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# **The Technical Viability of Microalgal Biodiesel**

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Rubisco, the most abundant protein on earth, sequesters CO<sub>2</sub> from the atmosphere [1]. Two billion years ago it was responsible for the Great Oxidation Event.



## ABSTRACT

Biodiesel is the most energy dense renewable storage medium in terms of volumetric capacity. A large-scale introduction of this fuel could theoretically substitute petrodiesel entirely, but is to date bottlenecked by a limited feedstock supply.

A proposed solution are microalgae. They are endowed with high growth rates, accumulate large amounts of lipids and can be cultivated on non-arable land. Nevertheless, microalgae have yet to be commercially exploited as a biodiesel feedstock.

This thesis aims to examine the technical viability of microalgal biodiesel. The literature review found that productivity is highly sensitive to environmental variables such as irradiance and temperature, but problems were also encountered in downstream processing due to the high water content of the culture medium. By replacing extraction and transesterification with hydrothermal liquefaction the production chain was shown to increase overall yields, but the technology has yet to reach sufficient maturity.

Based on the literature study, a large-scale production facility in Brazil was proposed. The biorefinery served as a model to assess the viability of supplying 20 % of Brazil's transportation fuel demand with microalgal biodiesel. To increase its performance, an anaerobic digestion process was integrated into the production chain.

The resulting model yielded a *technical potential* of 10.6 ton biodiesel ha<sup>-1</sup> y<sup>-1</sup>, an *energy return investment* of 1.8 and a *global warming potential* of 1.9 tonC (ton biodiesel)<sup>-1</sup>. By comparing these numbers to biodiesel from palm oil and to petrodiesel, it was concluded that microalgal biodiesel is unviable at present. Biological factors are seen as major inhibitors – productivity is negatively influenced by microalgae's response to suboptimal irradiances, temperatures and fertilizer utilization. If advances in phycology and genetic engineering are not contrived, effort should rather be directed towards the production of algae-derived high-value products and food.



## SAMMENDRAG

Av foreslåtte fornybare energibærere har biodiesel den høyeste volumetriske kapasiteten. Storskala produksjon kan potensielt erstatte fossil diesel fullstendig, men begrenses i dag av tilgangen på råstoff.

En mulig løsning er mikroalger. Høy vekstrate og oljeinnhold, samt muligheten til å kultivere dem på ikke-dyrkbare landområder, taler for mikroalger som biodieselryåstoff. Allikevel er de hittil ikke unyttet til kommersiell drivstoffproduksjon.

Denne oppgaven undersøkte det tekniske potensialet til biodiesel fra mikroalger. Litteraturstudien viste at produktiviteten til algene er svært sensitiv overfor solinnstråling, temperatur og næringstilgang. Det ble også funnet problemer ved øvrige deler av produksjonskjeden forårsaket av det høye vanninnholdet i algeslammet. *Hydrothermal Liquefaction*-teknologi kan erstatte deler av produksjonskjeden med den fordel at total biodiesel produksjon øker. Men teknologien er ennå ikke klar for å bli tatt i bruk.

Basert på litteraturstudien, ble det foreslått et storskala produksjonsanlegg i Brasil. Ytelsen til bioraffineriet evalueres for et produksjonsvolum tilsvarende 20 % av Brasils drivstofforbruk. Et biogassanlegg legges til produksjonskjeden for å bedre total ytelse.

Modellen viser at bioraffineriet har et teknisk produksjonspotensial på 10.6 ton biodiesel ha<sup>-1</sup> y<sup>-1</sup>, en *energy return investment* på 1.8 and et *global warming potential* på 1.9 tonC (ton biodiesel)<sup>-1</sup>. Etter en sammenlikning med biodiesel fra palmeolje og med fossil diesel, konkluderes det at satsing på storskala biodieselproduksjon fra alger ikke er forsvarlig i dag. I fremtiden kan dette endres hvis det gjøres fremskritt innen fykologi og genmanipulasjon. I mellomtiden bør produksjonen av andre algeprodukter som mat være i fokus.





## PREFACE

In his book *Collapse*, Jared Diamond [2] lists five factors detrimental to human societies and which historically have led to their fall. Two of the five are prominent today; human impact on the environment and climate change. A timely response to these detriments, Diamond argues, is paramount, as their effects are no longer imminent, but ongoing.

To mitigate the consequences, the Intergovernmental Panel on Climate Change [3] urges a drastic reduction fossil fuel usage. of greenhouse gas emissions. Although unable to induce a reversal, lower emissions may better the prospects of our future.

But climate change is not the sole threat. The current supply of fossil energy is finite. Hence, the present course is a non-sustainable course, and must inevitably change. The question is when. And how.

Fortunately, scientists show readiness to answer these questions. Over the course of this thesis, it was evident that recent research on renewable energy dwarves that on fossil fuels. There are of course a multitude of reasons for this; maturity, corporation-driven research, etc., but it does bear some promise. Moreover, many scientists open their papers with an introduction akin to this preface, meriting climate change mitigation or sustainability as their motivator.

The opportunity to partake in such research myself has been a great experience and the field of microalgal biodiesel proved an excellent conclusion to my five years as an Environmental Physics student. Over the course of the semester I was supervised by Dr. Marchetti, who expertly introduced me to the subject, and to whom I would like to express my gratitude. Dr. Marchetti has provided research material and invaluable feedback at every request, and without his help, this thesis would be riddled with mistakes. In this regard would also like to thank Vegard Holmefjord, whose Excel-wizardry and validation of mathematical models was of great help. Many others deserve mention, but I doubt they will ever read past the title.

As for the thesis itself, I set out with the rigorous scientific approach of attempting to disprove my hypothesis – that microalgal biodiesel is technically viable. Unfortunately, I succeeded. Microalgal biodiesel takes us no further from societal collapse. Though in the future it might.

Ås, June 2016

Magnus Rysstad Nyvold



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**GLOSSARY**

ACAD	Algae Cultivation, Anaerobic Digestion
Auxiliary energy	Energy required to run a process, excluding solar energy
CX:Y	X: length of hydrocarbon chain, Y: number of double bonds
EROI	Energy return on investment
GWP	Global warming potential
HTL	Hydrothermal Liquefaction
Large-scale production	20 % of Brasil's transportation fuel demand
OPS	Open Pond System
PBR	Photobioreactor
PSE	Photosynthetic Efficiency
Raw energy	Chemical energy of the biomass
Rubisco	Ribulose-1,5-bisphosphate carboxylase/oxygenase



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# 1 INTRODUCTION

## 1.1 MICROALGAL BIODIESEL

Microalgal biodiesel first gained recognition as a renewable fuel in the 1970s [4]. The field experienced a surge in interest and technological advances, culminating in the Aquatic Species Program, launched in 1978 by the United States Department of Energy [5]. In its prime, more than \$2.5 million were channelled into the program annually, until a drop in oil prices rendered microalgal biodiesel uneconomical [6]. The program was discontinued in 1996.

When the oil prices rose anew, a second round of research was initiated and by 2009 microalgal biodiesel could no longer be ignored. The oil and energy companies invested heavily in algae technology [7], but progress was slow and, as of 2016, most investors have jumped ship – the world economy no longer speaks in favour of microalgal biodiesel initiatives. Yet other factors do.

As an oil crop, microalgae are almost ten times as productive as the nearest contender. Viable algal strains are estimated to yield 58,700 kg/ha of oil annually. As a comparison, the best land crop, oil palm, accumulates 5,950 kg oil/ha per year [8]. In terms of biomass productivity, the microalgae's annual raw energy output ranges from 700 GJ ha<sup>-1</sup> to 1,550 GJ/ha, comparable to the highly productive sugarcane (1,230-1,460 GJ<sup>-1</sup>ha) [9].

These figures drew the attention of researchers because it widened a major bottleneck in biodiesel production – the supply of feedstock [10]. But it is not the only advantage associated with microalgal biodiesel. Other important benefits, compiled from reviewed literature, are listed below [11-17]

- Reduced use of arable land – cultivation systems can be installed where no land crops will grow
- Extraction of valuable co-products – some species of microalgae are already cultivated for their ability to synthesise desirable products (e.g. highly unsaturated fatty acids, certain proteins,  $\beta$ -carotene)
- Reduced use of freshwater – microalgal cultivation requires less freshwater than other biodiesel feedstocks if proper recycling measures are installed. Some microalgal strains can even be cultivated in saltwater
- Water treatment – microalgae can grow in sewage water, utilizing otherwise wasted nutrients

- Enhancement of favourable traits by genetic modification – microalgae are unicellular structures and they are easily manipulated once a gene of favourable characteristics is located
- Sequestration of carbon dioxide – industrial flue gases can be used to improve the growth conditions for the microalgae

In spite of these advantages, algal biodiesel is not yet viable for commercial production. This thesis aims to explore why. As the economic feasibility exhibits a volatility similar to that of the oil price, microalgal biodiesel will be evaluated based on technical parameters.

## 1.2 THESIS GOAL

The purpose of this thesis is to assess the technical viability of microalgal biodiesel. This undertaking requires a thorough review of literature on the field, which is intended to be extensive in scope but not in depth. The literature review lays the foundation for a model biorefinery used to calculate the technical potential, auxiliary energy demand and global warming potential of microalgal biodiesel. The conclusion of its viability is based on these parameters.

## 1.3 THESIS STRUCTURE

The thesis will follow the structure described below:

- Section 2.1 aims introduce the concept of biodiesel and its properties
- Section 2.2-2.6 investigates microalgae as a biodiesel feedstock and presents the entire production chain: cultivation, harvest, extraction and biodiesel production.
- Section 2.7.1 introduces three integrated systems and recommends one system for large-scale biodiesel production
- Section 2.7.2 discuss other processes that may be integrated with the production chain for synergetic benefit
- Section 3 describes a model biorefinery and details the method used to obtain the parameters: technical potential, auxiliary energy demand and global warming potential. The results are presented in section 4.
- Section 5 will discuss model limitations and the implications of the results, before the future of microalgal biodiesel is pondered.

## 2 THEORY

### 2.1 BIODIESEL

Renewable energy experiences a highly variable supply and is in dire need of a suitable energy storage option. A myriad of storage technologies exists, but they are all outcompeted by non-renewable petroleum based fuels upon which society today relies.

Biodiesel is the most energy dense renewable storage medium in terms of volumetric capacity [18]. Gravimetrically, it is surpassed by hydrogen, which long has been proposed as a medium for large-scale energy storage. However, hydrogen will require an entirely new infrastructure if it is to be considered a feasible storage option, whilst biodiesel simply substitutes petrodiesel [19]. This enables a rapid change to renewable, and storable, energy. Biodiesel is thus more likely to make an immediate impact on carbon emissions [20].

Biodiesel's main challenge is the limited, or costly, supply of feedstock, as it is derived from organic oils that rely on renewable photosynthetic growth [10]. In principle, biodiesel is considered renewable and a zero net carbon emitter. However, its renewability does depend on sustainably grown feedstock, and the actual net carbon emissions are never quite zero if the entire production chain is accounted for. Some fossil energy or derivatives thereof, are currently required for biodiesel production.

#### 2.1.1.1 *Properties of Biodiesel*

Although comparable in areas of use, biodiesel differs from petrodiesel in its chemical composition. While petrodiesel consists of hydrocarbons, biodiesel is made up of fatty acid alkyl esters [19]. Thus, their properties vary slightly, as shown in table x.

**Table 2.1:** Properties of petrodiesel and biodiesel

Properties	Petrodiesel	Biodiesel	References
Energy density (avg.)	42 MJ kg <sup>-1</sup>	37 MJ kg <sup>-1</sup>	[21-24]
Cetane number	40-55	50-60	[21, 23, 25]
NO <sub>x</sub>	Baseline	+ 10 %	[22]
CO	Baseline	Increase	[22]
Sulphur	10-500 ppm	<5 ppm	[22, 23]
Oxidative stability	Excellent	Poor	[21]
Lubricity	Good	Excellent	[21]
Cloud point	-5 °C	-5°C to + 15°C	[23]

Biodiesel can obtain a higher cetane number than petrodiesel, which implies that its ignition delay is lower, in turn leading to a more complete combustion. An engine running on biodiesel will thus emit less CO and unburned hydrocarbons [26]. Sulphur emissions are also lower, and biodiesel is consequently considered a reducer of local pollutants.

Biodiesel does face some issues regarding oxidative stability and cold flow properties, as seen in table x. But the cloud point can be reduced and the oxidative stability increased if feedstock with a certain lipid profile is chosen (section 2.2.4) [27]. In the aggregate, the properties of biodiesel do not hinder it from replacing fossil fuels.

#### 2.1.1.2 Biodiesel Generations

There are three different approaches to biodiesel production coined first, second and third generation. The first generation utilizes crops such as soybean, rapeseed and oil palm as a feedstock. Although still common today, first generation feedstock is criticised for competing with food production. This shortcoming gave rise to the second generation, where waste oils were transformed into biodiesel. However, the impurity of the products necessitates expensive catalysts, production methods and separation methods [28]. Moreover, the supply of waste oils is unlikely to meet any large-scale production demand [29]. As a result, a third generation was proposed, which attempts to rid the disadvantages of past generations. Here, the feedstock is grown on non-arable land and yields oil of both high quality and quantity, thereby avoiding the problems of the first and second generation.

Microalgae in particular was fronted as a fitting third generation biodiesel feedstock because of the aforementioned advantages. The next sections aim to explore this feedstock in detail, as well as the production chain necessary for efficient biodiesel production. Figure 2.1 shows a simple outline of the microalgal biodiesel's production chain. This outline will gradually be expanded throughout the thesis, and will toward the end serve as the framework for a model biorefinery.



**Figure 2.1:** Outline of the microalgal biodiesel production process

## 2.2 CULTIVATION OF MICROALGAE

This section aims to introduce the microalgae and their metabolism. Emphasis is thereafter put on the factors that influence the algal metabolism and growth rate, and under which conditions optimal growth can be achieved.

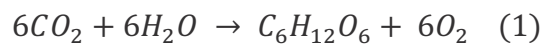
### 2.2.1 The Microalgae

Microalgae are single celled organisms inhabiting an aquatic environment. Characterized as phototrophic eukaryotes, they use the sun's energy to grow and reproduce [30]. Their photosynthetic efficiency may reach up to 5.4 % under ideal conditions, enabling rapid proliferation [16]. Additionally, the microalgae have steady access to nutrients dissolved in the fluid medium, which further promotes their growth.

As of 2015 more than 30,000 species of microalgae have been described and up to 700,000 species are believed to exist [31]. As discovered by the *Aquatic Species Program* [6], their individual characteristics differ immensely. It is therefore important to select microalgae with traits that are compatible with biodiesel production.

### 2.2.2 Biomass Productivity

A key characteristic of microalgae is the ability to efficiently synthesize organic compounds [32]. The first step in the process is the photosynthesis, which consists of two stages: the light dependent reaction and the Calvin cycle [33]. In the first stage, the microalgae captures sunlight in the visible spectrum, which excites certain electrons. The excitation energy is transferred through different carriers, before it powers the reduction of CO<sub>2</sub> into a sugar molecule. A reaction catalysed by the protein Rubisco. In short, the photosynthetic reaction can be represented by the following equation.



The sugar molecule, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, can be synthesized further, through different metabolic pathways, into an array of lipids and proteins. The efficiency of the entire process is called the photosynthetic efficiency (PSE). There are various definitions of PSE, some more complicated than others, but that of Schlagermann et al. [15] was chosen for this thesis, and specifies the ratio between the raw energy of the accumulated biomass and the insolation energy over a given period of time. It is simply defined as follows:

$$PSE = \frac{\mu}{I} \quad (2)$$

where

$\mu$  is the rate of biomass accumulation,  $W/m^2$ .

$I$  is the insolation,  $W/m^2$ .

Theoretically, the maximum PSE of microalgae is 12.4 % [32]. However, metabolic inefficiencies and reflection on the surface limit their achievable efficiency to 5,4% [16]. The exact magnitude of the losses will in practice depend on the conditions under which the algae grow. The factors that influence PSE and thereby the growth rate, are discussed in section 2.2.5.

### 2.2.3 Lipid Composition

In addition to the growth rate, the lipid content and the lipid composition will influence the viability of a microalgal strain. After the metabolic processes, the microalgae's volumetric lipid content lies in the range 20-50% (although some strains may contain up to 75% lipids, but they are usually associated with lower biomass productivity) [34].

Algal lipids are divided into two groups: polar and non-polar lipids [35]. The polar lipids present in algae are mainly phospholipids and glycolipids, which maintain cell membrane functions and contribute to metabolic processes. The non-polar lipids comprise the tri-, di and monoglycerides, waxes and free fatty acids. Triglyceride, the most abundant of all the algal lipids, serves as an energy store in the microalgae, and is easily converted to metabolic energy [36].

As the polar and non-polar lipids require different solvents for extraction, it is common to extract only the abundant triglycerides. Conveniently, triglycerides has a 99% conversion rate to biodiesel compared to less than 70% for the polar lipids, and the resulting biodiesel does not contain any sulphur, and lower amounts of nitrogen [37, 38]. After the extraction of the non-polar lipids, the free fatty acid content is normally low (<0.5%) and esterification will not be necessary. If, however, the algal oil is to be stored before conversion to biodiesel, the free fatty acid content will increase [39]. It is therefore important to keep the delay between oil extraction and biodiesel conversion to a minimum.

### 2.2.4 The Fatty Acid Profile

The fatty acid profile of an algal strain can indicate how suitable it is for conversion to biodiesel. Although studies are scarce, some fatty acids are said to result in biodiesel with more favourable qualities: Song et al. [40] report that algae with high content of the fatty acids C14:0, C16:0, C18:1, C18:2 and C18:3 convert to high quality biodiesel (better cold flow properties and higher cetane number). Ramos et al. [41] propose a similar relationship between fatty acid profiles and the quality of the biodiesel, but admit that research on the area is lacking. The



variety and complexity of algal lipids make it difficult to predict the performance of the biodiesel without conducting experiments [10]. Table 2.2 illustrates the variety of lipids found in three different algal species. Let it be noted that the listed profiles will vary even within the same species. *C. Vulgaris* serves as an example: Song et al. [40] report a C16:0 content of more than twice that of Talebi et al. [42], indicating just how challenging scientific rigour within the field of biology is.

**Table 2.2:** Fatty acids within the desired range for three microalgal strains.

Microalgal strain <sup>a</sup>	Fatty acid composition (%)							References
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	
<i>C. Vulgaris</i>	-	14.6	11.8	10.5	23.6	13.8	32.1	[42]
<i>N. Salina</i>	-	37.5	23.3	0.9	11.9	1.5	-	[43]
<i>P. Tricornutum</i>	4.5	25.8	37.5	1.3	-	5.1	2.0	[44]

<sup>a</sup> Proposed biodiesel feedstock algae are chosen and thus their lipid profiles comprise most of the desirable fatty acids

### 2.2.5 Growth Factors

Microalgae are versatile and grow in a vast array of environments. Although the ideal growth conditions differ among the species, certain factors are decisive for microalgal proliferation. Namely:

- Solar radiation
- Temperature
- CO<sub>2</sub>-supply
- Respiration losses

Their influence on growth rate can be expressed as follows

$$\mu = \mu_{max}f(I)f(T)f(CO_2)f(R) \quad (3)$$

where

$\mu_{max}$  is the maximum hourly growth rate under optimal conditions

$f(I)$  is a function describing the influence of insolation, ranging from 0 to 1.

$f(T)$  is a function describing the influence of temperature, ranging from 0 to 1.

$f(CO_2)$  is a function describing the influence of CO<sub>2</sub> concentration, ranging from 0 to 1.

$f(R)$  represents the night time respiration losses

Other factors will also influence the growth rate, but these relationships are complicated to model. Therefore, a qualitative investigation of the following factors will be performed.

- Nutrient supply
- Water supply
- Contamination

#### 2.2.5.1 *Solar Radiation*

Solar radiation drives the photosynthesis and is a prerequisite for algal growth. Its influence can be modelled using the Steele equation [45]

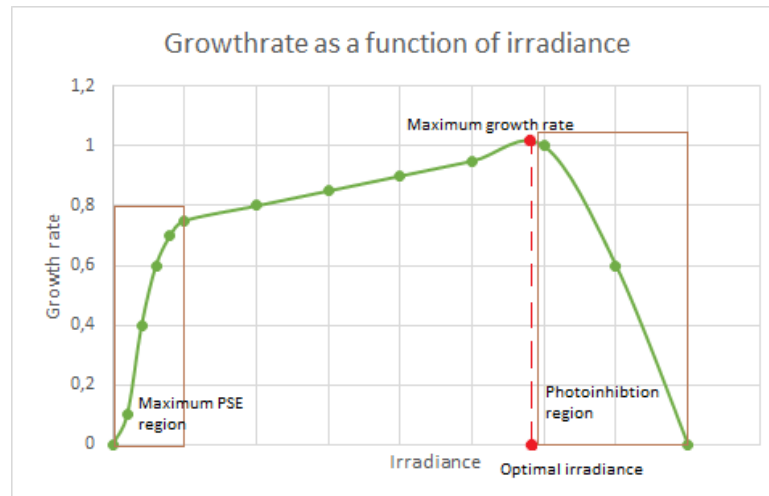
$$f(I) = \frac{I}{I_{op}} e^{\left(1 - \frac{I}{I_{op}}\right)} \quad (4)$$

where

$I$  is the insolation on the cultivation medium,  $\text{W m}^{-2}$ .

$I_{op}$  is the optimal insolation for maximum growth,  $\text{W m}^{-2}$ .

Irradiance exceeding the optimal level is associated reduced PSE [46]. The irradiance can also reach levels where it damages the algae's photosynthetic ability. To minimize these effects, high irradiance should be avoided: either by diluting the incoming radiation or by choosing a favourable geographical location for the cultivation system. The former is a feature of some photobioreactors (see section 2.3.2), while the latter can be achieved in locations like New Zealand, which is farther away from the equator and thus have lower insolation intensities. This inability to fully exploit high light intensities near the equator is a major disadvantage for algal biodiesel. Now, research points to methods to counter the effect – as explained next.



**Figure 2.2:** Irradiance effects on growth rate. The effect is illustrated using information from [47] and [48]. No numbers are provided for irradiance, as the value will depend on the specie of algae.

Photoinhibition occurs even for moderate light intensities because of the microalgae's large light-harvesting antenna. In their natural environment, the large antenna is likely to have evolved due to its shading effect. The algae, growing in mixed cultures, would benefit from a large antenna, as it ensures their own light capture while preventing light from reaching other species. In monocultures however, this competitive advantage becomes an inhibiting factor as the antenna captures more energy than the algae can utilize [46]. Such an over-abundance of energy can cause energy losses of up to 75 %, drastically reducing the PSE of the algae [49]. High light conditions may also lead to photoinhibition; a process where the light-harvesting antenna is severely damaged, resulting in reduced growth rates (as seen in figure 2.2) [50, 51]. The detrimental effects can be avoided by modifying the light-harvesting antenna: Perrine et al. [49] suggest that by reducing the circumference of the antenna “a two-fold increase in photosynthetic rate [PSE] at high-light intensities and a 30% increase in growth rate at saturating light intensities” are achieved. They postulated that a reduction (but not the elimination) of *chlorophyll b* would result in a smaller antenna and thus located the genome for its production and modified it with apparent success.

Another way to increase the PSE is done by exploiting the intermittent light effect. Photosynthetic organisms have been shown to increase their growth rate when exposed to intermittent light/dark cycles [51]. High cycle frequency (above 1 Hz) shows the highest increase in PSE [52]. It is difficult to achieve this effect in natural conditions, but by mixing the growth medium the intermittent light effect is approximated. The mixing has a secondary benefit: all algae are statistically exposed to sunlight. Evidently, insolation control is desirable if optimal growth should be achieved.

### 2.2.5.2 Temperature

Microalgal growth depends temperature of the growth medium. Instead of approximating the effect with a simple exponential function, another expression, which takes the dependence on irradiance into account, is used [53]

$$f(T) = \left( \frac{T_d - T}{T_d - T_{op}} \right)^\beta e^{-\beta \left( \frac{T_d - T}{T_d - T_{op}} - 1 \right)} \quad (5)$$

where

$T_d$  is the upper temperature limit for algal growth, °C.

$T_{op}$  is the optimal temperature, °C.

$T$  is the temperature of the growth medium, °C.

$\beta$  is a correlation parameter linking temperature and insolation.

Although the microalgae are versatile and can carry out photosynthesis in a wide range of temperatures, most algae show an optimal proliferation in the temperature range 20-35°C [54]. The difference between actual and optimal temperature can be used to calculate the influence of temperature on the growth rate.

The growth rate declines rapidly when the temperature approaches an upper limit. Because the optimal temperature and the upper temperature limit are quite close (*P. Tricornutum* has an optimal temperature of 23°C and an upper limit of 25°C [55]), it is concluded that higher temperatures are more detrimental to growth than lower temperatures.

### 2.2.5.3 CO<sub>2</sub>

Sufficient supply of CO<sub>2</sub> is paramount for a well-functioning photosynthesis. Because carbon accounts for almost 50 % of the algal biomass, 1.86 ton of CO<sub>2</sub> is required to produce 1 ton of biomass [8]. The effect of CO<sub>2</sub> concentration on algal growth can be described by a Monod kinetic equation [56]

$$f(CO_2) = \frac{[CO_2]}{K_{CO_2} + [CO_2]} \quad (6)$$

where

$[CO_2]$  is the concentration of CO<sub>2</sub> dissolved in the growth medium, kg m<sup>-3</sup>.

$K_{CO_2}$  is the CO<sub>2</sub> saturation constant, kg m<sup>-3</sup>.

Rubisco, the enzyme responsible for CO<sub>2</sub> sequestration, has a poor affinity for CO<sub>2</sub> under atmospheric conditions – working only at 30% of full capacity [57]. To utilize its full potential, it is advisable to install an additional supply of CO<sub>2</sub>, thereby increasing the carbon available in the growth-medium. The supply can come from industrial flue gases (given that the gases do

not contain heavy metals or other contaminants) or from an integrated biogas plant (see section 2.7.2). As CO<sub>2</sub> concentration is closely linked to the pH, the latter can help monitor the current CO<sub>2</sub> needs.

In addition, the competing ability of O<sub>2</sub> will influence the growth rate. Because the O<sub>2</sub>-concentration is higher than the CO<sub>2</sub>-concentration by a factor of 600, O<sub>2</sub> will compete with the CO<sub>2</sub> reaction catalysed by Rubisco. This effect can account for 30% of the reaction capability. By implementing an O<sub>2</sub> degassing system, growth rates can be increased further.

#### 2.2.5.4 *Nutrients*

Microalgae require nutrients to synthesize organic compounds. An array of nutrients are necessary for optimal proliferation (30 different metal ions are involved in the photosynthesis [33]), but two compounds are required in substantial amounts – nitrogen and phosphorus [32].

For each ton of algal biomass, 50-80kg nitrogen and 5 kg of phosphorus are required [58, 59]. Even though microalgae use fertilizer with an efficiency of almost 100% [16], the amounts required are vast and constitutes a large amount of total energy demand.

Atmospheric nitrogen is abundant, but its acquisition is energy demanding. The energy required for nitrogen production constitutes a substantial part of the total energy requirement as discussed in section 3. On the contrary, phosphorus is readily available in the ground, but the resources are limited and finite. An estimated 50-100 years of supply is remaining, the duration of which can be drastically extended through nutrient-recycling systems [60]. As a

conclusion, the success of algal biodiesel relies heavily on a system that efficiently recycles nutrients.

#### 2.2.5.5 *Nutrient Depletion Strategy*

Microalgae are shown to accumulate lipids at higher rates under environmental stress such as nutrient depletion, essentially shifting their metabolism from biomass productivity and cell division to lipid accumulation.

Especially the triglycerides, the lipids with the most favourable biodiesel properties, show a significant increase after a period of nutrient deprivation [61]. The robust alga *C. Vulgaris* more than doubled its lipid content under nitrogen deprivation, increasing its content from 18 % to 40 % [62]. But the results are not unanimous; the microalgae *Ulva Pertusa Kjellmann* experienced a relative increase in lipid content when nitrogen was in abundance [63].

Nutrient deprivation is often performed at the latter stages of the growth cycle, resulting in both higher lipid content and reduced use of fertilizer. The downside of nutrient depletion is that it negatively effects biomass accumulation. As the goal should always be to maximize lipid productivity, the optimal growth strategy for the specific specie must be chosen.

#### 2.2.5.6 *Respiration Losses*

When deprived of sunlight, the microalgae must use its energy reserves to uphold vital functions. This leads to respiration losses during the night, which can amount to losses in biomass of up to 35 % [64]. The respiration rate is species-specific and dependent on the temperature of the growth medium. Temperatures are positively correlated with the respiration losses, and should thus ideally be kept low, more specifically as close to 10 °C as possible, where respiration losses are less than 5 % [65].

#### 2.2.5.7 *Contamination*

Microalgal cultures are prone to contamination. Especially open systems will experience contamination from competing algal strains [6]. These strains may have less favourable properties and their success can decrease the overall productivity. The high nutritional value of the algae also attracts grazers and bacteria. Although the adverse effects of contamination are undisputed, there exist no figures of expected productivity losses, as its degree varies greatly from one system to another.

Cultivation of so-called extremophile species can help reduce contamination. Extremophile microalgae thrive in high-temperature or high-salinity environments. As these conditions are unsuitable for other algae, grazers and bacteria, contamination is largely avoided [9].

#### 2.2.5.8 *pH*

Most microalgae prefer a pH between 7 and 8, because Rubisco is most active in this range [66]. Therefore, excess amounts of CO<sub>2</sub> must be avoided, as it acidifies the growth medium [67]. And yet, some microalgae thrive in a growth medium of even higher pH. This can be advantageous for contamination control. One species, *Spirulina sp.* grows efficiently at pH greater than 10. The high pH hinders growth of other species and makes *Spirulina sp.* suitable for growth in Open Pond Systems (section 2.3.1) [68].

### 2.2.6 **Water Usage**

Microalgae require large amounts of water to grow. This is problematic in open systems, as the water evaporates from the ponds. Yet Dismukes et al. [9] state that the cultivation of microalgae in open ponds require less water than rapeseed agriculture as long as proper recycle measures are implemented.

### 2.2.7 Genetic Manipulation

Being unicellular and easy to cultivate, microalgae are amenable to genetic modification [69]. As of 2016, 20 microalgal genomes have been sequenced. That implies that if a gene is attributed to a certain characteristic, it can be modified. One example is the gene for *chlorophyll b* production. If suppressed, a smaller antenna size will be the result [49]. The associated benefit was discussed in section 2.2.5.1.

Genetic manipulation may solve another of algal biodiesel's challenges: When microalgae are grown as a biodiesel feedstock, they are put under stress conditions (e.g. nutrient deprivation) to enhance lipid accumulation [61]. This leads to a simultaneous drop in biomass accumulation and will reduce the overall productivity. A goal should be to deter this effect by manipulating the microalgae to synthesise high amounts of lipids also under optimal conditions.

## 2.3 CULTIVATION SYSTEMS

Algal growth is difficult to control in a natural environment and should therefore be conducted in a controlled cultivation system. The cultivation system is where the biomass accumulates before it is harvested and converted to biodiesel. A microalgal cultivation system should satisfy the conditions described in section 2.2: it must allow for sunlight exposure of all the algae and it should maintain a temperature within the optimal range. Moreover, the growth medium should contain the right amount of nutrients, and contamination should be avoided. At the same time, the system must be simple and frugal. A complicated system with high energy demands will not be viable for large-scale cultivation.

Cultivation systems used for algal biodiesel production are divided into two groups: open systems and closed systems, often called open ponds and photobioreactors respectively. This section will provide an overview of the two technologies and will, through a comparative analysis based on the aforementioned criteria, recommend a system for future large-scale cultivation.

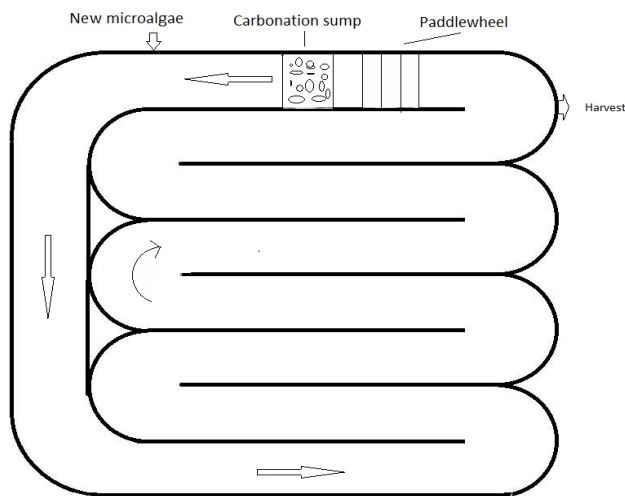


Figure 2.3: The Open Pond System



Figure 2.4: Photobioreactor drawn u. Solidworks

### 2.3.1 The Open Pond System (OPS)

The most common method for large-scale cultivation is the open pond system [70]. It consists of a basin of shallow water – no deeper than 0.3 meters, which is set in motion by a paddlewheel. The concentration of microalgae is kept constant by continuously extracting



growth medium for harvest. A carbonation sump can be installed to increase the CO<sub>2</sub> concentration and boost efficiency. Figure 2.3 shows a schematic of the system.

In an open pond system, the light intensity will change as a function of the pond depth. Accounting for this effect will yield a more accurate estimate of the influence of irradiance [71]

$$I(z) = \frac{1}{z} \int_0^z I_s e^{-K_e z} dz \quad (7)$$

where

$z$  is the pond depth, m.

$I_s$  is the irradiance, W m<sup>-2</sup>.

$K_e$  is the light extinction coefficient, related to the algal concentration, m<sup>-1</sup>.

This equation can be coupled with equation 4 to yield a complete expression for the influence of insolation on growth rate in open pond systems. The algal concentration is assumed constant. This means the effect can be approximated by taking the average of  $n$  depth increments.

$$f(I) = \frac{1}{n} \sum_{i=1}^n \frac{I_s (1 - e^{-K_e z_i})}{I_{op} K_e z_i} e^{\left(1 - \frac{I_s}{I_{op}}\right)} \quad (8)$$

where

$I_{op}$  is the optimal irradiance, W m<sup>-2</sup>.

$z_i$  is the pond depth of the  $i$ 'th increment, m.

Insolation as a function of depth

The flow in an open pond system should preferably be turbulent, as it will facilitate O<sub>2</sub> removal and ensure irradiance exposure of the entire culture [72]. Turbulent flow is achieved when the Reynolds number exceeds 4000, but as the transition region from laminar to turbulent flow is poorly defined, a Reynold's number of 8000 is assumed a minimum. Due to unpredictable hydraulic effects, open ponds often have to operate with a Reynolds number of more than 20,000 [73]. This necessitates a certain velocity of the growth medium. As a consequence, the paddlewheel consumes a large part of the auxiliary energy needed for cultivation [70]. The power demand of the paddlewheel per square meter can be calculated as follows [72]

$$P = \frac{9810 V^3 n^2}{d^3 e} \quad (9)$$

where

$V$  is the water's velocity

$n$  is Manning's roughness factor

$d$  is the pond depth

$e$  is the paddlewheel's efficiency

### 2.3.1.1 *Operation*

The open pond system is normally operated continuously during the day. When the culture medium has reached a sufficient density, it is removed for harvest while fresh culture medium is fed into the system [73]. The aim is to keep the concentration at a constant optimal level. The OPS must be cleaned to mitigate contamination, but due to large volumes they are only cleaned every other month [74].

### 2.3.1.2 *Advantages and disadvantages of the open pond system*

The main advantage of the open pond system is its simplicity. The system avoids overheating by replacing the evaporated water with water from a temperature stable reservoir (the sea, a river or a lake), eliminating the need for cooling systems. As the growth medium is in direct contact with the atmosphere, no system for gas exchange is needed. A system that supplies additional CO<sub>2</sub> could nevertheless be installed, distributed by a carbonation sump with low energy requirements for injection. As a result, the OPS has a low auxiliary energy demands compared to closed systems.

The disadvantages of the open pond system can be summed up as lack of control. It is difficult to ensure that the algal culture first introduced is not contaminated by invasive microalgal species or grazers. Altogether, this will influence the PSE of the system, as total yield is reduced. And, because an OPS is operated continuously, it is difficult to get rid of contamination. Furthermore, it is not feasible to closely monitor nutrient needs or to provide an optimal CO<sub>2</sub> supply (if such a system is incorporated), nor is it possible to distribute CO<sub>2</sub> and nutrients evenly throughout the cultivation system [72]. Lastly, the low biomass density results in inefficient harvesting – a subject addressed in section 2.4 [75].

Another previously thought shortcoming of the OPS was the inability to protect the culture medium against high insolation intensities, but new findings show that some microalgae can tolerate insolation above direct sunlight without efficiency losses [76]. Modification of the light harvesting antennae is also shown to counter the efficiency losses and to minimize the risk of photoinhibition (section 2.2.5.1).

### 2.3.1.3 *PSE of an Open Pond*

The simplest open pond systems achieve a PSE of 0.5%, which is about the same as oil producing land crops. If proper mixing and additional supply of CO<sub>2</sub> is added, the maximum PSE achieved is 2% [15].

### 2.3.2 Photobioreactor (PBR)

A PBR is made of a transparent material, serving as a confinement for the growth medium while allowing for sunlight to reach the microalgae unobstructed. The most common version is the tubular PBR, where the growth medium circulates in tubes and is exposed to sunlight or light from an artificial source. CO<sub>2</sub> is bubbled through the tubes, thereby maintaining optimal CO<sub>2</sub> levels and ensuring proper mixing of the growth medium. Frequent degassing of the system is necessary, as the O<sub>2</sub> that builds up during cell respiration can be detrimental to algal growth [77]. PBRs are prone to temperature rise when subjected to high irradiance levels. A system for cooling is in these cases required to prevent temperatures that are hazardous to the algae.

The PBR offers excellent control of most growth parameters: the temperature, CO<sub>2</sub>-supply, nutrient distribution and pH can all be monitored and optimized. Light dilution systems – systems that keep the incoming radiation at desired levels – can be installed, and show a significant impact on PSE under otherwise sub-optimal irradiance [78, 79]. In addition, the intermittent light effect (section 2.2.5.1) can be achieved by inducing turbulent flow by CO<sub>2</sub> bubbling [68]. All of this contributes to increasing the PSE of the system, making the tubular PBR the most efficient cultivation system, capable of achieving a PSE of 5 % [68].

But the increased PSE comes at a cost. System complexity and high auxiliary energy demand may offset the PBR's advantage [80]. Béchet et al. [81] illustrated this with a computer model of a large-scale PBR cultivation system in California, a region with favourable sun conditions. In order for the growth-medium temperatures to remain below 25°C, 18,000 GJ year<sup>-1</sup>ha<sup>-1</sup> of heat had to be removed. This equates to three times the raw energy of the accumulated algal biomass. Thus for the PBR to be viable, either thermophile microalgae must be cultivated, or the system must be submerged in a pool for cooling [82]. Both strategies will lead to reduced PSE.

### 2.3.3 Choosing the Right Cultivation System

The elevated control of the PBR leads to a significantly higher volumetric productivity. Reported values are 0.2–3.8 g L<sup>-1</sup> d<sup>-1</sup> for the PBR and 0.12–0.48 g L<sup>-1</sup> d<sup>-1</sup> for the OPS. However, Richmond [83] reports that there is little difference in terms of areal productivity. A large scale biodiesel facility would consequently favour the OPS, as it lowers the total energy demand – a claim which is supported by Richardson et al.[84]. On the other hand, if the extraction of valuable co-products is desired, the PBR is likely to be the better option due to the avoidance of contamination [85]. The exact goals of the production should always be taken into account when choosing a cultivation system. Section 2.7.1 will expand on this subject.

## 2.4 HARVESTING AND DEWATERING METHODS

Harvesting of microalgae is challenging due to the relative low density of algae in the growth medium. The solid content ranges from 0.5-1 kg m<sup>-3</sup> in OPSs and 2-9 kg m<sup>-3</sup> in PBRs, hence substantial amounts of water must be removed before the algal oil can be extracted [86]. Harvesting is usually performed in two stages: first concentrating to around 7-10 % dry solids, followed by a more complete drying process where the end-result is either an algal slurry (15-30 % solid content) or completely dried algae, depending on the oil extraction process. The first stage has the purpose of reducing the volume of the medium that needs to be processed, while still maintaining Newtonian fluid properties, thereby avoiding pumping problems [10]. The second stage prepares the algae for biodiesel production.

The simplest harvesting method is gravity sedimentation where particles separate from the liquid because of differences in density. The downside of sedimentation is the slow rate at which it occurs, causing the quality of the algal lipids to deteriorate. Deterioration of the lipids can inflict unwanted productivity losses (e.g. increase in free fatty acid content as shown by Chen et al. [39]). Therefore, other, more sophisticated harvesting methods are needed. There are three leading harvesting technologies, each with its own merits, which will be discussed in the following sections: flocculation, centrifugation and filtration.

**Table 2.3:** Comparison of different harvesting techniques

Technology	Solid content	Energy demand	Remarks	References
Flocculation	15 %	Low	Contaminates	[87]
Centrifugation	22 %	High	Reliable	[71]
Filtration	18-27 %	High for microalgae	Maintenance	[87]

### 2.4.1 Flocculation

A common method used for speeding up the harvesting process is flocculation. Flocculation exploits the charged nature of the microalgal cells [88]. A flocculation agent destabilizes the cells' repulsion forces, causing the microalgae to agglomerate – essentially forming large clusters that are easier to harvest [89].

Flocculation is the preferred harvesting method for the open pond systems owing to its low energy demand. It may also hold the advantage of high solid content of the resulting algal slurry, but reported numbers vary: Zeng et al. [90] (20-30 %), Danquah et al. [87] (15 %) Milledge et al. [86] (3-8 %). Because Danquah et al. [87] justify their claims through experiments, later assumptions will be based on this result. In reality, the solid content will depend on other factors such as type of microalgae, flocculation agent, cultivation system and the initial density of the growth medium.

Flocculation agents should be algae species-specific for optimal effect. The inorganic salt *aluminum sulfate* is shown to be a good flocculation agent for green microalgae such as *C. vulgaris*, causing up to 95 % of the microalgae to flocculate [91]. It is also widely available and can be obtained at low cost. However, inorganic salts will contaminate both the growth medium and the slurry. This can be avoided by using organic polymers (e.g. Chitosan), which show promise as flocculation agent for *C. vulgaris*, with the added advantage of low dosage requirements and better down-stream process characteristics [92]. Unfortunately, these flocculation agents are unavailable in large volumes and are more costly to produce [71, 92].

#### 2.4.2 Centrifugation

Centrifugation is the most reliable harvesting technique for algal biomass. All microalgae can be harvested equally well and there is no need for chemical additives. The centrifuge rotates at high speeds in order for particles of different densities to separate from the fluid – in a sense a sped up sedimentation process. The rate of separation and the solid content of the end product depend on the centrifuge's rotational speed, which again is linked to energy usage.

To obtain an algal sludge with a solid content of 22 %, Sadhukan et al. [71] calculated a energy consumption of 14 MJ kg<sup>-1</sup>. If it is assumed that the algae harvested is *C. vulgaris* with a triglyceride content of 27 % and that the chemical oil extraction yield is at 99 %, it implies that the specific energy consumption of algal oil is 52 MJ kg<sup>-1</sup>; 1.4 times its energy content. Hence, centrifugation is a harvesting technology reserved for biorefineries producing algal products of higher value than biodiesel [91].

#### 2.4.3 Filtration

Solid particles can be separated from water by passing the culture medium through a suitable filter. A wide variety of filters enables optimization of the filtering process. The filter's membrane size must simply be adjusted to the size of the microalgae. The smaller the size of the membrane/pores, the higher the pressure needs to be to force the medium through the filter. *Chlorella* cells have a diameter of 5-6 µm, and require micro filtration, which makes the process too energy intensive to be a viable harvesting method for microalgae [93]. For larger algae or for pre-flocculated cultures, filtration might prove feasible, but high maintenance costs are likely to be a limiting factor [90].

## 2.5 OIL EXTRACTION

After the algae are harvested, the triglycerides must be extracted and separated from the rest of the biomass. Oil can be extracted from the microalgae either mechanically, with a chemical solvent or in a super critical process. Mechanical extraction with an oil press avoids contamination of the end product, but requires the algal biomass to be dry. Drying requires large amounts of energy and is achieved either by solar drying, which is slow and land intensive, or by expensive freeze-drying. The low extraction yield (70 %) is another argument against mechanical harvesting. A more common approach is to first break the cell walls by homogenizing the microalgal cells and then chemically extract the lipids.

### 2.5.1 Soxhlet Extraction

The Soxhlet extraction is often used to extract the algal oils. Using hexane as a solvent, up to 99 % of the non-polar lipids (mainly triglyceride) are extracted and the unwanted polar lipids will not be included in the product. The main challenges of solvent extraction comprise the contamination of the end product, the health and safety risk associated with hexane, and solvent recovery. If valuable co-products are to be isolated from the biomass, they should be extracted before hexane is added to the algal slurry, otherwise contamination and quality deterioration may occur [94, 95].

### 2.5.2 Supercritical CO<sub>2</sub> extraction

The lipids can also be extracted in a process called supercritical-CO<sub>2</sub> extraction. The process operates at moderate temperatures (50 °C) to avoid degradation of the oil, and high pressure (200-250 bar). The pressure decides which components are extracted, enabling separation of high value products without the use of chemical additives [96]. But the operating conditions puts constraints on the technology.

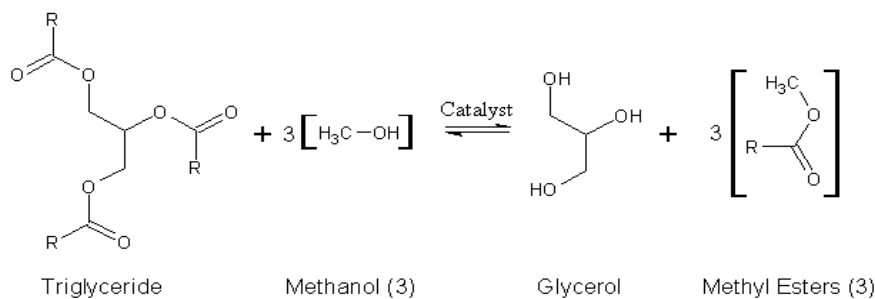
## 2.6 BIODIESEL PRODUCTION

After harvest and extraction, biodiesel production should be initiated as soon as possible to avoid degradation of the algal oil [39]. The oil is composed mainly of triglycerides, which can be converted to biodiesel through a process called transesterification. An emerging and alternative method for production, hydrothermal liquefaction, is also proposed.

### 2.6.1 Transesterification.

In the transesterification process, triglyceride undergoes a chemical conversion to fatty acid alkyl ester (FAAE) – conventionally named biodiesel. The triglyceride, composed of a glycerol molecule with three attached chains of fatty acids, has its fatty acids detached by an alcohol, forming FAAE and glycerol [97]. The reaction requires three moles of alcohol per mole of triglyceride to be in equilibrium. In practice, alcohol should be in abundance to ensure a complete reaction of all triglycerides.

Methanol is the preferred alcohol used for transesterification, as it is widely available and can be acquired at low cost. Moreover, triglycerides are readily dissolved in methanol as opposed to heavier alcohols. With methanol as a reactant, transesterification forms fatty acid methyl ester (FAME) [19, 98]. Figure 2.5 illustrates the transesterification reaction with methanol.



**Figure 2.5:** Transesterification of triglyceride using methanol.

The reaction is catalysed for it to be completed within a reasonable timeframe. Homogenous alkali catalysts, often NaOH or KOH, are commonly used [19, 98]. A conversion rate of >98 % can be achieved for a reactor operating at 60°C and atmospheric pressure [99], making it a suitable catalyst with respect to conversion rate, operating conditions and reaction time. Problems do arise downstream as the alkali solution must be neutralized and water washed for purification. Secondly, the homogenous catalysts contaminate the glycerol, reducing its quality and value. The catalyst is also difficult to recover and recycle.

Solid heterogeneous catalysts can solve many of the downstream challenges associated with alkali homogenous catalysts. As long as they do not fragment, they are easily removed and recycled and do not contaminate the glycerol or the biodiesel [100]. Heterogeneous catalysts require higher amounts of alcohol in the reaction chamber and higher reaction temperatures, adding to costs and energy use. This disadvantage however, may be countered by the removal of processing steps such as water washing and neutralization of the products.

### 2.6.2 Waste Management

For every ton of biodiesel, 100 kg of glycerol is produced. High grade glycerol would sell as a pharmaceutical product, but increased supply may render glycerol purification uneconomical. New ways to exploit glycerol have hence emerged.

One proposal is to use the glycerol to activate the catalyst (Mangesh Avhad, personal communication), but due to low dosage requirement this process will have limited impact on glycerol management.

Another possibility is heterogeneous esterification of glycerol in the presence of gold catalyst. Marchetti [101] observed a conversion rate of 77 % when using 10 % (w/w) catalyst. Limitations of the technology were stated to rely on the reusability of the catalyst, and more work is needed.

Glycerol can also serve as a hydrogen source. There are different ways to produce hydrogen from glycerol, but the most studied is the steam reforming process where the glycerol reacts with water vapour in the presence of a catalyst [102]. The major hurdle of the production process is that crude glycerol impedes the performance of the catalyst, and a purification step will be necessary.

As seen, glycerol has many potential uses. A few hurdles must still be overcome if these options are to be considered viable. A large-scale biodiesel production initiative would likely discard the glycerol by burning it in an industrial furnace as this is the least energy-intensive approach.



### 2.6.3 Supercritical Transesterification Process

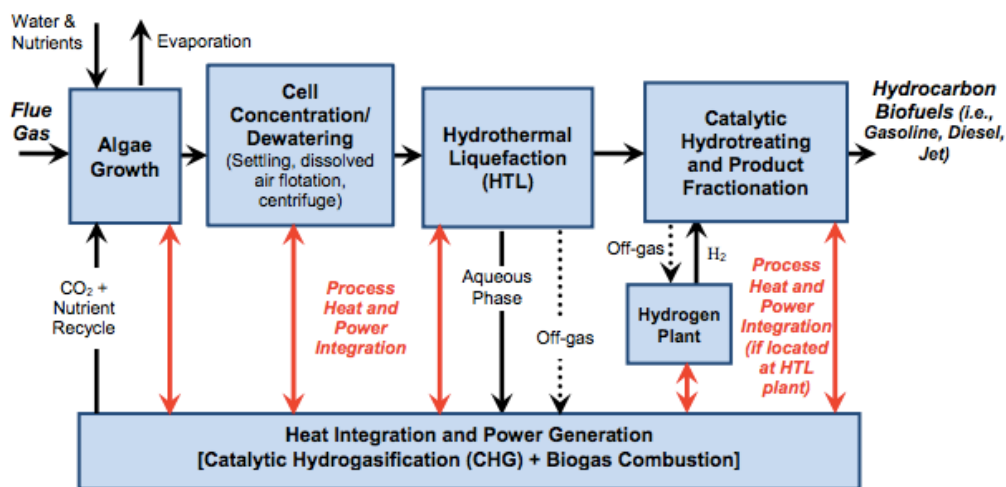
Biodiesel can also be produced by transesterification using supercritical methanol. Because the triglycerides and methanol are in single phase, there is no need for catalysts – the reaction spontaneous [103]. Compared to the homogenous catalytic method, Kusdiana et al. [104] claim that the supercritical process is simpler, has a higher yield and will produce glycerol of higher quality. But as with most supercritical processes, engineering challenges are limiting the viability [105].

### 2.6.4 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is an alternative biodiesel production method. The technology is defined by Toor et al. [106] as a “medium-temperature, high-pressure thermochemical process, which produces a liquid product, often called bio-oil or bi-crude”. HTL has a major advantage with respect to algal biodiesel: water acts as a reactant, enabling direct transformation of wet biomass, in turn lowering harvesting requirements [107]. Furthermore, proteins and carbohydrates also undergo transformation to bio-oil, not just lipids, implicating that lipid content in the algae is of secondary importance and algal strains can be selected for their biomass productivity alone.

If HTL is developed into an energy efficient process, it may become a truly disruptive technology for algal biodiesel. As of now, no large-scale HTL-operations exist and most research is conducted on laboratory-scale reactors [108]. Because HTL is carried out at 280-370°C and 10-25MPa, there are many engineering challenges associated with further development of the technology [109]. Under these conditions, the need for corrosion-resistant alloys adds to the costs, as do the feed pumps that must function under high pressure, not to mention the energy required to maintain the operating conditions [106, 110]. Until the hurdles are overcome, conventional transesterification will be the superior method for biodiesel production.

The chemistry of HTL is complicated and will depend on the molecule undergoing the liquefaction. Toor et al. [106] provide thorough explanation of most processes, but acknowledge that some of the mechanisms are poorly understood. In principle, large organic molecules in the biomass are cleaved and broken down into smaller compounds in the presence of water – they hydrolyse. The ultimate goal is to remove unwanted components such as nitrogen and phosphorus as well as oxygen, and then let the remaining hydrogen and carbon form hydrocarbons. The hydrocarbons make up the bio-oil with energy content similar to that of crude fossil oil (30-40 MJ/kg). The bio-crude can be refined further to extract hydrocarbons of desired length.



**Figure 2.6:** A schematic of microalgal biofuel production using HTL [111]. Reproduced with permission from the National Energy Laboratory

The reported conversion rates differ with respect to the input biomass. For microalgae >70 wt.% is reported by Jones et al. [111], whilst a continuous flow reactor system obtained a conversion rate of 40-60 wt.% [108]. The resulting biocrude contains relatively high amounts of oxygen (5 %) and nitrogen (5 %) and must be purified before it is refined into fuel.

The by-products comprise char, minerals and aqueous HTL-phase. The formation of char in particular is unwanted. Even though catalysts are not necessary for HTL, they have been shown to suppress the formation of char, in turn increasing the total biocrude yield [106]. But more research on HTL is necessary should an ideal catalyst to be recommended. The same goes for HTL technology itself, which has not yet reached maturity.

## 2.7 INTEGRATED SYSTEMS

As shown, different technologies are available for each production step. Be it cultivation, harvesting, extraction or biodiesel production, an optimal technology must be chosen and its dependence on the other production steps must be taken into account (e.g. flocculation will call for another extraction method than centrifugation). The challenge is to design an integrated system that functionally combines different technologies. The following section will explore three ways in which to do so. Thereafter, methods for integrating the system into other processes will be presented (sewage management, anaerobic digestion and CO<sub>2</sub> capture), before an argument is made in favour of the system best suited for large-scale algal biodiesel production.

### 2.7.1 System Integration Examples

The three systems that are about to be discussed all bear unique composition of products in addition to the biodiesel. System 1 emphasises on high-value by-products, which is reflected in its production chain. As a contrast, system 2 neglects the valuable by-products and is designed to maximize its *energy return on energy investment* (EROI) and to minimize maintenance requirements. As a consequence, its by-products are of lower quality. Lastly, system 3 make use of emerging technologies and yields a biocrude that can be refined into products similar to petroleum derivatives.

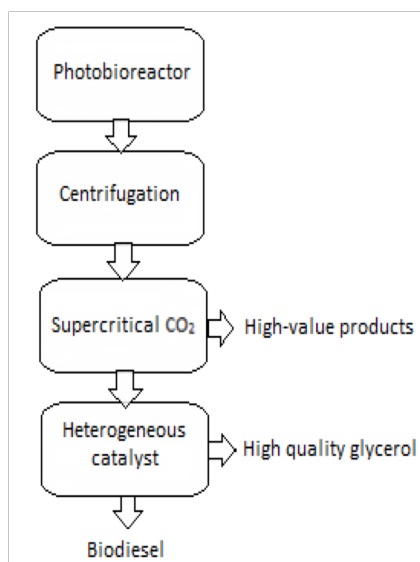


Figure 2.7: System 1

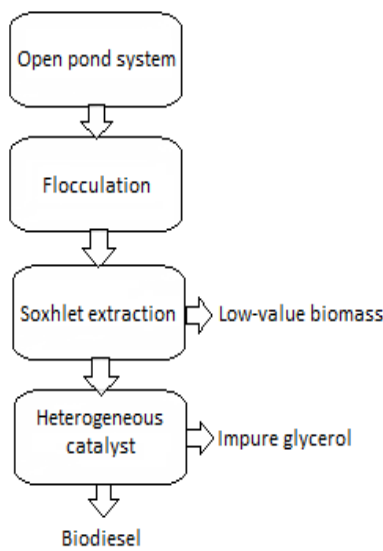


Figure 2.8: System 2

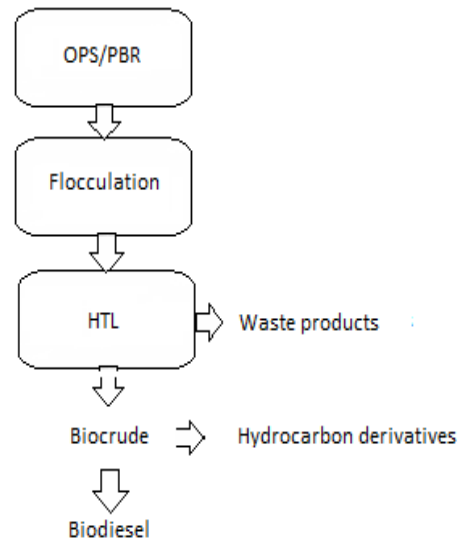


Figure 2.9: System 3

### 2.7.1.1 *System 1*

A system yielding high value products can afford higher auxiliary energy requirements and production costs. Valuable oils can be extracted, as can desired proteins. Moreover, no flocculation agents are used, nor any extraction chemicals. Combined with the use of heterogeneous catalyst, this ensures high-quality glycerol. So, although the EROI of the biodiesel may be lower, a positive profit margin can be reclaimed by selling the quality by-products. This system is excellent in a transition phase (especially with respect to research, as contamination is avoided), but will not facilitate large-scale biodiesel production [85]. Figure 2.7 shows a schematic of the system.

### 2.7.1.2 *System 2*

In order to produce the amounts of biodiesel defined as large-scale production, it is necessary to simplify the system. To follow the principles of agriculture: wheat is not grown in greenhouses. Biodiesel yield is prioritized and the system will use proven technologies with low auxiliary energy demand. The goal will be to maximize the energy return on energy investment (EROI) and reduce maintenance requirements.

### 2.7.1.3 *System 3*

System 3 is an attempt to predict a possible future system for algal biodiesel production. Emerging technologies should also be taken into account: Based on recent literature, many agree on HTL to be a disruptive technology *\*source\**. The ability to use water as a reactant solves one of the major hurdles of algal biodiesel: the slurry's water content. The advancement of HTL still relies on breakthroughs regarding the oxygen, nitrogen and phosphorus content of the bio-crude as well as issues with pumping under high pressure. A schematic of what such a system could look like is illustrated in figure 2.9. No calculations have been performed with this set-up as basis due to the many uncertainties associated with HTL.

## 2.7.2 **Integration with Other Processes**

As mentioned, algal biodiesel production can be integrated with other industrial processes for synergetic benefit. CO<sub>2</sub> and sewage containing phosphorus and nitrogen are normally considered waste products. Yet both have the ability to further the growth of microalgae and should be considered a resource. Different ways to exploit the industrial by-products have been proposed, while others are already implemented. Some of them are discussed here and cover most of the possibilities of process integration

### 2.7.2.1 The ACAD System

One way to combine different processes for enhanced performance is the *algae cultivation, anaerobic digestion* (ACAD)-system. ACAD is meticulously examined in Jon Eivind Strømme's [112] excellent master's thesis, and encompasses many clever ways in which to use waste and recycle nutrients. A short overview will be provided here.

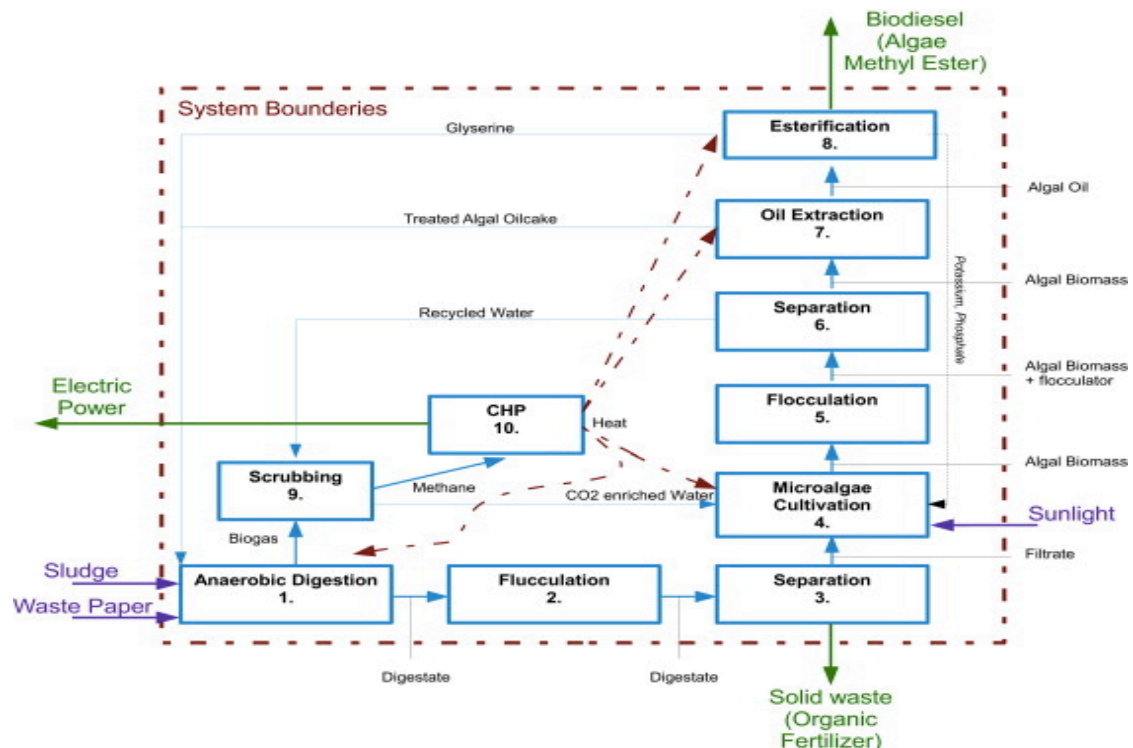


Figure 2.10: Schematic of the ACAD-system. Reproduced with permission from Strømme[112]

In essence, figure 2.10 shows

1. The organic waste decomposes anaerobically to form biogas and organic fertilizer.
2. The organic fertilizer is added to the microalgal culture.
3. The microalgae then undergo the process of harvest, extraction and transesterification.
4. After the algal oils are extracted, the remaining biomass is fed into the anaerobic digestion chamber.
5. Simultaneously, water removed in the harvesting process is used for water scrubbing of the biogas: the biogas, containing CO<sub>2</sub> and methane (CH<sub>4</sub>), is passed through the culture medium. Since CO<sub>2</sub> has a higher solubility in water than CH<sub>4</sub>, it will dissolve – efficiently cleaning the biogas (CH<sub>4</sub> is the desired product).
6. The CO<sub>2</sub> enriched water can now re-enter the cultivation system whilst the CH<sub>4</sub> can be burned on site for electrical power and/or heat for the ACAD system.
7. If the CH<sub>4</sub> is burnt onsite, the resulting CO<sub>2</sub> can be used to further increase CO<sub>2</sub> concentration in the cultivation system.

The ACAD system seamlessly combines many production steps to enhance the total performance. A performance of which John Morken [113] states the following: “The model shows that the ACAD biorefinery could be totally independent of external energy supplies”. This is under the assumption that sufficient sewage can be supplied.

#### 2.7.2.2 *CO<sub>2</sub> Capture*

Another symbiotic way to incorporate algal biodiesel into other processes is to use the microalgae to capture CO<sub>2</sub>. In this approach, industrial flue gases are passed through the photobioreactor contained algal medium, enhancing growth. The carbon footprint of the industrial process will consequently be reduced because the resulting biodiesel replaces fossil diesel. This concept is currently being implemented at Mongstad oil refinery, where they will use artificial lights to ensure continuous production [114]. The desired product is fish feed (omega-3 fatty acids), which has a higher value than biodiesel.

### 2.7.3 System Proposal

As seen, system integration plays an important role in biodiesel production. The set-up will greatly influence the composition of the products as well as the energy demand of the system. Based on the criteria set for large-scale biodiesel production, system 2 appears to be the only viable system that also utilizes proven technology. Therefore, system 2 will be the basis for the algae biorefinery model presented in section 3. Some of the combined processes presented in section 2.7.2 have also been added to the model, as they are shown (especially those presented in the ACAD-system) to have beneficial effects.

## 2.8 THEORY RECAPITULATION

Thus far, the motivation and technology behind algal biodiesel have been examined. Before embarking on the modelling of an algae biorefinery, a short summary of the presented theory is in order.

First, biodiesel and its properties were presented, as were the possible feedstocks used for its production. The feedstock microalga and its necessary growth conditions were then investigated and these growth conditions served as a basis when discussing two different cultivation systems – the photobioreactor and the open pond system, before the subsequent steps in the production chain were scrutinised – harvest, extraction and biodiesel production. In the end, all the steps were brought together in three distinct integrated systems, and each of them had its performance evaluated. Altogether, the theory lays the foundation for the model biorefinery, presented in the upcoming section.

### 3 MODEL BIOREFINERY

In this section, a crude model of an algae biorefinery is proposed. The technical potential of the biorefinery is calculated, and its performance is compared to that of best practice biodiesel and petrodiesel. A method description will precede the results, which are followed by a thorough discussion. The ultimate goal is to reach a conclusion on the viability of microalgal biodiesel.

#### 3.1 GOAL AND SCOPE

In short, the analysis aims to assess a model biorefinery's performance using the parameters technical potential, energy return on energy investment (EROI) and global warming potential (GWP). The scope of the analysis will be that of a *cradle-to-gate* life cycle analysis, which means that the distribution and burning of the fuel are left out of the calculations. The exact scope and system boundary are detailed in upcoming sections.

The *technical potential* is in this case defined as the biodiesel energy output under the given conditions, with the denomination  $\text{kWh m}^{-2} \text{y}^{-1}$ . In other words, the expected biodiesel yield of the model biorefinery that is about to be presented.

The *performance* of the model biorefinery is measured mainly by calculating the energy return on energy investment (EROI). The EROI is defined as the ratio between energy output and energy input. In the case of biodiesel, this implies the ratio of the biodiesel's chemical energy content to the auxiliary energy input. The higher the EROI, the better the performance of the system. Because the EROI of other liquid fuels is readily available, it makes for a simple comparison.

Yet, the EROI does not paint a complete picture of the biorefinery's performance. The EROI of fossil fuels, for example, is generally quite high, but their GWP is not included in the calculation. Therefore, GWP can be considered another parameter used to assess the performance.

Other factors, such as initial investment and continuous costs, will also influence the viability of the biodiesel, but their effects are omitted from the scope of this technical analysis. The main reason for leaving out the economics is the uncertainty. In a techno-economic analysis of algal biodiesel, cost estimates ranged from 0.42 to 72 USD  $\text{L}^{-1}$  [115]; highly inconclusive. That being said, the EROI does reflect the operating costs to a certain degree, as higher energy requirements lead to higher continuous costs.

The lack of empirical data implies that the end result cannot be considered exact, nor does the limited data allow for meaningful error margins to be calculated. The results should rather serve as insight into the yield and expenditure of the stipulated biorefinery within reasonable limits

## 3.2 METHOD

The following steps were undertaken to assess the algae biorefinery's performance.

1. Detail the model specifications and set the system boundary
2. Determine the system's biodiesel yield
  - a. Calculate biomass accumulation
  - b. Calculate biodiesel production
3. Determine auxiliary energy input
4. Determine global warming potential

The first step will include specifications of the model biorefinery and arguments for the model set-up. With a clearly defined model, it is possible to calculate the potential biodiesel production using appropriate theory. Data from literature is then used to determine the model's auxiliary energy requirements. The EROI is calculated on this basis. The global warming potential is obtained from the auxiliary energy demand and the specific GWP of Brazilian energy supply.

### 3.2.1 Model Specifications

Before the calculations can be performed, it is necessary to detail the system. System 2 from section 2.7.1 will serve as a framework for the model and will be expanded by determining the technologies and strategies which lead to optimal growth. Moreover, location, nutrient supply and waste management will influence the model and must be specified. Figure 2.11 shows a complete schematic of the model, underneath which the decisions are justified.



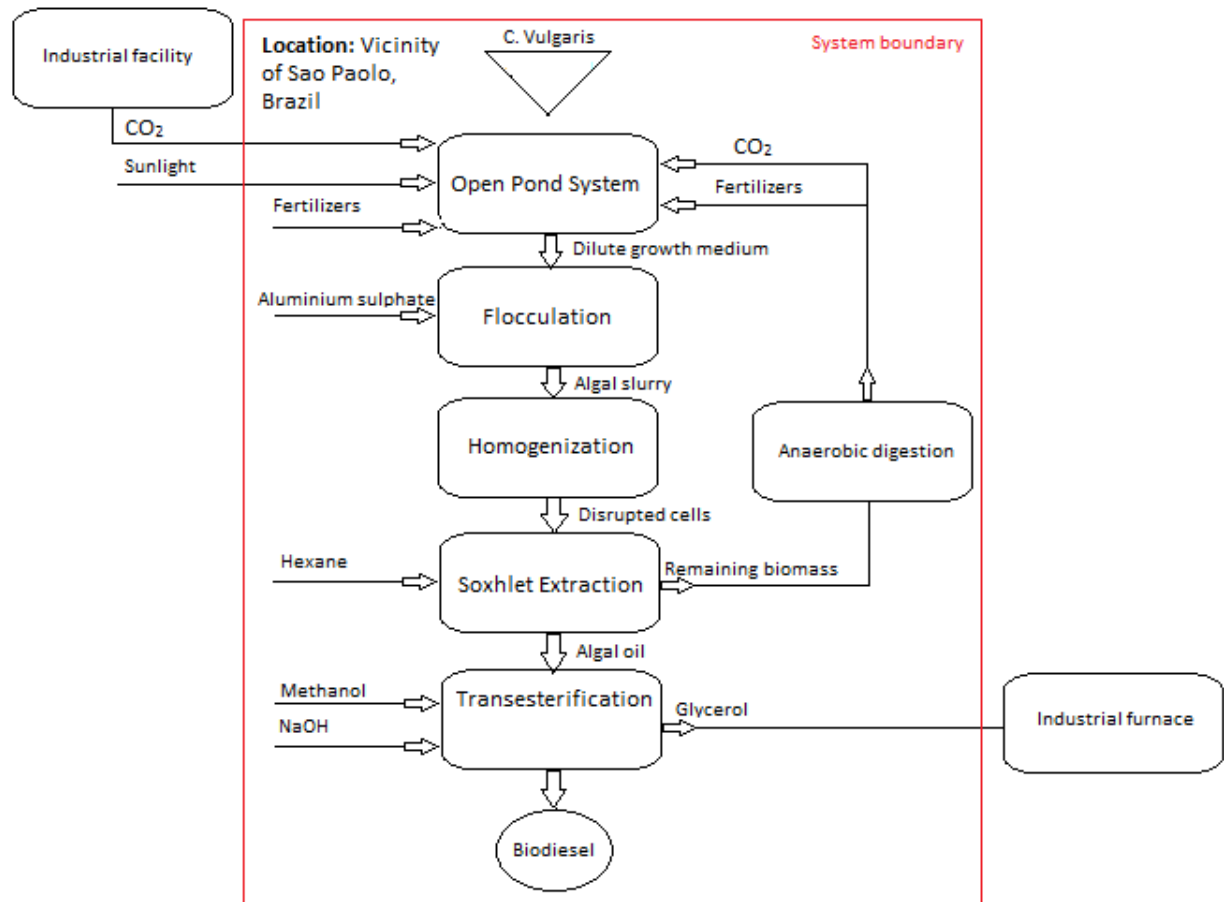


Figure 3.1: Model schematics

### 3.2.1.1 Location

The location is set to the vicinity of Sao Paolo, Brazil, due to favourable irradiance levels and temperatures. Initially, locations at latitudes farther away from the equator were assumed superior, but the benefit of long summers and low-light conditions were offset by long, cold winters. Desert regions were also investigated, as they experience the highest annual energy input from the sun, but were deemed unsuitable because they lack infrastructure and freshwater supply.

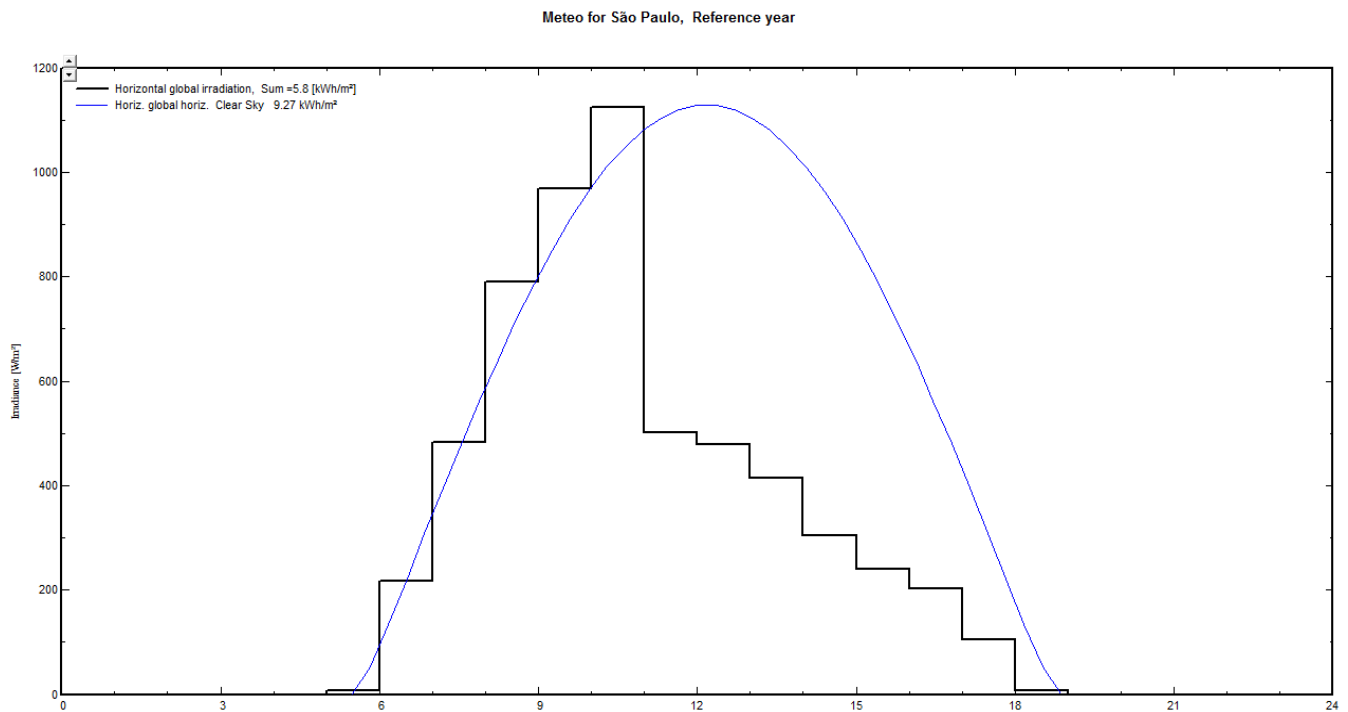
Brazil is a major producer of oil palm, utilizing the most productive oil crop that is grown at a large scale [116]. Cultivation of oil palm is however considered detrimental to both the local and global environment, and effort should be directed towards the development of new, better ways in which to produce oil and biodiesel. Microalgae might be the solution, but such a technological shift will require substantial restructuring and investment.

Certain factors indicate that Brazil is a suitable location for a shift to microalgal biodiesel. For one, biofuels, mainly bioethanol, already constitutes 40 % of Brazil's transportation fuel consumption (2012) [117]. Additionally, Brazil is the fourth largest biodiesel producer in the world [118]. The country's expertise should thus play in favour of a liquid biofuel initiative. Furthermore, the global warming impact of Brazilian electricity is significantly lower than the world average, owing to the large share of hydropower (>75 %). This will have a large impact on the overall GWP, as microalgal biodiesel is energy intensive to produce.

To be more specific regarding the location, the biorefinery must be located in an area of non-arable land. Otherwise, an important aspect of algal biodiesel will not be exploited – that it does not compete with food crops. Therefore, there should be no alternative use of the land that could mitigate global warming (planting of trees and the like), consequently the GWP of the land usage equals zero. However, the biorefinery was not located in Brazil's eastern semi-arid region. The reasons were the limited supply of freshwater and long distances to population centres where fuel is needed. Therefore, the vicinity of Sao Paolo was chosen, although no thorough investigation of available land area has been done. The fact that heavy rainfall in the region may overly dilute the ponds was not taken into account.

### 3.2.1.2 Insolation and Temperature Simulation

The software *PVsys* was used simulate irradiance and temperature. The program uses past meteorological data to simulate insolation, cloud cover and temperature at the chosen location over the course of a year. Hourly data accounts for the fluctuations throughout the day, and gives a better accuracy than daily averages. A graphical representation of data from an arbitrary day can be found in figure x.



**Figure 3.2:** PVsys output on an arbitrary day. Hourly irradiance levels

Figure x illustrates that insolation can reach very high levels at the chosen location. Problems may arise during peak hours, when the irradiance can exceed  $1 \text{ kW m}^{-2}$ . This puts the algae at risk of photoinhibition. The issue is addressed in due course.

### 3.2.1.3 Cultivation System

The argument for the open pond system has already been made, but certain aspects must still be determined. First, the effective area should be decided. This is the fraction of the entire biorefinery's area covered by the growth medium. No information on this could be found in the literature, so an area coefficient had to be assumed, somewhat unscientifically, by looking at pictures of open pond production facilities and estimating the areal distribution. It was approximated that 90 % of the area is occupied by growth medium.

#### 3.2.1.4 *Cleaning*

Open pond systems are prone to contamination and must be cleaned at regular intervals. Efficient cleaning systems can be installed to keep downtime to a minimum. Weissman et al. [72] argue that 360 days of operation per year can be used. Because this is the most elaborate study on open pond systems encountered, this figure will be replicated. The contamination coefficient, which accounts for maintenance downtime, is thus  $360/365 = 0.98$ . Cleaning is proposedly done

#### 3.2.1.5 *Mixing*

Mixing of the culture medium is important to ensure distribution of nutrients and CO<sub>2</sub>. A high water velocity in the raceway pond will increase mass transfer and improve growth conditions, but comes at a cost. Higher velocities will increase the paddlewheel's power demand. The optimal conditions (sufficient mixing at minimum power demand) are found to be 0.2 m s<sup>-1</sup> for a pond depth of 0.2 m [72].

#### 3.2.1.6 *Paddlewheel*

The water is put in motion by a paddlewheel, which constitutes a large part of the total auxiliary energy demand. Its specific power requirement depends on the factors described in equation 9. In this model, a concrete raceway pond is assumed with a Manning's roughness factor of 0.018 m s<sup>1/3</sup>, and the paddle's efficiency is set to 0.40 [72]. The approach neglects the hydraulic effect of a carbonation sump installed in the raceway. A slightly higher power demand than what is predicted by the equation should be expected in practice.

#### 3.2.1.7 *The Microalgae*

*C. Vulgaris* is one of the most studied microalgal strains when it comes to biodiesel, and it is the microalga of choice for the model. Although it has strong contenders in both the fast growing *P. Tricornutum* and the marine *D. Salina*, *C. Vulgaris* is preferred due to its versatility, growth rate, lipid profile and its ability to accumulate lipids under nutrient deprivation [40]. As opposed to *D. Salina*, *C. Vulgaris* is a freshwater microalga. Though this may sound like a major disadvantage, *D. Salina* would also require a supply of freshwater in order to avoid the detrimental salinity that is caused by evaporation in open ponds. The freshwater culture does however heighten the risk of contamination from invasive species. Therefore, versatility and contamination resistance is especially important. In this respect, *C. Vulgaris* has shown favourable characteristics and is known to survive under stress from viruses, bacteria, fungi and pollutants, as it rapidly repairs its DNA [119].

### 3.2.1.8 Growth Rate

The microalgae's growth rate will exert a large influence on the biodiesel yield. Incidentally, this figure was also the most problematic to acquire. Even when narrowed down to one specific microalga grown under nutrient deprivation in otherwise optimal conditions\*, the reported values did not conform. Again, experimental reports were favoured over information from review articles because detailed growth parameters were available. The maximum hourly growth rate of *C. Vulgaris* under nitrogen deprivation was found to be  $20 \text{ mg L}^{-1} \text{ h}^{-1}$  [120].

### 3.2.1.9 Lipid Profile

The lipid profile will influence the biodiesel quality, as indicated in section 2.2.4. *C. Vulgaris*' lipid profile is presented in table x and the favourable fatty acids are all present. *C. Vulgaris*' ability to yield quality biodiesel has been confirmed experimentally by Francisco [121].

### 3.2.1.10 Lipid Content

High lipid content is a desirable trait for microalgae as biodiesel feedstock. After a period of nutrient depletion, *C. Vulgaris* consists of 40 % lipids [120]. Literature is not entirely conclusive, but most results indicate that nutrient deprivation leads to the highest lipid productivity. In other words, enhanced lipid synthesis is beneficial even though it comes at the cost of reduced growth rate. Nutrient depletion also has the added benefit of reduced fertilizer consumption.

### 3.2.1.11 Irradiance

The growth rate is at a maximum only when irradiance is optimal. Sources vary, but for *C. Vulgaris* an optimal irradiance around  $250 \text{ W m}^{-2}$  was reported [47]. This irradiance level can be surpassed by a factor of four during the Brazilian summer, negatively influencing growth rates. Therefore, a method of antenna circumference reduction has been implemented, thereby improving light capture under high light conditions. A slight simplification of Perrine et al.'s [49] results has been made, and the optimal insolation after antenna modification is estimated to  $500 \text{ W m}^{-2}$ . It is assumed that the antenna-size is modified by selecting strains that contain lower amounts of *chlorophyll b*.

Because of *C. Vulgaris*' ability to efficiently repair its own DNA, any detrimental effects caused by high irradiance (abrupt decline of growth rate) are neglected. The intermittent light effect (section 2.2.5.1) is also omitted from the calculations as it is of little influence in open pond systems. Influence of sunlight will follow equation 4 and consequently the daily irradiance variation simulated in *PV-syst*. Night-time respiration losses are accounted for in the model.

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\* The lack of uniformity could be due to difficulties in determining the optimal conditions.

### 3.2.1.12 *Temperature*

For *C. Vulgaris* the optimal temperature is found to be 27 °C and the maximum temperature 33 °C [122]. The influence of the temperature is calculated using equation 5 and data from PVsyst. This approach has one shortcoming – it does not fully account for the effect of irradiance on the pond temperature. Evaporation and water replenishment will reduce fluctuations and help avoid detrimental temperatures, but deviations from air temperature are still to be expected [123]. An attempt was made to model these effects by assuming a correlation coefficient of 1.25, as per Sadhukhan [71].

### 3.2.1.13 *CO<sub>2</sub> supply*

The CO<sub>2</sub>-supply is assumed to come from an industrial facility in the vicinity of the ponds. Industrial flue gas consists mostly of nitrogen and water vapour; its CO<sub>2</sub> content being approximately 15 %. It also contains small amounts of sulphur, NO<sub>x</sub> and ash. The flue gas is therefore scrubbed to avoid contamination, after which it is distributed using a carbonation sump [72]. The industrial facility is assumed to provide the energy required for scrubbing, while the energy for CO<sub>2</sub> injection is set to 22.2 Wh per kg of CO<sub>2</sub> [124].

In the model biorefinery, optimal concentration of CO<sub>2</sub> used. That means that the Monod equation (equation 6) equals 1, which necessitates that a concentration of at least 65 μmol L<sup>-1</sup> is maintained and that the growth medium's pH is 8.5 [125]. For this to be sustained, the rate of CO<sub>2</sub> sequestration must be determined. The cultivation of one ton microalgae requires 2200 kg CO<sub>2</sub>. De Godos et al. [126] found that 66 % of the supplied carbon was taken up by the biomass. If assuming a CO<sub>2</sub> recycling degree of 44 % enabled by the anaerobic digestion [72], then 1870 gCO<sub>2</sub>/kg microalgae is required.

Oxygen levels are set below the growth inhibiting concentration of 25 mg L<sup>-1</sup> [127], and hence no degassing system is installed. Larger ponds subjected to high insolation are at risk of exceeding the limit. As this applies to the model at hand, the effect should have been accounted for. However, no data on expected oxygen levels could be found, so the detriment is neglected.

### 3.2.1.14 *Nutrients*

In a real scenario, a two-step growth process is common. First, the microalgae are grown with sufficient fertilizer, before it is transferred to a nutrient deprived pond. For the model, a constant growth rate under constant nutrient deprivation is assumed. The required fertilizer is estimated by looking at the composition of the microalgae. Under nutrient deprivation, the microalgae consist of 60 kg nitrogen and 5 kg phosphorus Chisti [8]. Nitrogen and phosphorus will be supplied using ammonium nitrate (34.5 wt.% nitrogen) and triple super phosphate fertilizer (18 wt.% phosphorus) respectively.

Nutrient recovery is paramount for the success of microalgal biodiesel, as fertilizer is costly and energy intensive to produce. An anaerobic digestion process is used to recover nutrients from the biomass. 76 % of the nitrogen and 50 % of the phosphorus is assumed recycled [128]. Using sewage water as an additional nutrient supply could reduce nutrient needs even further, but is considered too problematic due to the risk of contamination and distribution challenges.

Total fertilizer needs, under the assumption that distribution and uptake limitations are negligible [16], amount to 55 kg ammonium nitrate and 14 kg triple superphosphate per ton biomass.

#### 3.2.1.15 *Respiration losses*

*Chlorella* microalgae are shown to lose 5 % - 15 % of the accumulated biomass every night, depending on growth-medium temperature [65]. Night-time temperatures at the chosen location average out at 18 °C, hence 10 % of the biomass that is accumulated during the day is lost, should the results of Shah [64] be followed.

#### 3.2.1.16 *Growth strategy*

When the algal concentration in the ponds have reached 0.5-1 kg m<sup>-3</sup>, the system will be operated continuously during the day. Fresh medium is introduced as the old is harvested at a rate that keeps the concentration constant, as recommended by Chisti [73]. The open pond systems are flushed completely every 2 months, which is an efficient method to control contamination [62].

#### 3.2.1.17 *Harvesting*

Flocculation is chosen as the harvesting method because of its low energy demand. Flocculation is often followed by centrifugation to further concentrate the slurry. Yet Zeng et al. [90] have shown that a solid content of 15 wt.% is achievable after flocculation alone, which is sufficient for downstream processing. Tran et al. support this claim for *C. Vulgaris* specifically, stating that flocculation harvested *C. Vulgaris* show similar biodiesel conversion rates to centrifugation harvested *C. Vulgaris* [92]. As a result, energy intensive centrifugation is considered obsolete.

Biopolymer flocculants would surely be the best flocculant with respect to contamination. Unfortunately, they do not fit a large-scale production system, as the supply is limited. Instead, the inorganic salt *aluminium sulphate* is used, as it has proven to be an effective flocculation agent for harvesting of *C. Vulgaris* [91]. The energy required for its production amounts to 0.50 GJ/ton biodiesel.

### 3.2.1.18 *Cell disruption*

Before extraction, the cell walls are broken in a homogenizer. The homogenizer requires an auxiliary energy input of 1.7 GJ/ton biodiesel and it achieves a 96 % disruption rate [74, 129].

### 3.2.1.19 *Extraction*

The Soxhlet extraction is used to separate the non-polar lipids from the algal biomass. Close to 99 % of the triglycerides are recovered in the process [130]. An additional benefit is the ability to recycle the solvent – in this particular case, hexane. Energy requirements, also accounting for the production of hexane, is 2.1 GJ/ton biodiesel (see appendix section A.2.3).

### 3.2.1.20 *Transesterification*

The lipids are transesterified using methanol and a heterogeneous alkali catalyst, as this yields the fastest reaction time. The conversion rate is set to 99 %, which is not uncommon for industrial facilities. An estimated 3.2 GJ/ton biodiesel is required in this process (see appendix section A.2.4)

### 3.2.1.21 *Anaerobic digestion*

The biomass that is left after the removal of lipids is used to produce biogas in an anaerobic digester. The digester has a secondary benefit; it enables nutrient and CO<sub>2</sub> recovery at the aforementioned rates (section 3.2.1.13 and section 3.2.1.14). The energy it produces will contribute to lowering the auxiliary energy demand. The value is set to 10 GJ/ton biodiesel [74, 113].

### 3.2.1.22 *Waste management*

The market for pharmaceutical grade glycerol is quickly saturated. Any large-scale biodiesel production is likely to render glycerol purification uneconomical [131]. Energy-wise, glycerol burning in an industrial furnace is better than purification [74]. This is particularly valid for this model, as the chosen biodiesel production method yields low quality glycerol. The glycerol is treated as a pure waste product, meaning that any energy gained from burning the glycerol does not benefit the biorefinery



**Table 3.1:** Data used to determine the model's potential biodiesel yield per area.

Parameter	Units	Values	References
Max. growth rate	$\text{g L}^{-1} \text{h}^{-1}$	0.020	[120]
Lipid content	-	0.40	[120]
Pond depth	m	0.20	[125]
Light extinction coef.	$\text{m}^{-1}$	30.3	[71]
Optimal insolation	$\text{W m}^{-2}$	500	[15, 49]
Insolation	$\text{W m}^{-2}$	variable	PVsyst
Optimal temp	$^{\circ}\text{C}$	27	[132]
Maximum temp	$^{\circ}\text{C}$	35	[132]
Temp	$^{\circ}\text{C}$	variable	PVsyst
Correlation factor	-	1.5	[71]
Respiration losses	-	0.10	[65]
Area coef.	-	0.90	This thesis
Contamination coef.	-	0.98	[72]
Harvest recovery	-	0.95	[90]
Cell disruption rate	-	0.96	[74]
Lipid extraction recovery	-	0.99	[130]
Oil to biodiesel conversion	-	0.99	[99]
Energy content biodiesel	$\text{MJ kg}^{-1}$	37	[24]

### 3.2.2 Calculation approach

#### 3.2.2.1 Potential Biodiesel Yield

Equipped with the system specifications it is possible to calculate the potential biodiesel yield. The yield was obtained by first calculating the microalgal growth rate with equation 3, 5 and 8 using the information from table 3.1 and weather data from PV-syst. Then, downstream losses, also listed in table 3.1, were accounted for. Detailed calculations can be found in the appendix (A.1).

#### 3.2.2.2 Auxiliary Energy Demand

The auxiliary energy demand was found for each described process. Most are retrieved from literature, but some have to be calculated as they are specific for the model refinery. Detailed calculations can be found in the appendix (A.2)

#### 3.2.2.3 EROI

The EROI of the biodiesel from microalgae is determined by the ratio between biodiesel yield and auxiliary energy demand. The EROI of biodiesel and fossil diesel are found in literature, and they are all compared in table x.

#### 3.2.2.4 *Global Warming Potential*

In order for the biorefinery's GWP to be determined, it is necessary to calculate the GWP of the Brazilian energy mix. It was assumed that all auxiliary energy was supplied by Brazilian electricity with the exception of the production of fertilizer, methanol and hexane. Because Brazil has a large share of renewable energy (>75 % hydropower), the GWP is lower than what would be expected in most countries. A more detailed explanation of GWP calculations can be found in the appendix (A.3).

## 4 RESULTS

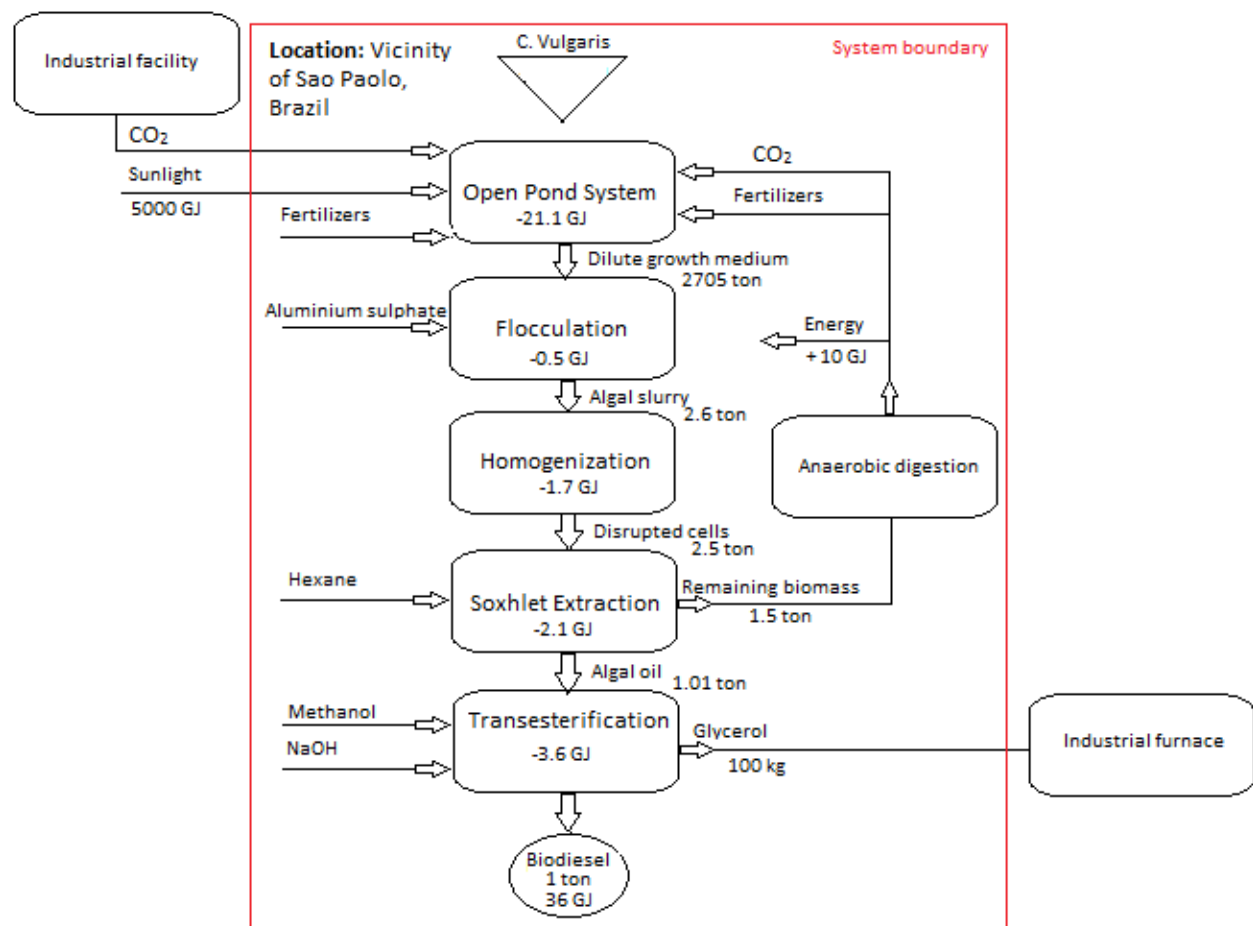
This section provides an overview of the important results. The technical potential, auxiliary energy demand, EROI and GWP are listed in table 4.1. Figure 4.1 outlines the energy and mass flows in the system. The results are commented and discussed in the next section.

**Table 4.1:** The most important results from the model and its comparators

Parameter	Units	Microalgae <sup>a</sup>	Palm oil <sup>a</sup> [8] [133]	Fossil <sup>b</sup> [134]
Technical potential	Ton fuel ha <sup>-1</sup> y <sup>-1</sup>	10.7	4.0	-
Auxiliary energy	GJ (ton fuel) <sup>-1</sup>	20.1	7.0	2.0
EROI	-	1.8	5.3	20
GWP	tonC (ton fuel) <sup>-1</sup>	1.9	2.0	2.9

<sup>a</sup> Energy content of biodiesel: 37 MJ/kg

<sup>b</sup> Energy content fossil diesel: 42 MJ/kg



**Figure 4.1:** Energy flow overview



## 5 DISCUSSION

### 5.1 MODEL LIMITATIONS

Although attempts have been made to propose a reasonable model, it will be subject to certain limitations. Prior to the discussion of the results' effect on present and future viability, the validity of the results is investigated.

#### 5.1.1 Potential Biodiesel Yield

An often cited figure, that of Chisti [8], states that the biodiesel yield from microalgae with a lipid content of 30 % is 41 ton ha<sup>-1</sup> y<sup>-1</sup>\*. This is four times higher than the biodiesel yield found for the biorefinery above. Possible reasons for the discrepancy should be investigated.

The microalgae's growth rate has a major influence on biodiesel yield. Therefore, the credibility of the chosen growth rate had to undergo some scrutiny before it was accepted as a model parameter. By using the optimal insolation of 500 W m<sup>-2</sup>, the maximum photosynthetic efficiency was calculated to 5.3 %, which is an efficiency comparable to that of closely monitored photobioreactors. The chosen growth rate is consequently considered reasonable.

If the deviations from Chisti's results do not stem from an erroneous growth rate, the cause may be the irradiance influences. Calculations show a productivity loss of 76 % inflicted by non-optimal irradiance. This number may be subjected to different sources of error: the mathematical model itself, unfavourable location, and a negative influence caused by the optimal irradiance value.

As for the mathematical model, the Steele equation was combined with Beer-Lambert's law to equate the influence of irradiance. Although this is a crude approach, it does according to Sadhukhan et al. [71] provide a good approximation. Especially when hourly irradiance data is available, which is the case for this model.

The effect of irradiance at the chosen location was examined by running simulations for numerous other locations. Neither a change to higher nor lower latitudes had a positive effect of significance on productivity. In most cases, a productivity decrease of 5 % or more was shown.

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\* Derived from 58 700 L ha<sup>-1</sup> y<sup>-1</sup> algal oil produced, assuming density 0.88 kg L<sup>-1</sup> and accounting for 80 % downstream losses, in accordance with Chisti's suggestions.

Slight alterations of the optimal insolation value were also tested, which resulted in a productivity improvement of 1 % at best. When set at reasonable values, the optimal insolation constant had little influence on productivity. It rather sets a limit for photoinhibition. There is evidently little reason to believe that the potential yield is underestimated.

There are, however, indications pointing in the opposite direction; that the potential biodiesel yield is overestimated. First off, the estimates of Chisti necessitate a photosynthetic efficiency of 7.2 % (microalgal oil content 30 %) and 11.7 % (microalgal oil content 70 %), and thus seem to be extrapolated from carefully controlled experiments. Hoekman et al. [135] support this claim, stating that potential yields based on small-scale operations should be regarded as speculative.

Thus, the scalability of Chisti's yields is improbable. Schlagermann et al. [15] argue that the photosynthetic efficiency of microalgae has a maximum value of 5.4 % in practice. Whether an open system or photobioreactors are used is unimportant. The photobioreactor is superior in terms of volumetric productivity, but its areal productivity is similar to that of the open pond system [83]. This strengthens the view that Chisti's yields are at present unobtainable in practice.

The yields projected by the model biorefinery may also be overestimated. As mentioned in the section 3.2.1.12, some temperature effects have not been accounted for and the predicted 12 % loss caused by non-optimal temperatures would be higher in a real scenario. Moreover, the assumption that CO<sub>2</sub> and fertilizers are supplied optimally is unlikely to be valid for an open pond system. Limited control and monitoring, as well as the delay in the distribution system will create sub-optimal conditions with a negative effect on growth rate.

In the aggregate, the system efficiency of 0.74 % (percentage of solar energy converted to biodiesel) is within the estimates of the literature. Its prerequisite – a PSE of 2 % – corresponds to the upper limit of open ponds with additional carbon supply (section 2.3.1), which indicates, again, that the model yields reasonable results, yet may slightly overestimate the potential biodiesel yield. In all likelihood, some effects have escaped the scope of this thesis, possibly related to the maximum growth rate and irradiance effects.

### 5.1.2 Auxiliary Energy Demand

The auxiliary energy demand influences the viability of a production chain. In an attempt to reduce the energy expenditure, certain energy sinks were omitted from the model, although the literature were not entirely conclusive on the matter [10, 62, 70, 74, 90]. Where disagreements were found, it was always ruled in favour of the low-energy route. This deserves some justification.

Omitted energy sinks:

- Centrifugation
- Pre-growth in closed system
- CO<sub>2</sub> allocation

#### 5.1.2.1 *Centrifugation*

Although it is stated in the literature that flocculation alone is sufficient for harvesting microalgae [92], most practical processes include dewatering by centrifugation. This may be a consequence of contamination avoidance, as large-scale refineries aim at producing an edible product\* and excessive use of flocculants should be avoided. For biodiesel production, centrifugation is far too energy demanding for it to be a viable dewatering method (see section 2.4.2). The reliance on the recent review by Zeng et al. [90] was in place, and the centrifugation step was hence omitted.

#### 5.1.2.2 *Pre-growth in protected environment*

Before the algal strain is introduced into the open ponds, they are cultivated briefly in a protected environment. As shown earlier, growth in more closely monitored systems are associated with higher energy demand. The exact volume of the pre-growth culture medium could not be found and is assumed to constitute a negligible share of the total volume. The energy required for this step was left out of the calculations with a presumably low impact.

#### 5.1.2.3 *CO<sub>2</sub> allocation*

The entire energy cost associated with CO<sub>2</sub> production was allocated to the industrial facilities outside the system boundary, based on the assumption that CO<sub>2</sub> is a waste product. For large-scale production, this may no longer be the case, as the demand is likely to exceed the accessible supply. Burning the biogas on-site will help recycle some CO<sub>2</sub> (66 %), but a substantial amount of carbon still leaves the system. If an additional source of CO<sub>2</sub> proves necessary, it will close to double the auxiliary energy demand [74]. The success of microalgal biodiesel is thus highly dependent on the industry it is trying to outcompete – the carbon emitters.

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\* No large-scale microalgal biodiesel production is carried out as of May 2016

### 5.1.3 EROI

In spite of the model's limitations, the estimated EROI of the modelled algal biorefinery falls within the range stated by Zaimes and Khanna [136]: 0.81-2.01. However, the EROI would be lower had the aforementioned energy sinks not been omitted from the calculations. In comparison, the EROI of biodiesel from oil palm is at 5.31 substantially better, indicating that a switch to algal biodiesel is unfeasible if solely looking at energy expenditure. Fossil diesel is better yet, by a factor of four, underlining why this is today's fuel of choice.

### 5.1.4 GWP

Microalgal biodiesel has a lower GWP than both best practice biodiesel and fossil diesel. Still, it is only marginally better than biodiesel from palm oil. Additionally, microalgal biodiesel is energy intensive and therefore sensitive to the GWP of the auxiliary energy production. The model biorefinery will in this particular case reap the benefits of Brazil's energy mix. If the production were moved to a different location, the GWP would not be as favourable. Moreover, the omitted energy sinks will impact the GWP like it impacts the auxiliary energy demand, and the GWP is likely to have been underestimated.

## 5.2 VIABILITY OF MICROALGAL BIODIESEL

The model biorefinery shows that microalgal biodiesel cannot be viable based on productivity alone – its low EROI being a serious shortcoming. Nor can benefit from a substantial GWP reduction, as it is only 5 % better than its nearest contender; biodiesel from palm oil. Consequently, algal biodiesel has to rely on other advantages if it is to be recommended for large-scale production in Brazil.

Areal efficiency and the utilization of non-arable land are important arguments for a microalgal biodiesel initiative. Using the fuel consumption in Brazil, 2005 (48 million ton oil equivalent [137]), it was estimated that a 20 % coverage would require 0.1 % of the country's land area, based on the biorefinery's yield. About 4 % of Brazil is semi-arid [138], meaning that enough land should be available for production. However, the viability of the land would have to be investigated more closely before it is deemed fit for cultivation of microalgae.

The extraction of high value products could give an edge to microalgal biodiesel over its competitors. But the presented biorefinery is not suited for such an operation. As a conclusion, the large-scale integration of this biorefinery is not technically feasible at this point. The field of microalgal biodiesel calls for new breakthroughs, which will be the emphasis of the next section.



### 5.3 THE FUTURE OF MICROALGAL BIODIESEL

The aquatic species program concluded that the challenges facing microalgal biodiesel are not engineering-related, but biological [6]. This is still the case. Biodiesel yields are limited by inefficiencies connected to the microalgae's metabolism and its inability to grow efficiently under varying light conditions. Moreover, growth inhibiting conditions are necessary for the algae to accumulate lipids, which reduces their over-all output. Genetic modification could potentially limit these inefficiencies, and will play a decisive part in the future of microalgal biodiesel [69].

However, some engineering challenges do remain. Were HTL to prove technically feasible, it would drastically better biodiesel yields. By using the cultivation steps of the presented model and replacing the extraction and transesterification process with HTL, a 110 % increase in product yield and 30 % reduction in auxiliary energy demand was shown based on numbers from Jones [111]. The resulting EROI is 2.64. The increase could be even higher by switching to a more productive microalga. For illustrative purposes figure x shows the area of Brazil needed if the country were to cover 20 % of its fuel demand by using thermally liquefied algal oil.



**Figure 5.1:** Area required to supply 20 % of Brazil's fuel supply based on results from this thesis. Map reproduced with permission from Google.

This system is still not likely to perform well enough to outcompete petrodiesel at present. In the future, however, things may look very different. As oil fields become less accessible, the EROI of fossil fuels will inevitably drop. On the contrary, sustainably grown microalgal biodiesel has the potential to increase its EROI. There is much to gain by development of new technology. The ACAD system, for example, has the potential to be self-sufficient with energy [113]. Coupled with genetically modified microalgae and HTL technology, biodiesel from the versatile aquatic feedstock may prove truly disruptive.

Until then, algae cultivation should divert its attention to one of its other benefits – food production. Although outside the scope of this thesis, it is evident that microalgae can contribute to our dietary needs by making use of previously assumed non-arable land. And, as long as enough waste-CO<sub>2</sub> is available, microalgae will grow efficiently [139]. A paradox even, that microalgal biodiesel is dependent on the very emissions it attempts to mitigate.

## **6 CONCLUSION**

Despite the long list of advantages, microalgal biodiesel performs poorer than its contenders in terms of EROI. Having only a marginally better GWP, it will not regain its appeal and cannot be recommended for large-scale biodiesel production. In the future, this may change if the microalgae are genetically modified to perform efficiently under varying environmental conditions. But until then, effort should be directed toward cultivation of microalgae for food and other high-value products.



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## APPENDIX

### A.1 Biodiesel yield

Growth calculations are performed by first obtaining the influence factors of temperature and sunlight. These are used to scale the maximum growth rate. Data from PV-syst were managed in Microsoft Excel and resulted in the following influences

$$F(T) = 0.87$$

$$F(I) = 0.24$$

$$F(R) = 0.90$$

Nutrient and CO<sub>2</sub> levels are considered optimal. Average growth rate throughout the year is thus (equation 3):

$$\mu = 0.02 \text{ g L}^{-1}\text{h}^{-1} \times 0.87 \times 0.24 \times 0.90 = 0.0038 \text{ g L}^{-1}\text{h}^{-1}$$

Using the pond depth of 0.2 m the areal biomass productivity is calculated

$$\begin{aligned} \text{Areal productivity} &= 0.0038 \text{ g L}^{-1}\text{h}^{-1} \times 1000 \text{ L m}^{-3} \times 0.20 \text{ m} \\ &= 0.75 \text{ g m}^{-2}\text{h}^{-1} \end{aligned}$$

The annual biomass production is calculated using the number of sun hours derived from PVsyst (4580h). Area is transformed to hectares.

$$\begin{aligned} \text{Annual biomass productivity} &= 0.75 \text{ g m}^{-2}\text{h}^{-1} \times 4580 \text{ h} \times 10000 \text{ m}^2\text{hec}^{-1} \\ &= 34\,000 \text{ kg hec}^{-1} \end{aligned}$$

The biomass is subject to losses listed in the table below before it is converted to biodiesel.

**Table A.1:** Conversion losses

Loss mechanism		Factor	Reference
Lipid content	-	0.40	[120]
Area coef.	-	0.90	
Contamination coef.	-	0.98	[72]
Harvest recovery	-	0.95	[90]
Cell disruption rate	-	0.96	[74]
Lipid extraction recovery	-	0.99	[130]
Conversion rate/ratio?	-	0.99	[99]

Using the factors in the table, a downstream loss coefficient of 0.32 is calculated.

$$\text{Biodiesel yield} = 34\,000 \text{ kg hec}^{-1} \times 0.32 = 10.6 \text{ ton ha}^{-1}$$

## A.2 Auxiliary energy demand

Table x lists the auxiliary energy demand of the processes assessed in this thesis. Most are retrieved from literature, but some had to be calculated as they were specific for the model refinery.

**Table A.2:** Data on the auxiliary energy demand of different processes. Found in literature.

Process	Energy [GJ/ton biodiesel]	References
Harvest	0.50	[74]
Cell disruption	1.7	[74]
Extraction <sup>a</sup>	2.1	[62]
Refining	0.70	[74]
Transesterification <sup>b</sup>	3.2	[62, 74]
Anaerobic digestion	- 10	[74, 113]
Fertilizer	9.5	This thesis
Paddlewheel	9.5	This thesis
Pond cleaning,	2.1	[74]
CO <sub>2</sub> injection	0.50	[140]
Total	19.8	

The energy required for fertilizer, paddlewheel, transesterification and some elements of the extraction process had to be calculated. The calculations are shown here.

### A.2.1 Paddlewheel

Equation 9 was used to calculate the paddlewheel's power demand per area

$$P = \frac{9810 \times \left(0.20 \frac{\text{m}}{\text{s}}\right)^3 \times \left(0.018 \text{ m s}^{-\frac{1}{3}}\right)^2}{(0.20 \text{ m})^{1/3} \times 0.40} = 7.9 \text{ W m}^{-2}$$

The paddlewheel is assumed to operate only during the day; operating hours equal 4580 h. Total annual energy demand equates to:

$$36 \text{ kWh m}^{-2}\text{y}^{-1} = 10 \text{ MJ m}^{-2}\text{y}^{-1}$$

The annual biodiesel productivity is used to calculate energy expenditure per ton biodiesel.

$$\frac{10 \text{ MJ m}^{-2}\text{y}^{-1}}{0.0011 \text{ ton biodiesel m}^{-2}\text{y}^{-1}} = 9.5 \text{ GJ (ton biodiesel)}^{-1}$$

## A.2.2 Fertilizer

Fertilizers, especially nitrogen is energy intensive to produce. It was argued in section 3.2.1.14 that 42 kg of ammonium nitrate and 14 kg triple superphosphate is required per ton algae. The number is based on the composition of the microalgae (60kg N/5kg P) and the fertilizers' recycle rate (76%/50%) as well as the nutrient content of the fertilizer (34.5%/18%). For nitrogen:

$$\frac{60 \text{ kg}}{0.345} \times (1 - 0.76) = 42 \text{ kg}$$

As this is per ton algal biomass it was adjusted to per ton biodiesel. The downstream losses are 0.32. The fertilizer needs per ton biodiesel are 132 kg and 44 kg for N and P-fertilizer respectively.

The energy required to manufacture (N)/acquire (P) the fertilizer is found to be 49.25 MJ/kg for N-fertilizer (urea) and 18.81 MJ/kg for P-fertilizer (triple superphosphate). The respective energy requirements are 6.5 and 0.83 GJ/ton biodiesel.

## A.2.3 Extraction

Heat and electricity requirements were derived from literature [62]. Hexane manufacture had to be accounted for. 20 kg hexane per ton biodiesel is required. Hexane production requires 37.5 MJ/kg.

$$20 \frac{\text{kg}}{\text{ton}} \times 37.5 \frac{\text{MJ}}{\text{kg}} = 0.75 \frac{\text{GJ}}{\text{ton}}$$

## A.2.4 Transesterification

Heat and electricity requirements were derived from literature [74]. The energy required for methanol production had to be estimated. The methanol demand was set to 114 kg/ton biodiesel and the specific energy demand of its production to 12.5 MJ/kg. The energy needed is

$$114 \frac{\text{kg}}{\text{ton}} \times 12.5 \frac{\text{MJ}}{\text{kg}} = 1.4 \frac{\text{GJ}}{\text{ton}}$$

### A.3 Global warming impact

The global warming impact of electricity could have been retrieved from literature. However, due to the large share of renewable energy (hydropower) in Brazil, such a number would largely overestimate the GWP. Therefore, information on Brazilian electricity production was gathered.

**Table A.3:** GWP of Brazilian electricity.

	Share total production	GWP [g-C/kWh]	Fraction GWP [g-C/kWh]	Ref.
hydro	72.1%	15	10,8	[141]
Coal	1.4%	1000	14	[141]
Nat. Gas	10.6%	600	63,6	[141]
Oil	4.4%	800	35,2	[141]
Biomass	5.4%	50	2,7	[141]
Total	94%	-	126	

The production methods of the 6 % imported energy was neglected and the fraction GWP was divided by 0.94 and converted to gram CO<sub>2</sub> equivalents per mega Joule [g-C/MJ].

$$GWP \text{ Brazilian energy mix} = \frac{126 \frac{\text{gC}}{\text{kWh}}}{0.94} \times 0.278 \frac{\text{kWh}}{\text{MJ}} = 37 \frac{\text{gC}}{\text{MJ}}$$

The GWP of the Brazilian energy mix is used to calculate the global warming potential of the processes where energy in the form of electricity is required. That encompasses everything but the energy required for manufacturing of fertilizer, methanol and hexane. These are calculated separately.

**Table A.3:** GWP of processes.

Process	Energy [GJ/ton biodiesel]	GWP [kg -C/ton biodiesel]	Ref.
Harvest	0.50	19	[74]
Cell disruption	1.7	62.9	[74]
Extraction <sup>a</sup>	2.1	78	[62]
Refining	0.70	26	[74]
Transesterification <sup>b</sup>	1.8	67	
Paddlewheel	9.5	351	
Pond cleaning	8.6	318	[74]
Waste management	5.6	207	[74]

<sup>a</sup> Number does not include production of methanol

<sup>b</sup> Number does not include hexane production



For the production of N fertilizer, P fertilizer, hexane and methanol, GWP is taken from literature and is not calculated using the Brazilian energy mix's GWP. Their specific GWP is listed below.

**Table A.3:** GWP of compound production.

Compound	Required mass [kg/ton biodiesel]	Specific GWP [gC/kg]	GWP [kgC/ton biodiesel]
N-fertilizer	132	2940	388
P-fertilizer	44	1160	51
Hexane	20	861	17
Methanol	114	2836	323

The total global warming potential is 1907 kg/ton biodiesel



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