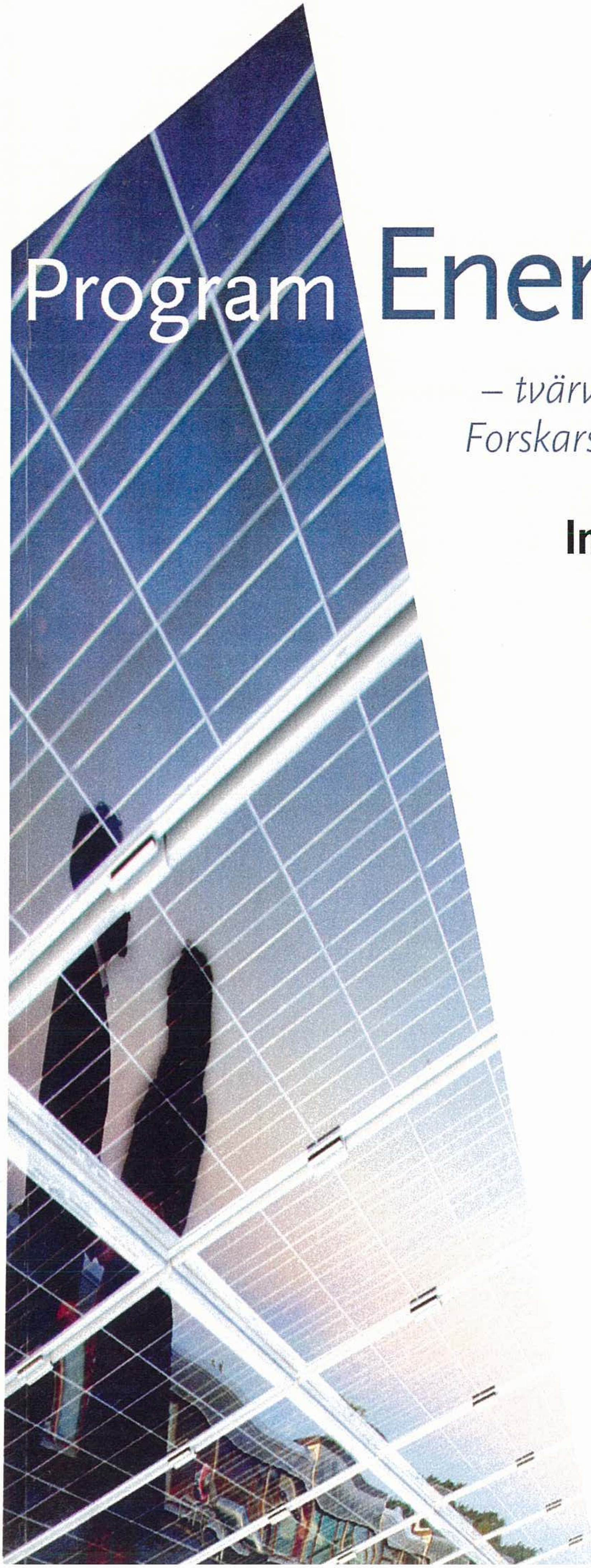

# Program Energisystem

*– tvärvetenskap i samhällets tjänst*
*Forskarskola och forskningsprogram*

# Integrated Algae Cultivation for Biofuels Production in Industrial Clusters

Viktor Andersson
Sarah Broberg
Roman Hackl

Arbetsnotat Nr 47
November 2011-11-15
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Forskning och forskarskola

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# Abstract

Declining fossil resources and the issue of climate change caused by anthropogenic emissions of greenhouse gases make global action towards a more sustainable society inevitable. The EU decided in 2007 that 20 % of the union´s energy use should origin from renewable resources by the year 2020. One way of achieving this goal is to increase the utilisation of biofuels.

Today 2$^{nd}$ generation biofuels are being developed. They are seen as a more sustainable solution than 1$^{st}$ generation biofuels since they have a higher area efficiency (more fuel produced per area) and the biomass can be cultivated at land which is not suitable for food crops. One of these 2$^{nd}$ generation biofuels are fuels derived from microalgae.

In this study a thorough literature survey has been conducted in order to assess the State-of-the-Art in algae biofuels production. The literature review showed the importance of a supplementary function in conjunction with algae cultivation and therefore algae cultivation for municipal wastewater treatment and capturing $CO_2$ emissions from industry was included in the study. It was assumed that all the wastewater of the city of Gothenburg, Sweden, was treated by algae cultivation.

A computer model of the whole production process has been developed, covering; algae cultivation in conjunction with wastewater treatment, algae harvesting and biofuels production. Two different cases are modelled; a first case including combined biodiesel and biogas production, and a second case investigating only biogas production. Both cases have been evaluated in terms of product outputs, $CO_2$ emissions savings and compared to each other in an economic sense.

Utilising the nutrients in the wastewater of Gothenburg it is possible to cultivate 29 $kt_{algae}$/year. In the biogas case it is possible to produce 205 $GWh_{biogas}$/year. The biogas/biodiesel case showed a production potential of 63 $GWh_{biodiesel}$/year and 182 $GWh_{biogas}$/year. There is a deficit of carbon in the wastewater, hence $CO_2$ is injected as flue gases from industrial sources. The biodiesel/biogas case showed an industrial $CO_2$ sequestration capacity of 24 $kt_{CO2}$/year while in the biogas case 22.6 $kt_{CO2}$/year, could be captured. Estimating the total $CO_2$ emissions savings showed 46 $kt_{CO2}$/year in the biodiesel/biogas case and 38 $kt_{CO2}$/year for the biogas case. The importance of including wastewater treatment in the process was confirmed, as it contributes with 13.7 $kt_{CO2}$/year to the total $CO_2$ emissions savings.

Economic comparison of the two cases showed that biodiesel in conjunction with biogas production is advantageous compared to only biogas production. This is mainly due to the higher overall fuel yield and the high willingness to pay for biodiesel. The total incomes from biodiesel/biogas sales were calculated to 221 million SEK/year and 193 million SEK/year for biogas. It was found that the higher incomes from biodiesel/biogas sales repay the increased investment for the biodiesel process in approximately 3 years.



*Keywords: Biofuels, algae cultivation, wastewater treatment, $CO_2$ capture, industrial cluster, biorefinery*

# Acknowledgements

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We would like to thank Dr. Eva Albers at the department of Industrial Biotechnology at Chalmers University of Technology and Adj. Prof. Jörgen Ejlertsson working at the department of Water and Environmental Studies at Linköping University and Scandinavian Biogas AB for their input in the startup of this project.

Thanks also to our supervisors; Thore Berntsson, Magnus Karlsson and Simon Harvey for their guidance throughout the working process. We would also like to thank the Swedish Energy Agency for making this project possible by financing the Energy Systems Programme.

# Contents

# Abbreviations

ATP – Adenosine Triphosphate

BOD – Biological Oxygen Demand

CAPEX – Capital Expenditures

$CH_4$ – Methane

COD – Chemical Oxygen Demand

DAF –Dissolved Air Floatation

DH – District Heating

EU – European Union

FAME – Fatty Acid Methyl Ester

FFA – Free Fatty Acids

GHG – Green House Gases

HRAP – High Rate Algae Pond

IE – Industrial Ecology

IPCC – Intergovernmental Panel on Climate Change

IS – Industrial Symbiosis

NG – Natural Gas

NGCC – Natural Gas Combined Cycle

OPEX – Operating Expenditures

PBR – Photobioreactor

RME – Rapeseed Methyl Ester

SAF – Suspended Air Flotation

SSU – Source Separated Urine

STP – Specific Theoretical Potential

TOC – Total Organic Carbon

TS – Total Solids

VS – Volatile Solids

WW – Wastewater

WWT – Wastewater Treatment

WWTP – Wastewater Treatment Plant

# 1 Introduction

The increasing use of fossil resources for both energy and manufacturing purposes is accepted to be unsustainable. It results in increasing emission of Green House Gases (GHG), mainly $CO_2$, which are understood to be the reason for rising atmospheric temperature, causing a major change of the earth's climate. Fossil resources are also limited and their availability is assumed to peak within the next decades, which is a serious threat to the worlds' energy security. Because of these reasons the European Union (EU) has in 2007 decided on converting itself into a highly efficient, low carbon economy in order to fight climate change, increase EU's competitiveness and guarantee energy security for the region. As a result the so-called "20-20-20" targets were set and became binding in June 2009 within the EU. The targets imply:

- GHG emissions reduction of at least 20% compared to the levels of 1990.
- On average 20% of the EUs energy use should come from renewable resources.
- Reduction of primary energy use by 20% by implementing energy efficiency measures (European Comission 2010).

Based on the EU directive for the promotion of the use of renewable resources, Sweden has set a target that the share of renewable in the transport sector should be at least 10 % in 2020 (Näringingsdepartementet 2010).

By applying these measures the goal is to keep the increase in atmospheric temperature below 2° C. According to a report published by the Intergovernmental Panel on Climate Change (IPCC) in 2007 (Pachauri & Reisinger 2007) a cut in $CO_2$ emissions in the developed world of 50 – 85 % by 2050 is necessary to achieve the 2° C target. Figure 1 shows $CO_2$ emissions from different sectors between 1971 and 2008. It can be seen that electricity and heat generation stands for the highest emissions, followed by transport and industrial/construction emissions.

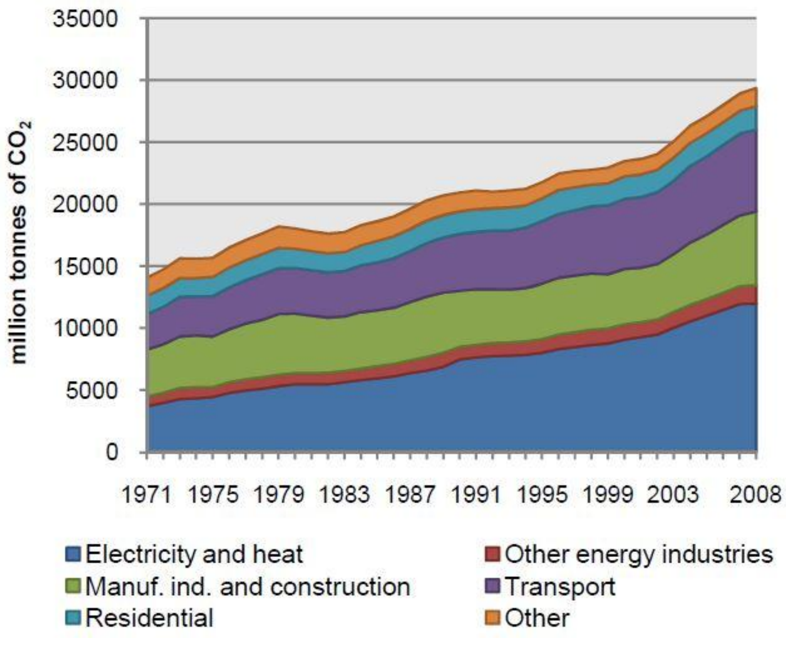


Figure 1 $CO_2$ emissions by sector 1971 to 2008 (IEA 2010).

As stated above it there are major challenges in order to fight climate change and at the same time stay competitive. This makes the development of a whole range of new technologies inevitable. Several potential options to achieve the targets are being suggested, reaching from an increasing share of renewable electricity production from e.g. wind, water, solar and biomass, investment in energy efficiency measures in industry and the building sector and increased decarbonisation of the transport sector by either electrification or alternative renewable fuels.

It is estimated that biomass can contribute by 20 - 90 % to the world energy supply (Berndes et al. 2003). Today biomass for energy purposes is mainly used for space heating, 1st generation biofuels, biogas and cogeneration of electricity. Other potential uses are next generation biofuels, chemicals, materials, pharmaceuticals, fats, dyes etc. In order to reach the EU targets the share of biomass in energy and materials generation has to be increased.

First generation biofuels like Rapeseed Methyl Ester (RME), ethanol from e.g. corn or sugar cane, biogas from anaerobic digestion of food residues and crops etc. are currently used globally as a substitute for fossil transportation fuels. Even though biofuels today only represents e.g. 0.3 % of the world's diesel consumption its use is growing rapidly. First generation biofuels have several drawbacks:

- Increased competition with food.
- Low area efficiency.
- Poor carbon balance depending on the means of production (e.g. extensive use of fertilizers and clearing of rainforest can even result in increased $CO_2$ emissions).

Especially the increasing pressure on arable land by food and biofuels crops (peak soil) resulted in increased criticism on 1st generation biofuels (Schenk et al. 2008).

Because of these drawbacks, efforts for implementation of 2nd generation biofuels are taken. These are in particular biofuels derived from lignocellulosic materials (via e.g. fermentation or gasification) and microalgae. According to Schenk et al. (2008) 2nd generation biofuels have a higher net energy output and biomass to biofuel efficiency, lower water demand and require less arable land to produce the same amount of fuel.

This report focuses on the production of biofuels from microalgae. Biofuels from microalgae are a promising alternative to conventional fossil fuels and a complementation to first generation biofuels. Chisti (2007) reports a 15 – 300 times higher oil yield from microalgae compared to traditional land based crops like rapeseed and palm oil. Figure 2 shows the biodiesel production rate of different biomass sources. It can be seen that algae has by far the highest production rate.

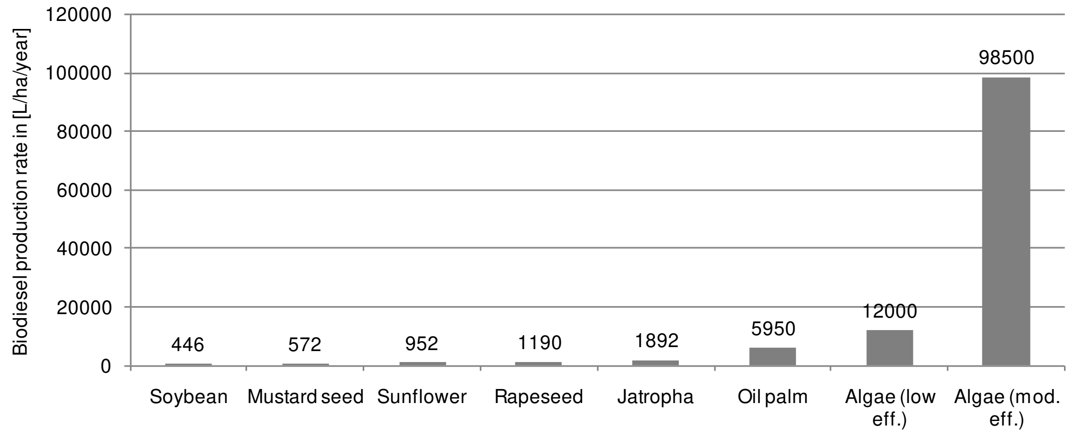


Figure 2 Biodiesel yields for different biomass sources; Algae (low efficiency) based on algae growth rate of 10 $g/m^2/day$ and 30 % Triacylglyceride[1] (TAG); Algae (moderate efficiency) based on algae growth rate of 50 $g/m^2/day$ and 30 % TAG; Real, current algae cultivation systems are within the low and mod. algae growth rate range, e.g. Seambiotic Israel (20 $g/m^2/day$ and 8 - 40 % TAG), HR BioPetroleum Hawaii (50 $g/m^2/day$ and 30 % TAG); Data taken from (Schenk et al. 2008).

Taking the global oil demand and the globally available arable land area into account and using the biodiesel yield from Figure 2, the percentage of arable land which is necessary to replace all oil by biodiesel can be calculated, which is shown in Table 1.

Table 1 Area necessary to replace the worlds' oil demand with biodiesel from different sources of biomass and resulting percentage of arable land necessary to produce the biomass.

| **Biomass** | **Area to produce global oil demand in [ha*$10^6$]**[2] | **Percentage of worlds arable land to provide global oil demand in [%]**[3] |
|---|---|---|
| Soybean | 11620 | 842 |
| Mustard seed | 9060 | 656 |
| Sunflower | 5440 | 394 |
| Rapeseed | 4350 | 315 |
| Jatropha | 2740 | 198 |
| Palm oil | 870 | 63 |
| Algae (low eff.) | 430 | 31 |
| Algae (mod. eff.) | 50 | 4 |

It can be seen that there are very large differences between the different sources of biomass and that algae even if a low production rate is assumed is still the most efficient in terms of cultivation area.

A summary of the advantages of microalgae for biofuels production is given below:

- Higher area efficiency compared to conventional land based crops (Clarens et al. 2010; Schenk et al. 2008).
- Can be grown on land unsuitable for agriculture (Savage 2011).
- Can utilise waste- and saltwater (Schenk et al. 2008).

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[1] Triacylglycerides are esters consisting of glycerol and three fatty acids. They are transformed into biodiesel via transesterification (Chisti 2007).
[2] Global oil demand in 2011: 5182102 L*$10^6$/year (IEA 2011)
[3] Global area of arable land in 2008: 1 380.5*$10^6$ ha (FAO 2011)

- Can be used in conjunction with wastewater treatment (WWT) (Rawat et al. 2010).
- Can be harvested all year round (Schenk et al. 2008).
- Production of non-toxic, biodegradable fuels, e.g. biodiesel (Rawat et al. 2010).
- No need for herbicides/pesticides (Rawat et al. 2010).
- Possible to extract other compounds, like pharmaceuticals, fats, dyes, sugars, fine chemicals (Mata et al. 2010).

Despite the advantages, the cultivation of algae for biofuels and other purposes is not without controversy. Soon to be published work by Razon & Tan (2011) states that two processes producing biogas and biodiesel from different microalgae show a large energy deficit, meaning that the processes need more energy than the energy output in the products.

Another study conducted by Clarens et al. (2010) analysed algae, corn, switchgrass and canola based biofuels according to the following categories:

- Land use.
- Energy use.
- GHG emissions.
- Water use.
- Eutrophication.

The study came to the result that land based biomass has lower environmental impacts in most of the categories analysed.

Only in land use and eutrophication potential algae where advantageous compared to the analysed land-based biomass sources. While corn, canola and switchgrass cultivation decreased global GHG emissions, algae cultivation emitted more $CO_2$ than what was taken up by during cultivation.

The results of the studies by Razon & Tan (2011) and Clarens et al. (2010) are very much depending on the underlying assumptions, but general conclusions can be drawn:

- It is essential to use $CO_2$ and nutrients from alternative[4] sources for algae cultivation.
- The overall fresh water and energy demand of the process needs to be decreased.

The studies discuss several alternatives to tackle these challenges:

- Nutrients can be recycled within the process and/or recovered from wastewater. The later would also decrease the fresh water demand of the process.
- $CO_2$ can also be recycled and/or obtained from flue gases from nearby power station or other industrial sites.

[4] Instead of artificial fertilizers addition.

- Process integration can be used to increase heat recovery within the algae biorefinery and also to increase heat integration with the surrounding infrastructure in order to minimise energy use.

From an economic point of view it is not economically feasible to produce biofuels from algae with today's technology, unless the process is combined with another, like WWT or the production of valuable by-products (Savage 2011). A similar conclusion has been drawn by Pittman et al. (2011).

# 2 Background

This chapter presents information regarding the area of this case study, Hisingen in Gothenburg, Sweden. The concept of Industrial Symbiosis (IS), which is applied in this case study, is also introduced.

## 2.1 Industrial Symbiosis

In recent years the concept Industrial Ecology (IE) gained interest in the work towards a sustainable consumption of the world's resources. The concept was highlighted in an article in the late 1980´s where the authors argue that industrial processes should be looked upon as integrated systems, industrial ecosystems, where the use of energy and materials is optimized, the waste generation is minimized and the effluents from one process works as the raw material in the next process. They emphasize that it is important not to study the individual processes in isolation, rather to see the system as a whole. Inspired by the nature the authors claim that the individual manufacturing processes contribute to the industrial ecosystem and therefore the whole system should be studied in order to seek an optimal system (Frosh & Gallopoulos 1989).

Industrial ecology operates at different levels, at the facility level, at the inter-firm level and at the regional or global level. Looking at the inter-firm level the subset known as Industrial Symbiosis (IS) is found. The goal with IS is that the collective benefit the actors in the network provide should be greater than the benefit achieved without collaboration (Chertow 2000). Chertow (2007) set up a criterion, called "3-2 heuristic", aiming to describe the minimum criteria to be fulfilled to be classified as IS. The author defines it as at least three units must be involved in an exchange of at least two different types of resources. Figure 3 shows an example of this minimum criterion.

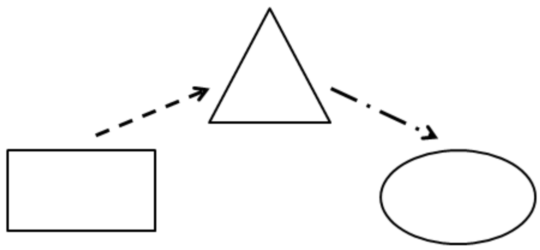

Figure 3 An example of the minimum criteria for industrial symbiosis, 3-2 heuristic, where three units exchange two types of resources (Chertow 2007).

Collaborations of this type will affect the amount of resources used, both material and energy, and the amount of waste and pollutants generated by the industries. Collaboration and resource optimization among collocated actors, in the form of IS, may lead to environmental benefits.

## 2.2 Gothenburg and the area of Hisingen

Gothenburg is the second largest city in Sweden with a population of around 500 000 inhabitants. The city is situated on the Swedish west coast. One of the most industrialized areas in Gothenburg is Hisingen. Volvo AB, Volvo Cars, ST1 refinery, Preem refinery, Gryaab Wastewater Treatment Plant (WWTP) and a Natural Gas

Combined Cycle power plant[5] (Rya NGCC plant) are some of the industrial sites located here today. These sites all contribute to the $CO_2$ emissions in the area. One way to reduce the $CO_2$ emissions in Gothenburg is therefore to reduce the emissions on Hisingen.

The three largest sources of $CO_2$ emissions in the area are the two refineries, Preem and ST1, and the Rya NGCC plant. The $CO_2$ emissions from these three industries are listed in Table 2. As seen in Table 2, in total the three plants emit 1 644 000 ton $CO_2$/year. In addition to this, the energy company Göteborg Energi has launched a project (GoBiGas) for a new gasification plant using wood as raw material (Göteborg Energi 2011a), that will result in additional access to $CO_2$.

The plants on Hisingen also produce large amounts of excess heat. Today the NGCC plant and the refineries deliver heat to the District Heating (DH) system. The amount delivered to the DH system can be found in Table 2. Although the excess heat from the refineries and the NGCC plant today are delivered to the DH system the industries may have additional excess heat with lower temperatures than required for the DH system, i.e. lower than approximately 90 °C.

Table 2 The three large sources of $CO_2$ at Hisingen and their respective emissions and delivery to DH system (Göteborg Energi 2011b; Nyström 2010; Hegerland et al. 2008).

| **Site** | **Emissions [ton $CO_2$/year]** | **Emissions recoverable [ton $CO_2$/year]** | **Heat delivered to DH system [MW]** |
|---|---|---|---|
| Preem refinery | 544 000 | 484 000 | 59 |
| ST1 refinery | 500 000 | No record | No record |
| Rya NGCC plant | 600 000 | 600 000 | 294 |

Gryaab is responsible for the WWT in the region of Gothenburg. On average, the treatment plant received 3 880 liters of water for purification per second during 2010 (Gryaab 2011). Gryaab currently use the sludge from wastewater treatment for biogas production with an annual output of approximately 60 GWh. In order to increase the methane yield they use co-digestion with food waste collected from the region. The biogas is upgraded to meet the requirements for vehicle fuel by the energy company Göteborg Energi (Gryaab 2011).

One of the major advantages with cluster collaborations and process integration at Hisingen is the short distances. ST1 refinery, Gryaab and Rya NGCC plant are practically neighbors and Preem refinery is only a few kilometers away and these industries can therefore be looked upon as a cluster, see Figure 4. Hackl & Harvey (2010) list several advantages with integration of a biorefinery in an industrial process cluster.

[5] A power plant holding one or more gas turbine generators that make use of excess heat in the turbine exhaust gas resulting in a high thermal efficiency. Additional electric power is produced since steam produced in the heat recovery steam generators powers a steam turbine (Northwest Power Planning Council 2002). In a natural gas combined cycle power plant the turbines are fueled with natural gas.

The biorefinery can:

- Make use of existing infrastructure.
- Use/supply available excess heat.
- Offer products (biorefinery products) to be used as raw material elsewhere in the cluster.
- Use existing process knowledge.

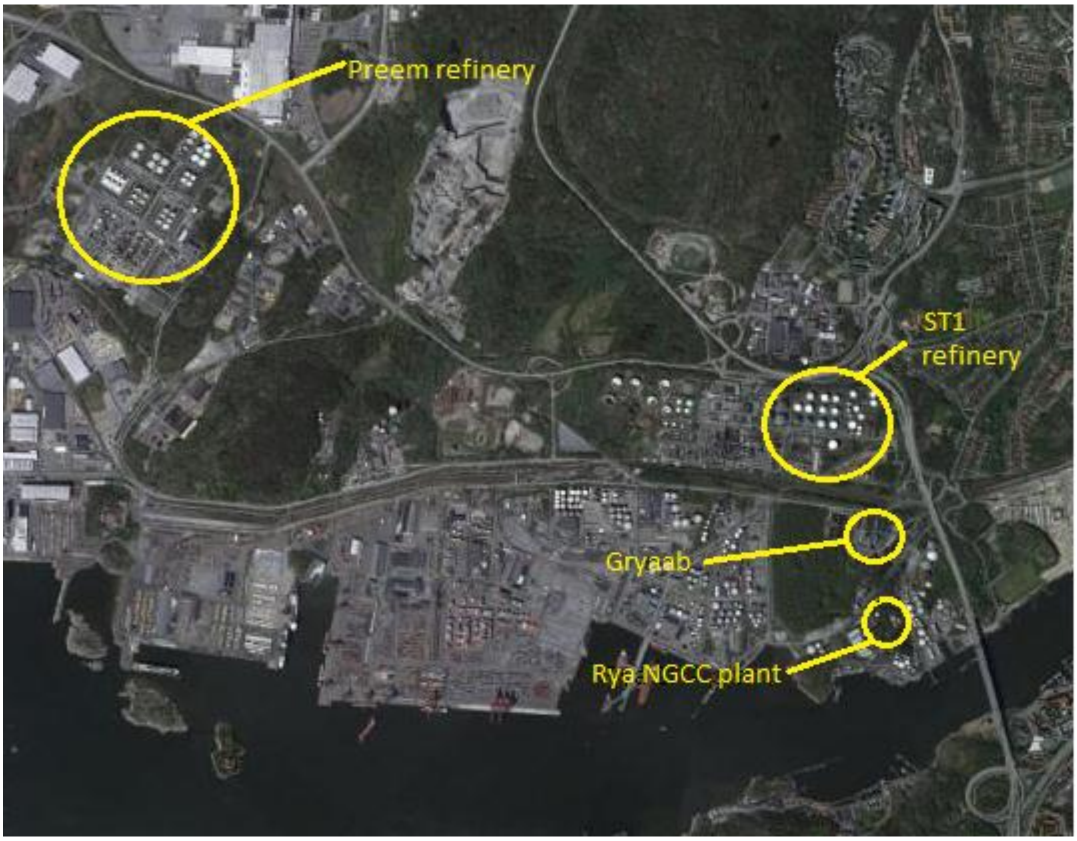


Figure 4 The plant sites at Hisingen; Preem refinery, ST1 refinery, Gryaab WWTP and Rya NGCC plant © Lantmäteriet Gävle 2011. Medgivande I 2011/0072.

In the development of biorefinery concepts one advantage, as listed above, is that the existing infrastructure system can be used. The natural gas network in Hisingen could be used if biogas is produced.

# 3 Objective and research questions

## 3.1 Objective and assignment

The objective of this research project is to investigate the potential of a future possible biorefinery concept. Algae cultivation for biofuels production in Gothenburg, Sweden, is studied with regard to prevailing climate conditions and necessary resources. Algae cultivation needs nutrients, above all in the form of carbon, nitrogen and phosphorous. An alternative nutrient source in form of wastewater will be studied in order to avoid the cost of these substances as well as the energy use and environmental impact associated with the production of these nutrients. More specifically, the assignment includes:

- A-State-of-the-Art study of algae cultivation, harvesting techniques and microalgae-based biofuels.
- A review of the climate conditions in Sweden, and more specific in Gothenburg, as the base in this case study.
- A study of microalgae cultivation in municipal wastewater to meet the nutrient demand in an inexpensive way in combination with wastewater treatment.
- A process integration of algae cultivation, wastewater treatment, excess heat usage and biofuels production.

The objective is to investigate the possible reductions in $CO_2$ emissions and energy demand by algae carbon fixing using $CO_2$ and excess heat from nearby industrial sources. Water from a municipal WWTP will be used as a nutrient source and the final product in the form of biofuel will be a useful energy source.

The study will discuss whether there is a potential for the assumed biorefinery concept in Gothenburg, and if further investigation is worthwhile. This will be done based on product outputs, economic evaluation and environmental consequences. The aim is also to show the differences in product outputs, energy requirements and $CO_2$ balances when using two different production routes within the biorefinery when the same cluster conditions are assumed in form of access to wastewater, $CO_2$ and a excess heat.

## 3.2 Research questions

The focus of this project will be on the following research questions:

- What is the status of using cultivated algae biomass as a renewable energy source? A State-of-the-Art review.
- What are the limitations for algae cultivation in terms of climate (sunshine hours, solar insolation and temperature) in Gothenburg?
- What amounts of nutrients are available in the wastewater and how much algae biomass can be grown using these nutrients? Is it possible to achieve the same water quality with wastewater treatment by microalgae as with conventional wastewater treatment? How large cultivation area is required?
- What conditions are offered in the region in terms of $CO_2$?
- What amount of biodiesel and biogas can be produced?
- Is single biogas or combined biodiesel and biogas production economically advantageous?
- How much $CO_2$ can be recovered from flue gases for microalgae cultivation?
- What are the global $CO_2$ emissions consequences of algae cultivation for biofuels production?

# 4 Methodology

The main activities of the project are summarized in Figure 5.

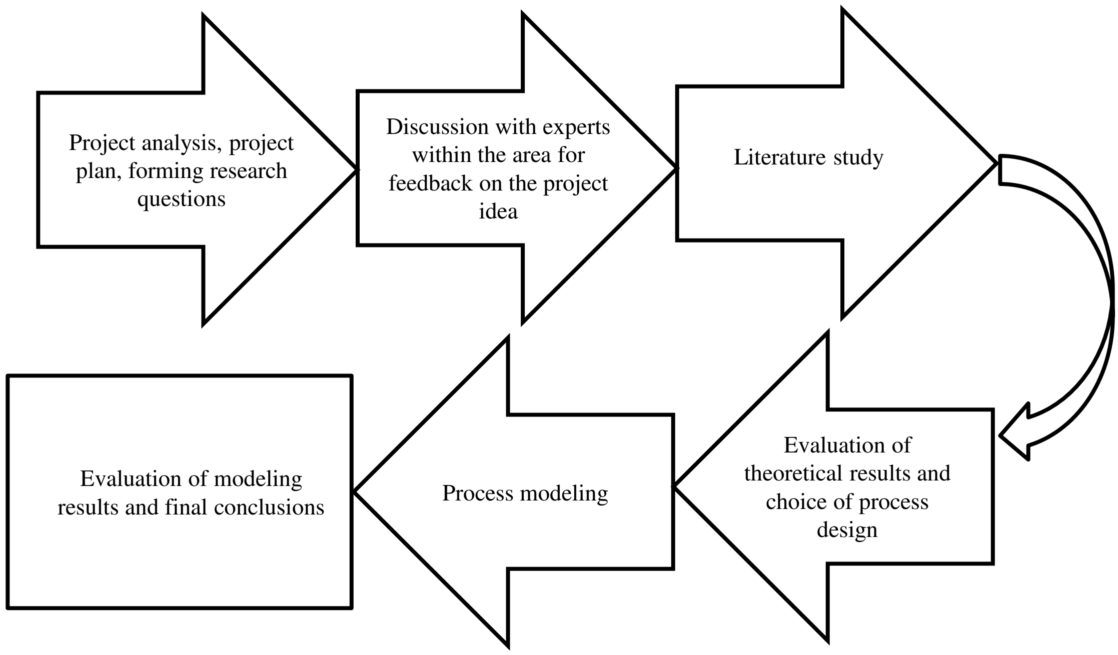


Figure 5 Overview of the main activities in this project.

In order to evaluate the project idea the project plan has been discussed with experts working within the area. In the spring of 2011 we visited Dr. Eva Albers at the department of Industrial Biotechnology at Chalmers University of Technology. Dr. Albers works in laboratory scale investigating algae for ethanol production. Discussions were also held during the spring with Adj. Prof. Jörgen Ejlertsson working at the department of Water and Environmental Studies at Linköping University and Scandinavian Biogas AB. These conversations have given new input to the design of the project.

In order to get an overview of the State-of-the-Art status of algae based biorefineries a comprehensive literature review covering algae cultivation, algae harvesting, climate conditions, biofuel production and WWT by microalgae has been performed. The literature data has then been compiled and evaluated.

Microsoft Excel models have been used to model algae cultivation, harvesting and biofuel production in order to examine the potential of the concept. The modeling results have been evaluated with regard to process integration, product outputs, economic viability and global $CO_2$ emissions consequences.

## 4.1 Data collection

In order to perform a comprehensive case study an extensive amount of data must be gathered. This data include process parameters, economic data and knowledge about the sociotechnical system where the process operates. In this work, such data has been gathered from State-of-the-Art reports and scientific articles regarding biofuel production from algae biomass. Where there has been lack of necessary data, contact has been taken with relevant companies or authorities. In order to better understand the system aspects of the process, consultations with experts within the area of algae cultivation have been conducted.

Since the technique is not yet fully deployed, it has been difficult to obtain experimental data above lab scale level for the process modeling. The solution to this problem has been to look at other simulation results and compare them to the lab scale experiments that have been conducted.

## 4.2 Process modeling

A Microsoft Excel model of the process was constructed in order to create a tool for analysing the whole algae cultivation for the biofuels production process. Based on the data collected from literature, expert advice and personal communication with plant personnel a process model was constructed. Due to the vast amount of process options available a qualified choice of process design had to be made. This was done based on expert recommendations published in different articles and reports on the subject.

The process chosen consists of different unit operations, reaching from different technologies for algae cultivation via biofuels production to $CO_2$ separation. Literature data and actual plant data for the performance and operating conditions of the different unit operations was gathered and fed into the Excel model.

Figure 6 shows the functionality of unit operations in the process model. The input to the unit operation consists of a set of values, e.g. mass flow, temperature and concentration of different substances. The input to the unit operation was used to calculate the output stream. The unit operation contains equations and data which were used to calculate the output stream from the input. It is also possible to use several input streams and construct a set of outputs.

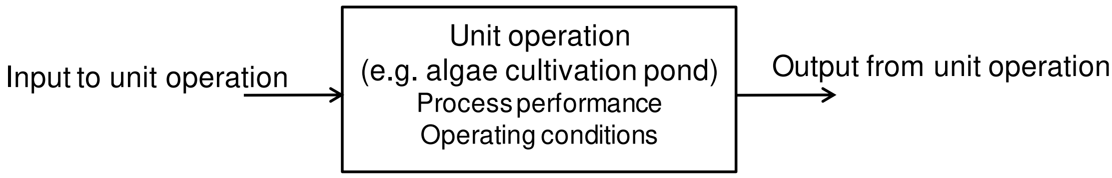


Figure 6 Functionality of unit operations in the process model.

The whole process model consists of several unit operations which are interconnected by input and output streams.

The main results of the model are:

- Amount of product (biofuels) output.
- Heat and electricity demand of the process.
- Necessary amount of external $CO_2$.
- Quality of treated wastewater (WW).

The results from the model can be used to evaluate different process options which are described in the next section.

## 4.3 Case study

A case study has been used in this project as a tool in the comparison of two different production pathways. As a crucial step in the study the unit that was studied and the system boundaries were defined.

This project contained two case studies; Figure 7 shows the two different cases.

a) Algae cultivation for WWT and production of biogas and biodiesel.
b) Algae cultivation for WWT and production of biogas.

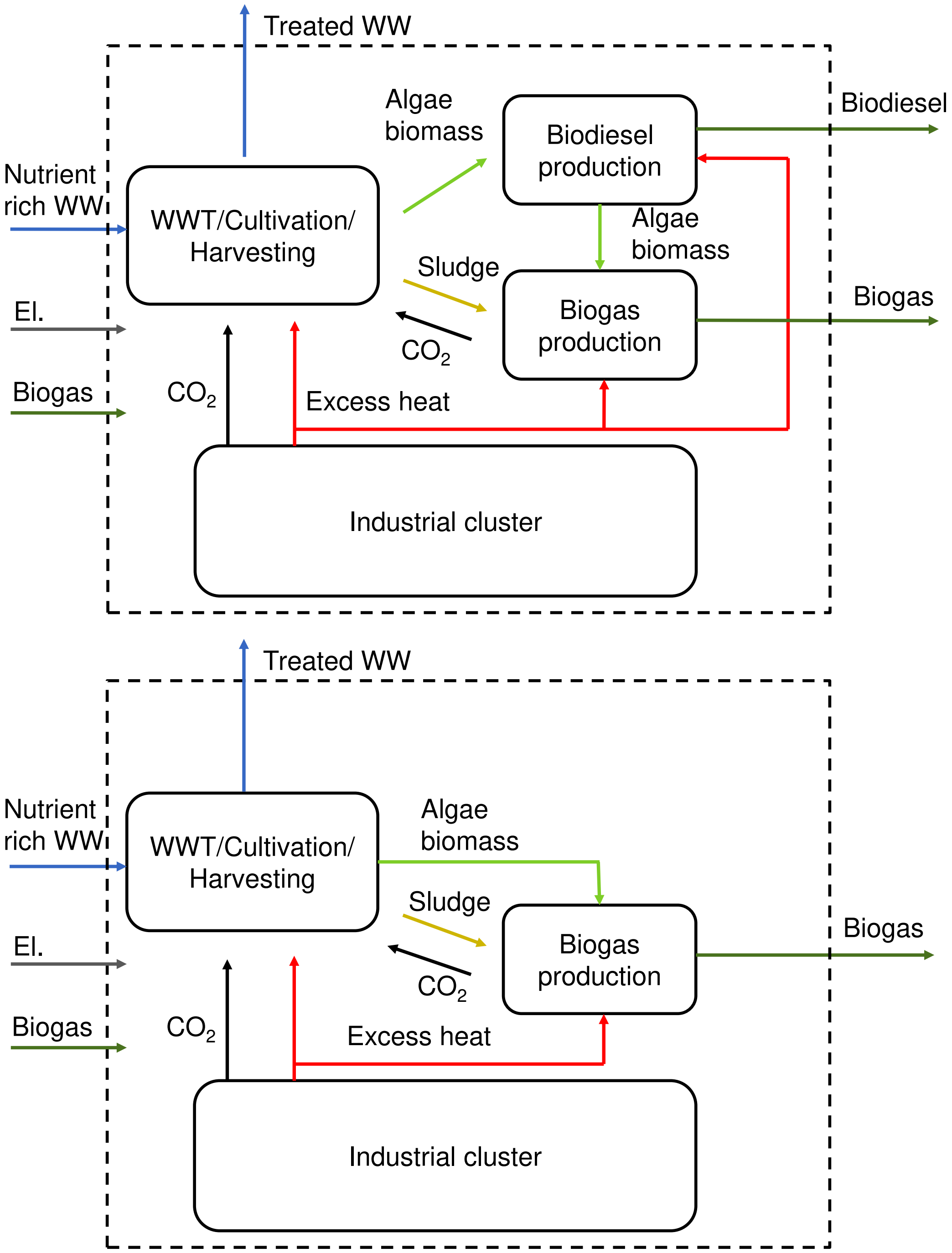


Figure 7 Material and energy flows for a) algae cultivation in conjunction with WWT and biodiesel and biogas production and b) algae cultivation with WWT and biogas production. Both processes assumed in conjunction with an industrial cluster.

It was assumed that the same amount of algae was produced in both cases, which is the amount possible to cultivate with the nutrients available in the WWTP in Gothenburg.

Both cases assumed the industrial cluster on Hisingen (presented in section 2.2) as source of excess heat and additional $CO_2$. It was also assumed that biogas can be delivered to either the natural gas grid where it replaces natural gas, or to the biogas tank station at Hisingen.

The two production process pathways, following algae cultivation, define the differences in the two case studies. In the first case, the algae cultivated were transferred to a biodiesel production plant extracting the lipids in the algae biomass and using transesterification to produce biodiesel and the byproduct crude glycerol. The algae residues were then further processed in a biogas production plant where crude biogas was produced and upgraded into biogas. In the second case the algae biomass was directly transferred to the biogas production plant from the algae cultivation.

In both cases it was assumed that the $CO_2$ produced and separated in the biogas upgrading step could be used for algae cultivation.

The system boundary was in these two case studies drawn so that the system includes the industrial cluster, offering excess heat and $CO_2$, and the WWT and biofuel production units.

The two cases were studied with regard to their performances. In this study their performances were evaluated with regard to the following aspects. This will be further described in the following sections.

- Product outputs.
- Energy requirements.
- $CO_2$ emissions.
- Economics.

## 4.4 $CO_2$ emissions evaluation

This section describes how $CO_2$ emission balances were calculated and compared. Figure 8 illustrates the fuel and carbon flows with and without the algae WWT/biofuels production process.

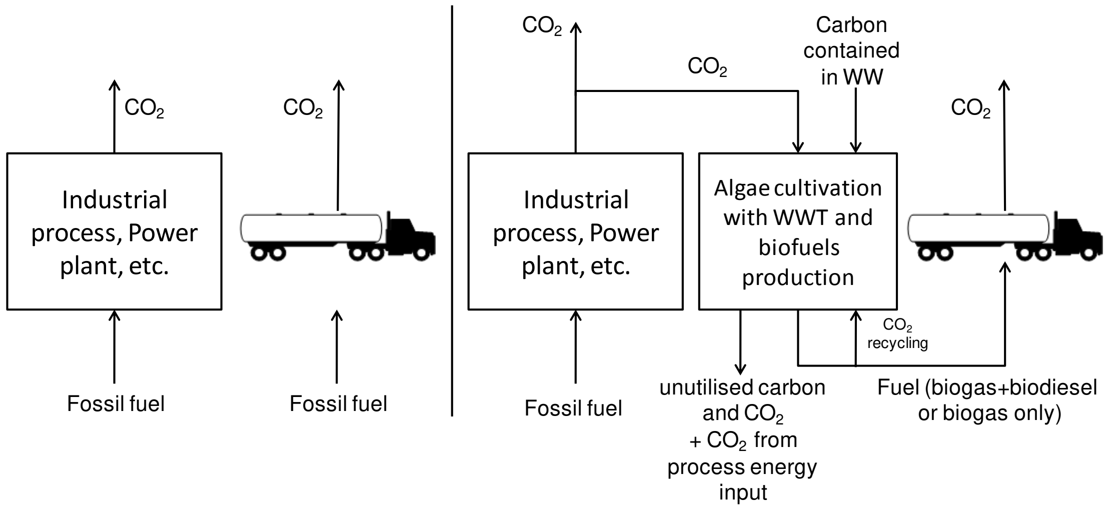


Figure 8 Fuel and carbon flows with and without algal biofuels.

To the left no algae cultivation and biofuels production is assumed. It can be seen that both industrial processes and the transportation sector use fossil fuels. In the case to the right biofuels are produced in the algae WWT/biofuels production process. These fuels in return replace fossil fuels.

In both cases (combined biodiesel and biogas and single biogas production) carbon is an important nutrient for algal growth. Carbon is assumed to be added from different sources:

- Carbon contained in the incoming WW.
- $CO_2$ from biogas upgrading.
- $CO_2$ from flue gases from the industrial cluster.
- From atmospheric, this is however neglected.

Not all the carbon sent to the process ends up in the biofuels produced (see unutilised carbon and $CO_2$ in Figure 8). Losses are due to:

- Not all carbon from the WW is removed.
- Not all $CO_2$ sent to algae cultivation from industrial sources is taken up.
- Losses of algae during algae harvesting.
- Conversion losses during biofuels production.

The biofuels produced in the presented process are in turn assumed to replace fossil fuels in the transportation and/or industrial sector. The amount of $CO_2$ savings by replacing fossil diesel and natural gas are shown in Table 3.

In order to compare the $CO_2$ emissions performance of the two processes the energy inputs to the processes and the related $CO_2$ emissions have to be considered. This is done by subtracting the $CO_2$ emissions from energy inputs to both processes from the $CO_2$ emissions saving by replacing fossil fuels, calculated above. WWT is another function of the presented processes, despite biofuels production. Therefore the $CO_2$ emissions consequences by replacing conventional WWT with WWT by algae cultivation are also taken into account. In conventional WWT biogas is produced by digestion of primary and secondary sludge from the WWT process. This amount of biogas also has to be subtracted from the $CO_2$ savings by replacing fossil fuels in order to calculate the total $CO_2$ emissions reduction. The following equation summarizes the calculations:

$$\begin{aligned}
&Total\ CO_2\ emissions\ reduction = \\
&+ CO_2\ emissions\ reduction\ by\ replacing\ fossil\ fuels \\
&- CO_2\ emissions\ from\ energy\ inputs\ to\ the\ algae\ biofuels\ process \\
&+ CO_2\ emissions\ from\ process\ energy\ input\ to\ conventional\ WWTP \\
&- CO_2\ emissions\ reduction\ of\ biofuels\ produced\ in\ conventional\ WWT\ (biogas)
\end{aligned} \tag{1}$$

The total amount of electricity used in the conventional WWTP was estimated to 37 500 MWh/year and the amount of biogas produced is ca. 60 000 MWh/year (Davidsson 2011; Göteborg Energi AB 2011).

Table 3 $CO_2$ emissions data for emissions reduction by replacing diesel and natural gas.

| Energy carrier | Value | Unit | Comments |
|---|---|---|---|
| Biodiesel | 258 | $kg_{CO2}$/MWh | Calculated from emissions of diesel combustion (Engineering ToolBox 2011), corrected by difference in energy content 35/32.6 (see section 5.4.1) |
| Biogas | 230 | $kg_{CO2}$/MWh | Emissions for combustion of natural gas (Engineering ToolBox 2011) |

The energy inputs to the process are in the form of heat and electricity. $CO_2$ emissions from energy input are calculated depending on the energy carrier (electricity or heat). Emissions from electricity and heat consumption are shown in Table 4.

Table 4 $CO_2$ emissions from electricity and heat use.

| Energy carrier | Value | Unit | Comments |
|---|---|---|---|
| $CO_2$ emissions from electricity use | 722 | $kg_{CO2}$/MWh | Assuming marginal electricity from coal power (Harvey & Axelsson 2010) |
| $CO_2$ emissions from heat use (>90 °C)[6] | 287.5 | $kg_{CO2}$/MWh | Assuming natural gas as fuel and a boiler efficiency of 0.8 |

## 4.5 Economic evaluation

The two cases are evaluated in relation to each other. This means that all costs that are equal between the cases, e.g. cultivation pond and harvesting equipment, are neglected. This is done since the large uncertainties remain regarding the costs of these process steps. Revenues for the two processes are compared, and an estimation of the difference in capital cost and operating cost between them is performed. There are several equipment units that differ between the two alternatives, which give rise to a significant difference in capital costs (Doucha et al. 2005; Schenk et al. 2008). Capital costs are assumed to follow the formula for upscaling shown in Equation 2 (Asp et al. 2008).

$$\frac{Cost_A}{Cost_B} = \left(\frac{Capacity_A}{Capacity_B}\right)^{0.7} \quad (2)$$

[6] It is assumed that industrial excess heat can be delivered from the cluster to the process to cover the processes energy demand at a temperature below 90 °C. Industrial excess heat is considered as $CO_2$ neutral in this study.

When calculating the capital costs, an annuity factor of 0.1 will be used to predict the yearly costs coming from capital costs. This implies a strategic investment with permission to have a long pay-back time. Operating costs include costs for electricity, heat and raw material in form of reactants and catalysts.

When capital costs are obtained for another year than 2011, these will be recalculated to 2011 prices, by the Chemical Engineering Plant Cost Index (CECPI). The equation can be seen in equation 3.

$$Cost_{2011} = Cost_{YearX}\left(\frac{CECPI_{2011}}{CECPI_{YearX}}\right) \quad (3)$$

The same is done for operating costs, but instead of using the CECPI, the Consumer Price Index (CPI) will be used. Numbers for years 2009 - 2011 are found in Table 5.

Table 5 CECPI and CPI for the years 2009-2011.

| **Year** | **CECPI** | **CPI** |
|---|---|---|
| 2009 | 521.9 | 299.7 |
| 2010 | 550.8 | 303.5 |
| 2011 | 575.8 | 310.2 |

Some costs are neglected, e.g. abandoning costs. These costs are assumed not to differ between the two different cases. In Table 6 the values and different sources of information regarding incomes and costs are presented.

Table 6: Income and cost parameters for the biorefinery.

| Type | Value[7] | Unit | Source |
|---|---|---|---|
| Biogas selling price | 10.70 | SEK/$m^3$ | (Ekendahl et al. 2010; Lundquist et al. 2010) |
| Biodiesel selling price | 7 420 | SEK/$m^3$ | (Lindh 2010) |
| Electricity price[8] | 500 | SEK/MWh | (Harvey & Axelsson 2010) |
| Lipid extraction (Capital costs) | 72.4 | MSEK/Process size of 19.2 $m^3$/h | (Pokoo-Aikins et al. 2009) |
| Lipid extraction (Operating costs) | 1 690 | SEK/$m^3$ | (Ekendahl et al. 2010) |
| Transesterification (Capital costs) | 106.2 | MSEK/process size of 4 730 $m^3$/h[9] | (Davis et al. 2011) |
| Transesterification (Operating costs) | 970 | SEK/$m^3$ | (Ekendahl et al. 2010) |
| Biogas production (Capital costs) | 4.25 | MSEK/(yr process size 300 $m^3$/h) | (Chen et al. 2010) |
| Biogas production (Operating costs) | 66 400 | SEK/(yr process size 36 $m^3$/h) | (Chen et al. 2010) |
| Biogas upgrade (Capital costs) | 14.1 | MSEK/Process size 1 040 $m^3$/h | (Chen et al. 2010) |
| Biogas upgrade (Operating costs) | 36 500 | SEK/(yr process size 1 040 $m^3$/h | (Chen et al. 2010) |

7 Exchange rate of 6.64 SEK/US$ (Nordea 2011)

8 Used for calculations of operating costs for cultivation. Using an exchange rate of 9.04 SEK/€ (Nordea 2011).

9 In order to obtain comparable figures from in (Davis et al. 2011), a re-calculation must be performed. This is due to that (Davis et al. 2011) uses a lipid content of 25 wt-%, whereas this work assumes a lipid content of 30 wt-%. Therefore the figure used in this work should be lower, since smaller equipment units are needed. The correction factor is assumed to be 25/30

# 5 Literature Study

In this chapter, necessary technical background information to the processes applicable within the project will be presented. The chapter presents information regarding algae cultivation and different harvesting techniques, a review of different upgrading routes for algae and the possibility for algae cultivation in municipal wastewater. In addition, the climate conditions in Sweden are presented.

## 5.1 Algae cultivation

Algae are simple organisms that differ from regular plants in many ways. They exist in several forms with different complexity and size. The size can range from 0.2 µm in diameter in picoplankton to large leaf-like formations that can measure up to 60 m in length. Algae are mainly aquatic and most of them belong to the group classified as microalgae (Barsanti & Gualtieri 2005). Further use of the word algae in this report refers to the group of microalgae. Microalgae can be classified into green algae, blue-green algae, diatoms and golden algae (Demirbas & Fatih Demirbas 2011). They are microscopic, unicellular organisms that can be found in freshwater as well as marine environments (Demirbas 2010). Using the sunlight as an energy source and $CO_2$ as a carbon source they produce algae biomass (Barsanti & Gualtieri 2005; Demirbas & Fatih Demirbas 2011).

Algae complete an entire growth cycle every few days. The algae growth follows the algae growth curve presenting the different phases; lag phase, exponential growth phase, linear growth phase, stationary growth phase and death phase. The amount of biomass is doubled typically within 24 hours under optimal growth conditions (enough nutrients, sunlight etc.), while in the exponential phase it only takes about 3.5 hours. Figure 9 shows the growth curve of algae biomass. The curve also shows that when the amount of biomass increases the availability of nutrients decreases (Mata et al. 2010).

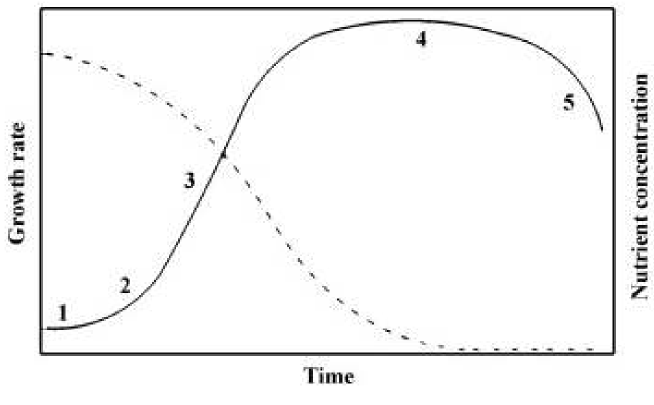


Figure 9 Representation of algae growth in batch culture (solid line) and nutrients concentration (dashed line). Recognized phases: (1) lag phase, (2) exponential phase, (3) linear growth phase, (4) stationary growth phase and (5) death phase (Mata et al. 2010).

The conversion of sunlight energy into chemical energy is a two-step process. The carbon-fixation reactions can occur both in the presence or absence of light and are therefore known as the dark reactions while the light reactions need illumination to occur. As a result of photosynthesis oxygen is formed. The conversion into chemical energy follows the following reaction (Ho et al. 2011):

$6CO_2 + 6H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6O_2$

There are several factors affecting the algae growth and their ability to perform photosynthesis and the conversion into algae biomass. As can be seen in the reaction above the photosynthesis requires $CO_2$, water and sunlight to take place. In addition nutrients are necessary for the algae growth (Pokoo-Aikins et al. 2009). For the production of cellulose, starch and oil the use of microalgae is a good option since they are able to produce these substances in large quantities (Schenk et al. 2008). In order to provide good growth conditions for algae a water temperature of 20 – 35 °C is required, depending on algae species (Pokoo-Aikins et al. 2009; J. B. K. Park et al. 2011). Temperature studies shows that algae can easily withstand temperatures up to 15 °C lower than their optimal growth temperature while a temperature of 2 – 4 °C higher than their optimal can cause algae death (Mata et al. 2010).

There is a need for sunlight as an energy source in order for algae to perform photosynthesis. Despite variations in solar radiation during the hours of the day, during the days of the year and depending on the geographic location of the cultivation there is a need to exploit the natural solar radiation in order to minimize the expenses for cultivation (Demirbas 2010). Both the quantity and quality (wavelength) of the light affects the growth. The light intensity decreases exponentially with the depth in the water. The rate of photosynthesis increases linearly with the intensity of light. This increase occurs until a plateau is reached. However, at high light intensities an inhibition of the photosynthesis can occur (Darley 1982). Microalgae have a maximum solar energy conversion capacity of about 4.5 %, meaning that only 4.5 % of the solar energy that reaches the algae is converted into biomass (Walker 2009).

The $CO_2$ demand varies under different conditions. Approximately 50 % of algae biomass in dry weight consists of carbon, where the main carbon source is $CO_2$ (Demirbas 2010). $CO_2$ is the dominant nutrients in algae growth. Stoichiometrically the $CO_2$ demand in algae varies between 1.65 up to 2 $CO_2$/kg dry biomass. This figure could rise as a consequence of high oil or starch content within the algae. The partial $CO_2$ pressure in the air is not sufficient (0.032 kPa) to achieve high growth rates. Since the optimal value is 0.1 kPa (Posten & Schaub 2009).

To improve the growth of algae $CO_2$ can be provided using an external carbon source, e.g. flue gases resulting from combustion (Posten & Schaub 2009). Flue gases from a small power plant are already today being used as the carbon source in microalgae cultivation (Doucha et al. 2005). In a study conducted in Umeå in Sweden algae are grown in combination with WWT. Flue gases are added to the cultivation from a cogeneration plant (Avfall Sverige 2009). A study done by (F. Kaštánek et al. 2010) showed that the productivity when using flue gases instead of a mixture of air and $CO_2$ did not differ significantly, i.e. no inhibition or limitation in algae growth was found. In addition, the study showed that no accumulation of harmful products from the flue gas did occur in the microalgae biomass (Doucha et al. 2005; F. Kaštánek et al. 2010). $CO_2$ sequestration, i.e. the capture of $CO_2$, has been studied in large pond systems under optimal conditions and has then shown high efficiency. Up to 99 % of the $CO_2$ was captured. Other studies show $CO_2$ sequestration by algae of 4 g per liter and day at a growth rate of algae of 2.5 g per liter and day. $CO_2$ has been shown to have a prime importance of the total economics of algae cultivation (Doucha et al.

2005). The ability to make use of flue gases as a carbon source in algae cultivation can therefore be of great interest.

Algae need nutrients for biomass formation. Nitrogen and phosphorous are two important substances needed in this process. As in the case of $CO_2$ demand the fraction of nitrogen can differ depending on the oil and starch content. A high value of oil or starch in the algae biomass reduces the mass fraction of nitrogen that normally lies around 0.1 – 0.14. There are two options for providing the algae with the nutrients they need for growth. Either the necessary nutrients are added or the algae can be grown in a medium already containing the required nutrients (Posten & Schaub 2009). The water may for example be provided from WWTPs in the area. Using the approximate molecular formula of microalgae, $C_{106}H_{181}O_{45}N_{15}P$, the minimal requirement of the different nutrients for algae growth can be estimated and calculated (Davis et al. 2011). Reduced availability of nitrogen and phosphorous may result in that the dry weight of lipids doubles or triples. Algae will continue to grow until there is a limitation of nutrients. Despite this limitation the photosynthesis will take part leading to an accumulation of starch and lipids, holding an important function for survival during unfavorable conditions. The cell division stops while the accumulation of starch and lipids occurs in the same rate as in the presence of nutrients. To obtain high lipid content in algae it is therefore good to perform algae cultivation in a medium where the availability of nutrients varies (Schenk et al. 2008).

### 5.1.1 Algae culture systems

There are several alternatives for microalgae culture systems. Algae can be grown in open or closed systems. There are several pros and cons with these systems. In the process of algae cultivation the design of an efficient cultivation system is the most important step. Due to the microalgae photosynthesis the reactors should be designed so that the algae will be reached by the solar radiation (Ho et al. 2011).

Scaling up production of microalgae has received increased attention since they have expected to be a promising raw material for biofuels and their ability for $CO_2$ fixation. For example, Phycal is a Hawaiian company that has received funds to build a pilot scale pond of 34 acres and is expected to break ground in late 2011 or in 2012. Another company is Blue Petroleum that uses Photobioreactors (PBR) to capture $CO_2$ from a refinery in Spain. For scaling up microalgae production, open systems such as lakes or ponds are interesting because they are less technically complex than closed systems. Despite their large production capacity, open ponds results in lower productivity than closed systems caused by several factors. These systems are dependent on the sun as an energy source and they are as a consequence more sensitive to variations in solar radiation, in regard to both the amount of light reaching the algae necessary for photosynthesis and the water temperature. The depth of the ponds affects the amount of light reaching the algae. Vapor losses, $CO_2$ diffusion to the atmosphere and the risk of cultivation contamination are some of the disadvantages with open systems (Ho et al. 2011). Open ponds have been shown to result in an average of 20 $g/m^2/d$ dry biomass per year (Posten & Schaub 2009).

There are three main designs of open cultivation systems; raceway ponds, circular ponds and inclined systems. Raceway ponds are built like an endless loop using paddle wheels to agitate the culture. In the circular ponds the culture is circulated by using a rotating arm while the inclined system uses pumping and gravity flow to mix the culture (Mata et al. 2010). The most common design, the raceway pond, normally operates continuously feeding the pond in front of the paddle wheel with water and nutrients and harvesting the algae behind the wheel. The rectangular pond is commonly made of concrete using baffles to guide the flow around the pond along the oval channel. The water is agitated using the paddle wheel resulting in that the algae are kept suspended in the water (Demirbas 2010; Schenk et al. 2008).

Studies have shown that more nutrients are needed in open ponds systems (T. J. Lundquist et al. 2010). In addition the depth of the pond is limited because the algae need to be reached by the solar energy to grow and perform photosynthesis (Mata et al. 2010). An optimally designed raceway pond should have a depth of 10 – 50 cm to ensure that the algae are exposed to the sunlight (Jorquera et al. 2010). The shallow ponds entail some difficulties that need to be kept in mind when using these culture systems. As a consequence of the depth the ponds occupy large land areas and make it more challenging to control the evaporation and the water temperature (Mata et al. 2010). Typically the raceway pond size lies between 0.2 – 0.5 hectares (Demirbas 2010). If there is a high availability of water the water loss through evaporation might not be a problem. Figure 10 illustrates a raceway pond.

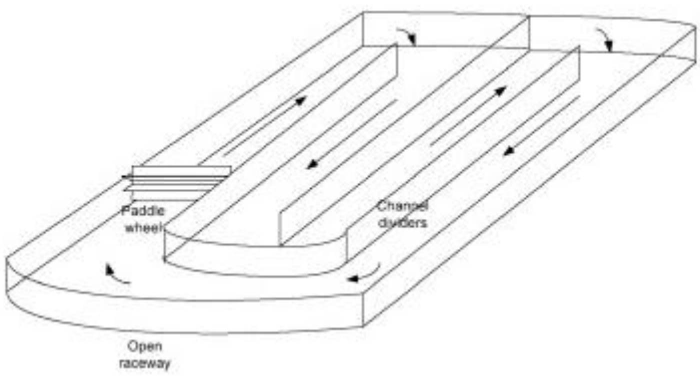


Figure 10 Illustration of a raceway pond (Jorquera et al. 2010).

A closed system overcomes many of the disadvantages presented for open systems. In closed systems, known as closed PBR, the risk of contamination are small and the amount of light reaching the algae is high due to the large surface area. The systems offer a regulated and controlled cultivation environment. PBRs offer great opportunities to optimize the cultivation environment in regard to algae strain. The efficiency of $CO_2$ fixation increases as a consequence of good mixing possibilities, good gas transfer and good light distribution. On the other hand, up scaling of these closed systems have other disadvantages (Ho et al. 2011), e.g. generally the closed systems are more expensive than open ponds and there are limitations regarding the size (Demirbas 2010). Still there are several advantages including high process control, the ability to prevent contamination of the biomass and high biomass productivity (Ho et al. 2011).

Closed PBRs are known for their high efficiency, but currently does not apply to large scale production. There are several types of closed PBRs holding various pros and cons. Plate-type systems are most attractive for large scale outdoor cultivation but the temperature control is poor. Column systems are also relatively low-cost but have a small illumination surface area. Vertical tube systems are relatively low-cost systems but it is hard to control the temperature (Ho et al. 2011). Successful algae cultivations have been performed using a 1000 – 2000 L tubular system operated for long periods (Mata et al. 2010). The tubular PBR consists of transparent tubes that are typically placed in parallel to each other or flat above the ground to maximize the illuminated surface area. The tubes are made of glass or plastic with a diameter usually less than 0.2 meter enabling the sunrays to reach the middle of the tube. The system consists of a reservoir where the mixing is taking place in order to increase the gas exchange and ensure nutrients distribution. The algae broth circulates between the reservoir and the reactor (the tubes) where the algae are illuminated with solar radiation (Demirbas 2010).

Using closed PBRs cell densities between 2 – 20 g/L can be achieved (Demirbas 2010; Posten & Schaub 2009). Figure 11 illustrates a flat-plate PBR and tubular PBR where the degassing column is used to remove oxygen.

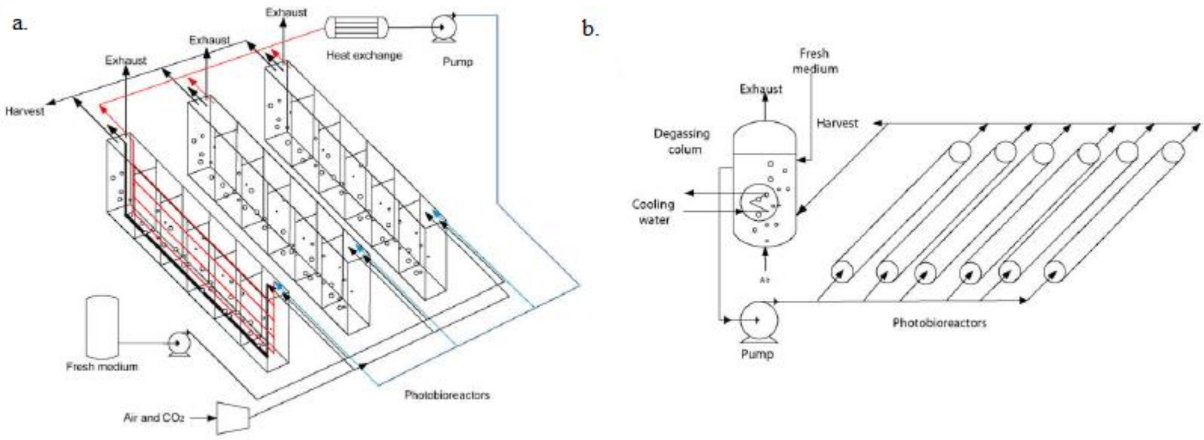


Figure 11 a) A flat-plate PBR b) A tubular PBR (Jorquera et al. 2010).

Combining open and closed systems in a so called hybrid system can improve the performance of the algae production and increase the yield. The selected strain of algae is first grown in a closed bioreactor and the algae broth is then transferred to the open pond. Using an inoculum large enough for the pond reduces the risk of contamination since it allows the strain to establish in the pond before the unwanted species. Cleaning the ponds in between also reduces the risk of contamination since the unwanted species sooner or later will dominate the open system (Demirbas 2010; Schenk et al. 2008).

The cost and energy demand of PBRs is one of the big disadvantages for using these systems. Flat plate PBRs have been reported to have less energy demand than horizontal tubular PBRs. Raceway ponds do not require that much energy for mixing, around 4 $W/m^3$ (Jorquera et al. 2010). Jorquera et al. (2010) performs a life-cycle analysis for microalgae biomass production comparing the energy use of open ponds versus closed PBRs. Figure 12 illustrates the process inputs and outputs for the algae cultivation process.

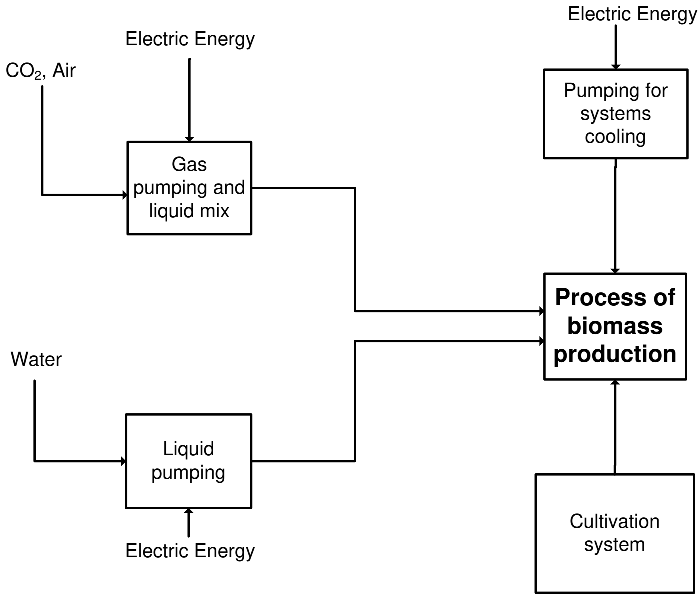


Figure 12 Illustration of the process inputs and outputs plus the energy use for the algae cultivation process (Jorquera et al. 2010).

Jorquera et al. (2010) compares raceway ponds, flat-plate PBRs and tubular PBRs using a production level of 100 000 kg biomass dry weight as the base level so that the three systems could be compared. The alga cultivated in the different culture systems is *Nannochloropsis* sp. Table 7 summarizes some important parameters used in the study.

Table 7 Process inputs and outputs plus the energy use for the algae cultivation process (Jorquera et al. 2010).

| **Variable** | **Raceway ponds** | **Flat-plate PBR** | **Tubular PBR** |
|---|---|---|---|
| Annual biomass production (kg/year) | 100 000 | 100 000 | 100 000 |
| Volumetric productivity (g/L/d) | 0.04 | 0.3 | 0.6 |
| Illuminated areal volume ($m^{-2}$) | 300 | 50 | 14.5 |
| Biomass concentration (g/L) | 0.4 | 2.7 | 1.02 |
| Space required ($m^2$) | 26 000 | 10 000 | 10 700 |
| Reactor volume required ($m^3$) | 7 800 | 1 000 | 490 |
| Energy demand ($W/m^3$) | 3.7 | 53 | 2 500 |

## 5.1.2 Climate conditions

In order to provide good growth conditions for algae and for photosynthesis to occur there is a need to investigate the air temperature and the solar radiation reaching Sweden throughout the year. Depending on geographic region or even specific locations these parameters will vary. The air temperature affects the water temperature which should range between 20 – 35 °C, depending on algae species, are needed for an optimal growth condition (Pokoo-Aikins et al. 2009; Park et al. 2011). Insolation and temperatures including seasonal variations are important parameters since they affect the algae productivity as well as the length of the season that could reach up to almost 300 days per year. Figure 13 presents the temperature zones assumed to be suitable for high algae productivity (within the square). The regions that fall within the blue square has an average temperature above 15 °C which is assumed to be the lower temperature limit for offering favorable cultivation conditions (Lundquist et al. 2010).

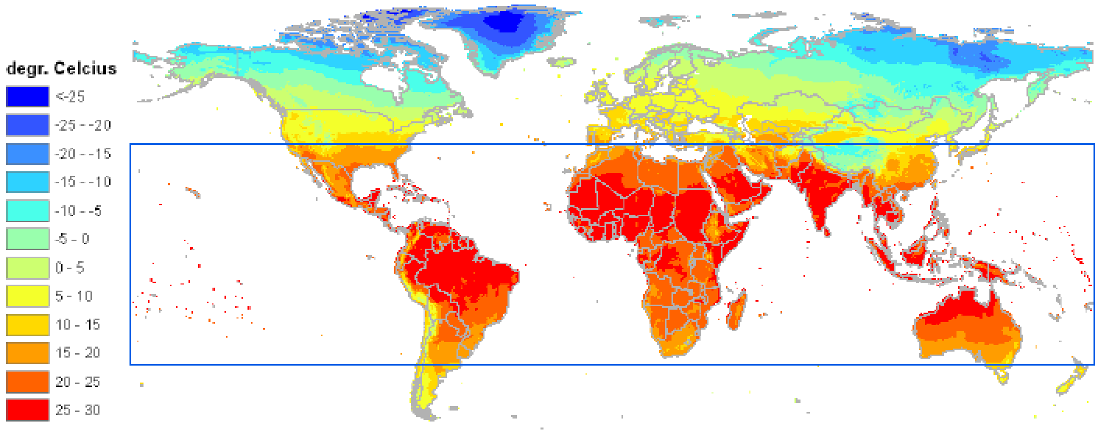


Figure 13 Average temperatures below 15 °C are assumed to be the temperature limit for high algae productivity. The regions that fall in the blue square have an average temperature exceeding this number (Lundquist et al. 2010).

As can be seen in the figure Sweden does not fall within this square. There are three temperature interval presented in the country. The south of Sweden has an average temperature ranging between 5 – 10 °C, the middle between 0 – 5 °C and in the north -5 – 0 °C. Since low temperatures will result in low cultivation pond temperatures and since the average temperature in Sweden fall below the temperature limit for high algae productivity it may be interesting to look at the possibility of using available excess heat to warm up the cultivation ponds.

In some parts of the world, where the temperature reach or even exceed 40 °C, the conditions are also not optimal since the temperatures are too high for algae cultivation. A high temperature may also result in high evaporation and thereby water losses (Lundquist et al. 2010). By placing the algae production in Sweden, too high temperatures will not be a problem disturbing the cultivation.

Figure 14 shows the average temperature in Sweden between the years 1961 – 1990 (SMHI 2011b; SMHI 2011c).

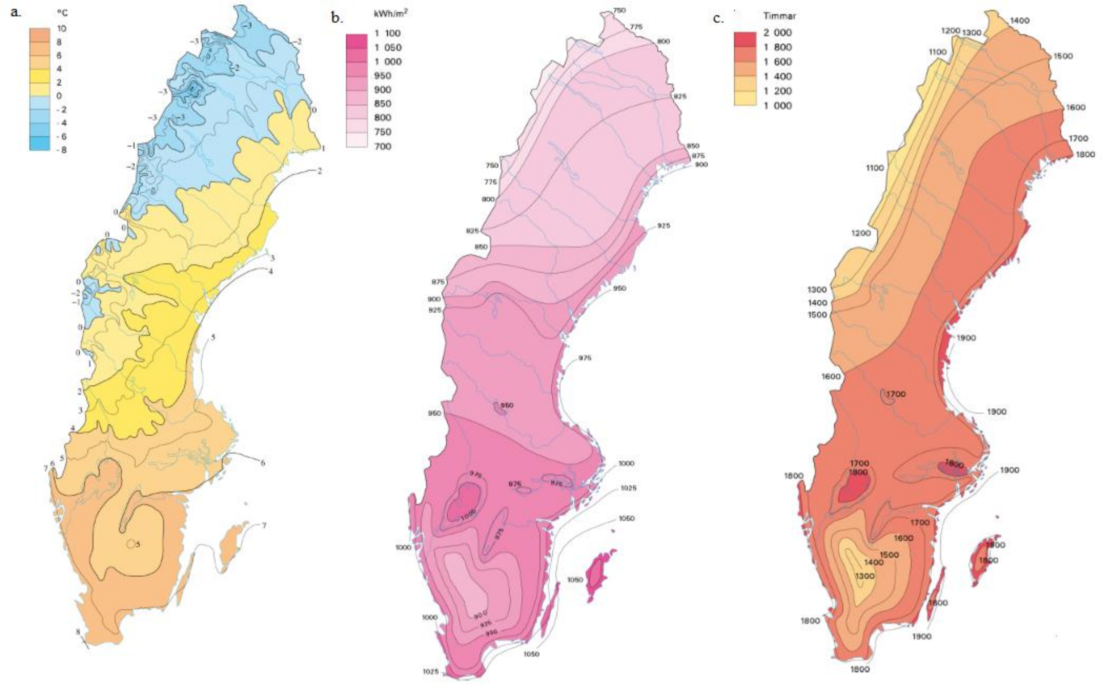


Figure 14 An illustration of the a. annual average temperature in Sweden b. total solar insolation during one year in Sweden and c. average amount of sunshine hours in Sweden between the years 1961 – 1990 (SMHI 2011b; SMHI 2011c).

Table 8 Observed temperature data in Gothenburg in Sweden during 1973 – 2010 (SMHI 2011a).

| **Year** | **Month** | **Temperature, °C** |
|---|---|---|
| 1973 | January | 1.2 |
| | May | 11.2 |
| | July | 18.9 |
| | September | 12.5 |
| 1983 | January | N.A |
| | May | 11.5 |
| | July | 18.3 |
| | September | 13.1 |
| 1993 | January | 2.2 |
| | May | 14.6 |
| | July | 15.0 |
| | September | 10.8 |
| 2003 | January | -1.1 |
| | May | 11.9 |
| | July | 19.4 |
| | September | 14.6 |
| 2010 | January | -5.5 |
| | May | 11.3 |
| | July | 19.5 |
| | September | 12.9 |

As can be seen in Figure 14 the annual average temperature does not exceed the temperature of 15 °C, assumed to be the limit for favorable conditions for algae cultivation. Collected temperature data by SMHI (2011c) (The Swedish Meteorological and Hydrological Institute) between 1961 – 1990 shows that during the months May to October the average temperature is only a few degrees below the assumed limit. During the summer months from June to August the average temperature exceeds 15 °C. The winter months in Sweden are cold and during January to April and November to December, the temperature is lower. It is in the southern parts of Sweden that temperatures are highest throughout the year.

The town of Gothenburg is located on the west coast of Sweden. The temperature variations in Gothenburg between 1973 and 2010, for four months spread over the year, can be found in Table 8. The temperature in Gothenburg broadly follows the trend described above.

The second important climate factor affecting the efficiency of algae cultivation is total solar insolation. Sweden´s insolation during the period 1961 – 1990 is illustrated in Figure 14. In general the temperature follows the solar insolation, and consequently the southern parts are receiving the most solar insolation throughout the year.

Based on the average monthly solar insolation from 1961 – 1990 in Gothenburg (SMHI 2011d), the approximate average solar insolation per day is calculated by dividing the monthly insolation by the number of days in each month. The average daily solar insolation for the period is illustrated in Figure 15.

As shown in Figure 13 the southern parts of the US are within the square and are therefore considered an appropriate area for algae cultivation. Among the areas with the highest potential in the US is the Central Valley of California. In order to discuss the amount of solar insolation in Sweden the solar insolation in the south of California is also presented in Figure 15.

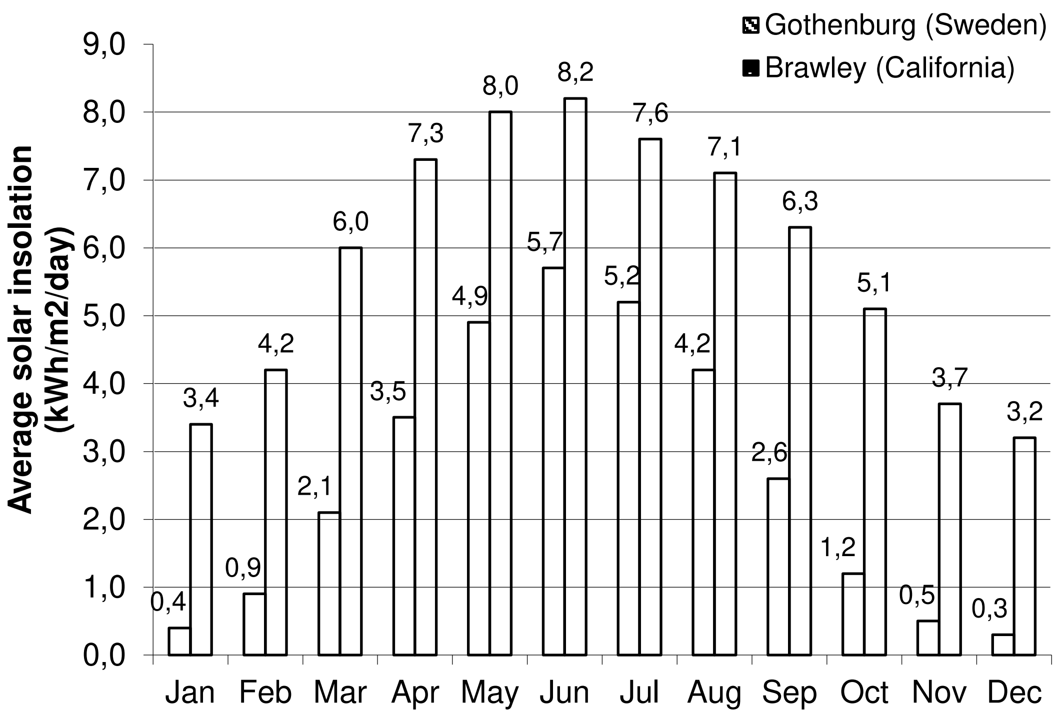


Figure 15 Average daily solar insolation in Gothenburg (1961 – 1990),and average insolation per day at Brawley, Imperial Country, California (1995 – 2009) (Lundquist et al. 2010).

The average daily solar insolation in Sweden is lower than the daily solar insolation in the area of southern California. The lowest average daily solar insolation in California was measured in December and measures 3.2 kWh/m$^2$. Following December is January with a solar insolation of 3.4 kWh/m$^2$. There are five months in Sweden measuring a number exceeding the January solar insolation in California. April to August measures an insolation ranging between 3.5 – 5.7 kWh/m$^2$/day. The highest average daily insolation in Sweden can be found in June, measuring 5.7 kWh/m$^2$. The closest comparable number in Californian can be found in March (6.0 kWh/m$^2$) or October (5.1 kWh/m$^2$).

The number of sunshine hours is thought to affect the productivity of the algae cultivation more than the amount of solar insolation (Lundquist et al. 2010). The average number of sunshine hours in Sweden is presented in Figure 14. Following the trend with higher temperatures in south of Sweden the most sunshine hours are found mainly in the south of the country or along the east coast.

Looking closer to the area of interest in this project, the area of Gothenburg, the amount of sunshine hours per day are presented in Figure 16. These figures are based on the monthly average amount of sunshine hours (SMHI 2011d) from 1961 – 1990. During the cold months there are less sunshine hours than during the months where the temperature is higher. The average sunshine hours per day of California, US, are also presented in Figure 16. The monthly average sunshine hours are measured in the area of San Diego, California, located about 200 km from Brawley, California (The Weather Network 2011). The monthly average is used to calculate the daily average. The monthly amount of sunshine hours is divided by the amount of days in each month.

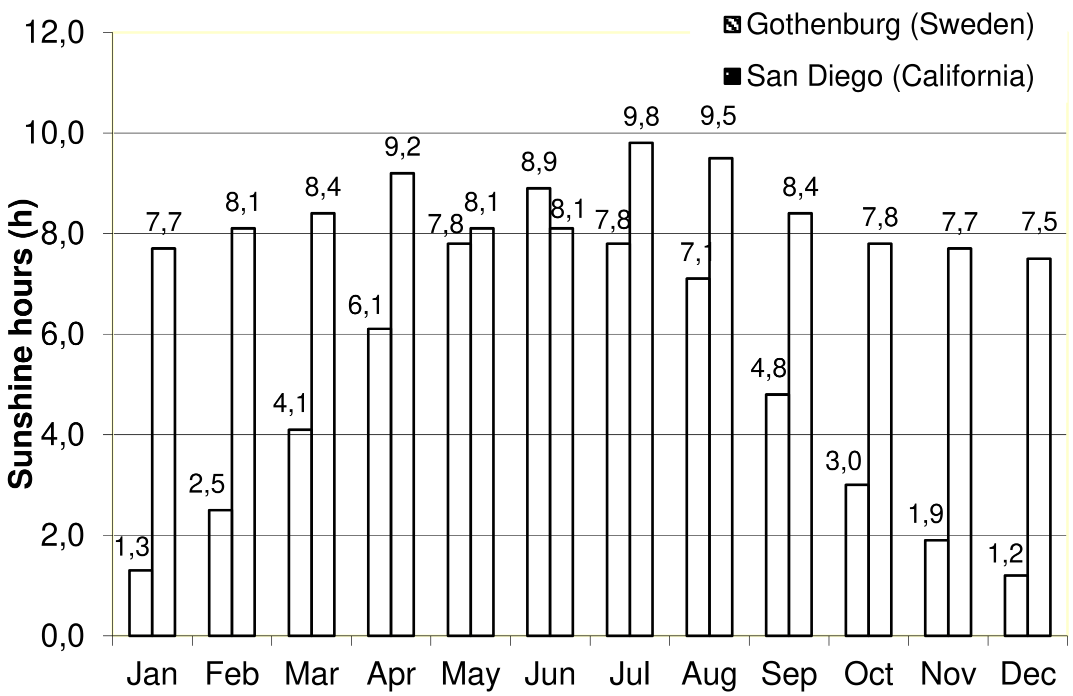


Figure 16 Approximate average daily sunshine hours in Gothenburg, Sweden (1961 – 1990) and San Diego, CA, US, (1961 – 1990).

The number of sunshine hours in Gothenburg varies during the months of the year from 1.2 – 8.9 hours per day. In San Diego the monthly variations are not that great ranging from 7.5 – 9.8 hours per day. During May to July the number of sunshine hours in Gothenburg do not fall below the lowest amount of sunshine hours in San Diego, measured in December. Even if the number of hours is less than in California during the rest of the year there are still several months in Sweden having a high number of sunshine hours.

## 5.2 Algae harvesting

One of the main difficulties with algae production is harvesting. After cultivation more than 99 wt-% of the algae/water mixture consists of water (Wiley et al. 2011). Separating the algae from the water in the culture system is difficult has a high energy demand. Approximately 20 – 30 % of the total cost of algae biomass originates from harvesting. The method used depends on the algae species, the cell density and usually the culture conditions (Demirbas 2010). The chosen harvesting techniques also depend on how the algae will be treated after harvesting, i.e. oil extraction for biodiesel production or anaerobic digestion. Different downstream production processes have different demands regarding the water content (Ho et al. 2011).

No single technique has proven to be the universal solution to the harvesting problem. In order to harvest the algae in the best way it is common to combine several methods (Mata et al. 2010). The harvesting methods can be grouped into primary and secondary harvesting techniques. As a first step in the harvesting process, a primary harvesting technique, e.g. sedimentation and flotation, is used to separate the algae biomass from the growth media. Secondary techniques are then used to further increase the solids content i.e. thicken the slurry. Primary harvesting results in a solid content ranging from 0.5 – 6 wt-%, while 10 – 20 wt-% are achieved with secondary harvesting. What techniques that should be used and if single primary or combined primary and secondary techniques should be used depends on requirement of the production process of the final product (Wiley et al. 2011). Techniques used for harvesting and biomass concentration include (Demirbas 2010; Ho et al. 2011):

- Centrifugation.
- Flocculation.
- Flotation.
- Sedimentation.
- Filtration.

To facilitate harvesting of microalgae the algae needs to form large agglomerates (Wiley et al. 2011). The choice of harvesting method is important, both in terms of cost and energy efficiency, for the production process to be economically viable. From an environmental perspective it is important to reduce the energy use to avoid that the energy use during production exceeds the energy supply in the final product.

The surface of the microalgae is usually negatively charged, preventing them from sticking together in the broth. In order to overcome this, coagulation agents are added. This method is called flocculation (Ho et al. 2011). Flocculation is used to facilitate the harvesting by aggregating the algae and increase the particle size. It is commonly combined with filtration, centrifugation or sedimentation[10] (Mata et al. 2010; Schenk et al. 2008). Various flocculants can be used for the purpose of increasing

[10]This leads to faster sedimentation due to the increased particle size.

flocculation. The choice of flocculant depends on the final product since it is important that it does not affect the final product negatively. The optimal flocculant should be inexpensive, nontoxic and should only need to be added in low concentrations. The salts $FeCl_3$, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ are common flocculants and the metal ion efficiency increases with increased ionic charge. Nontoxic polymers such as polyelectrolyte or chitosan can also be used as flocculants (Ho et al. 2011). The use of these chemicals turns the harvesting method into an expensive method and the chemicals can disturb further downstream processes (Pittman et al. 2011; Ho et al. 2011). When using raceway ponds for algae cultivation a neighboring pond is used for harvesting (Schenk et al. 2008).

Among alternative flocculation methods, where one can avoid chemical induced flocculation, is bio-flocculation, sometimes also called auto-flocculation. Using the effect of spontaneously aggregation of several algae species, chemical flocculants can be avoided. The aggregation leads to that the aggregates descend to the bottom of the pond facilitating the harvesting of the algae biomass (Pittman et al. 2011). In some algae species bio-flocculation may be induced by limiting the availability of nutrients such as C or N, i.e. exposing them to stress conditions (Pittman et al. 2011; Craggs et al. 2011). Following the harvesting bio-flocculation can be further combined with sedimentation and/or centrifugation. The drawback with sedimentation lies in the small size of the microalgae resulting in a slow settling rate (Pittman et al. 2011). Centrifugation on the other hand is an energy intensive harvesting technique, using 3 $kWh_e/kg_{algae}$, but offers a rapid method with a high harvest efficiency of 95 % (Pittman et al. 2011; Craggs et al. 2011). Bio-flocculation is the harvesting technique with the lowest costs available on the market today, making it interesting and worth further research (Craggs et al. 2011). The algae cultivation is transferred to a container, below ground, where the algae, during six hours, are settling to the bottom. So far it has not been tested in a large scale process, but numerous laboratories studies have been carried out as well as pilot scale projects in the US as well as New Zealand (Lundquist et al. 2010).

The use of sedimentation for large scale biomass production is difficult since the process is time-consuming and requires large surface areas (Schenk et al. 2008). Since using the gravitation force it results in a slow sedimentation. The drawbacks presented have led to a poor credence for the method used for algae biomass production. The method is inexpensive and combined with flocculation it may increase the efficiency in harvesting (Wiley et al. 2011).

In the study conducted by (Lundquist et al. 2010) the solids concentration is increased following bio-flocculation by using a gravity thickener assuming a capture efficiency of 95 %. Thickening is a technique used to remove water and thereby increasing the solids concentration. Gravity thickener is the most common thickening method and is today used in wastewater plants for sludge thickening. The floor in the circular thickener tank is steeply sloping and uses gravity to collect the settled solid in the center of the tank (Turovskiĭ & Mathai 2006), generating a higher solids concentration at the bottom of the tank. The sludge is transferred to the gravity thickener and due to the gravitational forces the solids settle at the bottom from where it can be collected and the supernatant is removed from the side of the thickener (Sperling 2007). Using gravity thickener results in solids concentrations of 2 – 3 wt-% (Lundquist et al. 2010; Turovskiĭ & Mathai 2006). Since gravity is used, the operational cost is low (Turovskiĭ & Mathai 2006).

Floatation is a technique where various methods are used to form foam that floats at the surface that can then be removed. The method is currently too expensive for large scale use (Ho et al. 2011). Algae have a tendency to float on the water surface as a result of the oxygen released during photosynthesis. To increase the efficiency several methods can be used to increase the amount of algae floating on the surface (Polprasert 1996). With Dissolved Air Floatation (DAF) small air bubbles are injected under high pressure, increasing the solubility of gas. The bubbles rise to the surface making the algae accumulate and aggregate on the water surface. Froth floatation combines bubbling with air with a change in pH which results in a foam containing algae on the water surface (Ho et al. 2011). Suspended Air Flotation (SAF) is based on the same basic principle as DAF. SAF uses smaller bubbles than DAF and a surfactant, to lower the surface tension between the water surface and the algae, instead of pressure. The absence of a pressure requirement leads to a lower energy demand and the method is thereby cheaper to operate. The algae containing froth are removed from the water surface using skimming (Wiley et al. 2011). Flotation is usually combined with flocculation since it increases the interaction with the bubbles (Ho et al. 2011; Schenk et al. 2008).

Centrifugation is suitable for growing algae used for high value products. The use of centrifugation for large scale production is difficult since the process is very costly with a high energy demand (Schenk et al. 2008; Ho et al. 2011). It has been estimated to use 3000 $kWh_{el}/ton_{algae}$. But to use centrifugation as a second harvesting method has been shown to be useful. Algae in a concentration of 10 – 20 g/L can be concentrated by centrifugation to 100 – 200 g/L. Using this second step of harvesting can be good when the following downstream processes requires a low water content (Schenk et al. 2008).

Conventional filtration is only suitable for relatively large microalgae in the size of >70 µm. Filtration uses vacuum to filter the suspension (Pittman et al. 2011). The efficiency of the harvesting technique is low and a common problem when using this method is filter clogging. The clogging is a problem during large scale production and the method suffers from high maintenance costs. (Schenk et al. 2008). Microfiltration and ultrafiltration are alternative filtration methods that can be used when harvesting smaller algae species though it suffers from drawbacks. The membranes used in this process must frequently be replaced and there is a great need for pumping, which requires large amounts of energy making the method expensive (Pittman et al. 2011).

A summary of the performance and the energy requirements for some of the methods presented in this report can be found in Table 9.

Table 9 Performance and energy demand of algae harvesting systems (Wiley et al. 2011).

| **Harvesting process** | **Final slurry (% total solids)** | **Energy input ($kWh/m^3$)** | **Sources** |
|---|---|---|---|
| Sedimentation | 0.5 – 3 | 0.1 | (Wiley et al. 2011). |
| DAF | 3 – 5 | 1.5 – 20 | (Wiley et al. 2011). |
| SAF | 3 – 5 | $3 \cdot 10^{-3}$ [11] | (Wiley et al. 2011). |
| Centrifugation | 10 – 22 | 0.9 – 8 | (Wiley et al. 2011). |
| Bio-flocculation | 1.5 [12] | N/A | (Lundquist et al. 2010) |
| Gravity thickener | 2 – 3 | N/A | (Lundquist et al. 2010; Turovskiĭ & Mathai 2006). |

The above described harvesting methods; centrifugation, flocculation, flotation, sedimentation and filtration are all used today in conventional wastewater treatment, see Section 5.3.1.

When producing biofuels a relatively inexpensive method suitable for large scale production is required. Gravity sedimentation enhanced with flocculation has been recommended as the most appropriate method for this purpose (Ho et al. 2011).

## 5.3 Algae cultivation in municipal wastewater

The uncontrolled discharge of wastewater to the environment leads to an "over-load" and thereby to a disruption of natural recycling processes like photosynthesis, respiration and nitrogen fixation.

Therefore the treatment of municipal and industrial wastewaters is an important task which needs to be performed in order to conserve the aquatic environment. Untreated wastewaters contain potentially harmful substances such as (Rawat et al. 2010):

- High levels of organic material.
- Pathogenic microorganisms.
- Large amount of nutrients.
- Toxic compounds (heavy metals etc.).

### 5.3.1 Conventional wastewater treatment

Conventional WWT is a combination of processes intended to generate water of sufficient, defined quality from municipal, industrial and other WWs with a known composition. It is important that the effluent from the WWTP can be discharged into a receiving body of water (mainly surface waters like rivers), without deteriorating it. The complexity of the treatment is strongly dependent on the receiving water. The

[11] Scalability of the figure is uncertain. Data obtained from small-scale experiments.
[12] Assumption made by Lundquist et al. (2010).

Urban Wastewater Treatment Directive (91/271/EEC) gives values for the minimum requirements for discharges from urban WWTP. Values for different WWTP effluent parameters are given in Table 10 (The council of the European Communities 1991).

Table 10 Requirements for discharges of urban WWTP. The values presented are valid for high WW flows (>100000 p.e.). Total phosphorus and nitrogen values only apply to discharges to sensitive waters (The council of the European Communities 1991).

| **Parameters** | **Concentration** | **Minimum percentage of reduction in relation to the influent load** |
|---|---|---|
| $BOD_5$[13] at 20 °C (without nitrification) | 25 mg/L $O_2$ | 70 % - 90 % |
| COD[14] | 125 mg/L $O_2$ | 75 % |
| Total suspended solids | 35 mg/L | 90 % |
| Total P | 1 mg/L P | 80 % |
| Total N | 10 mg/L N | 70 % - 80 % |

The following objectives are fulfilled by WWT (Gray 2010):

- Conversion of potential harmful substances in the WW into products that can be safely disposed into a receiving body of water without altering its quality.
- Protection of public health.
- Efficient and economic disposal of WW.
- Recovery of valuable components in the WW, like nutrients and energy.

[13] Biological Oxygen Demand
[14] Chemical Oxygen Demand

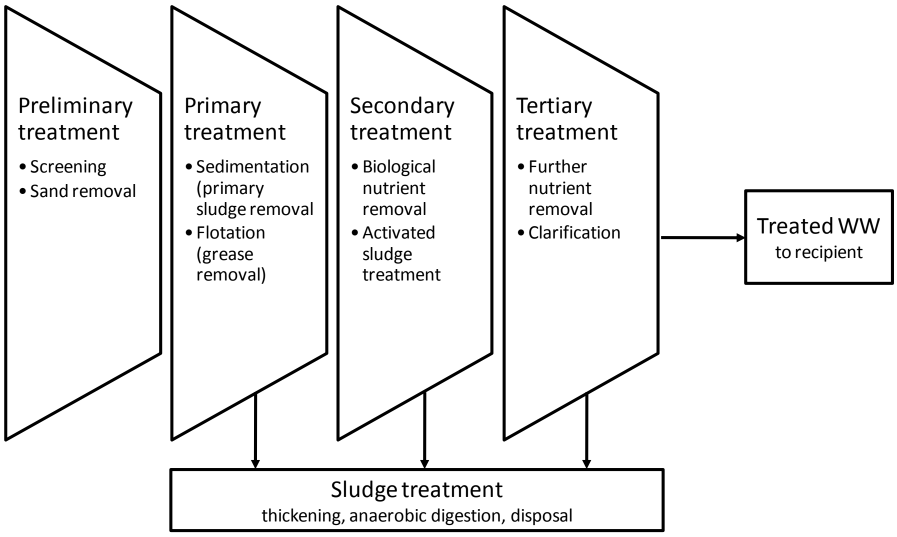


Figure 17 Summary of typical treatment process steps for municipal and industrial WWs. Depending on the influent and required effluent quality not all the steps have to be selected.

Depending on the demands on water quality WWTP have different cleaning steps, as shown in Figure 17. The different stages apply a variety of treatment processes, which can be categorised in (Rawat et al. 2010):

- Physical; sedimentation, flotation, filtration, centrifugation.
- Chemical; adsorption, disinfection, dechlorination.
- Biological; anaerobic digestion, biological nutrient removal (e.g. denitrification).

Figure 17 gives an overview of possible treatment process steps generally applied for treatment of municipal and industrial WWs. Generally the whole process can be divided in preliminary, primary, secondary and tertiary WWT. Additionally treatment of sludge obtained is applied to sludge from primary, secondary and tertiary treatment. Preliminary treatment involves the removal of materials like solids (e.g. cotton swabs and wood), grit, oil and grease by means of e.g. flotation and screening. In primary treatment the so-called primary sludge is removed from the WW by sedimentation. Secondary treatment usually involves biological treatment of the WW, where micro-organisms oxidise the dissolved and colloidal organic matter present in the WW. Tertiary treatment is used to further improve the water quality after biological treatment. Specific compounds are e.g. chemically removed (Gray 2010). In sludge treatment the sludge separated in different processes from the WW is treated separately in order to be able to dispose it. Treatment methods often used are dewatering by pressing, centrifugation etc. and anaerobic digestion to lower the amount of organic carbon and recover part of the energy contained by the sludge.

### 5.3.2 Wastewater treatment by microalgae

Using algae for treating wastewater has been discussed and is already applied since 40 years. An extensive amount of work has been conducted on investigating the use of algae to remove nutrients (mainly nitrogen and phosphorous) in a controlled manner. Also removal of heavy metals (Wang et al. 2009), pathogens and others contaminants have been investigated (Rawat et al. 2010).

Different studies show that the use of fertilizers for algae cultivation has a large negative impact on the sustainability and economics of such a process. Clarens et al. (2010) states that around 50 % of the energy use and GHG emissions from algae cultivation are associated with fertilizer production. Nigel Quinn, an agricultural engineer at the Lawrence Berkley National Laboratory states that economically algae cultivation for biofuels production will not be feasible if not another function (like wastewater treatment or production of valuable by-products) is fulfilled within the process (Savage 2011). Other studies also suggest wastewater treatment in combination with algae cultivation as a way to enhance the environmental and economic performance of the process. Table 11 shows experimental data on nutrient removal from different WW sources by microalgae (Craggs et al. 2011; Razon & Tan 2011; Park et al. 2011; Schenk et al. 2008). Algae cultivation serves two purposes by improving water quality and producing biomass for further utilisation as e.g. biofuels.

In a study performed by Clarens et al. (2010) three different types of partially treated wastewater were evaluated for algae cultivation:

- Secondary effluent from an activated sludge treatment plant with biological nutrient removal (N and P).
- Secondary effluent from a conventional activated sludge treatment plant with nitrification.
- Hydrolysed Source Separated Urine (SSU) in a 3.5 % solution.

Table 11 Literature data on major nutrient removal from WWs by different algae species.

| **Species** | **WW-source** | **Total N removal** | **Total P removal** | **Carbon removal** | **Retention time** | **Reference** |
|---|---|---|---|---|---|---|
| Algae+bacteria (*Chlorella*+*Nitzchia*) | Domestic WW after settling | 92 % | 74 % | 97 % BOD<br>87 % COD | 10 h | (McGriff Jr. & McKinney 1972) |
| *Chlorella pyrenoidosa* | Domestic WW after settling | 94 % | 80 % | NA | 13 days | (Tam & Wong 1989) |
| *Chlorella pyrenoidosa* | Domestic and industrial WW | 60-70 % | 50-60 % | 80-88 % BOD<br>70-82 % COD | 15 days | (Aziz & Ng 1992) |
| Cyanobacteria | Domestic effluent after secondary treatment + swine WW after settling | 95 % | 62 % | NA | 1 day | (Pouliot et al. 1989) |

SSU has been shown to be a very interesting option to be used as fertilizer for algae cultivation because of its high nutrient (especially N) density. Because of the non-existing infrastructure for SSU collection it is unfortunately not a viable option at the moment. In all three wastewaters it was found that the lifecycle burdens investigated (land use, energy use, GHG emissions, water consumption, eutrophication potential) were decreased compared to the base case which assumes algae cultivation by addition of fertilizers.

Another study conducted by (Wang et al. 2009) investigated the cultivation of *Chlorella* sp. algae in different streams of a municipal wastewater plant. The streams were:

- Before and after primary treatment.
- After the activated sludge tank (effluent).
- After sludge centrifugation (centrate).

The results of the study show that algae cultivation in the centrate after sludge centrifugation is a very promising alternative. WWT with algae before and after primary treatment gave better nutrient removal than effluent treatment after the activated sludge tank, but still current activated sludge treatment has better performance. Effluent treatment after activated sludge treatment (tertiary treatment) showed less promising results because of strong phosphorous limitation in this kind of wastewater. As a conclusion from this it can be said that treatment of centrate by algae after sludge centrifugation is a good option to both reduce nutrient content and produce biomass for biofuels production. Another advantage of this treatment method is that algae showed a high uptake of metal ions from wastewater.

In summary, algae cultivation for biofuels production combined with wastewater treatment has several advantages compared to single purpose cultivation implying the addition of fertilizers and water to the process. As wastewater treatment is inevitable, algae cultivation is a good alternative to utilise nutrients in the wastewater for biomass cultivation instead of wasting them, as is the case in today's activated sludge and other processes. Also from a cost perspective a combination of the two processes is advantageous. Nutrient, water and $CO_2$ addition in commercial algae farms accounts for 10 – 30 % of the total production costs. A combination of the processes makes nutrient and water addition unnecessary, thereby decreasing the production costs (Park et al. 2011).

WWT in combination with algae cultivation can be performed as described in the following. Figure 18 shows the different process steps. Screened WW is first treated in a pond similar to the primary treatment in conventional domestic WWT. Primary sludge is removed in a sedimentation tank and sent to anaerobic digestion. The primary treated WW has a lower solids concentration. Another positive effect of primary treatment of WW is an increase in photosynthetic efficiency in the following High Rate Algae Pond (HRAP), because the WW is clarified. Additional organic material is supplied to biogas production by anaerobic digestion (Lundquist et al. 2010).

HRAP are shallow (0.3 – 0.5 m), paddle-wheel mixed ponds (Craggs et al. 2011; Rawat et al. 2010). Their construction is very similar to raceway ponds, which are described in section 5.1.1 with the difference of HRAP having an outlet for the treated WW, while in raceway ponds water is continuously circulated. HRAP are designed to promote algae growth.

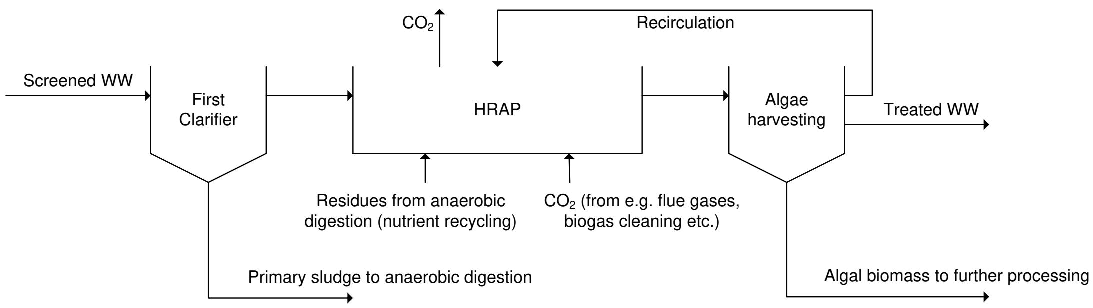


Figure 18 Process flow sheet of the WWTP with algal biomass production (Lundquist et al. 2010).

Figure 19 shows a HRAP, which enables the addition of $CO_2$ in order balance the C to N ratio in the WW.

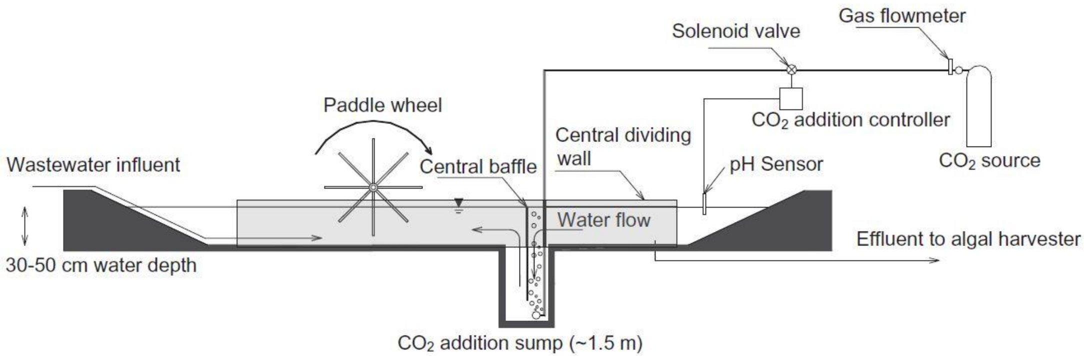


Figure 19 High rate algae pond with $CO_2$ addition (Park et al. 2011).

The concept of photosynthetic oxygenation, which is applied in the HRAP for nutrient removal, is shown in Figure 20. In the HRAP oxygen is consumed by bacteria to remove the BOD. Oxygen to the HRAP is supplied from the atmosphere and internally by algae photosynthesis. Carbon, nitrogen and phosphorous are consumed during algae growth while $O_2$ and biomass is produced (Rawat et al. 2010).

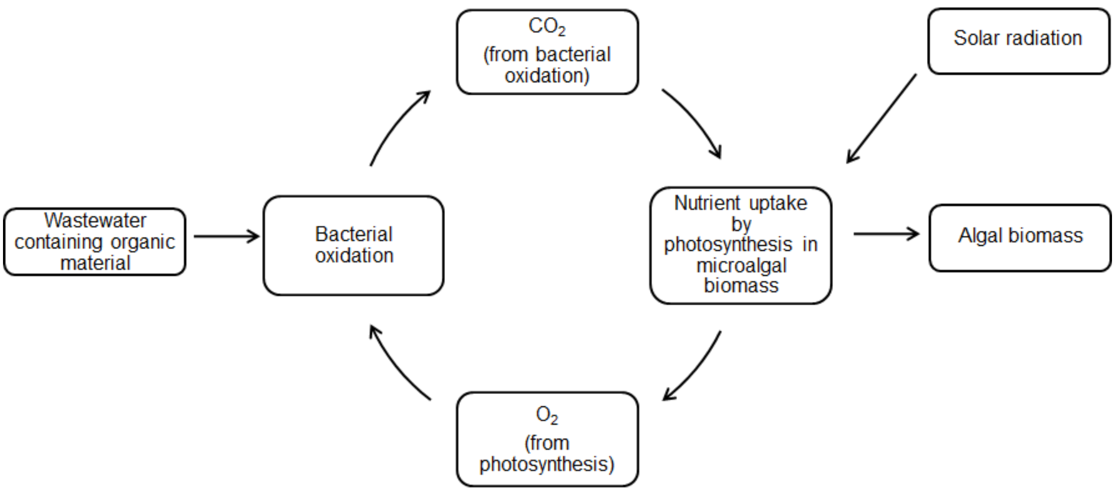


Figure 20 The process of photosynthetic oxygenation in BOD removal (Rawat et al. 2010).

HRAP is recommended by Lundquist et al. (2010) as the only viable solution for algae cultivation in large-scale at low-costs.

According to Lundquist et al. (2010) conventional WWT ponds (unmixed) are not suitable because of their inability to control algae culture. Also algae harvesting in such ponds is difficult and makes the use of flocculants necessary, which are expensive and may have a negative influence on the later biofuels production processes.

Due to the high costs of PBR systems it is at the moment not very likely that these types of cultivation systems will be used for large scale algae cultivation. One potential use today is as inoculation system for the HRAP in order to promote growth of desired algae species. HRAP are seen as the by far most cost effective reactors for liquid waste in combination with cultivation of photo-autotrophic biomass (Rawat et al. 2010). After the HRAP the treated WW is sent to a settling pond for separation of algae and treated WW (Schenk et al. 2008; Lundquist et al. 2010).

One limitation to algae cultivation in WW is the lack of carbon present in most domestic WWs to enable efficient nitrogen removal (Lundquist 2008; Craggs et al. 2011; Park et al. 2011). A typical C to N ratio in domestic wastewater is 1:0.5, while algae ideally demand a C to N ratio of 1:0.1 – 1:0.2[15]. N to P ratios generally are not a limiting factor for algae cultivation in wastewaters as algae can handle a wide range of ratios, ranging from ca. 4:1 to almost 40:1 (Craggs et al. 2011). Therefore $CO_2$ addition can be advantageous and has already been shown to double the algae productivity. Potential sources of $CO_2$ include:

- Flue gases from heat and power generation plants (on- or off-site).
- $CO_2$ from biogas produced by anaerobic digestion of algae residues and primary sludge (Heubeck et al. 2007).
- Chemicals, cement, steel, ethanol, natural gas and petroleum processing.

Another problem utilising algae from a WWTP is that harvesting of algae is generally difficult. Nowadays flocculation is used, which is expensive and also the flocculants have a negative influence on the use of algae in further processing steps (Benemann 2011).

According to Craggs et al. (2011) WWT by algae cultivation can be achieved at much lower capital and operating costs than conventional WWT (25 to 33 % of the costs of secondary-level activated sludge treatment).

A summary of advantages and disadvantages of algae cultivation in WW is given in Table 12.

[15] Depending on if the amount of N is a limiting factor (low availability of N increases the oil content of algae)

Table 12 Advantages and disadvantages of WWT by cultivation of microalgae (Lundquist et al. 2010; Lundquist 2008; Tchobanoglous et al. 2002; Craggs et al. 2011).

| **Advantages** | **Disadvantages** |
|---|---|
| – Sufficient amount and ratio of N and P in WW (total N: 20 – 85 mg/L, total P: 4 – 15 mg/L) and a substantial amount of C (TOC[16]: 80 – 290 mg/L)<br>– Algae achieve good WWT (metals and nutrients removal)<br>– Combination of WWT and biofuels production gives an increased income<br>– Process has a lower energy demand than the conventional WWT process<br>– Reduced fresh water consumption<br>– Lower capital and operating costs than conventional WWT | – High costs for removing algae from effluent (microalgae rarely settle → costly more advanced technologies necessary)<br>– Flocculants can have a negative influence on the biomass to biofuels process<br>– Suspended solids limits are not met<br>– Algae WWT interferes with disinfection of WW<br>– Larger area needed than conventional WWT process<br>– Not all process steps are commercially available |

## 5.4 State-of-the-Art Technologies for microalgae-based biofuels production

Microalgae can be processed into a large variety of biofuels, including hydrogen, biodiesel, bioethanol and biogas (Posten & Schaub 2009). Before processing into more advanced fuels, the algae dry content must be increased. After harvesting the water content of the algae slurry is still high (>80 wt-%). In order to reach a high dry content (up to 85 wt-% dry weight) mechanical dehydration and thermal drying can be applied (Xu et al. 2011). This is however not necessary if using wet extraction of lipid, or if producing biogas, where the moisture content can be high (Posten & Schaub 2009).

Figure 21 shows how different parts of the microalgae are suitable for different types of biofuel production. $CO_2$ is not a part of the algae, but the algae takes up $CO_2$ and makes hydrogen instead of performing the photosynthesis.

[16] Total Organic Carbon

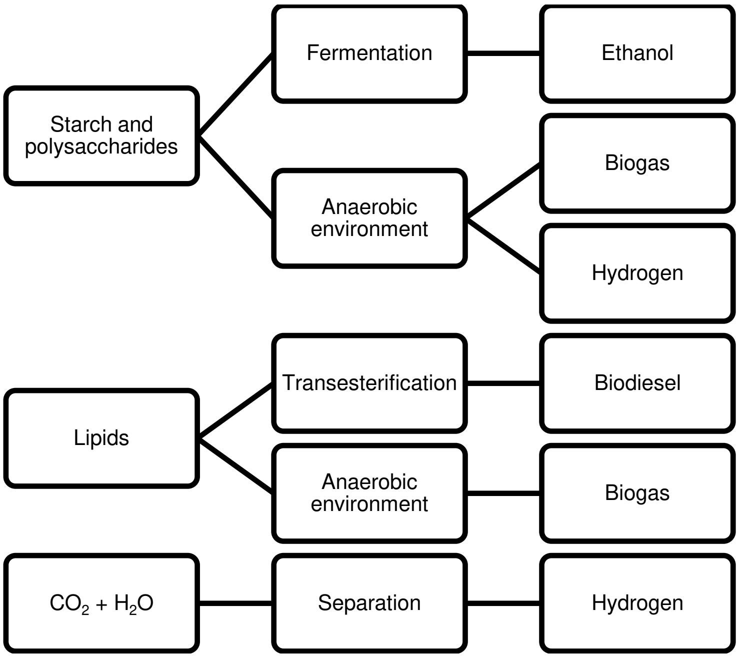


Figure 21 Possible routes for different parts of the microalgae into fuels (Posten & Schaub 2009).

### 5.4.1 Biodiesel

Biodiesel is becoming increasingly important as a near-market biofuel (Schenk et al. 2008). Diesel is used for the absolute majority of all vehicles used in agriculture and transport of goods, and biodiesel can be adapted to the existing infrastructure. From this background it is not surprising that biodiesel production in the EU has gone from 500 000 tonnes in 1998 to 9 000 000 tonnes in 2009 (Astals et al. 2011). Biodiesel can replace petroleum diesel in regular engines, but has a lower energy density, 32.6 MJ/L instead of 35 MJ/L for petroleum diesel (Posten & Schaub 2009). Therefore 1 L of biodiesel cannot replace 1 L of petroleum based diesel, but it is nevertheless convenient. It is estimated that in order to cover 50 % of the transport fuel need of the United States, 2.5 % of the existing cropping area could be enough if biofuels from microalgae are used (Chisti 2007).

Biodiesel is produced from vegetable oil that is transesterified. The triglycerids in the oil react with methanol (Chisti 2007). The optimal methanol:oil ratio in order to drive the reaction towards biodiesel production is 6:1, and the conversion is approximately 98 wt-% basis (Pokoo-Aikins et al. 2009). This is the process that is seen as the viable route in foreseeable future (Chisti 2007). The by-product glycerol constitutes approximately 10 wt-% of the initial raw matter (Astals et al. 2011). The glycerol and biodiesel phases differ in density, and the denser glycerol can be separated in a decanter and go on to purification steps. However, the value of glycerol is decreasing due to increased availability and the biodiesel industry has turned from considering glycerol as a desirable co-product into regarding it as waste (Fountoulakis et al. 2010).

The triglycerids in microalgae is in the form of lipids. A lipid content of 20 – 50 wt-% of dry biomass is common, but by adjusting the cultivation the lipid content can reach up to 80 % (Chisti 2007). After extraction and drying, these can be processed into biodiesel. The first step of lipid extraction is the disruption of the cell walls, which can be achieved either via mechanical or non-mechanical action (Mata et al. 2010). Examples of cell disruptive actions are homogenization, bead mills, autoclave, freezing and osmotic shock. After cell disruption, the lipids must be extracted. Normally this is done via solvent extraction using butanol, hexane, ethanol or a hexane-ethanol mixture (Ehimen et al. 2009; Mata et al. 2010). Direct transesterification can be done but is unsuitable for transesterification of wet biomass (Johnson & Wen 2009). Biodiesel production from algae is rather expensive, and lipid extraction processes that do not demand drying are needed (Chisti 2008).

A process diagram of the biodiesel production process can be seen in Figure 22.

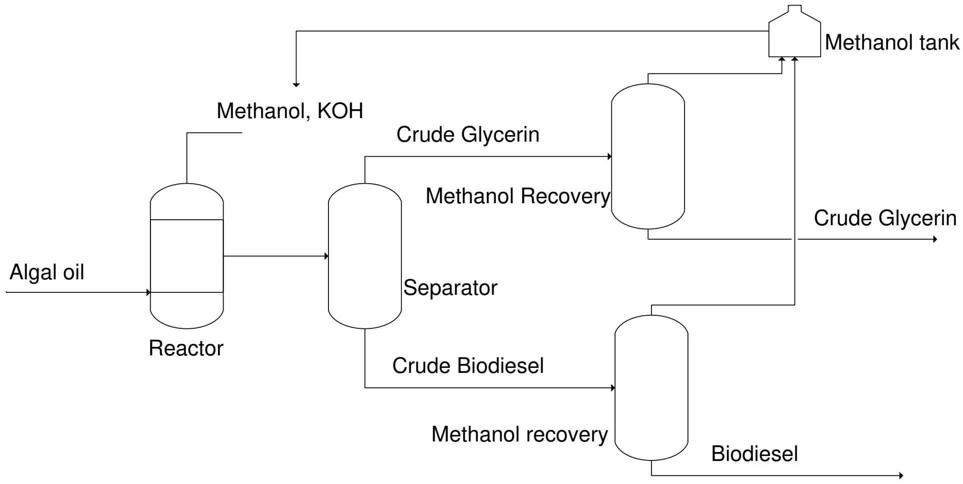


Figure 22 The biodiesel production process.

## 5.4.2 Biogas

Biogas can be used for a range of applications, but perhaps the most common options are on-site combustion for heat and electricity production, as transportation fuel or to be transferred to the natural gas grid replacing natural gas. The later options requires purification of the biogas.

Biogas can be processed from virtually any biomass by digesting under anaerobic conditions. The product is a mixture of methane (common values are 60 – 75 %) and $CO_2$ with traces of other gases. If the gas should be used as transport fuel, the fraction of methane must be higher than 95 % (Energigas Sverige 2011). To clean the gas to this extent is an energy demanding process, the most common of which is water scrubber absorption. A process scheme for biogas production and cleaning is shown in Figure 23.

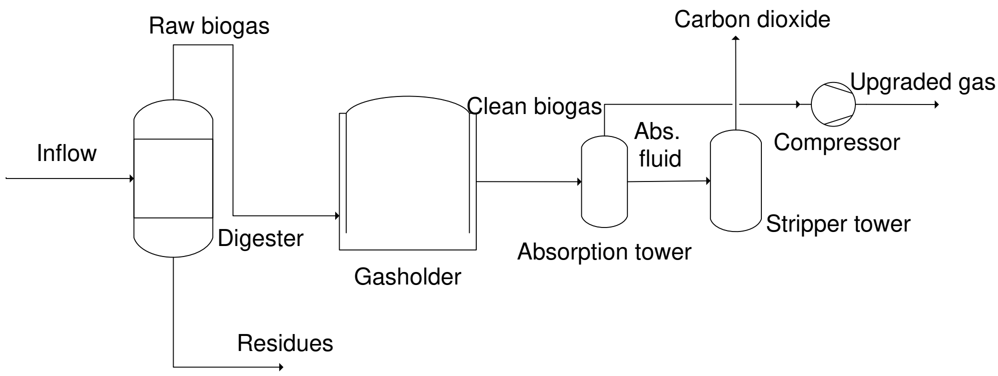


Figure 23 The route from algal slurry to natural gas grade biogas (Jacobsson 2009).

Not only methane and $CO_2$ is formed in the process, but also ammonia. The nitrogen is important in making the anaerobic flora function, and the optimal C/N ratio has been claimed to be 15 – 30 (Ehimen et al. 2009). However, recent studies have shown best results at a ratio of 12.44 (Ehimen et al. 2011). Ammonia changes the alkalinity and hence the pH of the digester, which favours the reaction towards methane (Sialve et al. 2009). However, if the substrate contains too much nitrogen it can cause free ammonia to occur in the digester. This may cause disruptions in the process since ammonia can diffuse across the cell membranes (Golueke et al. 1957).

Algal biomass with a theoretical composition of $C_{106}H_{181}O_{45}N_{15}P$, has a C/N weight ratio of 6.1 (Davis et al. 2011), which is lower than the recommended shown above. However, if the algal biomass is cultivated in a nitrogen deprived environment, the fraction of lipids in the biomass increases (Chisti 2007). Since nitrogen mainly originates from proteins this means that the fraction of nitrogen decreases and the C/N ratio increases.

The proportion on methane in biogas produced from algae is approximately 69 – 75% (Sialve et al. 2009). This is regarded as a relatively high yield compared to other substrates and therefore a suitable substrate. One problem with biogas production from microalgae is that the cell of the algae can withstand the enzymes produced by the anaerobic flora (Sialve et al. 2009). There can be intact cells even after 30 days, since algae can be very resistant to hydrolysis (Golueke et al. 1957). This represents a disadvantage from a methane yield perspective, and it can also result in ongoing photosynthesis creating oxygen in the digester. Therefore, the substrate should go through some kind of cell disruptive process before retting.

Pretreatment processes could include e.g. thermal or ultrasonic pretreatment, but also extraction of lipids for other fuels, leaving the cell wall destructed (Chisti 2007; Sialve et al. 2009). Thermal pretreatment has been reported to increase the methane yield by up to 33 % when heating the substrate to 100 °C for 8 h (Sialve et al. 2009). It has also been shown that with increasing temperature in the digester, the algae resistance against anaerobic bacteria declines (Golueke et al. 1957).

Chisti et al (2007) suggested that biodiesel should be produced from the lipids in the microalgae. The extraction would result in broken cell walls, but also in a loss of lipids. This increases the protein fraction in the substrate, giving problems with ammonia formation and pH. One option to solve this could be to co-ret the glycerol formed when the algae oil is transesterified. Glycerol was until recently seen as a valuable by-product in biodiesel production and should therefore have been purified and turned into commercial grade glycerol (Pokoo-Aikins et al. 2009). However, as stated by Astals et al. (2011) the explosion in biodiesel production has created a surplus in the market for glycerol. Moreover, the glycerol originating from biodiesel production (approximately 10 wt-% of initial raw matter) is crude glycerol which is expensive to upgrade and therefore out of the feasible range for small and medium sized plants (Astals et al. 2011). An alternate use for this glycerol is needed, and in order to avoid transport costs and also to have the benefit of improving the substrate, co-digestion with the extraction residues could be a viable option. Glycerol codigestion has also been investigated in Ehimen et al. (2011), where a >50 % increase in methane production was shown. Waste paper has also been suggested as a low-nitrogen source for co-digestion (Sialve et al. 2009).

After digestion, several material flows can be re-used in the algae cultivation. If the biogas should be upgraded to transport fuel, either an upgrading facility could supply almost pure $CO_2$ to the system, or a PBR system could be used to upgrade the gas up to 97 % (Heubeck et al. 2007). If the biogas is combusted on site, and hence not so thoroughly cleaned, the flue gas can act as a $CO_2$ source for the algae cultivation (Pokoo-Aikins et al. 2009). In both cases the $CO_2$ is reused in the cultivation process. In addition to recycling $CO_2$, the digester residues contain large amounts of nitrogen and phosphorous that can be recycled to the cultivation (Sialve et al. 2009). Fertilizer for the algae cultivation is the third largest contributor to energy demand of the process, and reducing this is a vital part of getting a positive net energy balance (Razon & Tan 2011).

### 5.4.3 Biohydrogen

Biohydrogen is a part of the decarbonisation-of-fuel route towards lower $CO_2$ emissions in the transport sector (Andress et al. 2011). There has been a great interest in creating a hydrogen based energy system. This debate may have declined, but hydrogen still possesses great potential in the battle against anthropogenic $CO_2$ emissions.

Microalgae can produce hydrogen via a simple two step reaction  shown in equantion 4 (Schenk et al. 2008).

$$H_2O \rightarrow 2H^+ + 2_e^- + {}^1/_2\, O_2$$
$$2H + 2_e^- \rightarrow H_2 \qquad (4)$$

The first reaction is present in all photosynthesis, but the second reaction is mediated by a special enzyme present in only a few species of microalgae (Schenk et al. 2008). The second reaction needs anaerobic conditions to take place otherwise Adenosine Triphosphate (ATP) production would occur instead.

A major advantage when producing hydrogen is that it quickly goes into gas phase instead of accumulating in the culture (Schenk et al. 2008). This way the product never builds up to levels that could be toxic to the algae. Another advantage of hydrogen production is that it can give a net fresh water gain, up to 610 $m^3$ annually from a 1 000 $m^3$ PBR (Schenk et al. 2008).

In order to get hydrogen production from microalgae economically feasible, the photon conversion efficiency should rise from currently approximately 1 % to 7 % (Schenk et al. 2008). To increase the natural efficiency by a factor 7 may be a bit optimistic, but already results with up to 2 % photon conversion efficiency has been demonstrated, on a laboratory scale (Posten & Schaub 2009). Hydrogen production is today considered as a promising technology for the future, but not yet fully developed (Schenk et al. 2008).

### 5.4.4 Bioethanol

Conversion of sugar to ethanol is perhaps currently the most common way to produce biofuel. The fuel is easy to use with existing infrastructure, and is easy to store (Hirano et al. 1997). Store capacity is a benefit compared to biodiesel. The ethanol is produced via a two step reaction catalysed by yeast (Demirbas 2010). First sucrose is converted through hydrolysis into glucose and sucrose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \qquad (5)$$

Then the glucose and fructose are converted into ethanol:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (6)$$

Today corn is the dominant feedstock for ethanol production, but this has been heavily criticised since the ethanol production then directly competes with food supply. Second generation ethanol generally means ethanol produced from wood, but there are indications that microalgae is a promising feedstock for ethanol production (Hirano et al. 1997). The large amount of starch in the algae can be converted into ethanol using the same process as described above. Some algae species have reported starch fractions up to 50 wt-% of dry mass (Hirano et al. 1997). However, a number of algae strains not only produce starch, but also produce ethanol from intracellular starch when exposed to dark and anaerobic conditions (Hirano et al. 1997). This enhances the energy efficiency of the starch to ethanol process.

# 6 Modelling

In this chapter the underlying assumptions for the different process options for algae cultivation in municipal WW in combination with biofuels production are described.

## 6.1 Algae cultivation

An important factor during production of biofuels from microalgae is to make the production process economically viable. A recent study has shown that a lot of work is still to be done in the area of algae biofuels production to get the process economically viable (Savage 2011). Therefore, it is of great interest to keep the production costs low. For the cultivation process to fulfill this requirement the construction of the plant needs to be inexpensive and the operating costs need to be minimal. Algae can be cultivated in open (ponds) or closed (PBR) systems. In this study the algae cultivation will be modeled using open ponds and HRAP due to the following:

- No transparent material are needed and therefore they can be built in a variety of materials which leads to lower construction costs (Schenk et al. 2008)
- Production of high value products in PBR can be economically viable. Biofuels are classified as low value products and therefore the economic margins are much lower (Schenk et al. 2008).
- A comprehensive study of biodiesel production in open and closed systems (using a requirement of 10 % rate return) shows that the required selling price of biodiesel when using PBR systems are twice the selling price when using open ponds. The production cost using three alternative growth scenarios were compared and in all cases the PBR systems were more expensive (Davis et al. 2011).
- HRAP are considered to be the most cost effective system for wastewater treatment and capturing of solar energy (Rawat et al. 2010).

To keep the cost of algae cultivation low it is important to consider the availability of nutrients. Wastewater offers many of the nutrients needed for algae to grow. For biofuel production from algae biomass to become economically viable with the technology available today the cultivation must be done in collaboration with other processes, e.g. wastewater treatment (Savage 2011). It is assumed that algae will be grown in WW since they offer a low cost nutrient source and at the same time reduces the use of fresh water. The structure and the assumptions made regarding the modeling of algae cultivation will be described below.

Algae cultivation is divided into the following process steps:

- WW pretreatment and primary sludge removal.
- Algae cultivation in HRAP.

In the first step of modelling algae cultivation process in municipal WW, the composition of municipal WW is determined. WW composition and concentrations can vary strongly depending on location and also over time (Schenk et al. 2008). In order to estimate the potential for algae cultivation in Gothenburg, average data for incoming sewage water to the WWTP in Gothenburg is considered, see Table 13. 8 000 hours of annual operation is assumed.

Table 13 Wastewater composition in Gothenburg's WWTP (Davidsson 2011; Gryaab AB 2011).

| **Parameter** | **Value** | **Unit** |
|---|---|---|
| $BOD_7$ | 156 | $mg/L_{WW}$ |
| TOC | 83 | $mg/L_{WW}$ |
| COD | 360 | $mg/L_{WW}$ |
| Total N | 30.8 | $mg/L_{WW}$ |
| Free ammonia | 19.2 | $mg/L_{WW}$ |
| Total P | 3.9 | $mg/L_{WW}$ |
| Grease[17] | 100 | $mg/L_{WW}$ |
| Average flow rate[18] | 3 833 | $L_{WW}/sec$ |

The first step in WWT assumed in this study is the preliminary treatment where only gross solids are removed from the WW. This treatment has no influence on the general water pollutant concentration. This is followed by the primary treatment, were the so-called primary sludge, oil and grease are removed by sedimentation and floatation respectively. This serves the following purposes:

- Solids reduction to avoid sedimentation in following treatment steps.
- Increase photosynthetic efficiency in the following algae cultivation by clarifying the WW.
- Reducing the BOD.
- Provide additional sludge to anaerobic digestion.

In order to estimate the composition of the primary treatment effluent, pollutant reduction factors as shown in Table 14 are used. Not all the components of WW are affected; concentrations of colloidal and dissolved components are unchanged.

Table 14 Pollutant reduction during primary treatment of domestic WW.

| **Pollutant** | **Reduction factor** | **Comments** |
|---|---|---|
| BOD | 0.31 | (Pescod 1992), average reduction of the "City of Davis" and "San Diego" WWTP |
| TOC | 0.28 | (Pescod 1992) |
| COD | 0.30 | (Marani et al. 2004) |
| Total N | 0.20 | (Pescod 1992), average reduction of the "City of Davis" and "San Diego" WWTP |
| Total P | 0.26 | N/A→average of BOD, TOC and total N reduction was taken |
| Grease | 0.65 | (Pescod 1992) |
| Suspended solids | 0.5 – 0.7 | (Pescod 1992) |
| Colloidal and dissolved constituents are not affected | | |

Applying the reduction factors in Table 14 to the WW data shown in Table 13, the following results for nutrient concentration in primary treatment effluent are obtained,

[17] Value for grease was not available for Gothenburg, therefore the medium value for WWs from Tchobanoglous et al. (2002) was used.
[18] Average flow rate is taken for June 2010 to May 2011 (Gryaab AB 2011).

see Table 15. The primary treatment effluent is send to the HRAP, where algae cultivation is conducted.

Table 15 Estimated composition of primary treatment effluent.

| Parameter | Value | Unit |
|---|---|---|
| BOD | 107.6 | $mg/L_{WW}$ |
| TOC | 59.9 | $mg/L_{WW}$ |
| COD | 360 | $mg/L_{WW}$ |
| Total N | 24.6 | $mg/L_{WW}$ |
| Total P | 2.8 | $mg/L_{WW}$ |
| Grease | 35 | $mg/L_{WW}$ |

In order to reach the desired degree of sedimentation a typical retention time of 1.5 to 2 h and an overflow rate of circa 40 $m^3/m^2$/day is necessary. A typical depth of 4.3 m for primary treatment ponds was used in other studies (Lundquist et al. 2010; Tchobanoglous et al. 2002).

The sludge obtained from primary treatment is sent to anaerobic digestion. The composition of the primary treatment sludge can be found in Table 16.

Table 16 Estimated primary sludge composition.

| Parameter | Value | Unit |
|---|---|---|
| BOD5 | 48.4 | $mg/L_{WW}$ |
| TOC | 23.1 | $mg/L_{WW}$ |
| COD | 0 | $mg/L_{WW}$ |
| Total N | 6.2 | $mg/L_{WW}$ |
| Total P | 1 | $mg/L_{WW}$ |
| Grease | 65 | $mg/L_{WW}$ |

The primary treatment effluent is then entering the secondary treatment, which in this case is conducted in HRAP. These are shallow, paddlewheel-mixed ponds and have a significantly higher algae productivity compared to conventional facultative ponds which are used in WWT today (Craggs et al. 2011). In Table 17 the general assumptions considering operating conditions and nutrient uptake by microalgae are summarised. Data is based on experimental data and results from previous studies (Craggs et al. 2011; Lundquist et al. 2010; Kadam 2001; Oonk & Van Harmelen 2006; Park et al. 2011; Pittman et al. 2011; Wang et al. 2009).

In order to estimate the algal growth rate/productivity, experimental values are used in this study, as shown in Table 17 (12 – 40 $g/m^2$/day). Growth rates will be used to estimate the cultivation pond size. 12 – 40 $g/m^2$/day corresponds well to the theoretical, maximum algal productivity in Gothenburg ($P_{max}$), which can be calculated as shown in equation (7) (Park et al. 2011). For results, see Figure 29.

Table 17 General assumptions for HRAP operating conditions and nutrient uptake.

| **HRAP as secondary treatment** | low | high | | **Source** |
|---|---|---|---|---|
| Assumed depth of HRAP | 0.3 | | m | (Lundquist et al. 2010) |
| Temperature | 20 | 35 | °C | (Park et al. 2011) |
| Assumed growth rate | 12 | 40 | $g/m^2/day$ | |
| Electricity demand Paddle wheel | 80 | | $kWh/ML_{WW}$ | (Craggs et al. 2011); average value (80 $kWh/ML_{WW}$) used |
| Electricity consumption Flue gas injection | 0.0222 | | $kWh/kg_{CO2}$ | (Kadam 2001) |
| Nutrient uptake rate by microalgae | | | | |
| $CO_2$ uptake from flue gases | 0.8[19] | | | (Oonk & Van Harmelen 2006; Pittman et al. 2011; Wang et al. 2009) |
| pure $CO_2$ uptake | 0.9 | | | |
| BOD5 reduction | 0.9 | | | |
| TOC | 0.9 | | | |
| COD reduction | 0.85 | | | |
| Total N reduction | 0.92 | | | |
| Total P reduction | 0.8 | | | |

$$P_{max} = \frac{I_0 \bullet \eta_{max}}{algae\ heating\ value} \tag{7}$$

Where $I_0$ = Average solar radiation and

$\eta_{max}$ = maximal, theoretical light utilization by algae

Table 18 Parameters for calculating maximum algal productivity.

| **Theoretical algal productivity (Park 2011)** | **Symbol** | **Unit** | **Value** | **Source** |
|---|---|---|---|---|
| Average solar radiation | $I_0$ | $kWh/m^2/d$ | Figure 15 | (SMHI 2011b) |
| Maximal, theoretical light utilization by algae | $\eta_{max}$ | | 0.045 | (Walker 2009) |
| Heating value of algae | | kJ/g | 21 | (Park et al. 2011) |

In order to be able to calculate the amount of algae that can be produced from the nutrients available in the WW the general composition of algae has to be estimated. The composition is shown in Table 19. Starting with the elemental formula

[19] According to Oonk & Van Harmelen (2006) the removal rate for pure $CO_2$ is 0.9 and somewhat lower for flue gases. Therefore 0.8 is assumed in this study.

($C_{106}H_{181}O_{45}N_{15}P$), the weight distribution of different elements was calculated (Davis et al. 2011).

The total mass of algae generated is calculated based on the average annual WW flow of a typical WWTP. In this case the GRYAAB WWTP in Gothenburg, Sweden is used. WW flow data from June 2010 to May 2011 was used (Gryaab AB 2011). An annual average flow of 3.83 $m^3/s$ was calculated.

Table 19 Estimated algae composition.

| **Component** | **No. of atoms** | **Molecular weight** | **Weight** | **wt-%** |
|---|---|---|---|---|
| | | [g/mol] | [g] | |
| C | 106 | 12 | 1272 | 52.69 |
| H | 181 | 1 | 181 | 7.50 |
| O | 45 | 16 | 720 | 29.83 |
| N | 15 | 14 | 210 | 8.70 |
| P | 1 | 31 | 31 | 1.28 |

Calculating the C:N:P weight ratio in both, the WW and the algal biomass the following results are obtained:

- WW: C : N : P = ca. 23.7 : 10 : 1
- Algal biomass: C : N : P = ca. 41 : 6.8 : 1

Based on this results it can be concluded, that the amount of carbon in the WW is not sufficient to fully utilise the algae growth potential and thereby reach maximum nutrient reduction in the WW. Therefore additional carbon has to be added from external sources (see Section 5.3.2). The difference in the N : P ratio (10 : 1 in WW; 6.8 : 1 in algae with the estimated composition as shown in Table 19) is a less severe problem, as real algal biomass shows N : P ratios ranging from 4 : 1 to 40 : 1 and therefore a complete N and P uptake of these nutrients by algae can be assumed (Craggs et al. 2011).

The following equations are used to calculate the total mass of algae cultivated in the WW.

N supply limiting:

$$Total\ mass\ algae\ cultivated = \frac{Mass\ ratio\ P\ in\ WW \bullet Total\ vol.\ flow\ WW}{Mass\ of\ P\ per\ mol\ algae} \quad (8)$$

P supply limiting:

$$Total\ mass\ algae\ cultivated = \frac{Mass\ ratio\ N\ in\ WW \bullet Total\ vol.\ flow\ WW}{Mass\ of\ N\ per\ mol\ algae} \quad (9)$$

The additional amount of C per mol algae and the total mass flow of C to compensate for the lack of carbon in WW, was calculated depending on if N or P supply is the next limiting factor after carbon.

N supply limiting:

$$\frac{Additional\ mol\ C}{mol\ algae} = \frac{Total\ mol\ C}{mol\ algae} - \frac{mol\ P / mol\ algae}{mol\ P / L_{WW}} \bullet \frac{mol\ C}{L_{WW}} \quad (10)$$

P supply limiting:

$$\frac{Additional\ mol\ C}{mol\ algae} = \frac{Total\ mol\ C}{mol\ algae} - \frac{mol\ N / mol\ algae}{mol\ N / L_{WW}} \bullet \frac{mol\ C}{L_{WW}} \quad (11)$$

Carbon supply to the HRAP can originate from different sources, as shown in Section 5.3.2. Flue gases and $CO_2$ from biogas cleaning are assumed as $CO_2$ source in this study. The $CO_2$ removal rate by microalgae from flue gases and pure $CO_2$ was estimated in order to determine the necessary flow of flue gases to supply enough $CO_2$ for algae cultivation to cover the C deficit of the WW. The underlying assumptions regarding flue gas conditions are given in Table 20.

Table 20 Flue gas conditions and $CO_2$ removal rate assumed for flue gas used for $CO_2$ addition (NTNU 2010; Lundquist et al. 2010).

| | **Value** | **Unit** |
|---|---|---|
| Flue gas composition | | |
| $N_2$ | 74.5 | mol% |
| $O_2$ | 12.7 | mol% |
| $H_2O$ | 8.1 | mol% |
| $CO_2$ | 3.8 | mol% |
| Ar | 0.9 | mol% |
| Temperature | 43 | °C |

Oxygen to satisfy BOD is obtained from:

- Photosynthesis of algae.
- Oxygen in flue gases.
- Oxygen diffusion from the atmosphere.

The size of the HRAP is estimated by assuming a low and a high growth rate scenario based on commercial WWT and algae production, as described above.

In the following a summary of the outcomes of the cultivation model is given:

- Amount of additional C necessary for optimal algae growth.
- Amount of flue gas necessary to supply C deficit.
- Amount and composition of HRAP effluent.
- Amount of algae biomass cultivated with the given nutrient levels.
- Area required for algae cultivation in combination with WWT.

## 6.2 Algae harvesting

The aim of the harvesting process is to increase the algae concentration. The algae concentration typically is < 0.5 $g_{algae}/L_{WW}$ after the cultivation (Craggs et al. 2011; Pienkos & Darzins 2009).

Algae harvesting is an important factor in the whole process and accounts for approximately 20 – 30 % of the total production costs. Cost-effective harvesting of algae is one of the major limitations in the utilisation of algae for biofuels production. Therefore cheap and efficient technologies have to be applied to perform this process step. Depending on the final product output, different final dry contents are applicable (~20 wt-% for biodiesel production (wet extraction) (Davis et al. 2011), 4–12 wt-% for biogas production (Lundquist et al. 2010)).

Flocculation in combination with sedimentation is seen as a cost-effective way to harvest algae, but adding chemical flocculants might interfere with later stages in the biofuels production process (Rawat et al. 2010). Bio-flocculation, flocculation without adding any chemicals has been observed in WWT HRAPs (Craggs et al. 2011) and demonstrated on pilot scale (Lundquist et al. 2010). Bio-flocculation together with sedimentation is a low-cost and low-energy demanding process option for algae harvesting.

The algae harvesting process assumed in this study is illustrated in Figure 24. The general assumptions for the different process steps are given in Table 21 and Table 22.

The dry content of algae harvested by sedimentation is still very low (<0.5 %). In order to upgrade the algae slurry, further processing has to be applied in order to increase the dry biomass content. Gravity thickening is commonly applied in WWTPs for sludge concentration, which means that it is a proven technology and especially interesting for algae harvesting because of its low operating costs due to the use of gravity (Lundquist et al. 2010; Turovskiĭ & Mathai 2006).

A final increase of the dry content before wet algae oil extraction is necessary. Other studies, like (Lundquist et al. 2010) assume solar drying as a method to decrease the algae slurry's water content. This is deemed not to be applicable in Gothenburg due to the high area needed and the local climate conditions. Therefore centrifugation is, despite its relatively large electricity consumption, used to increase the dry content of the algae slurry and thereby decrease downstream production costs in the biofuels production processes (Davis et al. 2011).

Bio-flocculation has been demonstrated on pilot scale, but still has to be proven on large scale (Lundquist et al. 2010). According to (Craggs et al. 2011), 50 – 90 % of algae biomass can be removed by bio-flocculation and sedimentation.

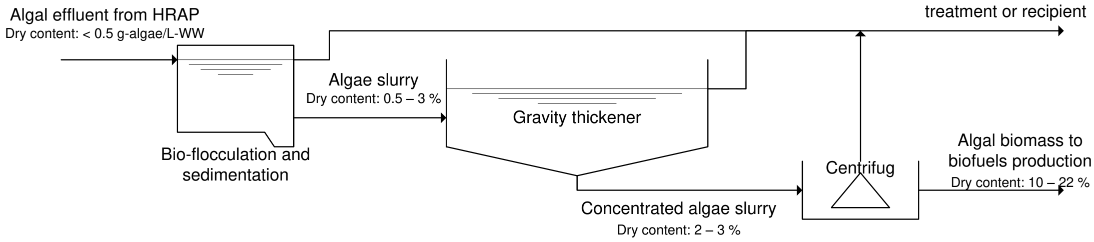


Figure 24 Process flowsheet of the algae harvesting process.

The algae/WW mixture enters the bio-flocculation/sedimentation unit. A continuous below-ground clarifier is assumed for this unit operation (Lundquist et al. 2010). After sedimentation the slurry is sent to a gravity thickener, where the algae concentration is further increased.

Table 21 General assumptions for bio-flocculation/sedimentation tank and gravity thickener.

| Bio-flocculation/sedimentation | Value | Unit | Source |
|---|---|---|---|
| Algae removal rate | 0.9 | | (Craggs et al. 2011) |
| Retention time | 6 | h | (Lundquist et al. 2010) |
| Output solids concentration | 0.015 | $g_{algae}/g_{WW}$ | |
| Electricity demand | 0.1 | $kWh/m^3$ | (Wiley et al. 2011) |
| Gravity thickener | | | |
| Algae removal rate | 0.95 | | (Lundquist et al. 2010) |
| Retention time | 4 | h | |
| Output solids concentration | 0.03 | $g_{algae}/g_{WW}$ | |
| Electricity demand | 0.1 | $kWh/m^3$ | |

In order to further increase the algae dry content prior the following biofuels production processes, centrifugation is assumed in this study.

Table 22 General assumptions for centrifugation process.

| Centrifugation | Value | Unit | Source |
|---|---|---|---|
| Algae removal rate | 0.95 | | (Molina Grima et al. 2003) |
| Solids concentration | 0.2 | $g_{algae}/g_{WW}$ | (Davis et al. 2011; Wiley et al. 2011) |
| Electricity demand | 0.1 | $kJ/kg_{algae}$ | (Khoo et al. 2011) |

The algal biomass from centrifugation is sent to biofuels production. The treated WW from the different steps of the harvesting process is, if the pollution limits are fulfilled sent to the water recipient or further treatment is applied. Some algal biomass is contained in the WW.

In the following a summary of the outcomes of the harvesting model is given:

- Mass flow and dry content of algae after different harvesting steps.
- Electricity demand of the harvesting steps.
- WW flow from harvesting units to recipient/further treatment.
- Algae overflow/loss to treated WW.

## 6.3 Biofuels production

In order to choose the best way to utilize the algal biomass from the wastewater treatment it has to be established what criterions that the process should meet. One is of course material efficiency. The available cultivation area for biomass is scarce, which makes it important to utilize as large share of the biomass as possible. This is why e.g. only biodiesel production is not viable. In the assumptions made in this study, the lipid content is assumed to be 30 %. To only utilize 30 % of the biomass is not acceptable. In Figure 25 the possible outputs of different fuels from 1 kg of algae biomass are given. It can be seen that the highest yield of fuels are obtained when co-producing biogas and biodiesel production. The next highest yield is when only biogas is produced. Noticeable is that simultaneous production of bioethanol and biogas results in lower yield than only producing biogas.

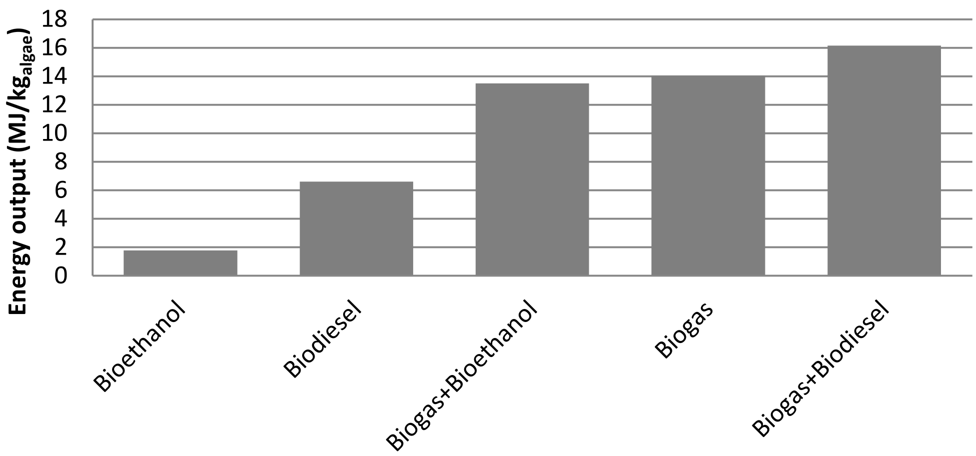


Figure 25 Possible outputs of 1 kg algae biomass from different process routes (Harun et al. 2011).

The process should also be as energy efficient as possible, preferably from a net energy perspective. The $CO_2$ emissions should also be lowered as much as possible. Taking care of other environmental issues such as eutrophication and water use is important, but is not within the scope of this study.

The economics are very important, if the process does not generate profit, it will need subsidies and risks not being built. The high willingness to pay for biodiesel can to some extent be explained by the ease with which biodiesel can be implemented in existing infrastructure.

### 6.3.1 Biodiesel production

The modeling of the biodiesel process is based on the outputs from the harvesting model.

In the model, the following steps will be covered:

- Pretreatment.
- Extraction of lipids.
- Butanol recovery.
- Transesterification.
- Methanol recovery.

As input to the model, a flow with algae biomass with a dry content of 20 wt-% enters a stirred ball mill[20] for pretreatment before the lipid extraction (Xu et al. 2011). 0.5 MJ of electricity is assumed to disrupt the cell walls of 1 kg of algae biomass (Xu et al. 2011). This amounts to a total electricity demand of the process of approximately 3.2 GWh/year or 0.4 MW.

The slurry then proceeds to the extraction reactor, where butanol is added in order to extract the lipid content of the algae. Before it enters it is heated up to 90 °C. This is because heat is known to further disrupt the cell walls, and the extraction process is supposed to be carried out at 90 °C (Lundquist et al. 2010; Ehimen et al. 2009). The algal slurry is assumed to enter at a temperature of 25 °C, which is just below the temperature in the pond. The heat capacity of algal biomass has been approximated

[20] The ball mill is partially filled with balls of metal. When the mill rotates the balls grind the algae, causing cell walls to disrupt.

with that of wheat straw, which is 1.46 kJ/kg/K (Chen et al. 2011). The extraction can take place at temperatures up to near boiling point of butanol (Nagle & Lemke 1990). The lipid rich butanol and the algae residue slurry are separated through disk stack centrifugation (Davis et al. 2011). The electricity demand of this process is assumed to be equal to the dewatering step in harvesting, 360 $kJ/kg_{algae}$ (Khoo et al. 2011). The butanol and algae are then separated in a stripper column (Davis et al. 2011). In this step, a lipid loss of 5 % to the water phase is assumed. The temperature in the stripper is assumed to be butanol boiling point, which is 118 °C.

The algae residues are sent to the anaerobic digester for biogas production, while the algae oil-butanol solution is sent to a separation unit. The calculation of the composition of the residues is shown below.

Characteristics of the inlet to the extractor are given in Table 23.

Table 23 Characteristics of the WW stream coming into the extractor.

| **Parameter** | **Value** | **Unit** |
|---|---|---|
| Mass flow of algae | 811 | g/s |
| C:N:P ratio | 41:6.8:1 | |
| Molar mass algae | 2414 | g/mol |
| Lipid content of algae | 30 | wt-% |

The yield of lipids that can be extracted from the algal biomass is assumed to be 90 % (Pokoo-Aikins et al. 2009). The lipids extracted have a general composition shown in Table 24.

Table 24 Composition of algal oil extracted from the biomass (Ehimen et al. 2010).

| **Fatty Acid** | **Molar mass (g/mole)** | **% in sample ($x_{FA}$)** | **Molar mass contribution** |
|---|---|---|---|
| C16:0 | 256.42 | 4 | 11.21 |
| C16:1 | 254.41 | 0 | 1.12 |
| C18:1 | 282.46 | 62 | 174.59 |
| C18:2 | 280.45 | 20 | 55.92 |
| C18:3 | 278.43 | 12 | 34.02 |
| C20:1 | 310.52 | 1 | 3.79 |
| Molar mass (g/mole) | | 100 | 280.65 |

The anaerobic digester is sensitive to inlet composition, and therefore a C:N ratio for the residues must be calculated. This is done via subtraction of the amount of matter that goes to the transesterification. As can be seen in Table 24, the average molar mass of the algal oil is 280.65 g/mole. With a fatty acid mass flow of 230.5 g/s, this corresponds to a mole flow ($F_{AO}$) of 0.82 mole/s. Equation 12 is used to calculate how much carbon that is extracted.

$$F_C = F_{AO} \sum (x_{FA} \cdot N_C) \quad (12)$$

Where $N_C$ is the number of carbon atoms in the fatty acid.

From this the amount of carbon extracted can be calculated. The original amount of carbon in the algal biomass is reduced by the calculated extracted carbon contained in the algae oil, giving a C:N:P ratio in algae residues of 24.9:6.8:1.

In the transesterification reactor the molar ratio methanol:fatty acid should be 6:1. This results in a mass ratio of 1:4.4 (Pokoo-Aikins et al. 2009). In addition to this, 1 wt-% of NaOH is added as a catalyst. No pretreatment in order to neutralize Free Fatty Acids (FFA) is modeled, since the FFA content in microalgae is very low, approximately 0.05% (Pokoo-Aikins et al. 2009). The FFA content should stay below 1 wt-%, otherwise pretreatment is needed (Pokoo-Aikins et al. 2009). If the FFA content is high, a large amount of soap is formed during the transesterification (Georgogianni et al. 2008). This affects both the yield of biodiesel and the ease with which the glycerol and the biodiesel can be separated. The conversion rate is assumed to be 99.7%, and for every kg biodiesel that is formed, 0.1 kg of glycerol is also formed (Pokoo-Aikins et al. 2009). The glycerol formed during transesterification is separated in a decanter and is sent to the anaerobic digester, whereas the biodiesel is sent to a second reactor, a new decanter and then to a distillation column for further purification. Complete gravity separation in the decanter is achieved after a retention time of 2 h (Atadashi et al. 2011). Unreacted methanol is recovered via distillation. After the methanol recovery column, the biodiesel is washed with water to further clean it from residues of glycerol, methanol and soap. A final purity of 96.5 wt-% FAME (Fatty Acid Methyl Ester) is achieved (Atadashi et al. 2011). In the model, maximum allowed content of glycerol (0.24 wt%), methanol (0.2 wt-%) and water (500 mg/kg) is assumed (Atadashi et al. 2011; Berrios et al. 2011). The two reboilers in the distillation columns are at temperatures 97 °C and 44°C. Specifications of the heat demand in the two reboilers of the distillation columns are given in Table 25.

Table 25 Heat specifications for distillation columns in transesterification process (Pokoo-Aikins et al. 2009).

| **Column number** | **Reboiler temperature (°C)** | **Heat duty (kW)** |
|---|---|---|
| 1 | 97 | 490 |
| 2 | 44 | 1 410 |

The glycerol is not purified, but instead sent directly to the anaerobic digester at a purity of 85 wt-%. No biodiesel is assumed to follow the crude glycerol, which means that it consists of 15 % methanol and 85 % glycerol.

### 6.3.2 Biogas production

Two different cases have been modeled and the biogas production model in the two cases will be described in this section. In the first case the inflow to the biogas production comes from the previous process steps in the biorefinery. Primary sludge from the WW primary treatment stage, algae residues from the oil extraction step and crude glycerol, a byproduct from the transesterification step in the biodiesel production, are transferred to the digester for anaerobic digestion into biogas. In the second case there will only be two inflows, primary sludge and algae biomass. The lipids will in this case not have been extracted, but instead the algae will be transferred from the WW treatment directly to the biogas production. The inflows to the digester in the two cases can be seen in Figure 26.

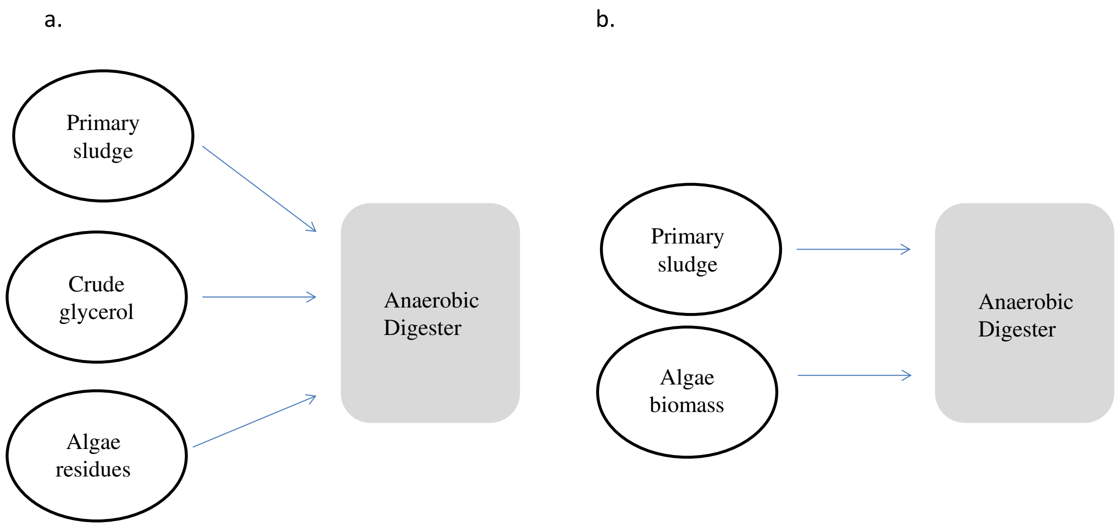


Figure 26 The inflows to the anaerobic digester in. a. the 1st case; combined biodiesel and biogas production, and b. the 2nd case; single biogas production.

This section will describe the biogas production models used to determine important process parameters. The following process steps will be described:

- Pre-treatment.
- Solids to digester.
- Conversion of organic matter.
- Output from digester.
- Biogas cleaning step – water scrubber.

Sialve et al. (2009) describes the advantage of pretreatment of algae biomass before added to the digester since it will increase the amount of organic material available to anaerobic digestion. With a pretreatment of the substrate of 8 hours at 100 °C the $CH_4$ production will increase by 33 %. In the combined biodiesel and biogas production there will be no specific pretreatment step before the algae biomass are transferred to the digester. However, in the oil extraction step, in the biodiesel production process, the algae biomass is heated up to 100 °C and therefore it is assumed to replace the algae biomass pretreatment step and consequently a 33 % increase in the $CH_4$ yield will be assumed. In the 2nd case, there will be a pretreatment step, where the algae biomass is heated to 100 °C, before the algae biomass is transferred to the digester. Due to this pretreatment step the specific theoretical methane potential will also in this case be assumed to increase with 33 %.

As previously described the combined biodiesel and biogas production case has three sources of solids inflow to the anaerobic digester. Starting at the primary sludge composition, the mass flow of grease, which is a carbon containing component in the primary sludge, can be calculated using the component concentration and the wastewater flow. The solids concentration in the primary sludge is assumed to be 5.5 %, equivalent to 2.64 ton/h (Davidsson 2011). Primary sludge contains several kinds of fat removed during primary WW treatment. In this model the grease is assumed to consist of oleic acid. Oleic acid has the empirical formula $C_{18}H_{34}O_2$ and is a fatty acid found in sources of animals as well as vegetables (World of Molecules 2011). Therefore the fatty acid is assumed to, in this study, be representative for the grease content in the primary sludge. The amount of COD[21] in the primary sludge is taken from Table 16. The mass flow of crude glycerol into the biogas production is the total amount of crude glycerol produced in the biodiesel production. Crude glycerol consists of 85 % glycerol and 15 % methanol. Finally, the mass flow of algae residues can be calculated using the mass flows of carbon, hydrogen, oxygen, nitrogen and phosphorous from the oil extraction. The solids concentration of algae biomass transferred to the biodiesel production is 20 % (Section 6.2) and since 27 % (Section 6.3.1) of the solids are extracted the solids content when transferred to the digester will be lower. In the second case the assumptions made regarding primary sludge is the same as in the first case. There will be no glycerol inflow since this case does not include any biodiesel production (see Figure 28). The amount of algae biomass will as a consequence be higher than in the first case since the lipids are not extracted. The solids concentration of the algae biomass when transferred from the harvesting to the anaerobic digester is 20 % (Section 6.2).

The content of organic material is described by the Volatile Solids (VS) content, which describes the amount of material that will be converted into biogas. Subtraction of the ash from the Total Solids (TS) gives the amount of VS (Sørensen et al. 2008). The VS content in oleic acid is 98.5 % (Luostarinen et al. 2009), in glycerol 850.3 $g_{VS}$/kg (Astals et al. 2011) and in methanol 99 % (Park & Park 2003). To calculate the VS content of the algae biomass (total algae biomass in the first case and algae residues in the second case) the ash content needs to be assumed. Razon & Tan (2011) list the composition of the algae *Nannochloropsis* sp. The species consists of approximately 30 % lipids, in line with the previous assumption regarding lipid content in the oil extraction model, approximately 30 % protein and 10 % carbohydrate. The ash content is approximately 27 %. The same ash content is assumed to apply for the algae cultivated in this project. The VS of the algae biomass can be calculated by subtracting the ash content from the mass flow of algae biomass into the digester. The ash content in the combined biodiesel and biogas production case will, however, be assumed to be higher since 27 % of the biomass has been extracted in the biodiesel production process. Looking at the VS of lipids it can be assumed that the ash content of the extracted lipids is negligible. Consequently, the ash content in the algae residues can be calculated by dividing the proportion of the remaining algae biomass (73 %) by the ash content in the total algae biomass (27 %).

Addition of organic substances to the digester, using co-digestion with several substances, is associated with high biogas production. An example of such a substance is glycerol. Fountoulakis et al. (2010) are studying co-digestion of sewage sludge and glycerol. They conclude that the added amount of glycerol should not exceed 1 % (v/v)[22] if the effect of glycerol addition should be positive. Glycerol is only available in the first case where biodiesel production is a part of the process. The

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[21] The amount of COD describes the amount of oxygen required to oxidize the organic material in the waste (Angelidaki et al. 2011).

[22] volume fraction, the volume of a constituent v divided by the volume of all constituents.

amount of available glycerol is considerable less than the amount of primary sludge and algae residues and since it does not exceed 1 % (v/v) all the produced crude glycerol is assumed to be transferred to the digester.

The primary sludge can be anaerobically digested without further drying steps. The dry content of the primary sludge is assumed to be 5.5 % (Davidsson 2011). The solids concentration of algae biomass is 20 % following harvesting. The solids concentration in the digester has been calculated using the total mass flow of solids transferred the total mass flow of crude glycerol and the total mass flow of water transferred to the digester. According to (Lundquist et al. 2010) the solids concentration normally ranges between 4 – 12 % when transferred from the digester.

The output from the digester, i.e. the biogas produced is assumed to consist of 70 % $CH_4$ and 30 % $CO_2$ (Collet et al. 2011). Using the $CH_4$ yield for each component transferred to the digester the total amount of $CH_4$ produced can be calculated. The specific theoretical $CH_4$ yield, $B_{o,th}$ ( $L_{CH4}/g_{VS}$), for oleic acid (grease in primary sludge), glycerol and methanol have been calculated using the following equation (Angelidaki et al. 2011).

$$B_{o,th} = \frac{(\frac{n}{2} + \frac{a}{8} - \frac{b}{4})22.4}{(12n + a + 16b)} \qquad (13)$$

Where n=carbon content, a=hydrogen content and b=oxygen content.

The C/N ratio of the substrate in the digester affects the biogas yield from the anaerobic digester and a value that is too high or too low will affect the yield negatively. Ideally the C/N ratio should be in the range of 15 – 30 to achieve the highest yield. Having a ratio higher than 30 may indicate that there is a deficit of nitrogen while a lower value than 15 may result in that ammonia ($NH_3$) could be formed resulting in an increased pH and thus a toxic inhibition of the microbial population in the digester. In both cases, if the C/N ratio is higher than 30 or lower than 15, the $CH_4$ yield may be lower than expected. (Ehimen et al. 2009) conclude in their study, that their C/N ratio for algae residues of 5.4 – 8.60 is lower than the recommended ratio and therefore there could be a risk of ammonia inhibition and an indication of that the organic material will not be completely degraded. Table 26 shows the amount of nitrogen and carbon available in the modelled digester and the calculated C/N ratio for the two cases.

As can be seen in Table 26, the C/N ratio in the digester in the two cases (5.9 and 7.5) also falls below the recommended value. Following the same reasoning as Ehimen et al. (2009) this might indicate that the organic material will not be completely degraded due to ammonia poisoning.

The temperature in the digester is assumed to be within the mesophilic temperature range at 35° C and the assumed digestion time is 14 days (Ehimen et al. 2011). The electricity demand of the mixing in the anaerobic digester is 0.108 kWh/kg dry solids (Collet et al. 2011).

Table 26 The total amount of carbon and nitrogen in the digester and the C/N ratio.

| | | **Value** | **Unit** |
|---|---|---|---|
| First case; combined biodiesel and biogas production | Total N in digester | 94.2 | g/s |
| | Total C in digester | 558.7 | g/s |
| | C/N ratio | 5.9 | |
| Second case; biogas production | Total N in digester | 94.2 | g/s |
| | Total C in digester | 707.7 | g/s |
| | C/N ratio | 7.5 | |

For the gas to be used as transportation fuel it needs to be upgraded to contain a $CH_4$ fraction higher than 95 % (Energigas Sverige 2011). This will be done by using a water scrubber. The method takes advantage of the fact that $CO_2$ is highly soluble in water whereas $CH_4$ is not. When bubbling the gas through pressurized water it results in a gas consisting of 96 % $CH_4$ (Collet et al. 2011) thus meeting the requirement for transportation fuel. The gas is fed at the bottom of the scrubber tower while the water enters the tower from the top. When the gas reaches the top of the tower the $CO_2$ has dissolved in the water and the gas consists mainly of $CH_4$. The $CO_2$ rich water then enters the next tower (the stripper tower) where the reverse absorption reaction takes place (Janssen et al. 2010). The $CO_2$ desorbs from the water as the solvent travels down the tower. The temperature in the process is 20 °C and the pressure in the scrubber tower is 8 bar and in the stripper tower 1 bar. 0.5 % of the $CH_4$ are lost during this upgrading process (Götz et al. 2011). The water used in the water scrubber process can be used again in the first scrubbing tower (Kapdi et al. 2005). Following desorption the $CO_2$ gas can be used as a carbon source in the algae cultivation. Using the $CH_4$ fraction in the upgraded biogas, the outflows from the digester and the amount of methane lost during the water scrubber process, the amount of upgraded biogas can be calculated as well as the amount of separated $CO_2$. The energy demand of the water scrubber is 0.170 kWh/m$^3$ biogas and the temperature in the scrubber process is 20 °C (Götz et al. 2011).

The energy content of biogas is determined by the $CH_4$ content. The energy density of $CH_4$ is 39.9 MJ/m$^3$ (Ehimen et al. 2009)

# 7 Results

## 7.1 Process design and integration

The two process designs are shown in Figure 27 and Figure 28. There are similar mass and heat integration in both cases. The cluster supplies heat to the cultivation pond, the pretreatment step and the anaerobic digester. To reduce the risk of contamination, the selected algae strain will first be grown in a closed PBR before being transferred to the open pond. $CO_2$ is added to the pond from the biogas upgrade facility as well as the industrial cluster, while the PBR is supplied with $CO_2$ via biogas upgrading, as described in Section 5.4.2. The $CO_2$ uptake from the industrial cluster is larger in case 1, since more biogas is produced in case 2. In case 1, the by-product glycerol is fed into the anaerobic digester together with sludge and algae residues.

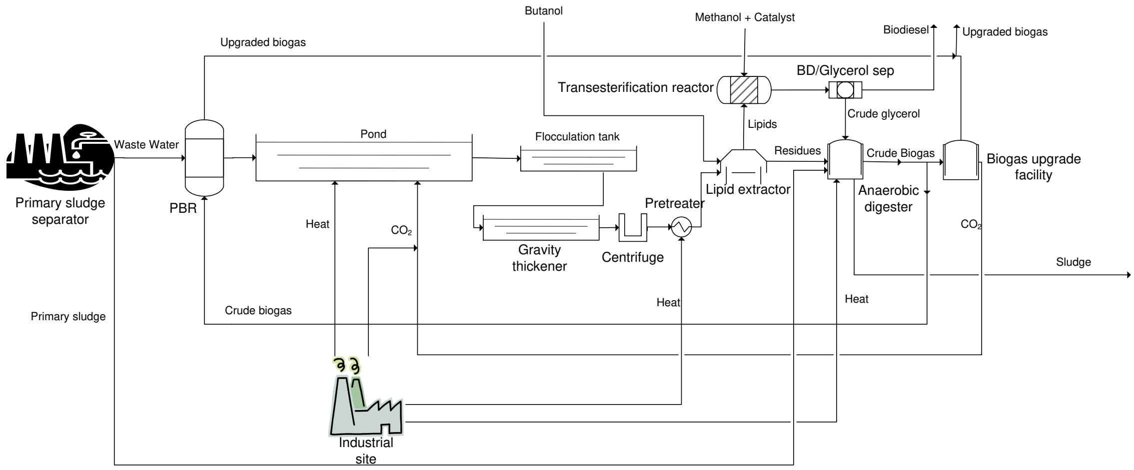


Figure 27 Process design for case 1; algae cultivation in WWTP and combined biogas and biodiesel production.

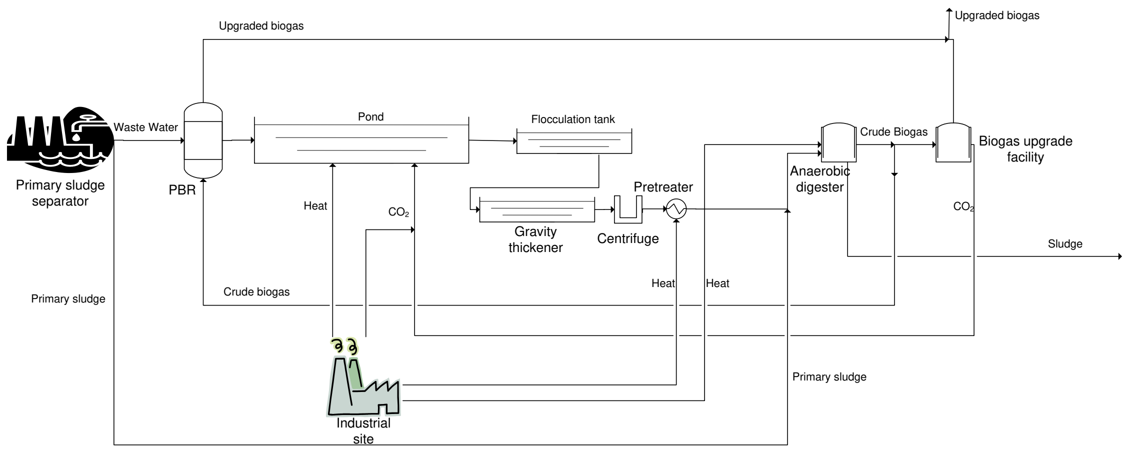


Figure 28 Process design for case 2; algae cultivation in WWTP and single biogas production.

## 7.2 Product outputs

### 7.2.1 Algae cultivation

The potential algae biomass that can be produced at the WWTP in Gothenburg was modelled. Based on underlying assumptions presented in 6.1 the model gave the following results for algae biomass output, algae concentration, carbon deficit in WW, $CO_2$ and flue gas addition for carbon compensation (see Table 27).

Table 27 Algae biomass output, algae concentration, carbon deficit in WW, $CO_2$ and flue gas addition for carbon compensation, assuming WW treatment with algae cultivation at the WWTP in Gothenburg.

| | **Value** | **Unit** |
|---|---|---|
| Algal biomass output | 28.8 | $kt_{algae}$/year |
| Algae concentration in WW | 0.26 | $g_{algae}/kg_{WW}$ |
| Carbon deficit in WW | 26.6 | $mol_C$/sec |
| $CO_2$ addition for carbon compensation | ca. 33.7[23] | $kt_{CO2}$/year |

Comparing the algae cultivation carbon deficit with e.g. the annual $CO_2$ emission of the PREEM refinery in Gothenburg it can be seen that algae cultivation can take up ca. 6.2 % of the refineries emissions.

The remaining pollutant concentration in the WW was also estimated and is given in Table 28. It can be seen, that the concentrations obtained for the different pollutants are below the requirements for discharge from local WWTPs defined by The council of the European Communities (1991) (see Table 10, Section 5.3.1).

Table 28 Remaining pollutant concentration in the WW after algae cultivation.

| **Pollutant** | **Value** | **Unit** |
|---|---|---|
| $BOD_5$ | 10.76 | mg/L |
| COD | 37.80 | mg/L |
| Total P | 0.57 | mg/L |
| Total N | 1.97 | mg/L |

The size of the HRAP was estimated by different algae growth rates. Average solar radiation for each month was taken from SMHI (2011b) as an average from the years 1961 – 1990, see Figure 15. Figure 29 shows the theoretical, maximum algal productivity ($P_{max}$) calculated for the city of Gothenburg, Sweden. It can be seen that from March to September[24] the productivity is within the assumed growth rates in this study (12 – 40 g/m$^2$/d).

[23] Assuming 8000 h/year of operation.
[24] Higher theoretical productivity in June.

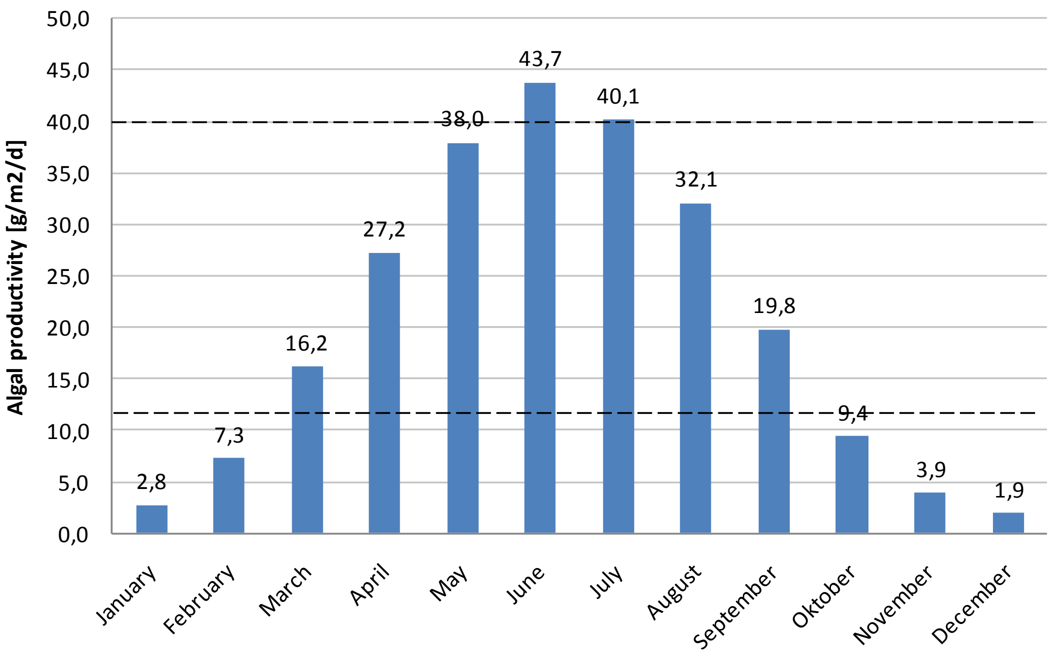


Figure 29 Theoretical maximum algal productivity considering the approximate average solar radiation in Gothenburg, Sweden (see Figure 15).

Using the different growth rates, the cultivation pond size was calculated, see Table 29.

Table 29 Estimated size of a HRAP to treat all the WW of the city of Gothenburg by algae cultivation. Low and high value assume different algae growth rates.

| **Growth rate** | | **Unit** |
|---|---|---|
| Low | High | |
| 12 | 40 | $g/m^2/day$ |
| 719 | 216 | ha |
| 1 027 | 308 | football fields[25] |

The electricity demand for algae cultivation consisting of electricity consumed by $CO_2$ injection and paddle-wheel of both the cases investigated. For the biogas/biodiesel case the electricity demand was calculated to 9 420 MWh/year, while the biogas only case had a consumption of 8 830 MWh/year. The difference is due to the higher amount of $CO_2$ from flue gases necessary in the combined biogas and biodiesel case. In the single biogas case, 22.6 $kt_{CO2}$/year have to be added from flue gases, while if biogas and biodiesel are produced 23.8 $kt_{CO2}$/year are needed. This means that a higher amount of flue gases has to be pumped to the HRAP.

[25] Assuming a football field of 100 x 70 m.

### 7.2.2 Algae harvesting

Upstream algae cultivation is followed downstream by algae harvesting. In this study a four step process, consisting of bio-flocculation, sedimentation, gravity thickening and centrifugation was assumed.

This section presents the main results from modelling the different harvesting process steps are given. Table 30 shows the results from the last stage of the harvesting process (centrifugation). After this the algal slurry is sent to further processing, e.g. algae oil extraction.

Table 30 Algal biomass output from the centrifugation harvesting stage.

| Parameter | Value | Unit |
|---|---|---|
| Solids concentration | 0.2 | $g_{algae}/g_{WW}$ |
| Total mass of algae | 23.4 | $kt_{algae}$/year |
| WW flow to oil extraction | 116 | $10^6$ $L_{WW}$/year |

Not all the algae cultivated (28.8 $kt_{algae}$/year) are sent to biofuels production due to some losses in the harvesting process. The algae carryover and the total flow of WW from algae harvesting to further treatment or the water recipient is shown in Table 31. It was determined that, that in total 5.4 $kt_{algae}$/year (ca. 18.8 %) of the algae cultivated are lost during algae harvesting.

Table 31 Treated WW flow from algae harvesting to further treatment or recipient.

| Parameter | Value | Unit |
|---|---|---|
| Total WW flow | 1.1 | $10^{11}$ $L_{WW}$/year |
| Algae flow in treated WW | 4.2[26] | $kt_{algae}$/year |

The electricity demand of the different process steps is summarised in Table 32.

Table 32 Electricity demand of the different algae harvesting process steps.

| Process step | Value | Unit |
|---|---|---|
| Bio-flocculation/sedimentation | 1380 | kW |
| Gravity thickener | 21.6 | kW |
| Centrifugation | 307.3 | kW |
| Total | 1708 | kW |
| | 13 670[23] | MWh/year |

### 7.2.3 Biodiesel production

The biodiesel model has two main steps, the lipid extraction and the transesterification. The model is based on assumptions described in Section 6.3.1.

The most important output from the biodiesel model is of course the product flow of biodiesel, 6 770 $m^3$/year which corresponds to approximately 63 GWh/year.

Table 30 shows the inflow to the model. The first step is the lipid extraction, where

[26] Difference (5.4 – 4.2 kt/year) is recycled to the cultivation HRAP.

90 % of the lipids present in the biomass follows the butanol. The calculated energy and mass flows for pretreatment and in the actual process are shown in Table 33 and Table 34 respectively.

Table 33 Energy flows for the lipid extraction process.

| Unit operation | Value | Unit |
|---|---|---|
| Cell wall disruption with stirred ball mill | 3.2 | GWh/year (electricity) |
| Heating with excess heat from cluster to extraction temperature | 9.5 | GWh/year |
| Heat demand for butanol recovery | 2.3 | GWh/year |

Table 34 Mass flows for the lipid extraction process.

| Unit operation | Mass flow [ton/year] |
|---|---|
| Make-up flow of butanol | 2 100 |
| Algae residues to anaerobic digester | 17 400 |
| Lipids flow to esterification reactor | 5 950 |

The algae residues are sent to the biodiesel production process. The lipids are entering the transesterification and purification process. Process parameters can be seen in Table 35 and Table 36.

Table 35 Energy flow in the transesterification process.

| Unit operation | Energy flow [GWh/year] |
|---|---|
| Heat duty in first methanol recovery column | 0.17 |
| Heat duty in second methanol recovery column | 0.5 |

Table 36 Mass flows and conversion rate in the transesterification process.

| | Value | Unit |
|---|---|---|
| Make-up flow methanol | 770 | ton/year |
| Recycle rate of methanol | 95 | % |
| Conversion rate for lipids → biodiesel | 99.7 | % |
| Biodiesel product output | 6 770 | $m^3$/year |
| Glycerol product output to digester | 710 | ton/year |

The biodiesel output has been purified in order to follow standards. The composition of the biodiesel can be seen in Table 37.

Table 37 Composition of the produced biodiesel.

| Substance | wt-% |
|---|---|
| FAME | 96.5 |
| Glycerol | 0.24 |
| Methanol | 0.1 |
| Water | 0.05 |
| Other trace elements | 3.11 |

### 7.2.4 Biogas production

The theoretical amount of biogas that can be produced, following algae cultivation at the WWTP in Gothenburg in the two studied cases was modelled. The models were based on the underlying assumptions presented in Section 6.3.2.

In the first case, the combined biodiesel and biogas production case, there are three different flows of substrates transferred into the digester to be anaerobically digested into biogas. Primary sludge is transferred from the wastewater treatment, algae residues are transferred from the oil extraction step in the biodiesel production and glycerol is transferred from the transesterification step in the biodiesel production process. In the biogas case there will be no glycerol transferred to the digester and the algae biomass will be higher since there will be no lipid extraction. The mass flow into the digester in the two cases can be seen in Table 38.

To determine the amount of material that will be converted into biogas the VS for each inflow has been calculated. The VS has been calculated using the conversion coefficient for each substance. The conversion coefficient and the amount of VS in the digester are listed in Table 38.

Table 38 The mass flow into the digester, the VS conversion coefficient and the VS flow into the digester for the two cases.

| Case | Substrate | Mass flow into digester | VS conversion coefficient | VS flow into digester |
|---|---|---|---|---|
| Case 1; combined biodiesel and biogas production | Algae residues | 605 g/s | 36.1 % ash | 387 g VS/s |
| | Glycerol | 21 g/s | 850.3 g VS/kg | 18 g VS/s |
| | Methanol | 3.7 g/s | 99 % | 3.7 g VS/s |
| | Grease in primary sludge | 249 g/s | 98.5 % | 245 g VS/s |
| | COD in primary sludge | 414 g/s | | |
| | Dry solids in primary sludge | 733 g/s | | |
| Case 2; biogas production | Algae biomass | 811 g/s | 26.9 % ash | 593 g VS/s |
| | Grease in primary sludge | 249 g/s | 98.5 % | 245 g VS/s |
| | COD in primary sludge | 414 g/s | | |
| | Dry solids in primary sludge | 733 g/s | | |

The solids content is calculated to determine if there is a need of further pretreatment steps to increase or decrease the solids content in the digester. According to T. J. Lundquist et al. (2010) the solids concentration normally ranges from 4 – 12 % in the digester. The solids concentration in the digester for the two cases can be seen in Table 39.

Table 39 Solids concentration in the digester.

| Case | Value | Unit |
|---|---|---|
| Case 1; combined biodiesel and biogas production | 7.8 | % |
| Case 2; biogas production | 8.9 | % |

The amount of biogas produced is determined using the Specific Theoretical methane Potential (STP) for the different substrates. In the case of COD and algae the methane potential have been found in the literature while for grease, glycerol and methanol it has been calculated using Equation 7 presented in section 6.3.2. In both cases the pretreatment step results in a 33 % higher $CH_4$ yield from algae biomass. The STPs are presented in Table 40.

Table 40 Specific theoretical methane potential.

| | Value | Unit |
|---|---|---|
| Algae (pretreated) | 0.40 | L $CH_4$/g VS |
| Glycerol | 0.35 | L $CH_4$/g VS |
| Grease | 1.01 | L $CH_4$/g VS |
| COD | 0.39 | L $CH_4$/g COD |
| Methanol | 0.52 | L $CH_4$/g VS |

The methane yield was calculated using values from Table 40, and via the assumption of a crude biogas concentration of 70 % $CH_4$ and 30 % $CO_2$ the amount of $CO_2$ produced in the process was calculated. The process yield of raw biogas is 23.6 $Mm^3$/year in the combined case and 26.6 $Mm^3$/year in the single biogas case.

To upgrade the biogas to follow the requirements for transportation fuels (≥95 % methane fraction) (Energigas Sverige 2011) a water scrubber will be used as a cleaning step, resulting in a gas containing 96 % methane (Collet et al. 2011). The amount of upgraded produced biogas and the amount of separated $CO_2$ can be determined using this number. The output from the water scrubber can be seen in Table 41 as well as the energy content of the upgraded biogas.

Table 41 Biogas production process output; Amount of upgraded biogas, $CO_2$ outflow and energy content of produced biogas.

| | | Value | Unit |
|---|---|---|---|
| Case 1; combined biodiesel and biogas production | Upgraded biogas | 17.1 | $Mm^3$/year |
| | $CO_2$ outflow | 11.0 | kt/year |
| | Energy content of produced biogas | 181.8 | GWh/year |
| Case 2; biogas production | Upgraded biogas | 19.3 | $Mm^3$/year |
| | $CO_2$ outflow | 12.4 | kt/year |
| | Energy content of produced biogas | 205.3 | GWh/year |

The amount of biogas produced at the WWTP today is approximately 60 GWh/year (Gryaab 2011), corresponding to approximately 9.5 million $m^3$/year, with a methane fraction of 63 %. The substrate from the digester is mainly sludge from the wastewater treatment process (97 %) while the rest (3%) is food waste (Davidsson 2011). The energy demand of the different process steps is summarized in Table 42.

Table 42 Energy demand for different biogas process steps.

| Case | Process step | Value | Unit |
|---|---|---|---|
| Case 1; combined biodiesel and biogas production | Anaerobic digester (mixing) | 4.16 | GWh/year |
| | Anaerobic digester (heating) | 4.89 | GWh/year |
| | Water scrubber | 2.90 | GWh/year |
| | Total | 11.96 | GWh/year |
| Case 2; biogas production | Anaerobic digester (mixing) | 4.80 | GWh/year |
| | Anaerobic digester (heating) | 3.60 | GWh/year |
| | Water scrubber | 3.28 | GWh/year |
| | Total | 11.68 | GWh/year |

## 7.3 Economic evaluation

Given the different cost parameters given in Section 4.5, the two different cases are evaluated. The OPerating EXpenditures (OPEX), CAPital EXpenditures (CAPEX) and Annualized CAPital EXpenditures (Ann. CAPEX) for case 1 and 2 are shown in Table 43 and Table 44 respectively.

Table 43 Costs for additional equipment in case 1.

| **Process step** | **CAPEX [kSEK]** | **Ann. CAPEX [kSEK/yr]** | **OPEX [kSEK/yr]** |
|---|---|---|---|
| Lipid extraction | 25 540 | 2 550 | 12 000 |
| Transesterification | 8 970 | 900 | 6 890 |
| Total | 33 670 | 22 340 | |

From Table 43 it can be seen that lipid extraction is the most expensive step of the process. Therefore the conclusion can be drawn that much research must be aimed at lowering the costs for this process. Both the capital costs and in particular the operating costs are very high.

Table 44 Costs for enlarged equipment in case 2.

| **Process step** | **CAPEX [kSEK]** | **Ann. CAPEX [kSEK/yr]** | **OPEX [kSEK/yr]** |
|---|---|---|---|
| Biogas production | 5 240 | 520 | 720 |
| Biogas upgrade | 5 680 | 570 | 10 |
| Total | 10 450 | 1 820 | |

As can be seen in the tables it is more costly to produce biodiesel, mostly because of the lipid extraction step. Both the capital costs and the operating costs are higher for case 1. In addition to this, the biodiesel/biogas case consumes more electricity in the cultivation step, due to the fact that less pure $CO_2$ is available. This renders another 294 500 SEK/year to the operation costs for case 1. However, biodiesel production also increases the revenues. The sales for biofuel are accounted for in Table 45.

Table 45 Income from biofuel sale from the two cases.

| | **Case 1** | **Case 2** |
|---|---|---|
| Biodiesel sales [kSEK/yr] | 50 210 | - |
| Biogas sales [SEK/yr] | 170 910 | 193 050 |
| Total [kSEK/yr] | 221 120 | 193 050 |

The difference in revenues for the different cases is thus approximately 28 MSEK. This must be compared to the difference in total annual costs, which is approximately 20.5 MSEK, and the difference in capital costs; 23 MSEK. Looking at these figures, the best process option would be the combined biodiesel and biogas case. Biodiesel has a higher value on the market, and the biodiesel process also has a higher biomass-to-fuel efficiency than the biogas process, which yields 30% $CO_2$. Calculating with a straight pay-back time, it takes approximately 3.2 years before the higher costs for the biodiesel process have been neutralized by the higher revenue. It must be noted that the capital and operation costs presented in Table 43 and Table 44 are only numbers for the increased equipment costs needed in for the biogas/biodiesel case compared to the production of biogas only. It is thus not a complete economic evaluation of the entire process chain.

## 7.4 $CO_2$ emissions evaluation

$CO_2$ emissions consequences of producing biofuels in combination with algae cultivation in municipal WW the amount of $CO_2$ emissions avoided by replacing fossil fuels with fuels produced from algae is estimated. The savings for both cases are shown in Figure 30 Total $CO_2$ emissions reduction by replacing fossil fuels with biofuels from algal biomass cultivated in municipal WW

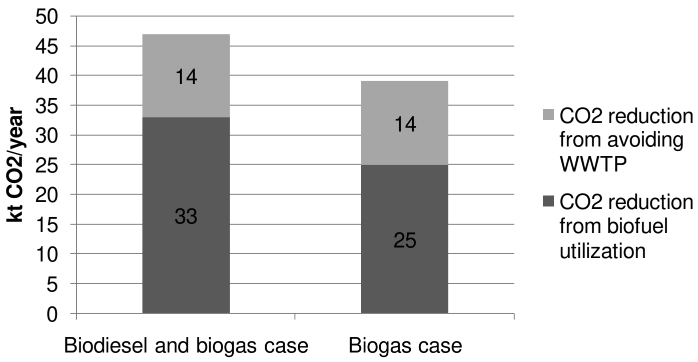


Figure 30 Total $CO_2$ emissions reduction by replacing fossil fuels with biofuels from algal biomass cultivated in municipal WW.

It can be seen that in the case where biogas and biodiesel are produced higher total $CO_2$ emissions savings are achieved. This is mainly due to the higher biofuels outputs from the biogas/biodiesel process.

Figure 30 illustrates also the $CO_2$ emissions reduction obtained by cultivating algae in conjunction with municipal WWT. WWT stands for ca. 13.6 kt of net[27] $CO_2$ emissions saving per year, corresponding to 34 % savings in the biogas case and 24 % for the biogas/biodiesel case. This illustrates the importance of combining algae biofuels production with WWT. If algae are cultivated without WWT the nutrients contained in the WW have to be replaced by artificial fertilizers, which in turn results in $CO_2$ emissions[28].

The $CO_2$ emissions reduction shown in Figure 30 correspond to 2.5 % in the biogas and 3 % in the biogas/biodiesel case of the main industrial $CO_2$ emissions of the industrial cluster on Hisingen (see section 2.2).

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[27] Net $CO_2$ emissions = $CO_2$ emissions from energy inputs (corresponding to ca. 27 $kt_{CO2}$/year)– $CO_2$ emissions saved by todays biogas production at the WWTP (corresponding to ca. 13.4 $kt_{CO2}$/year).
[28] $CO_2$ emissions from fertilizer production is not accounted for in this study.

# 8 Discussion

Biofuels production from algae biomass represents an interesting field within energy research. In this study, two different process paths have been evaluated from a techno-economic perspective.

One issue is that the assumed techniques, especially for cultivation and harvesting, are not yet fully developed. Lack of large-scale facilities constitutes lack of reliable data. The future research within the field of algae based energy is thus dependent on large-scale demonstration plants. Another related problem is that some of the process techniques are presently too expensive or not yet proven, e.g. bio-flocculation has not yet been tested on a large scale. This could very well prove that the product outputs are not competitive on the fuel market at this time. When more demonstration plants are built, and hence the knowledge about the techniques increases, the production costs are expected to decrease. For example the use of PBRs is today considered economically unfeasible, but could prove to be the most attractive option if issues regarding energy demand and capital costs are solved.

There are large uncertainties regarding how the growth rate is affected by the climate conditions in Gothenburg. The large variations in climate conditions in Gothenburg during different parts of the year make it hard to predict the algae growth rate. The wide span of 12 – 40 $g/m^2/day$ results in uncertain conclusions regarding the cultivation pond size. The climate conditions also rise questions regarding how large parts of the year the process is available. To have open pond systems operating in the winter would cause severe problems with heat losses and evaporation, and supporting light would probably also have to be supplied. A solution here could be to keep the old wastewater facility, so that regular wastewater treatment could occur during wintertime. Another solution could be to use PBRs, which have low evaporation losses, are less sensitive to contamination and more area effective. This could also decrease the need for supporting light since PBRs are more area effective.

Wastewater treatment with algae must also be subject to more research. The water quality requirement regarding nitrogen and phosphorous are met, but suspended solids are not taken care of in the presented process. This could mean that extra treatment after the algae cultivation is necessary. Release of algae could result in increased algae growth outside the algae cultivation site, and the effects of this should be further examined.

The area efficiency of algae biofuels should be compared to other second generation biofuel techniques such as gasification. It is often claimed that algae cultivation can use non-arable land, but despite this, non-arable land is not always used. Wastewater treatment with algae of the Gothenburg municipal wastewater did not decrease the emissions at Hisingen with more than approximately 3 %. At the same time, the cultivation occupies a lot of land. It would be interesting to see how $CO_2$ emissions would be affected if the same area was used for the production of other biofuels.

The large area demand can especially be an economic problem, as the WWTP in Gothenburg (and WWTPs in general) is located close to the city, meaning that land prices are high. Either the WW infrastructure has to be changed to be able to build an algae WWTP further outside the city, where more and cheaper land is available or a high price has to be paid for the land area needed, both increasing the capital costs of the plant.

It is not much known about public acceptance of this type of project, but public acceptance can be seen as an important factor. Due to the large land area needed severe landscape changes will occur and private land for the plant has to be acquired. Therefore the public opinion on such a project is important and should be further investigated.

# 9 Conclusions

The research questions presented in Section 3.2 will be answered below.

- Intensive research is conducted all around the world within the area of using cultivated algae as a renewable energy source. But still there is a need for more research in the area, and it has to be performed on large scale plants. The production costs for algae cultivation are currently too high and new solutions are needed to reduce the production costs. The development of PBRs to increase the efficiency in the cultivation could be a solution if the cost of these systems would go down and if they are developed for large scale production.
- Sweden offers a climate with cold winters. In order to carry out algae cultivation in this climate, heating of the cultivation ponds is required. In addition to the low temperatures, the solar insolation during the winters is low. The assumed productivity, of 12 – 40 $g_{algae}/m^2$/day is theoretically reached from March to September. Under the conditions assumed in this study it is therefore only possible to conduct seasonal algae cultivation.
- After primary treatment, where the primary sludge and grease are removed, the following concentrations of nutrients can be found in the wastewater: 59.9 $mg_{TOC}/L_{WW}$, 24.6 $mg_N/L_{WW}$ and 2.8 $mg_P/L_{WW}$ with an annual average WW flow at Gryaab WWTP in Gothenburg, Sweden of 3.83 $m^3$/sec. Due to carbon deficit 1171 $g_{CO2}$/sec needs to be injected. Algae cultivation using the nutrients in Gothenburg WW results in an algae biomass output following cultivation of 29 $kton_{algae}$/year.
- The pollutant concentrations in the treated WW are below the limiting value for discharge from a WWTP. The suspended solids concentration is however not affected by the algae cultivation since the algae cannot utilize these solids. In addition, 5.4 $kt_{algae}$/year (ca. 18.8 %) of the cultivated algae are lost during the harvesting process.
- Calculations of the cultivation area required to treat all the WW in the city of Gothenburg by algae cultivation has been made by using two different growth rates scenarios, 12 $g/m^2$/day and 40 $g/m^2$/day. The lower growth rate results in a need of a 719 hectare HRAP while the higher growth rate scenario requires a 216 hectare HRAP.
- $CO_2$ is available in large quantities in the cluster in form of flue gases from industry. PREEM refinery, ST1 refinery and the Rya NGCC plant totally emits about 1550 $kton_{CO2}$/year. In addition the biogas production process in the two cases results in 11 $kton_{CO2}$/year and 12.40 $kton_{CO2}$/year respectively. The need for added $CO_2$ in the algae cultivation is ca 33.7 $kton_{CO2}$/year, showing that there is a large surplus of $CO_2$ in the cluster.
- The combined biodiesel and biogas production case has the potential to produce ca. 63 GWh biodiesel and ca. 182 GWh biogas per year. The single biogas production case has the annual potential to produce ca. 205 GWh biogas.
- Of the two processes studied in this work, combined biodiesel and biogas production and single biogas production, it is more economically feasible to produce both biogas and biodiesel. The high willingness to pay for biodiesel and the high conversion rate of algae oil to biodiesel makes the revenues large enough to compensate the larger capital and operation costs of biodiesel.

- Due to an increased amount of available $CO_2$ from the biogas upgrading process in the case of biogas production the need of $CO_2$ from flue gases in this case is lower than in the combined biodiesel and biogas production case. 23.8 $kton_{CO2}$/year (flue gases) needs to be pumped to the HRAP in the combined production case while for the biogas case 22.6 $kton_{CO2}$/year is needed.
- The $CO_2$ emissions savings obtained from replacing fossil fuels with the biofuel from algae biomass cultivated in a WWTP sums up to 46 $kt_{CO2}$/year in the combined biodiesel and biogas production case and 38 $kt_{CO2}$/year in the biogas production case. The $CO_2$ emission saving of avoiding WWT stands for 13.7 $kt_{CO2}$/year, which shows the importance of combining the processes.

# 10 Future works

To determine the direction of future work, we briefly summarize the ideas which emerged during preceding critically review of the work. This chapter also briefly summarizes those ideas that has been considered interesting, but unfortunately did not fit within the time frame of this work.

*Sensitivity analysis.* A detailed sensitivity analysis should be performed on the model to examine how changes in various process parameters such as algae growth efficiency, nutrient availability and biofuels conversion efficiency affect the result, i.e. the amount of produced biofuels, the energy demand of the process and the $CO_2$ emissions savings. The sensitivity analysis also aims to investigate how the amount of excess heat and $CO_2$ available affects the outcome.

*Public opinion.* Large algae ponds will inevitably lead to landscape changes. This, and other factors may affect the public opinion, which should be further investigated.

*Inventory of the amount of excess heat.* The amount of excess heat in the cluster needs to be assessed in order to determine if there is enough available excess heat in the cluster to meet the heat demand in the biorefinery, as one of the assumptions in this study is that there is enough available excess heat below 90 °C. In addition, technical solutions for the excess heat transfer as well as the costs for these solutions needs to be further investigated.

*Area efficiency.* It is assumed that arable land is becoming more scarce in the future, and therefore the area efficiency of the modeled algae based biorefinery should be compared with other biorefineries using other raw materials than algae biomass.

*Economic analysis.* A detailed cost estimation for the whole algae wastewater treatment and biofuels production concept, including both investments and operating costs should be performed. In this way the pay-back time can be calculated. In addition a production cost of the produced algae based biofuels should be calculated. The economic evaluation should also take the cost savings of replacing the current WWT process into account.

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