 | 0 | Day 0 | 62.00 | 12.17 | 0.24 | 0.05 | - | - | - | 2.20 | 0.67 | - | 21.00 | 2.12 | - | 20.43 | 1.86 | - |
|  | 7 | AN_LN | 736.67 | 16.07 | 13.64 | 0.22 | 96.38 | 0.578 | D1-D5 | 4.60 | 0.47 | 4.43 | 23.81 | 1.40 | 22.95 | 19.23 | 2.38 | 18.53 |
|  | 7 | AN_HN | 695.00 | 17.32 | 14.88 | 0.08 | 90.43 | 0.632 | D1-D5 | 4.39 | 0.37 | 3.97 | 27.16 | 1.98 | 24.56 | 15.83 | 1.25 | 14.31 |
|  | 7 | HRAP_LN | 493.33 | 32.53 | 13.70 | 0.69 | 61.62 | 0.607 | D1-D5 | 5.23 | 0.33 | 3.22 | 33.63 | 0.50 | 20.72 | 21.96 | 1.17 | 13.53 |
|  | 7 | HRAP_HN | 563.33 | 37.86 | 9.58 | 0.34 | 71.62 | 0.623 | D1-D5 | 7.34 | 0.46 | 5.26 | 27.15 | 1.72 | 19.45 | 19.23 | 0.51 | 13.77 |
| EXPT 2 | 0 | Day 0 | 191.11 | 5.09 | 3.75 | 0.07 | - | - | - | 6.66 | 0.84 | - | 25.76 | 4.16 | - | 19.19 | 1.74 | - |
|  | 7 | AN_LN | 633.33 | 7.64 | 17.10 | 0.35 | 63.17 | 0.288 | D0-D4 | 3.15 | 0.50 | 1.99 | 29.09 | 1.38 | 18.38 | 16.32 | 0.46 | 10.31 |
|  | 7 | AN_HN | 621.67 | 5.77 | 16.15 | 0.28 | 61.51 | 0.231 | D0-D4 | 3.25 | 0.23 | 2.00 | 30.62 | 1.15 | 18.83 | 16.09 | 0.80 | 9.89 |
|  | 7 | HRAP_LN | 585.00 | 18.03 | 14.54 | 0.27 | 56.27 | 0.240 | D0-D4 | 4.85 | 0.27 | 2.73 | 24.58 | 0.36 | 13.83 | 17.38 | 2.15 | 9.78 |
|  | 7 | HRAP_HN | 506.67 | 2.89 | 10.65 | 0.25 | 45.08 | 0.167 | D0-D4 | 3.29 | 0.24 | 1.48 | 27.91 | 1.06 | 12.58 | 20.07 | 2.48 | 9.05 |
| EXPT 3 | 0 | Day 0 | 181.11 | 1.92 | 4.27 | 0.05 | - | - | - | 12.31 | 0.82 | - | 29.76 | 1.03 | - | 17.79 | 1.06 | - |
|  | 7 | AN_HL | 813.33 | 15.28 | 18.34 | 0.64 | 90.32 | 0.301 | D0-D4 | 5.23 | 0.46 | 4.72 | 40.10 | 1.74 | 36.22 | 15.98 | 0.00 | 14.44 |
|  | 7 | AN_LL | 533.33 | 5.77 | 13.55 | 0.48 | 50.32 | 0.236 | D0-D4 | 6.52 | 1.27 | 3.28 | 36.16 | 0.90 | 18.19 | 22.50 | 3.25 | 11.32 |
|  | 7 | HRAP_HL | 816.67 | 20.82 | 18.76 | 0.41 | 90.79 | 0.251 | D0-D4 | 5.43 | 0.92 | 4.93 | 32.23 | 0.46 | 29.27 | 14.29 | 0.71 | 12.97 |
|  | 7 | HRAP_LL | 580.00 | 10.00 | 14.95 | 0.24 | 56.98 | 0.192 | D0-D4 | 6.21 | 1.96 | 3.54 | 33.95 | 0.41 | 19.34 | 17.82 | 1.99 | 10.15 |
| EXPT 4 | 0 | Day 0 | 168.89 | 6.94 | 4.12 | 0.11 | - | - | - | 11.10 | 0.67 | - | 40.89 | 7.62 | - | 19.74 | 1.97 | - |
|  | 7 | AN_HL | 780.00 | 26.46 | 13.61 | 0.24 | 87.30 | 0.301 | D0-D4 | 7.22 | 0.29 | 6.30 | 32.43 | 1.11 | 28.31 | 16.67 | 2.22 | 14.55 |
|  | 7 | AN_LL | 596.67 | 15.28 | 14.17 | 0.09 | 61.11 | 0.231 | D0-D4 | 6.67 | 0.70 | 4.08 | 35.35 | 1.27 | 21.60 | 20.11 | 1.68 | 12.29 |
|  | 7 | HRAP_HL | 706.67 | 15.28 | 16.56 | 0.72 | 76.83 | 0.225 | D0-D4 | 7.30 | 0.31 | 5.61 | 32.75 | 0.28 | 25.16 | 15.09 | 0.82 | 11.60 |
|  | 7 | HRAP_LL | 496.67 | 15.28 | 11.03 | 0.31 | 46.83 | 0.164 | D0-D4 | 9.23 | 0.51 | 4.32 | 34.37 | 0.47 | 16.10 | 22.82 | 3.08 | 10.68 |

## 9.6 APPENDIX F: Aspen plus properties

The components used in modelling the cell disruption, lipid purification and upgrading stage are shown in the table below.

Table 50: Component representation in Aspen Plus

| Component | Comments |
|---|---|
| Hexane | Available in Aspen database |
| Methanol | Available in Aspen database |
| Lipid(TAG) | Aspen database component Triolein used |
| Residual lipid extracted algal biomass (LEALG) | Define Solid component<br>MW: 23.238<br>DHSFRM: -97,133,800 J/Kmole [1]<br>Solid density: 1.5 g/cc (taken as starch) [1]<br>Solid volume Polynomial (VSPOLY): see table 22<br>Solid heat capacity (CPSP01): see table 22 |
| Algal biomass (ALG) | Define Solid component<br>MW: 24.6264<br>DHSFRM: -130,500,000 J/Kmole [1]<br>Solid density: 1.5 g/cc (taken as starch) [1]<br>Solid volume Polynomial (VSPOLY): see table 22<br>Solid heat capacity (CPSP01): see table 22 |
| $MgSO_4$ | Available in Aspen database |
| $K_2HPO_4$ | Available in Aspen database |
| $NaNO_3$ | Available in Aspen database |
| $H_2O$ | Available in Aspen database |
| $CASO_4$ | Aspen database component Gypsum used to represent silica and clay for lipid purification; native Aspen component. |
| $H_3PO_4$ | Phosphoric acid for lipid purification. Available in Aspen database |
| $CO_2$ | Available in Aspen database |
| $H_2$ | Available in Aspen database |
| C1 | Available in Aspen database |

| | |
|---|---|
| C2 | Available in Aspen database |
| C3 | Available in Aspen database |
| C4 | Available in Aspen database |
| iC4 | Available in Aspen database |
| C5H12-2 | Available in Aspen database |
| C5H12-1 | Available in Aspen database |
| C6H14-2 | Available in Aspen database |
| C6H14-1 | Available in Aspen database |
| C7H16-2 | Available in Aspen database |
| C7H16-1 | Available in Aspen database |
| C7H14-6 | Available in Aspen database |
| C7H8 | Available in Aspen database |
| C8H18-3 | Available in Aspen database |
| C8H18-1 | Available in Aspen database |
| C8H16-8 | Available in Aspen database |
| C8H10-4 | Available in Aspen database |
| C8H10-1 | Available in Aspen database |
| C9H20-1 | Available in Aspen database |
| C9H18-1 | Available in Aspen database |
| C9H12-1 | Available in Aspen database |
| C10H22-E4 | Available in Aspen database |
| C10H22-1 | Available in Aspen database |
| C10H14-1 | Available in Aspen database |
| C10H12 | Available in Aspen database |
| C10H16O4-D1 | Available in Aspen database |
| C11H24 | Available in Aspen database |
| C12H26 | Available in Aspen database |
| C12H18-D3 | Available in Aspen database |
| C13H20 | Available in Aspen database |
| C14H22 | Available in Aspen database |
| C15H32 | Available in Aspen database |

| | |
|---|---|
| C16H34 | Available in Aspen database |
| C17H36 | Available in Aspen database |
| C18H38 | Available in Aspen database |
| C19H40 | Available in Aspen database |
| C21H44 | Available in Aspen database |
| C23H48 | Available in Aspen database |
| C24H38O4-D1 | Available in Aspen database |

[1]. Wooley and Putsche, 1996

The hydrodeoxygenated algal lipid product contain different compounds ranging from C1 to C24 range hydrocarbons. For modelling purpose a mixture of compounds in this hydrocarbon range are used to represent the hydrodeoxygenated product. The given percentages for each compound is estimated using information in table 3 and the percentage abundance of the hydrocarbon in the fuel range C5-C8( Naphtha range), C7-C13( Jet fuel range), C9-C19( Diesel range) and C20> (VGO range) are shown in below (Biller et al.,2015; Han et al.,2009; MSDS Naphtha; Shepherd et al., 2000). It is assumed that the percentage abundance of the hydrocarbon compound in the petroleum based fuel is the same as the bio-derived fuel.

Table 51**:** Components used to model the hydro-deoxygenated algal oil product.

| **Compound** | **Compound formula** | **wt.%** |
|---|---|---|
| $CO_2$ | CO2 | 0.05 |
| $H_2O$ | H2O | 0.05 |
| C1 | CH4 | 0.01 |
| C2 | C2H6 | 0.004 |
| C3 | C3H8 | 0.07 |
| iC4 | C4H10-2 | 0.02 |
| C4 | C4H10-1 | 0.016 |
| 2-METHYL-BUTANE | C5H12-2 | 0.008534 |
| N-PENTANE | C5H12-1 | 0.008534 |

| | | |
|---|---|---|
| 2-METHYL-PENTANE | C6H14-2 | 0.00512 |
| N-HEXANE | C6H14-1 | 0.059737 |
| 2-METHYLHEXANE | C7H16-2 | 0.010667 |
| N-HEPTANE | C7H16-1 | 0.01461 |
| METHYLCYCLOHEXANE | C7H14-6 | 0.025602 |
| TOLUENE | C7H8 | 0.041372 |
| 3-METHYLHEPTANE | C8H18-3 | 0.004731 |
| N-OCTANE | C8H18-1 | 0.004731 |
| ETHYLCYCLOHEXANE | C8H16-8 | 0.004731 |
| ETHYLBENZENE | C8H10-4 | 0.013265 |
| O-XYLENE | C8H10-1 | 0.030333 |
| N-NONANE | C9H20-1 | 0.012601 |
| N-PROPYLCYCLOHEXANE | C9H18-1 | 0.012601 |
| N-PROPYLBENZENE | C9H12-1 | 0.012601 |
| 4-METHYLNONANE | C10H22-E4 | 0.01564 |
| N-DECANE | C10H22-1 | 0.01564 |
| N-BUTYLBENZENE | C10H14-1 | 0.01564 |
| 1,2,3,4-TETRAHYDRONAPHTHALENE | C10H12 | 0.01564 |
| DIMETHYL-1,4-CYCLOHEXANEDICARBOX | C10H16O4-D1 | 0.01564 |
| N-UNDECANE | C11H24 | 0.096567 |
| N-DODECANE | C12H26 | 0.036108 |
| N-HEXYLBENZENE | C12H18-D3 | 0.036108 |
| N-HEPTYLBENZENE | C13H20 | 0.030862 |
| N-OCTYLBENZENE | C14H22 | 0.018366 |
| N-PENTADECANE | C15H32 | 0.012244 |
| N-HEXADECANE | C16H34 | 0.006122 |
| N-HEPTADECANE | C17H36 | 0.004081 |
| N-OCTADECANE | C18H38 | 0.00102 |
| N-NONADECANE | C19H40 | 0.000204 |

| | | |
|---|---|---|
| N-HENEICOSANE | C21H44 | 0.065711 |
| N-TRICOSANE | C23H48 | 0.065711 |
| DIISOOCTYL-PHTHALATE | C24H38O4-D1 | 0.065711 |
| **Total** | | 1.00679 |

Table 52: Components used to represent Naphtha

| **Naphtha** | **Compound formula** | **wt.%** |
|---|---|---|
| 2-METHYL-BUTANE | C5H12-2 | 4.329004 |
| N-PENTANE | C5H12-1 | 4.329004 |
| PIPERIDINE | C5H11N | 4.329004 |
| 2-METHYL-PENTANE | C6H14-2 | 2.597403 |
| N-HEXANE | C6H14-1 | 30.30303 |
| 2-METHYLHEXANE | C7H16-2 | 5.411255 |
| N-HEPTANE | C7H16-1 | 5.411255 |
| METHYLCYCLOHEXANE | C7H14-6 | 12.98701 |
| TOLUENE | C7H8 | 12.98701 |
| ETHYLBENZENE | C8H10-4 | 4.329004 |
| O-XYLENE | C8H10-1 | 12.98701 |
| Total | | 100 |

Table 53: Components used to represent Jet fuel

| **Jet fuel** | **Compound formula** | **wt.%** |
|---|---|---|
| N-HEPTANE | C7H16-1 | 2.0000 |
| TOLUENE | C7H8 | 8.0000 |
| 3-METHYLHEPTANE | C8H18-3 | 2.4000 |
| N-OCTANE | C8H18-1 | 2.4000 |
| ETHYLCYCLOHEXANE | C8H16-8 | 2.4000 |
| ETHYLBENZENE | C8H10-4 | 2.4000 |
| O-XYLENE | C8H10-1 | 2.4000 |
| N-NONANE | C9H20-1 | 4.6667 |
| N-PROPYLCYCLOHEXANE | C9H18-1 | 4.6667 |

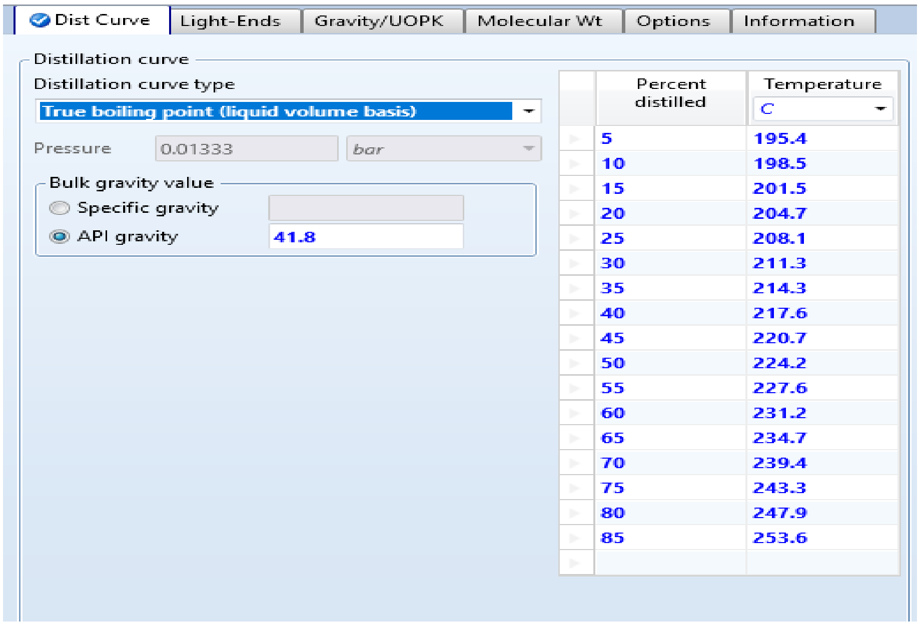
| | | |
|---|---|---|
| N-PROPYLBENZENE | C9H12-1 | 4.6667 |
| 4-METHYLNONANE | C10H22-E4 | 4.0000 |
| N-DECANE | C10H22-1 | 4.0000 |
| 1,2,3,4-TETRAHYDRONAPHTHALENE | C10H12 | 4.0000 |
| DIMETHYL-1,4-CYCLOHEXANEDICARBOX | C10H16O4-D1 | 4.0000 |
| N-BUTYLBENZENE | C10H14-1 | 4.0000 |
| N-UNDECANE | C11H24 | 20.0000 |
| N-DODECANE | C12H26 | 9.0000 |
| N-HEXYLBENZENE | C12H18-D3 | 9.0000 |
| N-HEPTYLBENZENE | C13H20 | 6.0000 |
| Total | | 100 |

Table 54: Components used to represent Diesel fuel

| **Diesel** | **Compound formula** | **wt.%** |
|---|---|---:|
| N-NONANE | C9H20-1 | 1.725328 |
| N-PROPYLCYCLOHEXANE | C9H18-1 | 1.725328 |
| N-PROPYLBENZENE | C9H12-1 | 1.725328 |
| 4-METHYLNONANE | C10H22-E4 | 3.933747 |
| N-DECANE | C10H22-1 | 3.933747 |
| 1,2,3,4-TETRAHYDRONAPHTHALENE | C10H12 | 3.933747 |
| DIMETHYL-1,4-CYCLOHEXANEDICARBOX | C10H16O4-D1 | 3.933747 |
| N-BUTYLBENZENE | C10H14-1 | 3.933747 |
| N-UNDECANE | C11H24 | 28.98551 |
| N-DODECANE | C12H26 | 9.31677 |
| N-HEXYLBENZENE | C12H18-D3 | 9.31677 |
| N-HEPTYLBENZENE | C13H20 | 6.21118 |
| N-OCTYLBENZENE | C14H22 | 9.31677 |
| N-PENTADECANE | C15H32 | 6.21118 |
| N-HEXADECANE | C16H34 | 3.10559 |

|  |  |  |
|---|---|---|
| N-HEPTADECANE | C17H36 | 2.070393 |
| N-OCTADECANE | C18H38 | 0.517598 |
| N-NONADECANE | C19H40 | 0.10352 |
| Total |  | 100 |

Four blend of assays which represents jet fuel, diesel, naphtha and lights are specified and blended. The mass fraction of each assay in the blended oil are represented using information table 23 (Chapter 4). Below shows, the information used to define each assay.



Distillation curve

Distillation curve type: True boiling point (liquid volume basis)

Pressure: 0.01333 bar

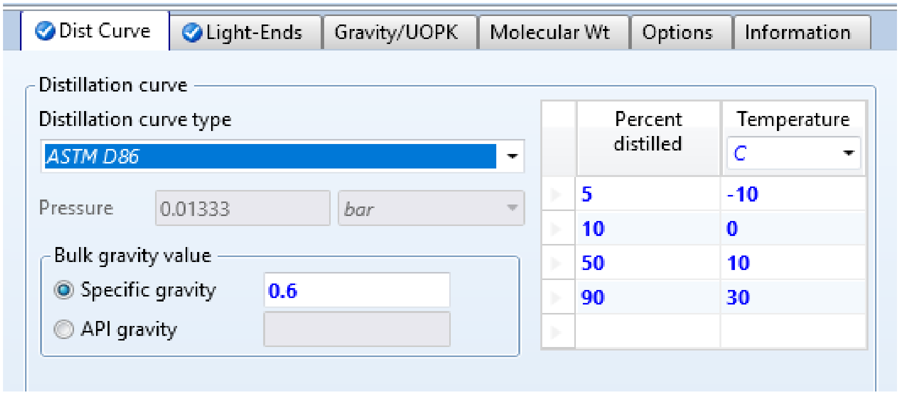
Bulk gravity value

○ Specific gravity

● API gravity: 41.8

| Percent distilled | Temperature C |
|---|---|
| 5 | 195.4 |
| 10 | 198.5 |
| 15 | 201.5 |
| 20 | 204.7 |
| 25 | 208.1 |
| 30 | 211.3 |
| 35 | 214.3 |
| 40 | 217.6 |
| 45 | 220.7 |
| 50 | 224.2 |
| 55 | 227.6 |
| 60 | 231.2 |
| 65 | 234.7 |
| 70 | 239.4 |
| 75 | 243.3 |
| 80 | 247.9 |
| 85 | 253.6 |

Figure 35 : Jet fuel true boiling point data obtained from Smith and Bruno, 2007



Distillation curve

Distillation curve type: ASTM D86

Pressure: 0.01333 bar

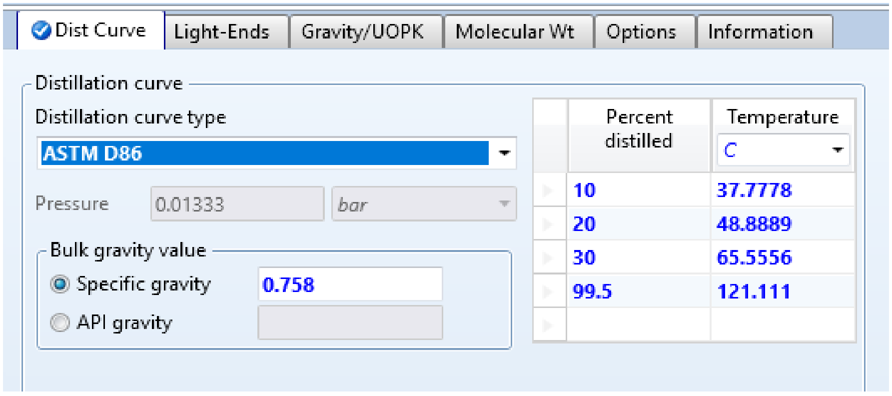
Bulk gravity value

● Specific gravity: 0.6

○ API gravity

| Percent distilled | Temperature C |
|---|---|
| 5 | -10 |
| 10 | 0 |
| 50 | 10 |
| 90 | 30 |

Figure 36: Light gases ASTM D86 data



Distillation curve

Distillation curve type: ASTM D86

Pressure: 0.01333 bar

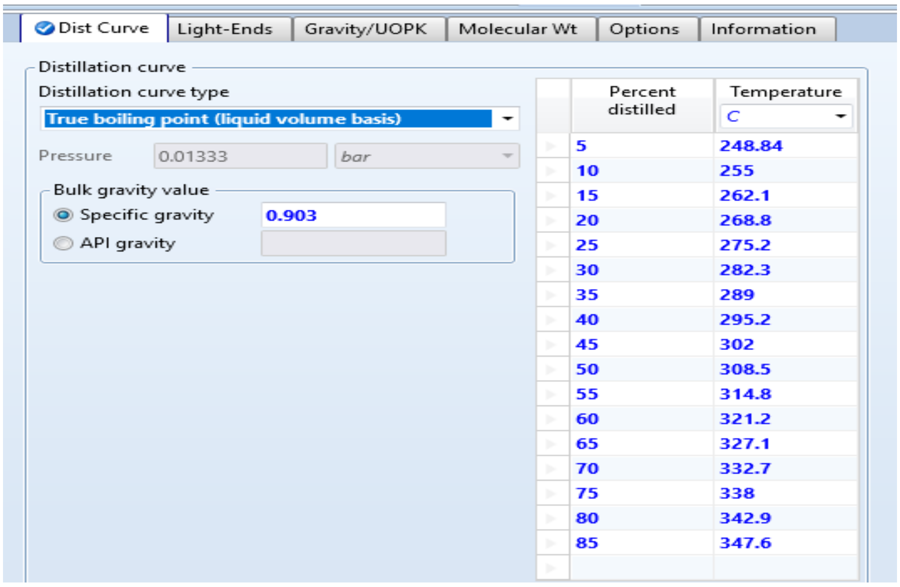
Bulk gravity value

● Specific gravity: 0.758

○ API gravity

| Percent distilled | Temperature C |
|---|---|
| 10 | 37.7778 |
| 20 | 48.8889 |
| 30 | 65.5556 |
| 99.5 | 121.111 |

Figure 37: Naphtha ASTM D86 data obtained from ACS, 2016



Distillation curve

Distillation curve type: True boiling point (liquid volume basis)

Pressure: 0.01333 bar

Bulk gravity value

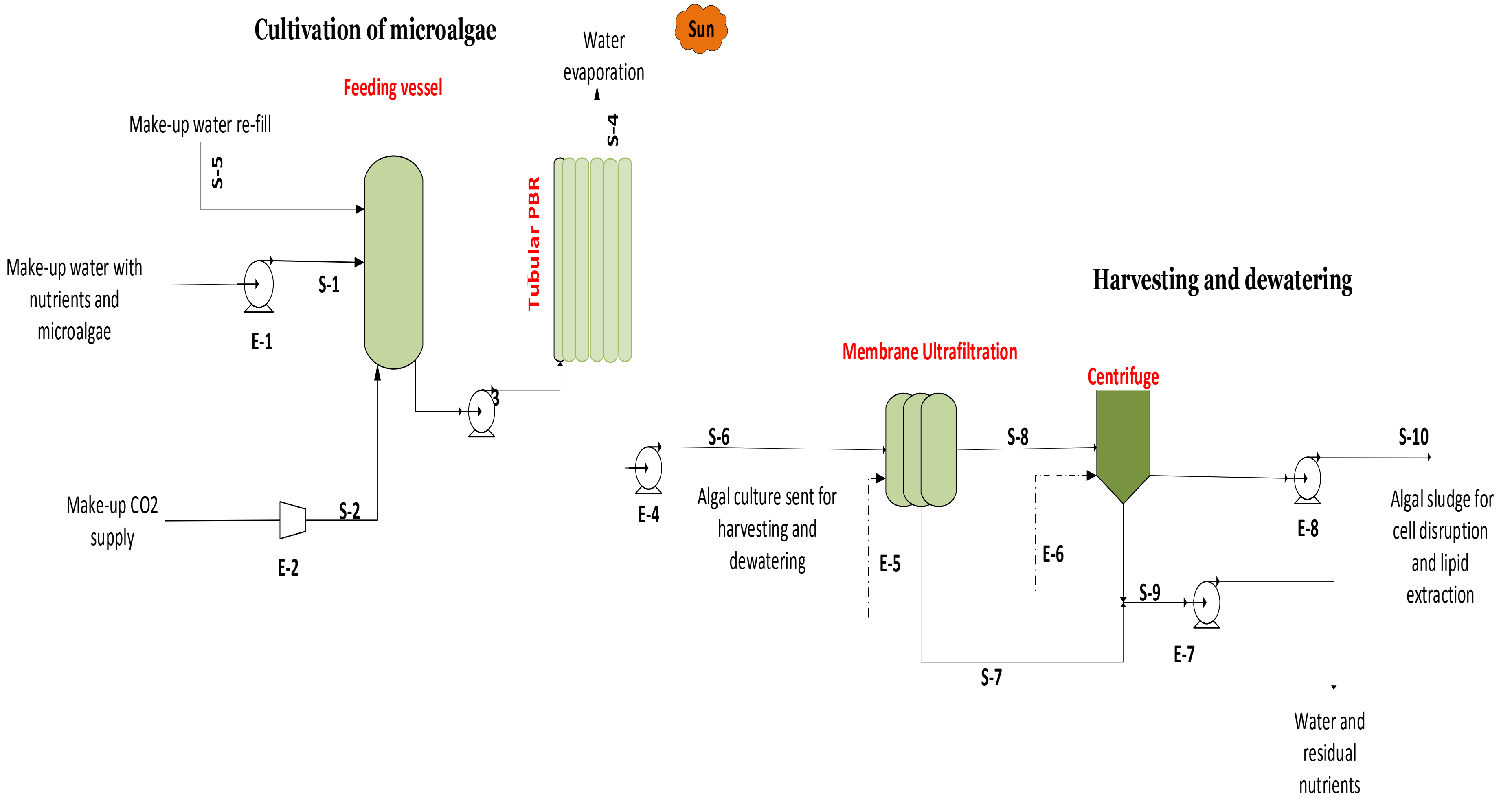
● Specific gravity: 0.903

○ API gravity

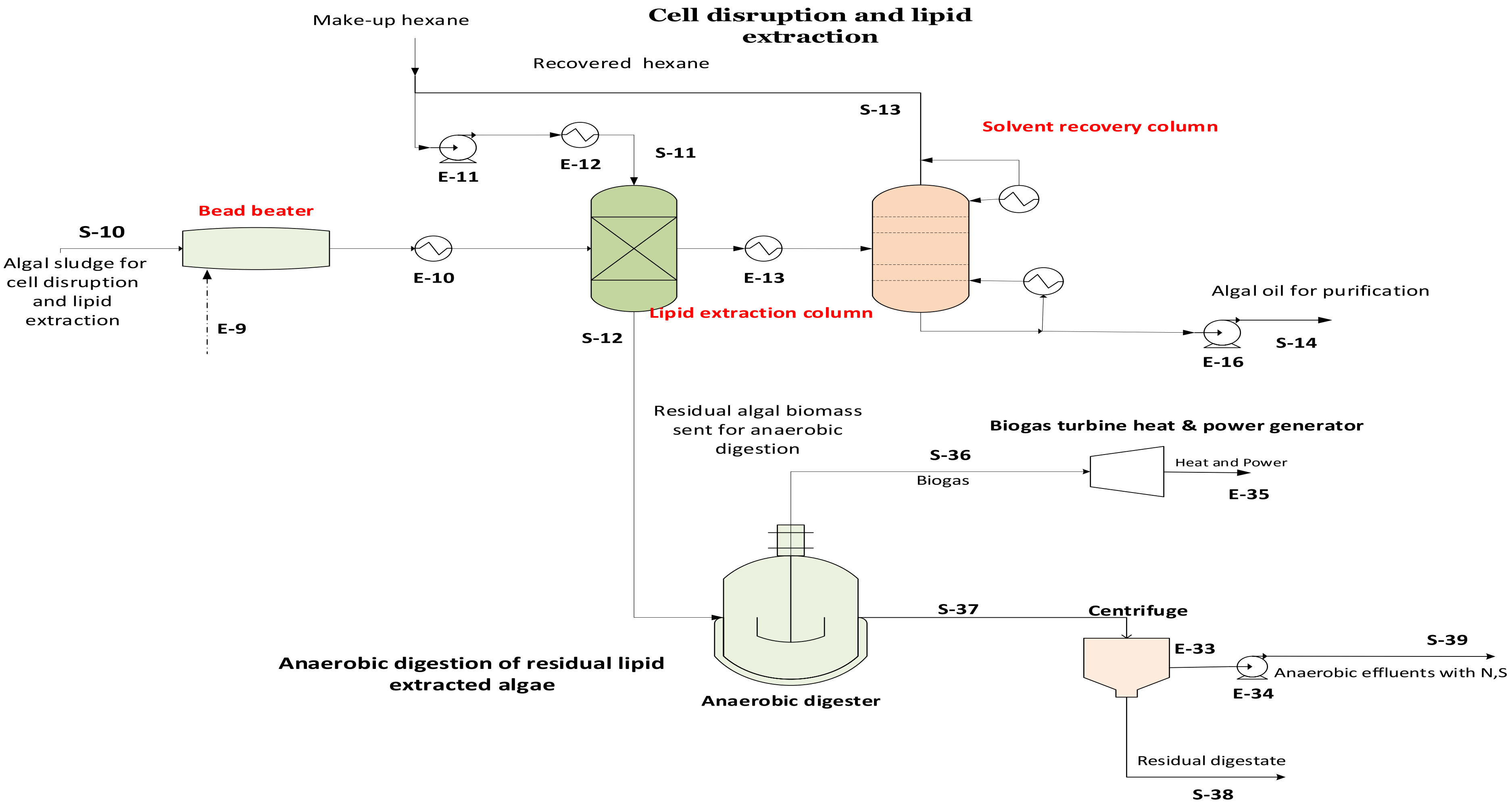
| Percent distilled | Temperature C |
|---|---|
| 5 | 248.84 |
| 10 | 255 |
| 15 | 262.1 |
| 20 | 268.8 |
| 25 | 275.2 |
| 30 | 282.3 |
| 35 | 289 |
| 40 | 295.2 |
| 45 | 302 |
| 50 | 308.5 |
| 55 | 314.8 |
| 60 | 321.2 |
| 65 | 327.1 |
| 70 | 332.7 |
| 75 | 338 |
| 80 | 342.9 |
| 85 | 347.6 |

Figure 38: Diesel true boiling point data obtained from Smith et al., 2008

## 9.7 APPENDIX G: Material balance and Energy requirement for the production of Algal bio-jet fuel.

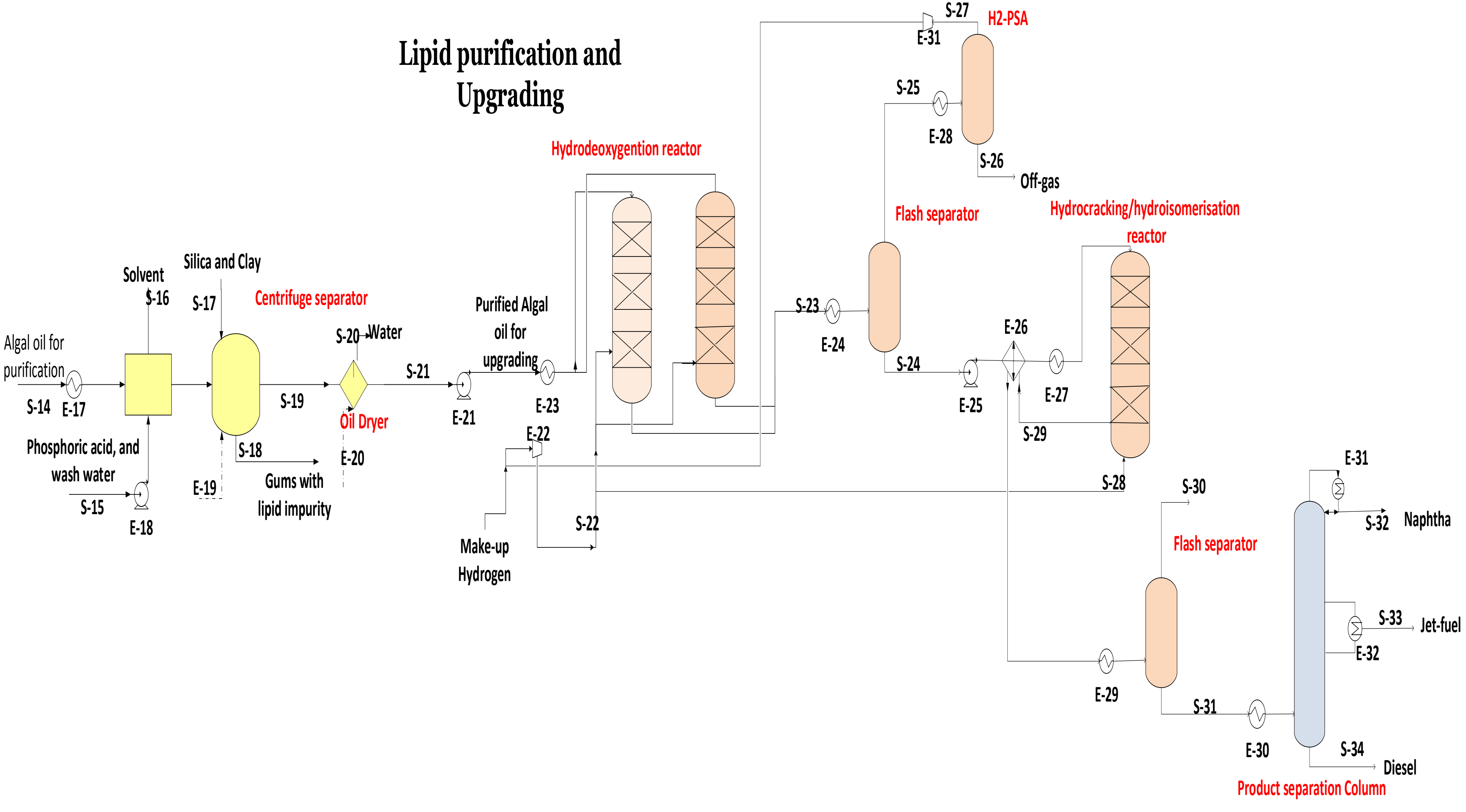


|  | S-1 |  | S-2 |  | S-3 |  | S-4 |  | S-5 |  | S-6 |  | S-7 |  | S-8 |  | S-9 |  | S-10 |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % |
| **Total** | 2,802,092 | 100 | 10,846 | 100 | 2,812,938 | 100 | 3,360 | 100 | 3,360 | 100 | 2,812,938 | 100 | 2,728,637.09 | 100.00 | 84,301.23 | 100.00 | 51,547.39 | 100.00 | 32,753.83 | 100.00 |
| Algae biomass | 1,400 | 0.05 | 0 | 0.00 | 1,400 | 0.05 | 0 | 0.00 | 0 | 0.00 | 6,564 | 0.23 | 66 | 0.00 | 6,498.80 | 7.71 | 130 | 0.25 | 6,369 | 19.44 |
| Algal Lipid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| OH | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 369 | 0.01 | 185 | 0.01 | 184.63 | 0.22 | 92 | 0.18 | 92 | 0.28 |
| Oxygen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 10,443 | 0.37 | 5,222 | 0.19 | 5221.51 | 6.19 | 2,611 | 5.06 | 2,611 | 7.97 |
| $NaNO_3$ | 1,291 | 0.05 | 0 | 0.00 | 1,291 | 0.05 | 0 | 0.00 | 0 | 0.00 | 55 | 0.00 | 28 | 0.00 | 27.57 | 0.03 | 14 | 0.03 | 14 | 0.04 |
| $MgSO_4$ | 52 | 0.00 | 0 | 0.00 | 52 | 0.00 | 0 | 0.00 | 0 | 0.00 | 12 | 0.00 | 6 | 0.00 | 6.21 | 0.01 | 3 | 0.01 | 3 | 0.01 |
| $K_2HPO_4$ | 77 | 0.00 | 0 | 0.00 | 77 | 0.00 | 0 | 0.00 | 0 | 0.00 | 31 | 0.00 | 16 | 0.00 | 15.68 | 0.02 | 8 | 0.02 | 8 | 0.02 |
| Hydrogen sulfide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Fresh water | 2,799,272 | 99.90 | 0 | 0.00 | 2,799,272 | 99.51 | 3,360 | 100.00 | 3,360 | 100.00 | 2,795,187 | 99.37 | 2,722,978 | 99.79 | 72,208.87 | 85.66 | 48,621 | 94.32 | 23,588 | 72.02 |
| Carbon dioxide | 0 | 0.00 | 10,846 | 100.00 | 10,846 | 0.39 | 0 | 0.00 | 0 | 0.00 | 276 | 0.01 | 138 | 0.01 | 137.95 | 0.16 | 69 | 0.13 | 69 | 0.21 |
| Hexane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methanol | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Residual lipid extracted biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Lipid impurity | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0 | 0.00 |
| Phosphoric acid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Wash water | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Silica | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Clay | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Hydrogen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $CO_2$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $H_2O$ ( by-product) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C1 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C2 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C3 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| iC4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Naphtha range( C5-C8) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Jet fuel range (C8-C13) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Diesel range (C14-C20) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Heavy hydrocarbon (C21+) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |


Cell disruption and lipid extraction
Make-up hexane
Recovered hexane
S-13
Solvent recovery column
S-11
E-11
E-12
Bead beater
S-10
Algal sludge for cell disruption and lipid extraction
E-9
E-10
E-13
Lipid extraction column
S-12
Algal oil for purification
S-14
E-16
Residual algal biomass sent for anaerobic digestion
Biogas turbine heat & power generator
S-36
Biogas
Heat and Power
E-35
S-37
Centrifuge
E-33
S-39
Anaerobic effluents with N,S
E-34
Anaerobic digestion of residual lipid extracted algae
Anaerobic digester
Residual digestate
S-38

| | S-11 | | S-12 | | S-13 | | S-14 | | S-36 | | S-37 | | S-38 | | S-39 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** | **Mass(kg/hr)** | **%** |
| **Total** | 31,844 | 100.00 | 30,781 | 100.00 | 31,997 | 100.00 | 1,820 | 100.00 | 5,100 | 100.00 | 23,070 | 100.00 | 6,716 | 100.00 | 16,667 | 100.00 |
| Algae biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Algal Lipid | 0 | 0.00 | 96 | 0.31 | 0 | 0.00 | 1,784 | 98.04 | 0 | 0.00 | 29 | 0.12 | 0 | 0.00 | 29 | 0.17 |
| OH | 0 | 0.00 | 92 | 0.30 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 92 | 0.40 | 0 | 0.00 | 92 | 0.55 |
| Oxygen | 0 | 0.00 | 2,611 | 8.48 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $NaNO_3$ | 0 | 0.00 | 14 | 0.04 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 14 | 0.06 | 6 | 0.08 | 8 | 0.05 |
| $MgSO_4$ | 0 | 0.00 | 3 | 0.01 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 3 | 0.01 | 0 | 0.00 | 3 | 0.02 |
| $K_2HPO_4$ | 0 | 0.00 | 8 | 0.03 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 8 | 0.03 | 0 | 0.00 | 8 | 0.05 |
| Hydrogen sulfide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Methane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 3,522 | 69.05 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Fresh water | 0 | 0.00 | 23,116 | 75.10 | 472 | 1.47 | 0 | 0.00 | 0 | 0.00 | 21,273 | 92.21 | 5,060 | 75.33 | 16,213 | 97.28 |
| Carbon dioxide | 0 | 0.00 | 69 | 0.22 | 0 | 0.00 | 0 | 0.00 | 1,578 | 30.95 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hexane | 15,922 | 50.00 | 157 | 0.51 | 15,763 | 49.26 | 2 | 0.13 | 0 | 0.00 | 157 | 0.68 | 157 | 2.34 | 157 | 0.94 |
| Methanol | 15,922 | 50.00 | 157 | 0.51 | 15,763 | 49.26 | 2 | 0.13 | 0 | 0.00 | 157 | 0.68 | 157 | 2.34 | 157 | 0.94 |
| Residual lipid extracted biomass | 0 | 0.00 | 4,458 | 14.48 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 1,337 | 5.80 | 1,337 | 19.91 | 0 | 0.00 |
| Lipid impurity | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 31 | 1.70 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Phosphoric acid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Wash water | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Silica | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Clay | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hydrogen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $CO_2$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $H_2O$ ( by-product) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C1 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C2 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C3 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| iC4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Naphtha range( C5-C8) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Jet fuel range (C8-C13) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Diesel range (C14-C20) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Heavy hydrocarbon (C21+) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |

# Lipid purification and Upgrading



| | S-15 | | S-16 | | S-17 | | S-18 | | S-19 | | S-20 | | S-21 | | S-22 | | S-23 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % |
| **Total** | 182 | 100.00 | 5 | 100.00 | 5 | 100.00 | 75 | 100.00 | 1,927 | 100.00 | 143 | 100.00 | 1,784 | 100.00 | 150 | 100.00 | 1,856 | 100.00 |
| Algae biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Algal Lipid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 1,784 | 92.59 | 0 | 0.00 | 1,784 | 100.00 | 0 | 0.00 | 0 | 0.00 |
| OH | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Oxygen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $NaNO_3$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $MgSO_4$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $K_2HPO_4$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hydrogen sulfide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Methane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Fresh water | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Carbon dioxide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hexane | 0 | 0.00 | 2 | 50.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Methanol | 0 | 0.00 | 2 | 50.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Residual lipid extracted biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Lipid impurity | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 31 | 40.99 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Phosphoric acid | 3 | 1.86 | 0 | 0.00 | 0 | 0.00 | 3 | 4.50 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Wash water | 178 | 98.14 | 0 | 0.00 | 0 | 0.00 | 36 | 47.40 | 143 | 7.41 | 143 | 100.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Silica | 0 | 0.00 | 0 | 0.00 | 2 | 33.33 | 2 | 2.37 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Clay | 0 | 0.00 | 0 | 0.00 | 4 | 66.67 | 4 | 4.74 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hydrogen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 150 | 100.00 | 0 | 0.00 |
| $CO_2$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 93 | 5.00 |
| $H_2O$ ( by-product) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 93 | 5.00 |
| C1 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 19 | 1.00 |
| C2 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 7 | 0.40 |
| C3 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 130 | 7.00 |
| iC4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 37 | 2.00 |
| C4 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 30 | 1.60 |
| Naphtha range( C5-C8) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 249 | 13.40 |
| Jet fuel range (C8-C13) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 649 | 35.00 |
| Diesel range (C14-C20) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 186 | 10.00 |
| Heavy hydrocarbon (C21+) | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 364 | 19.60 |

|  | S-24 |  | S-25 |  | S-26 |  | S-27 |  | S-28 |  | S-29 |  | S-30 |  | S-31 |  | S-32 |  | S-33 |  | S-34 |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % | Mass(kg/hr) | % |
| **Total** | 1,670 | 100.00 | 264 | 100.00 | 273 | 100.00 | 71 | 100.00 | 54 | 100.00 | 1,724 | 100.00 | 223 | 100.00 | 1,531 | 100.00 | 274 | 100.00 | 1,042 | 100.00 | 186 | 100.00 |
| Algae biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Algal Lipid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| OH | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Oxygen | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $NaNO_3$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $MgSO_4$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $K_2HPO_4$ | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hydrogen sulfide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Methane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Fresh water | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Carbon dioxide | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hexane | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Methanol | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Residual lipid extracted biomass | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Lipid impurity | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Phosphoric acid | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Wash water | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Silica | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Clay | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Hydrogen | 0 | 0.00 | 79 | 29.73 | 8 | 2.87 | 71 | 99.87 | 54 | 100.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $CO_2$ | 0 | 0.00 | 93 | 35.14 | 93 | 33.94 | 0 | 0.13 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| $H_2O$ ( by-product) | 0 | 0.00 | 93 | 35.14 | 93 | 33.97 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C1 | 19 | 1.11 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 19 | 1.08 | 19 | 8.33 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C2 | 7 | 0.44 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 7 | 0.43 | 7 | 3.33 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C3 | 130 | 7.78 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 130 | 7.54 | 130 | 58.33 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| iC4 | 37 | 2.22 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 37 | 2.15 | 37 | 16.67 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| C4 | 30 | 1.78 | 0 | 0.00 | 32 | 11.89 | 0 | 0.00 | 0 | 0.00 | 30 | 1.72 | 30 | 13.33 | 30 | 1.94 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| Naphtha range( C5-C8) | 249 | 14.89 | 0 | 0.00 | 20 | 7.47 | 0 | 0.00 | **0** | 0.00 | 274 | 15.88 | 0 | 0.00 | 274 | 17.88 | 274 | 100.00 | 0 | 0.00 | 0 | 0.00 |
| Jet fuel range (C8-C13) | 649 | 38.89 | 0 | 0.00 | 16 | 5.78 | 0 | 0.00 | 0 | 0.00 | 1,042 | 60.44 | 0 | 0.00 | 1,042 | 68.06 | 0 | 0.00 | 1,042 | 100.00 | 0 | 0.00 |
| Diesel range (C14-C20) | 186 | 11.11 | 0 | 0.00 | 3 | 1.02 | 0 | 0.00 | 0 | 0.00 | 186 | 10.77 | 0 | 0.00 | 186 | 12.12 | 0 | 0.00 | 0 | 0.00 | 186 | 100.00 |
| Heavy hydrocarbon (C21+) | 364 | 21.78 | 0 | 0.00 | 8 | 3.06 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |

| Components | **Energy requirement (kWh)** |
|---|---|
| E-1 | 15.61 |
| E-2 | 444.86 |
| E-3 | 0.71 |
| E-4 | 0.74 |
| E-5 | 109.15 |
| E-6 | 48.97 |
| E-7 | 0.73 |
| E-8 | 0.01 |
| E-9 | 636.88 |
| E-10 | 1,369.30 |
| E-11 | 0.13 |
| E-12 | 0.04 |
| E-13 | 67.63 |
| E-14 | 0.02 |
| E-15 | 0.04 |
| E-16 | 0.01 |
| E-17 | 32.58 |
| E-18 | 0.00 |
| E-19 | 1.83 |
| E-20 | 196.98 |
| E-21 | 0.01 |
| E-22 | 389.68 |
| E-23 | 73.87 |
| E-24 | 705.14 |
| E-25 | 0.28 |
| E-26 | 150.31 |
| E-27 | 183.71 |
| E-28 | 18.48 |
| E-29 | 68.94 |
| E-30 | 198.98 |
| E-31 | 158.74 |
| E-32 | 3.13 |
| E-33 | 15.40 |
| E-34 | 0.07 |
| E-35 | -799.33 |

## 9.8 APPENDIX H: Equipment Costing

| Source | EQUIPMENT NAME | Max. capacity | | No.of units/value | Unit Cost | Unit | Original cost ($) | Year of quote | Scaling exponent | Size ratio | Scaled cost | Purchase cost in 2015 ($) | Installed cost ($) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cultivation** | | | | | | | | | | | | | |
| Estimate from Beal et al., 2015 | Photobioreactors | 3 | $m^3$ | 934.0 | 396 | $/$m^3$ | 5,548,143 | 2010 | | | | 5,469,574 | 6,290,010 |
| Estimate from vendor Wilo LLC | Culture Feed pumps | 20 | $m^3$/h | 140.1 | 800 | €/unit | 153,555 | 2007 | | | | 158,698 | 182,503 |
| Estimate from vendor Wilo LLC | Circulation pumps | 20 | $m^3$/h | 70.1 | 300 | €/unit | 28,791 | 2007 | | | | 29,756 | 34,219 |
| Estimate from Vendor | Air blowers | 50 | $m^3$/h | 109.6 | 200 | €/unit | 30,018 | 2007 | | | | 31,024 | 35,678 |
| Estimate based on Brepols, 2010 | Culture medium preparation columns | 60 | $m^3$ | 46.7 | 12,000 | €/unit | 767,001 | 2007 | | | | 792,694 | 911,598 |
| Estimate from Beal et al., 2015 | Piping cost | | | | | | | | | | | 2,981,603 | 3,428,844 |
| | | | | | | | | | | | **SUBTOTAL** | **9,463,350** | **10,882,852** |
| **Harvesting and dewatering** | | | | | | | | | | | | | |
| Estimate based on Judd and Judd, 2010 | Membrane filtration | 65,351 | $m^3$/h | 65,351.5 | 160 | $/$m^3$ | 10,456,235 | 2007 | | | | 10,806,501 | 12,427,476 |
| Estimate based on Norsker et al., 2011 | Centrifuge separators | 52 | $m^3$/h | 0.0 | 500,000 | $/unit | 1,000,000 | 2007 | | | | 1,033,498 | 1,188,523 |
| Estimate from vendor Wilo LLC | Harvest pumps | 20 | $m^3$/h | 139.8 | 800 | €/unit | 111,807 | 2007 | | | | 115,553 | 132,886 |
| Estimate | Piping cost | | | | | | | | | | | 3,437,221 | 3,952,804 |
| | | | | | | | | | | | **SUBTOTAL** | **15,392,773** | **17,701,689** |
| **Cell disruption & lipid extraction** | | | | | | | | | | | | | |
| Estimate | Bead beater | 3000 | kg/hr | 10.9 | 55,000 | $/ unit | 600,487 | 2,015 | | | | 600,487 | 690,560 |
| Estimate from Vendor | Extraction column | 5,894 | kg/hr | 1.4 | 1,980,000 | $/ unit | 2,750,874 | 2013 | | | | 2,633,042 | 3,027,998 |
| Estimate based on Davis et al., 2014 | Solvent recovery reboiler | 5,599 | kg/hr | 0.3 | 150,000 | $/unit | 48,756 | 2009 | 0.7 | 0.3 | 68,304 | 71,065 | 81,725 |
| Estimate based on Davis et al., 2014 | Solvent recovery column | 5,599 | kg/hr | 0.3 | 714,000 | $/unit | 232,078 | 2009 | 0.6 | 0.3 | 363,797 | 378,505 | 435,281 |
| Estimate based on Davis et al., 2014 | Preheater exchanger | 1,162 | KW | 1.2 | 48,019 | $/unit | 56,585 | 2007 | | | 56,585 | 58,481 | 67,253 |
| Estimate from Vendor | Solvent storage | 20 | $m^3$ | 3.2 | 20,000 | $/unit | 63,995 | 2015 | | | | 63,995 | 73,594 |
| Estimate from Vendor | Product Pumps | 20 | $m^3$/h | 92.5 | 800 | $/unit | 74,027 | 2004 | | | | 90,492 | 104,066 |
| Estimate | Piping cost | | | | | | | | | | | 201,621 | 231,865 |
| | | | | | | | | | | | **SUBTOTAL** | **4,097,689** | **4,712,342** |

| Source | EQUIPMENT NAME | Max. capacity |  | No.of units/value | Unit Cost | Unit | Original cost ($) | Year of quote | Scaling exponent | Size ratio | Scaled cost | Purchase cost in 2015 ($) | Installed cost ($) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Additional purification and lipid upgrading** |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Estimate based on Davis et al., 2014 | Prior lipid purification (degumming /bleaching) | 24,757 | kg/hr | 0.1 | 6,400,000 | $/unit | 461,253 | 2013 | 0.8 | 0.1 | 780,526 | 747,093 | 859,157 |
| Estimate from Vendor | Hydrotreating reactors | 31,119 | kg/hr | 0.1 | 1,500,000 | $/unit | 258,015 | 2006 | 0.7 | 0.1 | 202,765 | 220,379 | 253,436 |
| Aspen Capital Cost Estimator | Hydrogen compressor | 30,390 | $m^3$/h | 0.1 | 1,385,600 | $/unit | 76,029 | 2011 |  |  | 76,029 | 70,486 | 81,059 |
| Estimate from Vendor | PSA | 31,119 | kg/hr | 0.0 | 12,000,000 | $/unit | 101,830 | 2013 | 0.7 | 0.0 | 425,860 | 407,618 | 468,761 |
| Aspen Capital Cost Estimator | Hydrotreater feed heater | 1,952 | kWh | 0.0 | 29,000 | $/unit | 1,097 | 2005 | 0.7 | 0.0 | 2,931 | 3,399 | 3,909 |
| Estimate based on Marker et al., 2005 | Hydrocracking unit (inc. fired heater,compressor,flash sep) | 10,732 | kg/hr | 0.2 | 30,000,000 | $/unit | 4,668,464 | 2007 |  |  | 4,668,464 | 4,824,849 | 4,824,849 |
| Aspen Capital Cost Estimator | Flash separator coolers | 1,952 | kWh | 0.4 | 46,300 | $/unit | 16,725 | 2005 | 0.7 | 0.4 | 68,102 | 78,982 | 90,829 |
| Aspen Capital Cost Estimator | Separation column | 31,978 | kg/hr | 0.0 | 183,700 | $/unit | 8,793 | 2005 | 0.6 | 0.0 | 29,656 | 34,394 | 39,553 |
| Aspen Capital Cost Estimator | Separation column reboiler | 771 | kWh | 0.0 | 22,400 | $/unit | 91 | 2005 | 0.7 | 0.0 | 948 | 1,099 | 1,264 |
| Aspen Capital Cost Estimator | Separation column condenser | 434 | kWh | 0.4 | 33,200 | $/unit | 12,143 | 2007 | 0.7 | 0.4 | 16,420 | 16,970 | 19,516 |
| Estimate from Vendor | Diesel product storage | 20 | $m^3$ | 1.6 | 20,000 | $/unit | 31,175 | 2015 |  |  |  | 31,175 | 35,851 |
| Estimate from Vendor | Naphtha product storage | 20 | $m^3$ | 2.3 | 20,000 | $/unit | 45,980 | 2015 |  |  |  | 45,980 | 52,877 |
| Estimate from Vendor | Bio-Jet fuel storage | 20 | $m^3$ | 2.3 | 20,000 | $/unit | 45,980 | 2015 |  |  |  | 45,980 | 52,877 |
|  | Piping cost |  |  |  |  |  |  |  |  |  |  | 305,277 | 351,069 |
|  |  |  |  |  |  |  |  |  |  |  | **SUBTOTAL** | **6,833,681** | **7,135,006** |
| **Anaerobic digestion** |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Estimate from Vendor | Anaerobic digester with pumps, blowers, | 10,000 | tonne | 1.4 | 600,000 | $/unit | 811,292 | 2015 | 0.7 | 1.4 | 741,087 | 741,087 | 852,250 |
| Estimate based on Norsker et al., 2011 | Centrrifuge separator | 72 | $m^3$/h | 0.2 | 500,000 | €/unit | 112,593 | 2007 | 0.8 | 0.2 | 151,706 | 156,788 | 180,306 |
| Estimate from vendor | Biogas heat and power generator | 1 | kW | 222.04 | 1,000 | $/KW generated | 222,037 | 2008 | 1 | 222.0 | 444,074 | 419,069 | 481,929 |
|  | Piping cost |  |  |  |  |  |  |  |  |  |  | 68,152 | 78,375 |
|  |  |  |  |  |  |  |  |  |  |  | **SUBTOTAL** | **1,385,096** | **1,592,860** |

## 9.9 APPENDIX I: **Discounted Cash Flow Rate of Return**

| Year | Fixed Capital investment (CAPex) | Working capital | Total capital cost | Loan interest payment | Loan Prinicpal | Loan Payment | Variable operating cost | Fixed operating Cost | Total production cost | Bio-jet fuel price($/L) | Forecast Fuel sales | Forecast By-product credit | Total annual sales |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -2 | 2,608,433 | 0 | 2,608,433 | 313,012 | 3,912,649 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| -1 | 19,563,245 | 0 | 19,563,245 | 2,660,601 | 33,257,517 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 10,433,731 | 3,823,528 | 14,257,258 | 3,912,649 | 48,908,113 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 0 | 0 | 0 | 3,912,649 | 45,532,011 | 7,288,751 | 18,103,309 | 5,459,973 | 23,563,282 | 5.89 | 37,569,160 | 2,657,782 | 40,226,942 |
| 2 | 0 | 0 | 0 | 3,642,561 | 41,885,821 | 7,288,751 | 20,327,012 | 5,459,973 | 25,786,985 | 5.89 | 37,569,160 | 3,543,709 | 41,112,869 |
| 3 | 0 | 0 | 0 | 3,350,866 | 37,947,936 | 7,288,751 | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 4 | 0 | 0 | 0 | 3,035,835 | 33,695,019 | 7,288,751 | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 5 | 0 | 0 | 0 | 2,695,602 | 29,101,870 | 7,288,751 | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 6 | 0 | 0 | 0 | 2,328,150 | 24,141,268 | 7,288,751 | 20,438,546 | 5,459,973 | 25,898,519 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 7 | 0 | 0 | 0 | 1,931,301 | 18,783,819 | 7,288,751 | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 8 | 0 | 0 | 0 | 1,502,705 | 12,997,773 | 7,288,751 | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 9 | 0 | 0 | 0 | 1,039,822 | 6,748,844 | 7,288,751 | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 10 | 0 | 0 | 0 | 539,907 | 0 | 7,288,751 | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 11 | 0 | 0 | 0 | 0 |  |  | 20,689,496 | 5,459,973 | 26,149,469 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 12 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 13 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 14 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 15 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 16 | 0 | 0 | 0 | 0 |  |  | 20,689,496 | 5,459,973 | 26,149,469 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 17 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 18 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 19 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 20 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 21 | 0 | 0 | 0 | 0 |  |  | 20,438,546 | 5,459,973 | 25,898,519 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 22 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 23 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 24 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 25 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 26 | 0 | 0 | 0 | 0 |  |  | 20,689,496 | 5,459,973 | 26,149,469 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 27 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 28 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 29 | 0 | 0 | 0 | 0 |  |  | 20,327,012 | 5,459,973 | 25,786,985 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |
| 30 | 0 | 0 | 0 | 0 |  |  | 20,577,963 | 5,459,973 | 26,037,936 | 5.8932 | 37,569,160 | 3,543,709 | 41,112,869 |

| Year | Depreciation charge | Depreciation | Annual cash income | Taxable income | Tax paid | Cash flow | Cumulative cash flow | Discount factor (10%) | Discounted cash flow (10% discount) | Cumulative discounted cash flow (NPV@10%) |
|---|---|---|---|---|---|---|---|---|---|---|
| -2 | 0 | 0 | 0 | 0 | 0 | -6,521,082 | -6,521,082 | 1.21 | -7890508.95 | -7890508.955 |
| -1 | 0 | 0 | 0 | 0 | 0 | -48,908,113 | -55,429,195 | 1.1 | -53798924.7 | -61689433.65 |
| 0 | 0 | 0 | 0 | 0 | 0 | -22,171,678 | -77,600,873 | 1 | -22171678.1 | -83861111.7 |
| 1 | 14.29% | 11,648,282 | 9,374,909 | -2,273,374 | 0 | 9,374,909 | -68,225,964 | 0.909091 | 8522644.34 | -75338467.36 |
| 2 | 24.49% | 19,962,662 | 8,037,133 | -11,925,529 | 0.00 | 8,037,133 | -60,188,831 | 0.826446 | 6642258.674 | -68696208.69 |
| 3 | 17.49% | 14,256,715 | 7,786,183 | -6,470,533 | 0.00 | 7,786,183 | -52,402,649 | 0.751315 | 5849874.181 | -62846334.51 |
| 4 | 12.49% | 10,181,039 | 8,037,133 | -2,143,906 | 0.00 | 8,037,133 | -44,365,516 | 0.683013 | 5489469.979 | -57356864.53 |
| 5 | 8.93% | 7,279,158 | 7,786,183 | 507,025 | 0.00 | 7,786,183 | -36,579,333 | 0.620921 | 4834606.761 | -52522257.77 |
| 6 | 8.92% | 7,271,006 | 7,925,599 | 654,593 | 152,107.50 | 7,773,492 | -28,805,841 | 0.564474 | 4387933.556 | -48134324.21 |
| 7 | 8.93% | 7,279,158 | 7,786,183 | 507,025 | 196,377.98 | 7,589,805 | -21,216,037 | 0.513158 | 3894769.822 | -44239554.39 |
| 8 | 4.46% | 3,635,503 | 8,037,133 | 4,401,630 | 152,107.50 | 7,885,025 | -13,331,011 | 0.466507 | 3678422.587 | -40561131.8 |
| 9 | 0 | 0 | 7,786,183 | 7,786,183 | 1,320,488.97 | 6,465,694 | -6,865,318 | 0.424098 | 2742085.241 | -37819046.56 |
| 10 |  |  | 8,037,133 | 8,037,133 | 2,335,854.76 | 5,701,278 | -1,164,040 | 0.385543 | 2198089.565 | -35620956.99 |
| 11 |  |  | 14,963,400 | 14,963,400 | 2,411,139.90 | 12,552,260 | 11,388,221 | 0.350494 | 4399490.633 | -31221466.36 |
| 12 |  |  | 15,325,884 | 15,325,884 | 4,489,020.04 | 10,836,864 | 22,225,085 | 0.318631 | 3452958.865 | -27768507.5 |
| 13 |  |  | 15,325,884 | 15,325,884 | 4,597,765.24 | 10,728,119 | 32,953,204 | 0.289664 | 3107553.903 | -24660953.59 |
| 14 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 43,430,372 | 0.263331 | 2758965.903 | -21901987.69 |
| 15 |  |  | 15,325,884 | 15,325,884 | 4,522,480.10 | 10,803,404 | 54,233,776 | 0.239392 | 2586249.03 | -19315738.66 |
| 16 |  |  | 14,963,400 | 14,963,400 | 4,597,765.24 | 10,365,635 | 64,599,411 | 0.217629 | 2255864.162 | -17059874.5 |
| 17 |  |  | 15,325,884 | 15,325,884 | 4,489,020.04 | 10,836,864 | 75,436,275 | 0.197845 | 2144015.787 | -14915858.71 |
| 18 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 85,913,443 | 0.179859 | 1884410.834 | -13031447.88 |
| 19 |  |  | 15,325,884 | 15,325,884 | 4,522,480.10 | 10,803,404 | 96,716,848 | 0.163508 | 1766442.886 | -11265004.99 |
| 20 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 107,194,016 | 0.148644 | 1557364.326 | -9707640.666 |
| 21 |  |  | 15,214,351 | 15,214,351 | 4,522,480.10 | 10,691,870 | 117,885,886 | 0.135131 | 1444798.563 | -8262842.103 |
| 22 |  |  | 15,074,934 | 15,074,934 | 4,564,305.18 | 10,510,628 | 128,396,515 | 0.122846 | 1291188.389 | -6971653.713 |
| 23 |  |  | 15,325,884 | 15,325,884 | 4,522,480.10 | 10,803,404 | 139,199,919 | 0.111678 | 1206504.259 | -5765149.454 |
| 24 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 149,677,087 | 0.101526 | 1063700.79 | -4701448.665 |
| 25 |  |  | 15,325,884 | 15,325,884 | 4,522,480.10 | 10,803,404 | 160,480,491 | 0.092296 | 997110.9581 | -3704337.706 |
| 26 |  |  | 14,963,400 | 14,963,400 | 4,597,765.24 | 10,365,635 | 170,846,126 | 0.083905 | 869733.2896 | -2834604.417 |
| 27 |  |  | 15,325,884 | 15,325,884 | 4,489,020.04 | 10,836,864 | 181,682,990 | 0.076278 | 826610.8991 | -2007993.518 |
| 28 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 192,160,159 | 0.069343 | 726521.9518 | -1281471.566 |
| 29 |  |  | 15,325,884 | 15,325,884 | 4,522,480.10 | 10,803,404 | 202,963,563 | 0.063039 | 681040.2009 | -600431.3651 |
| 30 |  |  | 15,074,934 | 15,074,934 | 4,597,765.24 | 10,477,168 | 213,440,731 | 0.057309 | 600431.3651 | -1.39698E-09 |