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Producing lipids, biogas and fertilizer from microalgae – conceptual design and techno-economic analysis

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Report Title: Producing lipids, biogas and fertilizer from microalgae - conceptual design and techno-economic analysis

Key words: microalgae, microalgae products, techno-economic assessment, CO_2 biofixation

Abstract

Biological CO_2 capture by microalgae is seen as a promising technology and has the advantage of producing biofuel/biomass simultaneously. The combination of biofuel/biomass production, CO_2 fixation and bio-treatment of wastewater underscore the prospect and potential of microalgae. This work concerns the optimal use of microalgal biomass, focusing on carbon capture and economic feasibility. Microalgal products are briefly reviewed as well as the carbon capture from industrial flue gas. Conceptual level techno-economic analysis is performed for four concepts that produce lipids, biofuels and/or fertilizer. The evaluated processes include open pond cultivation with industrial flue gas, harvesting, drying, cell wall disruption, extraction of lipids and anaerobic digestion. Process parameter and economic evaluation data, such as prices, specific power consumptions and the yields of unit operations, have been obtained mainly from literature. The results of this study indicate that microalgae-based production of selected products would be unprofitable with the assumptions used. Sectorial literature shows similar performance. The most significant factors affecting the profitability were high investment costs and other fixed costs, as well as the cost of heat in concepts where biomass was dried.

Espoo, June 2015

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1 Introduction

This study has been carried out in Work Package (WP) 6 of the Carbon Capture and Storage Programme (CCSP), a research program of CLEEN Ltd (Cluster for Energy and Environment). The aim of WP 6: 'Utilisation of microalgae for CO_2 capture and biogas/-fuel production', is to identify conditions for feasible and sustainable algal solutions. The objective of this study was to perform a techno-economic analysis of microalgae-based carbon capture concepts with selected product portfolios.

Microalgae are recognized as one of the oldest living microorganisms on Earth (Lam et al. 2012). They are a diverse group of microscopic, unicellular organisms, which can use either inorganic or organic carbon to produce biomass. This study addresses photoautotrophic microalgae production, that is, using sunlight as energy source and CO_2 as the carbon source.

An increase in atmospheric CO_2, derived from flue gas that originates from fossil fuel combustion, is a great challenge to worldwide environmental sustainability (Kumar et al. 2010). Available technologies for CO_2 removal/capture include physicochemical absorbents, injection into deep ocean and geological formations and geological formations, and enhanced biological fixation (Kumar et al. 2010). Biological CO_2 capture by microalgae is a promising technology, which has gained a lot of attention in recent years due to its advantage of producing biofuel/biomass simultaneously. Lipids and carbohydrates in microalgal biomass can be converted for example to biodiesel, bioethanol and biogas, which are alternatives to existing fossil fuels.

Microalgal biomass has several advantages over conventional energy crops. Microalgae can grow at exceptionally fast rates; the photosynthetic efficiency of microalgae is from 10–20 %, in comparison with 1–2 % for most terrestrial plants. Some algal species, during their exponential growth, can double their biomass in periods as short as 3.5 hours. (Lam et al 2012; Singh & Ahluwalia 2012) Apart from that some microalgal species are able to accumulate large quantities of lipids (Chisti 2007), which can be converted to biodiesel. Microalgae convert solar energy to chemical energy and utilize CO_2 from various sources, for example from flue gas, as a carbon source during photosynthesis. In addition microalgae can be cultivated on non-agricultural land, which decreases the competition of land for human food crops. Furthermore, algae can be cultivated in various water qualities, and their water usage is smaller than that of most terrestrial plants. (Brennan & Owende 2010) The combination of biofuel/biomass production, CO_2 fixation and bio-treatment of wastewater underscore the prospect and potential of microalgae.

Despite all the benefits of algal biomass production, significant challenges for the commercialization of large scale microalgae production still exist. These include the

high cost of cultivation and downstream processing operations, the potential for a negative energy balance after accounting for requirements in water pumping, CO_2 transfer, harvesting and extraction (Brennan & Owende 2010) and also complications associated with culture stability (Quinn & Davis 2015).

The objective of this study was to study the feasibility of options for the utilisation of algal biomass and perform a techno-economic analysis of microalgae-based carbon capture concepts with selected product portfolios. The focus is on mass production of algal biomass combined with CO_2 capture. The bulk algal products selected are biogas, lipids and fertilizers.

2 Microalgal biomass products

Historically microalgae were used already over 2000 years ago for surviving during famine. However microalgal biotechnology really began in the middle of last century and commercial cultivation started in the early 1960's. The chemical composition of microalgae allows their biomass to be utilised in several applications such as nutritional supplements, antioxidants, cosmetics, fertilizers, biomolecules for specific applications, biofuels, natural dyes and colorants, pharmaceuticals and polyunsaturated fatty acids (PUFA) (Spolaore et al. 2006, Singh & Ahluwalia 2013). One feature for microalgal research is the combined production of renewable energy with environmental solutions such as carbon dioxide capture and wastewater treatment (Brennan & Owende 2010). Figure 1 illustrates different possibilities for microalgal production systems. Here a short summary of commercial microalgal products and biofuel products is given; in chapter 5 selected products are discussed in more detail.

2.1 Commercial products of microalgae

Nowadays, there are numerous commercial applications of microalgae. Microalgae have been used to enhance the nutritional value of food and animal feed because of their chemical composition. They have been used in aquaculture and they are utilized in cosmetics. Moreover, they are cultivated as a source of highly valuable molecules. For example, their polyunsaturated fatty acid oils can be added to infant formulas and nutritional supplements and their pigments can be used as natural dyes. (Spolaore et al. 2006; Hudek et al. 2014)

Microalgae for human nutrition are marketed as tablets, capsules and liquids. They can also be used as ingredients in for example pastas, snack foods, candies and beverages. They act as a nutritional supplement or represent a source of natural food colorants. According to Spolaore et al. (2006) the commercial applications are dominated by four strains: *Arthrospira* (a cyanobacterium), *Chlorella, Dunaliella salina* and *Aphanizomenon flos-aquae*. Microalgae are used in human nutrition

because of their high protein content and high nutritive value and they also are described as providing various health promoting effects. (Spolaore et al. 2006)

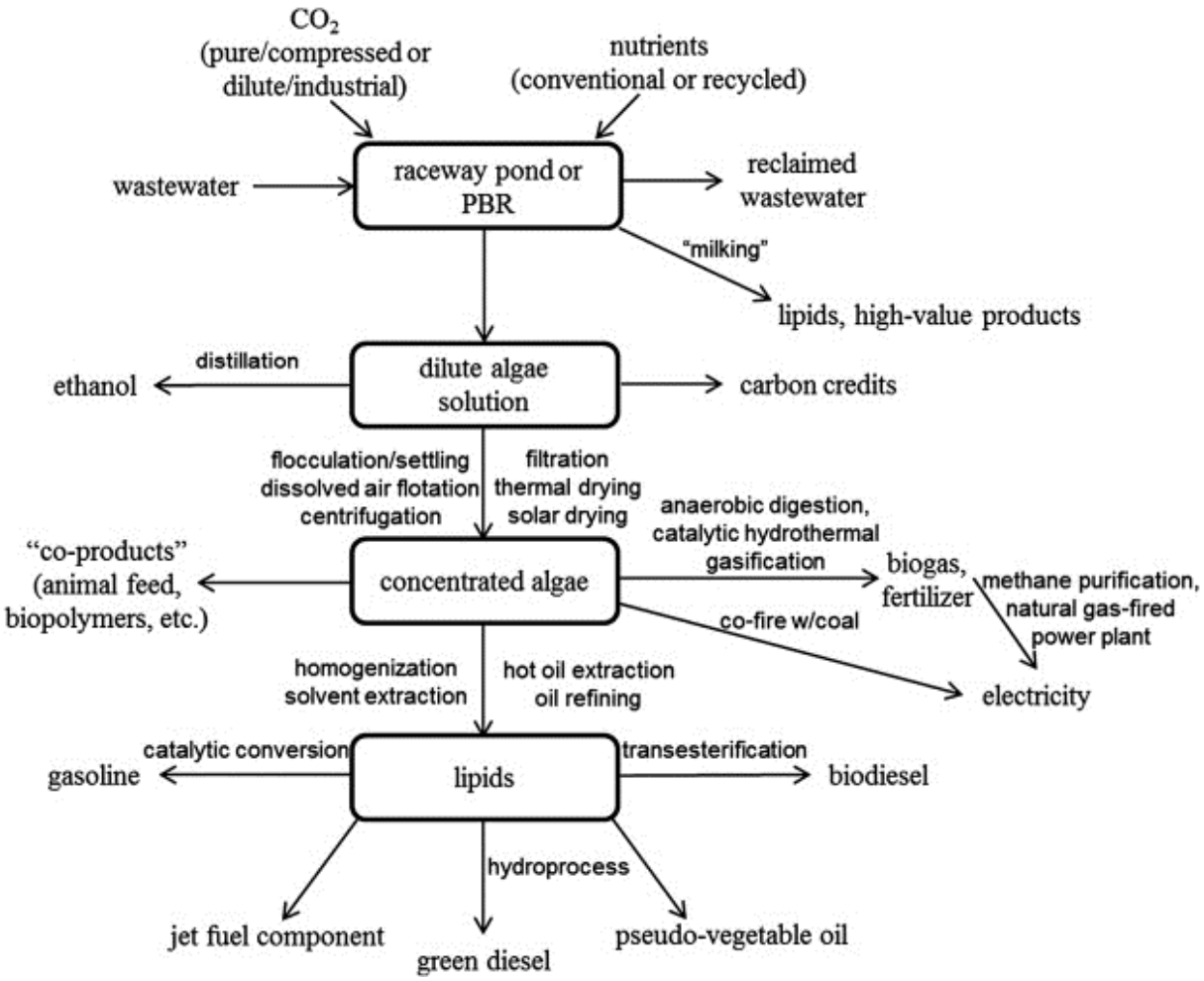

Figure 1. Different possibilities for microalgal production schemes. (Rickman & al. 2013)

In animal nutrition, microalgae are incorporated into the feed for a wide variety of animals, from fish to pets and farm animals. In year 2004 30% microalgae production was used for animal feed applications (Spolaore et al. 2006). Microalgae are important in aquaculture, being a natural food source for these animals. Microalgae are produced for molluscs, shrimps and fish, to be utilised as nutrition, and also for colouring the flesh of fish. Microalgae are also utilised for larval nutrition. While microalgae provide food for zooplanktons, they also help to stabilize and improve the quality of the culture medium. Nevertheless, despite the advantages of live microalgae in aquaculture, the current trend is to avoid using them. This is due to their high cost and the difficulty in producing, concentrating and storing them (Borowitzka 1997). The usage of algae as animal feed is based on their positive effect on the physiology (by providing a large profile of natural vitamins, minerals,

and essential fatty acids; improved immune response and fertility; and better weight control) and external appearance (e.g. healthy skin and a lustrous coat) of animals (Spolaore et al. 2006).

In the case of cosmetics, microalgal extracts can be found mainly in face and skin care products. Microalgae can also be found in sun protection and hair care products. Some cosmeticians have even invested in their own microalgal production system.

High value molecules are also extracted from microalgae, the most common of these are polyunsaturated fatty acids (PUFA), pigments and stable isotope biochemical (Spolaore 2006, Hudek et al. 2014). Currently, docosahexaenoic acid (DHA) is the only algal PUFA commercially available, however many potential ones exists. Economic competitiveness with other sources of PUFA limits the availability of algal PUFA. β-carotene and astaxanthin are the most important carotenoids used commercially. Their most important uses are natural food colorants (e.g. used in orange juice) and additives for animal feed (poultry, fish). Carotenoids also have applications in cosmetics. Some carotenoids have nutritional and therapeutic relevance of certain carotenoids is due to their ability to act as vitamin A. Commercially, microalgal carotenoids compete with the synthetic forms of the pigments. Although the synthetic forms are much less expensive than the natural ones, microalgal carotenoids have the advantage of supplying natural isomers in their natural ratio. (Spolaore et al. 2006)

According to Pulz & Gross in 2004 the microalgal biomass market produced about 5,000 tons of dry matter per year and generated a turnover of approximately US $ 1.25×10^9 per year (Pultz & Gross 2004). Based on Benemann (2013), the production amount today is three times larger, being 15,000 t/year microalgae. Also, according to Benemann (2013) the dominant cultivation system is the open pond (more than 99%), primarily raceway ponds with paddle wheel mixing.

2.2 Microalgal biofuels

The potential applications of microalgae, seen in research and demonstration stage are seen as much larger than existing applications. According to Benemann (2013), commodities (feed, fuels and chemicals) are not currently produced commercially from microalgae. The main challenges are the production costs that need to be reduced, a potential to negative energy balance, and the volumes that need to be increased many hundred-fold.

However, in recent years interest in microalgal cultivation and biomass production has increased in the renewable energy field. Extensive research has been conducted to develop the use of microalgae as an energy source and make algal oil production commercially viable. (Ghasemi 2012)

Figure 2 shows potential energy conversion processes from algal biomass to energy end-use. The conversion technologies can be divided into two categories: thermochemical conversion and biochemical conversion (Brennan & Owende 2010).

Thermochemical conversion includes the thermal decomposition of organic components in algal biomass. Different technologies include gasification, thermochemical liquefaction, pyrolysis and direct combustion.

Biochemical conversion of microalgal biomass includes anaerobic digestion to produce biogas, alcoholic fermentation to produce ethanol, and photobiological hydrogen production.

Biodiesel is a derivative of oil crops and biomass which can be used directly in conventional diesel engines (Brennan & Owende 2010). After the extraction process, the separated algal oil can be converted to biodiesel by transesterification, which produces biodiesel from algal oil and small-chain monoalcohols in the presence of catalysts.

A good summary of different conversion technologies can be found in Brennan & Owende (2010).

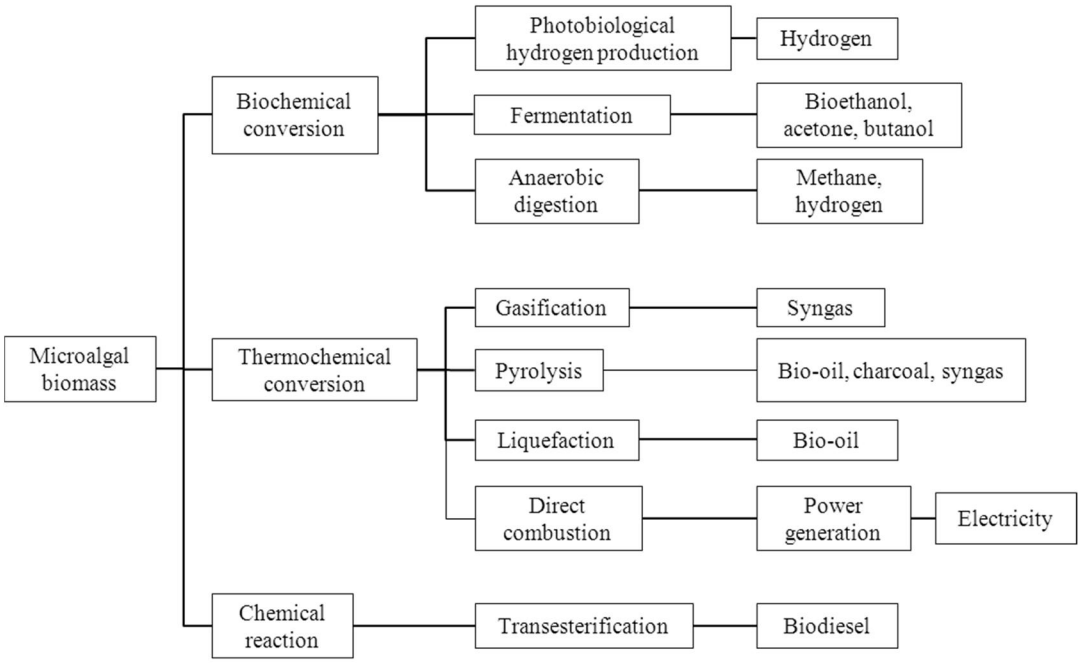

Figure 2. The algal biomass conversion technologies for different biofuel products. (Leino 2012)

3 Algal species selection

Microalgae are a diverse group of microscopic, photosynthetic organisms that typically grow suspended in water. Autotrophic microalgae use carbon dioxide (CO_2) and their growth is driven by same photosynthetic process adopted by terrestrial plants. (Razzak et al. 2013)

Successful algal biotechnology mainly depends on choosing the right alga with relevant properties for specific culture conditions and products. Some species and their general composition are listed in Table 1. The biodiversity of microalgae is enormous and represents an almost untapped resource. Microalgae are present in all existing earth ecosystems, not just aquatic but also terrestrial, representing a big variety of species living in a wide range of environmental conditions. It is estimated that more than 50,000 species exist, but only 30,000 have been studied and analysed (Mata et al. 2010).

Table 1. General composition of different microalgae, expressed as % of dry weight. (Becker 2007)

Alga	Protein	Carbohydrates	Lipids
Anabaena cylindrica	43–56	25–30	4–7
Aphanizomenon flos-aquae	62	23	3
Chlamydomonas rheinhardii	48	17	21
Chlorella pyrenoidosa	57	26	2
Chlorella vulgaris	51–58	12–17	14–22
Dunaliella salina	57	32	6
Euglena gracilis	39–61	14–18	14–20
Porphyridium cruentum	28–39	40–57	9–14
Scenedesmus obliquus	50–56	10–17	12–14
Spirogyra sp.	6–20	33–64	11–21
Arthrospira maxima	60–71	13–16	6–7
Spirulina platensis	46–63	8–14	4–9
Synechococcus sp.	63	15	11

In order to achieve the potential benefit from microalgae culture, it is important to pay attention to selection of the proper algal specie. Desired properties of algal species, taking into account the selected product portfolio, are listed in Table 2. Desired properties vary depending on the production purpose and production technology. According to Venteris et al. (2014), selection of the algal strain has a dramatic effect on the productivity and consequently feasibility of an algal facility.

Table 2. Desired algal species characteristics (Brennan & Owende 2010; Razzak et al. 2013; Ghasemi et al. 2012, Ward et al. 2014; Ho et al. 2011, Lam et al. 2012)

Efficient CO2 capture
- High productivity - Have high CO_2 capture capacity / CO_2 removal efficiency - Tolerant to high temperatures is a benefit - Tolerant to high CO_2 concentration - Adaptation of microalgae to high concentration of CO_2 - pH requirements of species and CO_2 solubility dependence on pH (High CO_2 concentration induces low pH) - Tolerance to SOx, NOx originating from flue gas
Cultivation
- Robust and able to survive shear stresses in case of PBR - Should dominate wild strains, especially in open ponds - Tolerant to wide range of temperatures (seasonal variation, flue gas) - High photosynthetic efficiency (PE) - Water: saline, fresh, brackish; Growth performance under selected cultivation water is important - Limited nutrient requirements
Harvesting / dewatering
- Ease of biomass harvesting is needed. - Self-flocculation characteristics of microalgae
LIPID
- High lipid productivity - Good lipid composition for bio-oil production - High lipid accumulation - Cell wall degradability and characteristics
BIOGAS

- High lipid content: good or bad?
  - Theoretical methane potential higher
  - High lipid concentration can be inhibitory
  - AD after liquid biofuel production
- Cell wall degradability and cell wall characteristics
- C/N-ratio of microalgal species is low (varies from 4.16 to 7.82 to 10), C/N ratio preferred for AD is 20 to 35, High nitrogen content may cause ammonia-nitrogen toxicity

FERTILIZER
- High biomass productivity - High N, P, K content

In order to maximise CO_2 capture with microalgae a rapid growth rate is an essential factor. While focusing on the lipid production, a high oil content of microalgae is also an important property. The most relevant groups of algae targeted for biodiesel production include the diatoms that make up a majority of phytoplankton in salt and brackish waters, green algae that are common in many freshwater systems, blue-green algae, which are actually bacteria that contain chloroplasts and are important

to nitrogen fixation in aquatic systems, and finally the golden algal species able to store carbon as oil and complex carbohydrates. (Ghasemi 2012) These species contain lipids from 20 up to 75 % of dry weight basis. In general, species with lower oil content grow faster than species with high oil content (Ghasemi 2012).

For biogas production from microalgae, the specie selection has also an important role. Strong cell wall of some microalgal species can effectively resist bacterial attack in anaerobic digestion and cells may pass through anaerobic digester and remain undigested. Microalgae with no cell wall or cell wall made from protein are reported to give higher gas yield (Ward et al. 2014).

4 CO_2 fixation using microalgae

The concepts and technologies used for CO_2 capture by algae have been reviewed by Teir (2014). The review also summaries photosynthetic processes, in which inorganic carbon in the form of CO_2 is converted to organic carbon, using energy from light as well the technologies used for CO_2 fixation. Since microalgae (phototrophic) use CO_2 in photosynthesis, their CO_2 fixation capability correlates positively with cell growth rate and light utilization efficiency (Ho et al. 2011, Razzak 2013). Figure 3 shows the CO_2 fixation ability of various microalgal species reported in recent literature.

The molecular formula of algae (varying between algal species) expresses the amount of carbon utilized per amount of algal biomass. Thus, the carbon fixation rate does not depend directly on the biomass dry weight.

Commonly used CO_2 fixation capacity is based on the approximate molecular formula of microalgae presented by Chisti (2007) giving fixation capacity of 1.88 t / t algae. According to Posten (2009) the carbon fraction varies from 0.45 for algae with high carbohydrate content up to 0.8 for oil rich cells. This gives a fixation potential of 1.65 to 2.9 t CO_2 per t algae. Furthermore, Van Den Hende et al. (2012) observed values from 1.81 to 2.37 in the experimental literature.

For the techno-economic evaluations of this study the average fixation capacity was calculated based on algal composition and the CO_2 fixation capacity of each main component in algae (Table 3 and

Table 4). The main components of algae are proteins, lipids and carbohydrates. Their average molecular formulas are given in Table 3. The fixation potential per kg algae is larger with high lipid content than with low lipid content, for example 60% lipid content would generate fixation potential of over 2.4 kg CO_2 per kg algae. This indicates that high lipid content of algae is favourable concerning CO_2 capture effectiveness, however this was calculated per kg algae while time i.e. growth rate

was omitted. As mentioned earlier lipid content and growth rate are said to be mutually exclusive properties.

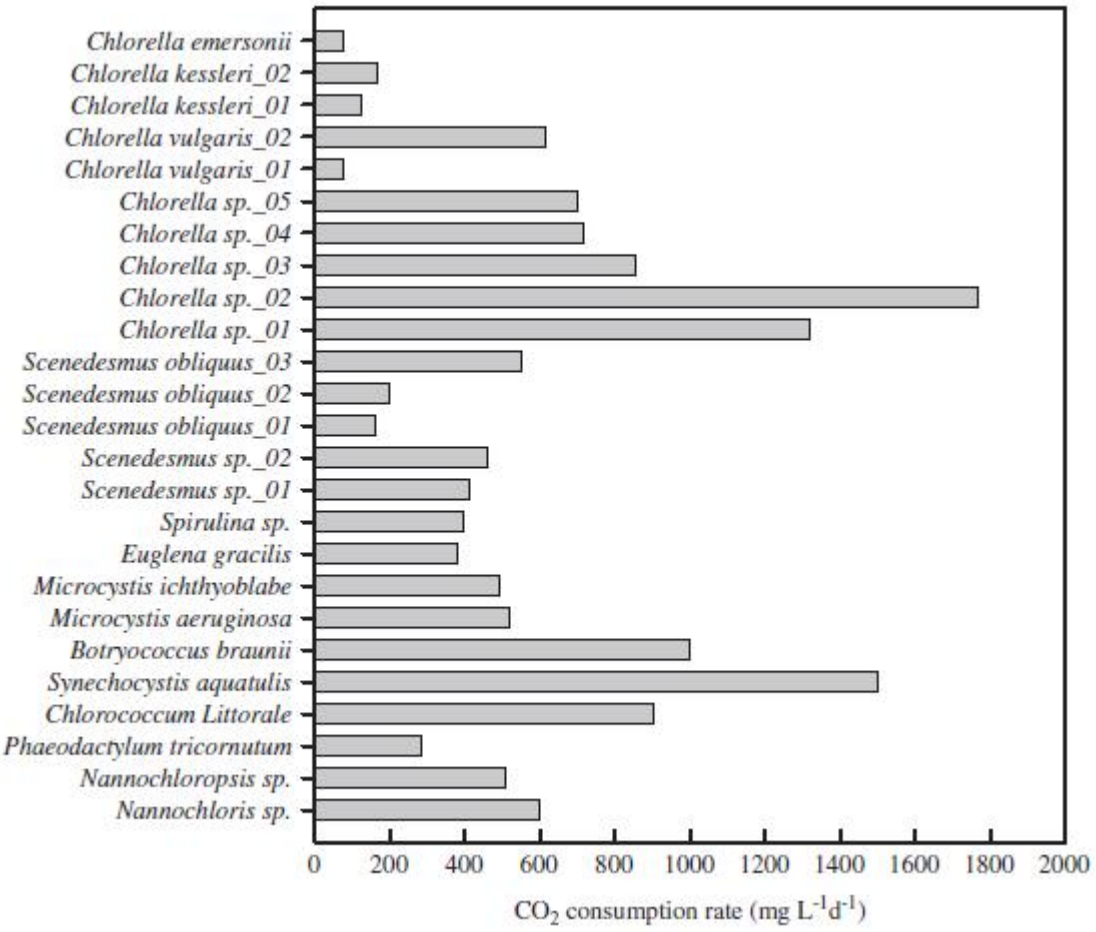

Figure 3. Microalgal CO_2-fixation ability (under batch operation) of 25 microalgal species reported in recent literature (Ho et al. 2011).

Usual sources of CO_2 for microalgae include: (i) atmospheric CO_2; (ii) CO_2 from industrial exhaust gases (e.g. flue gas and flaring gas); and (iii) CO_2 chemically fixed in the form of soluble carbonates (e.g. $NaHCO_3$ and Na_2CO_3) (Kumar 2010). In this study industrial flue gas is considered as the CO_2 source.

Table 3. Chemical composition of three main components of microalgae (Kwietniewska et al. 2014, Sialve et al. 2009, Heaven et al. 2011, Lardon et al. 2009) and their carbon capture potential.

Substrate	Composition	Carbon capture potential kg CO_2 / kg substrate
Protein	$C_5H_7NO_2$; $C_{4.43}H_7O_{1.44}N_{1.16}$	2.78-2.83
Carbohydrate	$C_6H_{12}O_6$; $(C_6H_{10}O_5)n$	1.47 – 1.63
Lipid	$C_{40}H_{74}O_5$; $C_{57}H_{104}O_6$	1.95 -1.96

Table 4. Carbon fixation potential of microalgae based on its three main components.

Alga composition			Carbon capture kg CO2 / kg
Lipids	Carbo-hydrates	Protein	Alga
10 %	45 %	45 %	1.89
30 %	35 %	35 %	2.10
60 %	20 %	20 %	2.41

4.1 Solubility of CO_2

In general CO_2 mass transfer between liquid and gaseous phases is slow and causes challenges for algal cultivation. As dissolution of CO_2 is slow, a significant amount of CO_2 may be outgassed from cultivation media. (Van Den Hende et al. 2012; Sonck 2012) Solubility of CO_2 decreases when salt concentration increases and decreases when temperature increases, potentially causing microalgal photosynthesis efficiency also to decline with increasing temperature (Ho et al. 2011).

Most microalgal species are capable of carrying out photosynthesis and cellular division at 15-30 °C, with optimal conditions at 20-25 °C. pH is an important factor which significantly affects the growth of the algae. Most microalgal species are favoured by neutral or slightly alkaline pH, whereas some species are tolerant to higher pH (e.g. *Spirulina platensis* at pH 9) or lower pH (e.g. *Chlorococcum littorale* at pH 4) (Kumar et al. 2010). The variation in pH affects the solubility and availability of nutrients, enzyme activity, and photosynthesis (Singh & Ahluwalia 2013). On the other hand, the dissolution of CO_2 tends to decrease pH, and also ammonia (NH_4^+) decreases pH due to the release of H^+ ions. Further, not only does pH affect the growth of microalgae, but also an increase in algal biomass may increase the pH of the solution. This increase is assumed to be due to the removal of hydroxide ions (OH-) from the cells, as a result of the intracellular conversion of bicarbonate into CO_2 for photosynthesis (Sonck 2012).

Carbon dioxide exists in water in different forms, see eq. (1). Bicarbonate is dominant in pH 6-10, commonly found in microalgae cultures.

$$CO_2(aq) + H_2O <-> H_2CO_3 <-> HCO_3^- + H^+ <-> CO_3^{2-} + H^+ \quad (1)$$

Microalgae utilise CO_2 via the Calvin cycle. Thus carbon exists also in the forms of bicarbonate and carbonate in water, not all of the dissolved carbon is directly

available in photosynthesis. However several species are also able to convert bicarbonate to CO_2. (Van Den Hende et al. 2012; Sonck 2012, Teir 2014)

4.2 Effect of CO_2 concentration

Atmospheric CO_2 levels (~0.04%) are not sufficient to support the high microalgal growth rates and productivities needed for full-scale biofuel production (Singh & Ahluwalia, 2013; Kumar et al. 2010). Actually, microalgal productivity in raceway ponds is limited to about 3 g/m^2-d when supplied only from atmospheric CO_2 diffusing into the ponds (Benemann 2013). High concentrations of CO_2 (1-15 %) have been reported to enhance microalgal growth rate compared to atmospheric CO_2 in several studies. For example an increment of 58% in growth rate, when using 15 % CO_2 instead of air, of *Nannochloropsis sp* has been reported (Lam et al., 2012).

The tolerance of various microalgal species to the concentration of CO_2 is variable; however several microalgal species have shown good tolerance to sparging with gas containing 5 to 20% CO_2, i.e., concentrations as in flue gas. Tolerance up to even 40 and 100% of CO_2 have been reported. (Van Den Hende et al. 2012).

A high concentration of CO_2 may, however, have an inhibitory effect on algal growth (Lam et al 2012). A high concentration of CO_2 induces low pH which may inhibit the growth rate. This pH reduction may have a substantial role in CO_2-related growth inhibition (Sonck 2012) as some species are also sensitive toward pH changes (Lam et al. 2012).

The CO_2 concentration in the gaseous phase does not necessarily reflect the CO_2 concentration to which the microalga is exposed during dynamic liquid suspension, as this concentration depends on the pH and the CO_2 concentration gradient created by the resistance to mass transfer (Kumar et al. 2010).

Growth rate evaluations of biomass are critical in assessment of CO_2 capture of waste gases in high concentration, as growth rate and CO_2 capture correlate positively with each other (Razzak 2013). However CO_2 capture is not directly measurable from growth rate as the chemical composition and carbon content of alga cell varies within different algal species.

4.3 Flue gas as a carbon source

Sonck (2012) has reviewed the utilization of flue gas as a carbon source for microalgae in his master thesis, thus only a short overview is given here.

There are two possible methods for supplying CO_2 from flue gas to algal cultivations: CO_2 can be either be first separated from flue gas and fed into the cultivation as pure CO_2 or flue gas can be used directly. Direct utilization of flue gas is essential to the profitability of microalgal CO_2 capture as separation of CO_2 causes significant

additional costs. (Sonck 2012) Flue gas contains typically CO_2 between 10 − 15 % in coal- and oil-fired power plants, and below 10 % in natural gas -fired power plants (Sonck 2012).

Utilization of flue gas as carbon source for microalgae sets further requirements to the selection of the algal species. This is not only due to high CO_2 concentration or the induced pH caused by high concentration of CO_2 as described earlier, but also the because of presence of other, potentially toxic, compounds in the flue gas (Lam 2012).

The trace acidic gases that flue gas contains may affect the pH of cultivation system. When the concentration of SO_2 is high (>400 ppm), the pH of the medium will decrease, potentially resulting in low productivity. Nitric oxide, NO at around 300 ppm (gas phase) does not directly affect microalgal growth because NO absorbed by the cultivation medium is changed to NO_2–, and thus can be further used as a nitrogen source of algae (Kumar et al. 2010). Although toxic effects from NOx and SOx not related to pH change also exist, however microalgae have been grown successfully in experiments conducted with gas containing CO_2, NOx and SOx in concentrations typical of flue gases (Sonck 2012).

Heavy metals originating from flue gas are also potential inhibitors of microalgal photosynthesis because they can replace or block the prosthetic metal atoms in the active site of relevant enzymes, or otherwise induce morphological changes in the microalgal cells that lead to physiological problems (Kumar et al. 2010).

In conclusion, the possibility of cultivation microalgae with flue gas has been reported in the experiment literature and there are also many research and demonstration projects on utilising flue gas to grow algae (Zhang 2015).

5 Selected microalgal products and CO_2 capture

Microalgae are currently cultivated in relatively small-scale systems, mainly for high value human nutritional products (Benemann 2013). In this study, large scale systems for low or medium cost commodities are evaluated. Several types of biofuels or biomass may be produced from algal biomass, each with a specific production process. For this study two different biofuels, or actually biofuel intermediates were selected; biogas and lipids, in addition fertilizer was selected to be in focus.

5.1 Lipids

Lipids can be extracted from algal biomass and further processed to biodiesel, and used directly in conventional diesel engines (Brennan & Owende 2010). The quantity and composition of lipids are key properties that determine biodiesel oxidative stability and performance properties (Zhang 2015).

5.1.1 Lipid content and lipid productivity

Microalgae have been identified as promising feedstocks for industrial-scale production of carbon-neutral biodiesel. Lipid productivity is said to be the most important feature of any microalgal oil production system (Griffiths & Harrison 2009; Quinn & Davis 2015).

In general, the algae can produce either lipids (*Nannochloropsis, Trachydiscus* and other members of *Eustigmaceae*) or starch (most *chlorococcal* and *volvocean* algae) as their energy and carbon reserves. From the renewable energy view, when selecting an algal strain it is important not only to choose an alga with high growth rate, but also one with the capability to achieve high lipid content (Pribyl et al. 2014).

Griffiths & Harrison (2009) have reviewed lipid content and productivity of different algal species from numerous articles. They also noted that lipid productivity is an under-reported variable, although it is a critical variable for the evaluation of algal species for biodiesel production. Lipid productivity is the product of lipid content and biomass productivity, hence, it is dependent on both. According to Griffiths & Harrison (2009) lipid content has not been shown to be a reliable indicator of lipid productivity, whereas a more dominant correlation was observed between biomass and lipid productivity. The faster growing species may have higher lipid productivity than those with higher lipid content. However, high lipid content may improve the efficiency of lipid production. Moreover, it is reported that accumulation of lipids and high growth rate of algal biomass are mutually exclusive characteristics (Pribyl et al. 2014).

A two-stage cultivation process has been suggested to enhance the lipid content in microalgal cells. (Lam et al., 2012, Ho et al., 2014). In the first stage, microalgae are grown rapidly in nutrient rich medium supplied with a high concentration of CO_2 to allow a high growth rate and high production. In the second stage microalgae is transferred into nutrient deficient media to increase the lipid content of the microalgae. Currently, nitrogen limitation is the most frequently used treatment to enhance lipid production in microalgae (Li et al. 2013). Other possibilities are silicon or phosphorous limitation. Lipid production is also being enhanced by improvements in lipid metabolic pathways using genetic engineering tools or optimizing utilisation of energy inputs, such as light intensity. Changes in salinity and pH have also shown to enhance the lipid content. (Pribyl et al. 2014)

The response of biomass productivity to nutrient limitation has been shown to vary widely between species. Table 5**Error! Reference source not found.** shows some recent achievements in lipid productivities using CO_2 as carbon source. However, cultivation of heterotrophic/mixotrophic algal species has been shown to have greater potential to increase lipid content than autotrophic species (Chen et al. 2015; Ghasemi et al. 2012). The lipid productivity of thermotolerant algae *Desmodesmus*

sp. F2 of 263 mg/L/d, reported by Ho et al. (2014), is among the highest levels of reported. In the study three day growth period and nitrogen depletion up to nine days after that were used.

Table 5. Overview of relevant recent achievements in maximal microalgal lipid productivities; only values exceeding 0.1 g / l /day using CO_2 as carbon source are presented (Modified from Pribyl et al. 2014)

Microalgal strain	Cultivation mode	Oil productivity (g l^{-1} d^{-1})	References
Chlorella vulgaris CCALA 256 (= *Chlorella minutissima* UTEX 2219)	Laboratory, tubes 50 ml Thin-layer PBR, 150 l	1.425±0.135 0.326±0.010	Přibyl et al. (2012a)
Chlorella minutissima UTEX 2219	Laboratory, flasks 650 ml	<0.155	Tang et al. (2011)
Chlorella vulgaris FACHB1068	Laboratory, 2 l	0.147	Feng et al. (2011b)
Chlorella zofingiensis ASU 2	Laboratory, tubes 300 ml	0.312	Chen et al. (2011b)
Chlorella sp.	Laboratory, PBR, 800 ml	0.114±0.016	Chiu et al. (2008)
Neochloris oleoabundans UTEX 1185	Laboratory, bottles 800 ml	0.133	Li et al. (2008)
Pseudochlorococcum sp. LARB 1	Laboratory, PBR 1.2 l	0.35	Li et al. (2011b)
Nannochloropsis oculata NCTU-3	Laboratory, PBR 800 ml	0.142	Chiu et al. (2009)
Nannochloropsis sp. F&M-M24	Outdoor PBR, 110 l	>0.250	Rodolfi et al. (2009)
Nannochloropsis sp.	Laboratory, columns 1 l	0.41	Pal et al. (2011)

5.1.2 Lipid extraction and further processing

The methods used for the extraction of lipid from microalgae can be divided into mechanical and chemical methods (Muburak et al. 2015). Chemical methods of lipid extraction include Soxhlet extraction, supercritical fluid extraction, and accelerated solvent extraction; mechanical methods include oil expeller, microwave assisted extraction, and ultrasonic assisted extraction. The chemical methods use organic solvents like n-hexane, which are toxic. The supercritical fluid extraction technology eliminates the use of toxic solvents and uses non-toxic CO_2 gas as solvent. Hexane (non-polar) has been used extensively throughout the world as a solvent for extracting vegetable oils.

Some species of microalgae have high lipid content; however, almost all species of microalgae have their lipids located inside the cells. The rigid cell walls and toughness of cell membranes of microalgae make the lipids not readily available for extraction. Cell disruption is often required for recovering intracellular products, such as lipids, from microalgae. According to Lee et al. (2012) the energy required for cell disruption may become a critical consideration in the production of low valued commodities such as biofuels.

A variety of methods is currently available for cell disruption. These techniques are divided into two main groups based on the working mechanism of microalgal cellular disintegration, i.e., (i) mechanical and (ii) non-mechanical methods. Mechanical methods include, among others, bead milling, high pressure homogenization, ultrasonication, and pulsed electric field. Non-mechanical methods can be chemical or enzymatic. (Günerken 2015). Mechanical treatments usually give some kind of

strong force, such as shear stress, acting on the cell wall, so that the cell wall is torn directly into pieces. Also combinations of mechanical and non-mechanical methods have been tested (Wang et al. 2015). Ultrasonication, high pressure homogenization and bead milling are the most widely used mechanical methods.

Removing water, beyond 10–30 wt-% dry biomasses, is energy intensive. Therefore, if a lipid extraction methodology can be applied to a wet feedstock, it can save a lot of energy.

Transesterification is the main method to produce biodiesel from lipids. It can be performed by a homogenous catalyst method where triglycerides react with short chain alcohols in the presence of acid or base catalysts. Other methods are based on heterogeneous catalysts, where unlike homogenous catalyst the heterogeneous catalyst can be recycled, and in-situ transesterification where extraction and transesterification are performed simultaneously (Lam et al. 2012; Brennan & Owende 2010).

5.2 Biogas

Anaerobic digestion (AD) is a process of decomposition of organic matter by bacteria into biogas in an oxygen free environment. Substrate, for example organic waste is converted to biogas containing methane (55-70%) and carbon dioxide (30-45%), and also traces from other gases such as hydrogen sulphide and water vapour. Anaerobic digestion occurs in three sequential stages of hydrolysis, fermentation and methanogenesis (Kwietniewska & Tys 2014, Brennan & Owende 2010, Costa & Mora 2011).

Optimal process conditions for biogas production are temperature 30-35°C, pH 6.8-7.5, a C/N ratio from 20 to 30, and time of digestion 20-40 days. The process is performed in high moisture content 80-90%. In the AD process, remineralisation of phosphorous and nitrogen occur and these nutrients remain in the residual. So the remaining residuals, containing both a liquid and solid phase, may be used as nutrients for algal cultivation, soil fertilizer and conditioners, animal feed or may be incinerated (Costa & Morais 2011, Ward 2014, Kwietniewska & Tys 2014).

There are different alternatives for using algae in anaerobic digestion. Pathways are illustrated in Figure 4. These include (i) direct digestion after harvesting algae, (ii) digestion after cell wall disruption and (iii) digestion after lipid is extracted for biodiesel production purposes.

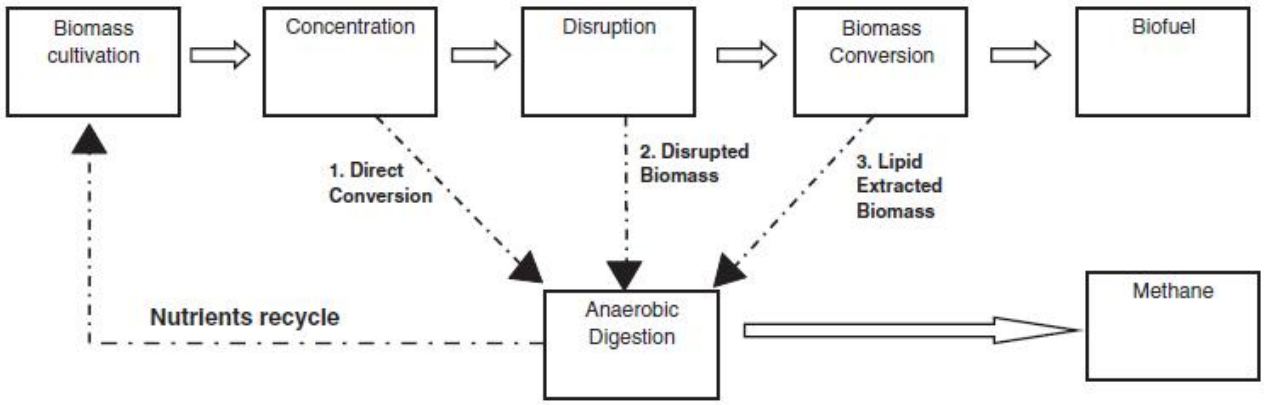

Figure 4. Conceptual visualisation of anaerobic digestion in algal biofuel production. (Ward 2014)

5.2.1 Theoretical yield

The theoretical yield of methane and carbon dioxide can be calculated from equation (1) (Bueswell et al. 1957).

$$C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 + \left(\frac{4a-b+2c+3d}{8}\right)CO_2 + d\,NH_3 \qquad (1)$$

The equation overestimates the biogas production, since it assumes 100% conversion of volatile solids (VS) to biogas and does not take into account the needs for organic matter degradation for bacterial metabolism and maintenance (Kythreotou et al. 2014). Table 6 shows the methane yield for three types of organic compounds in microalgae. Based on Ward et al. (2014) theoretical methane potential depends on the chemical composition of the used microalgal species, varying from 0.260 to 0.414 L/g VS destroyed.

Table 6. Specific methane yield for three types of organic compounds. (Kwietniewska et al. 2014)

Substrate	Composition	g COD · g-VS^{-1}	L CH_4 · g-VS^{-1}	CH_4 (%)
Proteins	$C_5H_7NO_2$	1.42	0.446–0.496	50
Lipids	$C_{57}H_{104}O_6$	2.90	1.014	70
Carbohydrates	$(C_6H_{10}O_5)n$	1.19	0.415	50

5.2.2 Experimental yield

Many experimental studies of anaerobic digestion of microalgae can be found in the literature. Methane yield ranging from 0.14 to 0.6 L/g VS (Ward et al. 2014; Uggetti et

al. 2014) are reported. The large variation is mainly due to strain specific cell wall properties.

5.2.3 Challenges

Cell walls of microalgae could protect the cell against the enzymes produced by the anaerobic consortium, and thus reduce the cell biodegradability. Indeed, some microalgal species are very resistant to hydrolysis, which drastically reduces their anaerobic biodegradability (Sialve et al. 2009). Carbohydrate based cell wall is reported to decrease gas production. Also, degradation of the cell walls is noted to correlate strongly with the amount of gas produced during digestion. (Ward et al. 2014; Kwietniewska & Tys 2014). For example Ward et al (2014) reported that cell wall disruption was needed to increase the methane potential of microalgae. Subjecting biomass to physicochemical treatment before digestion weakens the rigid cell wall structure and allows methanogens to consume the organic compounds inside the cell. Various mechanical, physical, thermal and chemical pre-treatment methods are applied for this purpose (Ward et al. 2014). Cell wall disruption is discussed earlier in chapter 5.1.2. However, these methods may have a high energy requirement, even as high or higher than the energy content of biogas gained from microalgal biomass. Due to this high energy demand, alternative low energy methods such as enzymatic or bacterial hydrolysis are also being investigated (Kwietniewska & Tys 2014).

Ammonia-nitrogen is produced from the biological breakdown of nitrogenous matter, mostly in the form of proteins and urea. **Ammonia-nitrogen toxicity** is a challenge in microalgal digestion.

Ammonia inhibits anaerobic digestion, but according to Ward et al. (2014) there is a large amount of conflicting information in the literature relating to the ammonia-nitrogen tolerance of anaerobic microbes. (e.g. 4200 mg/L has been inhibitory in some cases compared to 10 000 mg/L in other cases). Generally the toxicity is pH- and temperature dependent. An increase in pH or temperature can increase ammonia-nitrogen toxicity as these changes result the ammonium equilibrium toward free ammonia, which is the main cause of inhibition.

Highly proteinaceous composition of micralgae enhances the formation of a digested sludge with very a **low C/N ratio**.

The carbon/nitrogen ratio average for fresh water microalgae is 10.2 (Kwietniewska & Tys 2014). From reported experimental studies on microalgae digestion, the values such as 4.16 (*Spirulina maxima*) and 7.82 (*Tetraselmis*), can be found.

The preferred C/N ratio in anaerobic digestion is 20-35, thus when the C/N ratio is below 20 there is an imbalance between carbon and nitrogen availability for the anaerobic bacterial community and increased amount of free ammonia is released.

The commonly applied solution is to increase the C/N ratio by co-digestion with substrates containing low amounts of protein. (Ward et al. 2014; Kwietniewska & Tys 2014).

Lipids are attractive compound for AD as the theoretical methane yield of lipids is higher than that of other components of microalgae (proteins, carbohydrates). However, long chain fatty acids can cause inhibition to the anaerobic digestion process. Short chain fatty acids are not toxic themselves, however they might inhibit the AD process indirectly, because they may lower the pH to an undesirable level. (Ward et al. 2014; Kwietniewska & Tys 2014) It has been suggested that the conversion of microalgal biomass to methane rich biogas is energetically more favourable than lipid removal from microalgal biomass when the total lipid content is lower than 40% (Sialve et al. 2009). However, it has also been reported that the removal of lipids from microalgal biomass for liquid biofuel production prior to anaerobic digestion can be beneficial to the anaerobic digestion processes because of the inhibition from high lipid concentrations (Ward et al. 2014).

High salinity levels have been shown to be inhibitory as they may cause bacterial cells to dehydrate. Of mineral ions found in seawater, sodium is the strongest inhibitor to anaerobic digestion. However, the presence of sodium ions has also shown to reduce the inhibitory effect of ammonium-nitrogen. Electrical current have been used to overcome sodium inhibitory effect. Anaerobic microflora can also be adapted to salt environment and then the above mentioned inhibition effect may not occur (Ward et al. 2014; Kwietniewska & Tys 2014).

Oxidised **sulphur** compounds may be present in saline algae and saline waters. These sulphur compounds can produce hydrogen sulphide gas in anaerobic digestion, which, when present in gas, is corrosive and can cause damage to machinery, such as gas engine power generators, and piping. Except for sulphide, sulphur compounds below very high concentrations are not harmful to anaerobic bacteria. A small amount of sulphide in low concentration is needed for cellular metabolism by bacteria. (Ward et al., 2014; Kwietniewska & Tys 2014)

5.2.4 Nutrient recycling

Anaerobic digestion of algal biomass produces a nutrient-rich residual containing both nitrogen and phosphorus. The use of this residual from digested microalgal biomass is highlighted in many studies and has been proposed to be used as a nutrient source for further microalgae growth. Another benefit of integrating anaerobic digestion with algal cultivation is the ability of microalgal cultures to enhance the methane content of the biogas. Methane has been shown to be non-detrimental to microalgae growth and utilising the microalgae culture to strip carbon dioxide gas from the biogas would be beneficial. (Ward et al. 2014).

5.3 Biofertilizer

Historically, macroalgae have been used for soil fertilization in coastal areas all over the world (Pultz 2004). Algae biomass is known to improve water-binding capacity and the mineral composition of the soil, in addition to their nutritional content (Kumar et al. 2010; Skjånes et al. 2007). Increasing organic matter in soils may cause other greenhouse gas-saving effects, such as improved workability of soils, better water retention, less use (and consequently production) of mineral fertilizers and pesticides, and reduced release of nitrous oxide. Some conversion technologies, most notably pyrolysis, result in the formation of the solid charcoal residue biochar, that has potential agricultural applications as a bio-fertiliser (Brennan & Owende, 2010).

According to Benemann (2003) microalgae produced in algal facilities provide an opportunity to recover fertilizer compounds, both nitrogen and phosphorous, from wastewaters. Phosphorous removal is often limited by the amount of nitrogen present in wastewaters. Based on this N_2-fixing cyanobacteria is proposed for fertilizer production in a microalgal facility. N_2-fixing cyanobacteria have been studied for example in final “polishing” stage to remove P. (Benemann 2003).

According to Pultz (2004) a future trend seems to be the use of the biological activity of microalgal products against plant diseases caused by viruses or bacteria. It is likely that microalgae can be a source of a new class of biological plant protecting substances.

In the perspective of CO_2 capture, biofertilizer is a good product as fixed CO_2 in agriculture is estimated to have a retention time of 50–100 years (Skjånes et al. 2007), compared to the case where algal derived biofuels are burned releasing the CO_2 back to atmosphere.

6 Economic overview of algal based biofuels

Currently, algal biofuel or other large scale algal production utilizing industrial CO_2 has not been commercialized due to high costs associated with production, harvesting and oil extraction but the technology is progressing. In the future, crude algal oil may be an important renewable feedstock not only for energy and fertilizer but also for the chemical or food industries. Several start-up companies are already attempting to commercialize algal oil, mostly in the United States (Pribyl et al. 2014).

Techno-economic analysis represents a powerful tool that can be used to better understand the current commercial viability of microalgal systems. Quinn & Davis (2015) has reviewed the techno-economics of algae based biofuels (over forty assessments) and as result they summarize that a large variability exists in the results. These are mainly caused by differences in productivity assumptions, production pathways, growth architecture and financial inputs. They highlight the

productivity as a primary input from a process standpoint for techno-economic calculations. The values reported for lipid productivity varied from 2.3 to 136.9 m^3/ha/year in different studies. Differences between values are caused by the source of productivity, the lowest values originate from outdoor system currently operated (Lam & Lee 2012) and the highest are representing future potential usually scaled up from laboratory results (Chisti 2007, Mata et al., 2010). Also the choice between open race way ponds and photobioreactors (PBR) affects significantly the costs. According to Quinn & Davis (2015) review open race way pond systems are economically advantageous by more than a factor of 2. Delrue et al. (2012) also highlights the cultivation steps and productivity as major bottlenecks in microalgae based biofuel production, in addition to lipid accumulation and effective wet biomass technologies. According to Quinn & Davis (2015) the economic studies of PBR currently assume similar productivities and culture stability as modelled in open pond systems, which does not accurately capture the expected function of a large-scale PBR system as improved productivity and culture stability are expected compared to open systems.

As mentioned earlier, modelling of the productivity and growth of microalgae is a critical component in techno-economic assessments. Large variations in productivity assumptions (Figure 5) between different assessments directly contribute to large variation in the results. Biofuel cost between $1.65 and $ 33.16 per gal i.e. 0.34-7.00 €/l are reported in the literature. Figure 6, drawn by Quinn & Davis (2015), shows that the economic viability of microalgae biofuel systems is positively and drastically impacted by increased lipid productivity. In the literature most assessments of microalgal based biofuel production systems have relied on growth models extrapolated form laboratory-scale data, leading to large uncertainties in the data. According to Moody et al. (2014) and Quinn & Davis (2015) this type of growth modelling overestimates the productivity potential and fails to include biological effects, geographical location or cultivation architecture. Moody et al. (2014) determined a world average near-term lipid productivity of 17 m^3/ha/year, corresponding biomass yield of 9.4 g/m^2/day. The highest global lipid yields determined in the study by Moody et al., (2014) ranged between 24 and 27 m^3/ha/year (corresponding biomass yields of 13–15 g/m^2/day). The study used a validated outdoor photobioreactor to model the growth of *Nannochloropsis* and to determine the lipid productivity potential of microalgae around the world by integrating hourly meteorological data for over four thousand sites. In comparison to this, Weyr et al. (2009) have reported a thermodynamic theoretical best case practical yield of 40 m^3/ha/year. Values from both of these studies (Moody et al. 2014; Weyer et al. 2009) fall into the lower half of the values reported in Figure 5, indicating overestimation of productivity assumptions in some techno-economic analyses.

The techno-economic analysis becomes more rigorous if, instead of annual productivity, the seasonal variation in productivity is included. The variation in productivity between peak and minimum seasons can be 5-10 : 1 (Quinn & Davis 2015), giving an additional design aspect on processing equipment. When the performance of a process is season-dependent it causes over-sizing of the facility capacity for portions of the year, thus increasing the investment costs (ANL, NREL, PNNL 2012).

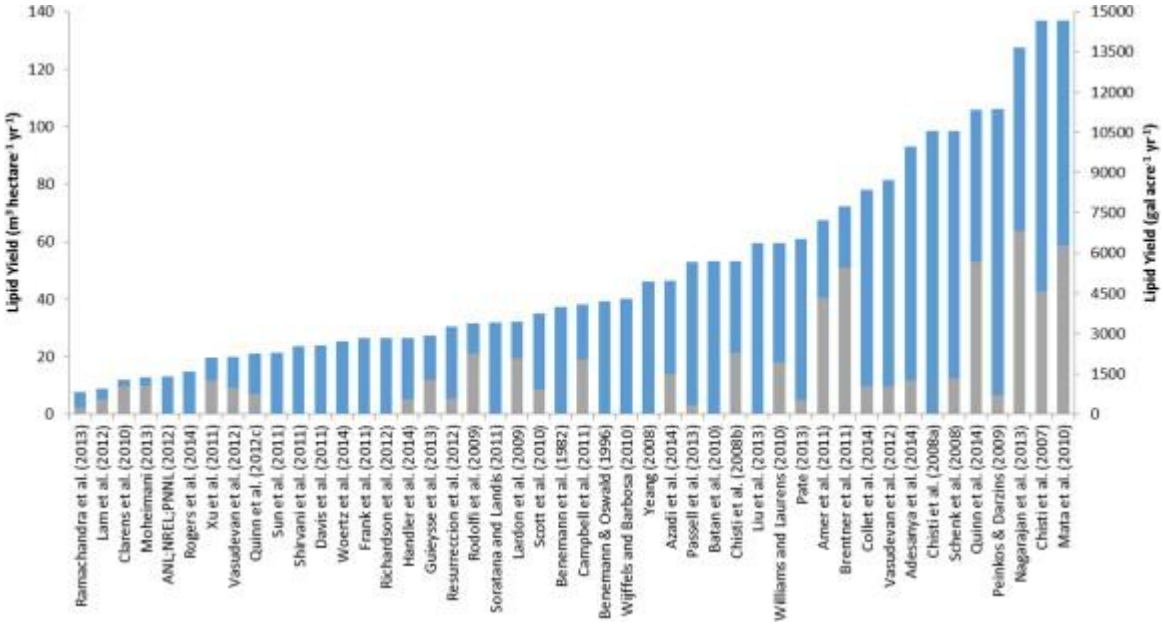

Figure 5. Lipid productivity assumptions for growth systems found in life cycle, techno-economic, and scalability assessments. Some studies report a range for the productivity with the high end reported and the low end illustrated in grey (Quinn & Davis 2015).

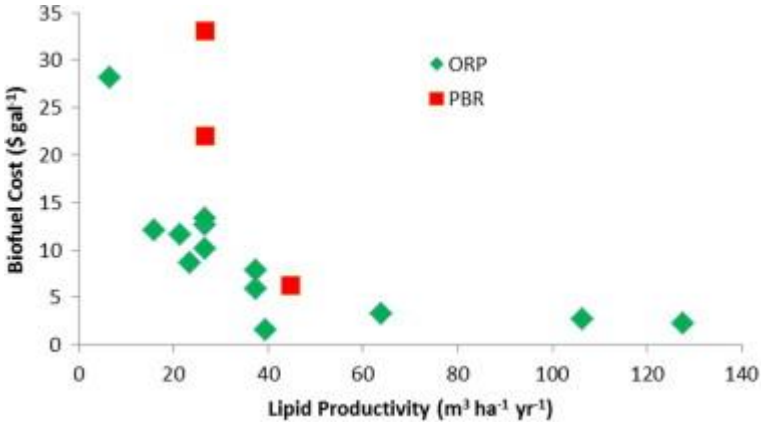

Figure 6. Comparison of lipid productivity to biofuel cost (2014 dollars) as reported in the literature (post 2007) with PBR and ORP growth architectures differentiated. (Quinn & Davis 2015)

CO_2 is essential in algal cultivation. According to Quinn & Davis (2015) challenges associated with the economical delivery and utilisation of gaseous CO_2 have typically been ignored or underestimated in TEA analyses. Typically the co-location of algae production facilities with an industrial carbon dioxide source is assumed without scalability implications. Quinn & Davis (2015) have reviewed that 80 milj. m^3 algae based oil can be produced when utilizing 20% of US waste carbon dioxide annually. Ribeiro & Silva (2013) pointed out that in many cases CO_2 could be provided for free, it could be paid or company producing CO_2 could pay the algal biomass producer to process CO_2. The existing and future carbon markets, coupled with more stringent limits of the emissions, may lead to companies increasingly paying to dispose off of their CO_2 emission, which may results in lower microalgal biomass production costs.

7 Conceptual level techno-economic analysis of selected microalgae-based carbon capture concepts

In the following we present four concepts for algal cultivation with industrial CO_2 and further processing of the algae for renewable energy and/or fertilizers. These concepts are named according to each product portfolio: BIOGAS, LIPID-BIOGAS, LIPID and FERTILIZER (Figure 7).

The study is a conceptual level techno-economic evaluation of the processes described later. Mass and energy balances are estimated. Usage of raw material, utilities, and need of chemicals are evaluated, and the variable production costs are estimated based on these. Also, estimates of capital expenses and fixed costs are calculated.

Fixed costs include (estimated based on Andersson (2009))

- operating labour costs

- administration and non-operating labour costs – 1.5 times operating labour costs
- Maintenance costs – 2 % of total capital investment cost
- Miscellaneous costs – 1 % of total capital investment cost
- Capital charge

Operating labour need is estimated from Lundquist et al. (2010) where it is 12 to 14 full-time operators for 100 ha algae facility. The process evaluated here is very large (4000 ha) and it is assumed that to build up such a large system several smaller sites are required. It is assumed that this bigger facility needs from 8 to12 persons per 100 ha depending on complexity. The following amounts of operators per 100 ha were selected; BIOGAS 10, BIOGAS-LIPID 12, LIPID 9, FERTILIZER 8.

Ten year straight line method is used to estimate annual capital charge.

7.1 Concept definitions

A schematic view of the concepts is shown in Figure 7.

In all concepts, similar technology for algal cultivation and harvesting was selected. We assume algae are grown in open raceway ponds, dewatered from solid content of 0.1% by settling, dissolved air flotation (DAF), and filtration to solid content of 20 %. For the concept BIOGAS only settling and DAF is needed.

In the concept of BIOGAS-LIPID, harvesting is followed by cell disruption and a wet extraction process. Residuals are sent to anaerobic digestion (AD) for biogas production and nutrient recycling. Solid residual from AD is dried and used as fertilizer.

The BIOGAS concept is similar to BIOGAS-LIPID concepts, excluding the LIPID extraction process and secondary harvesting.

In the LIPID concept, algal biomass is dried followed by lipid extraction. Residual biomass is utilised as biofertilizer.

In the FERTILIZER concept whole algal biomass is dried to be utilised as biofertilizer.

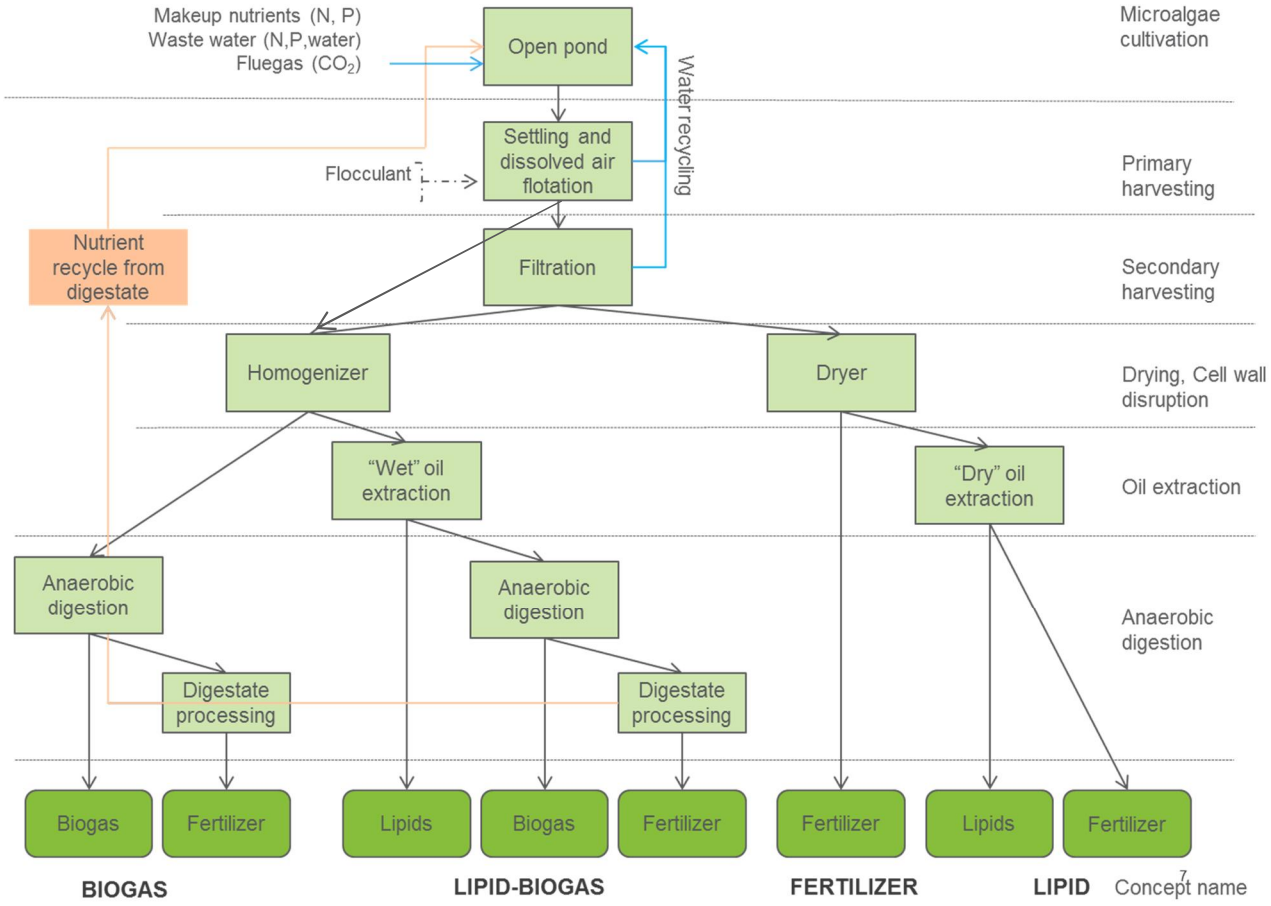

Figure 7. Schematic view of the concepts studied. Digestate processing includes phase separation and drying of solid digestate.

7.2 Initial data and assumptions for calculations

In the following chapters the selected technologies are presented along with the used assumptions. Power and energy consumption data, with references, are collected in Table 8. The yields of the unit operations are shown in Table 9.

7.2.1 Capacity and characteristics of algae

The choice of algal specie is influenced by indicators such as biomass productivity and lipid content; in the case of lipid production the lipid productivity is a key factor. Characteristics, such as ease of cultivation and harvesting are also vital for large-scale algae based production. The culture system, resources available, location and prevailing environmental conditions also govern the final choice of algal species, as well as the scope of production, which in this case is one of the three selected products in co-operation with CO_2 capture. The approach in this study is generic and based on modelling without own experimental data. Specific algal specie is not selected, but the assumed characteristics of algae are listed here.

Algae composition is modelled with their three main components; lipids, carbohydrates and proteins. The nitrogen and phosphorous content of algae are also calculated. Every concept includes two scenarios. Two levels of lipids (10% and 30%) are evaluated in the scenarios. Algae in the lipid rich scenario contain less protein than in the other scenario and they are assumed to contain correspondingly less nitrogen and phosphorous (Table 7).

Table 7. Algae composition in different scenarios.

	scenario 1	scenario 2
Lipid	30 %	10 %
Proteins	35 %	45 %
Carbohydrates	35 %	45 %
N	5.0 %	8.7 %
P	0.8 %	1.3 %

A realistic, but still optimistic value for biomass productivity 25 g/m^2/day is selected in this study. The value corresponds to 9 and 27 t/ha/year lipids (lipid content 10% or 30% respectively). The same biomass productivity is used for both lipid contents.

A large scale system is selected to be able to capture large amounts of CO_2. The selected capacity in the study (4000 ha raceway open ponds), utilizes 110 t/h CO_2 with 75% efficiency. This can be compared to an existing power plant, for example a coal fired power plant at Meri-Pori in Finland which generates 500 MW electric power and produces around 360 t/h CO_2. Hence, a 4000 ha open pond system would need the amount of CO_2 available from a power plant of approximately 150 MW.

7.2.2 Cultivation

Open raceway ponds are selected as cultivation architecture as these are at least two times more economic than photobioreactors (Quinn & Davis 2015). 95 % of the process water is circulated back to cultivation, 5 % is discharged as waste water from the system. The open pond depth is 0.2 m and evaporation from ponds is 0.06 cm/day (ANL, NREL, PNNL 2012).

Carbon dioxide for the cultivation comes from a nearby power plant, with input concentration of 12.5% CO_2. 75 % of CO_2 is estimated to be consumed by algae and the rest is lost to the atmosphere. Consumption of CO_2 by algae is calculated based on the main components of the algae and the algae composition of the two scenarios described earlier in Table 3 and Table 4. Based on these, the carbon capture in scenario one would be 2.10 kg CO_2 / kg algae and in scenario two 1.89 kg CO_2 / kg algae.

To provide CO_2 to the ponds, the technology presented by Lundquist et al. (2010) is utilised. This technology relies on sumps with depth of 1 m located in the ponds. CO_2 spargers, in the bottom of sumps, provide fine bubbles for efficient CO_2 transfer.

Municipal waste water is used as a water and nutrient source. Waste water nitrogen and phosphorous content is estimated to be as follow: N 35 mg/L, P 7.5 mg/L (Lundquist et al. 2010). The carbon balance may be affected also by organic carbon in waste water. This option is added to the model and algae may use waste water as an additional carbon source. Light is always used as an energy source, therefore both photoautotrophic and photoheterotrophic growth is possible. The amount of carbon in waste water is estimated based on its biological oxygen demand (BOD) 200 mg/l (Lundquist et al. 2010) and using a BOD/TOC ratio 1 (TOC total organic carbon) (Metcalf & Eddy 2003).

Additional nutrients urea and diammonium phosphate (DAP) are purchased when necessary.

Zero price/credit is assumed for make-up waste water used in cultivation and for the discharged waste water.

7.2.3 Harvesting and dewatering

Low cell densities and the small size of some algal cells make the recovery of biomass difficult (Brennan & Owende 2010). Generally harvesting process for microalgae is a two stage process including bulk harvesting and thickening. Bulk harvesting, or separation of biomass from water aims to concentration of 2-7% total solids. Technologies concerned with bulk harvesting include flocculation, flotation and gravity sedimentation. Thickening or mechanical water separation, concentrates the slurry using technologies such as centrifugation, filtration or ultrasonic aggregation. (Brennan & Owende 2010) According to Molina Grima et al. (2003) harvesting is responsible of 20-30 % of biomass production costs. The selection of harvesting technique depends on the specie of microalgae, the final desired product(s) and the processes subsequently used. Desired microalgal properties which simplify harvesting are large cell size, high specific gravity compared to the medium, and autoflocculation properties (Ho et al. 2011; Udumann et al. 2010). Power consumption of harvesting depends in addition to the technology used on the concentration factor as well as on the initial and final concentration.

We selected settling with dissolved air flotation (DAF) as the primary harvesting method. Harvesting is accomplished first in a simple settling tank that concentrates the algae to 1% (Beneman & Oswald 1996, Davis et al. 2011) via autoflocculation. In the next step flocculated algae are concentrated with DAF to 5%. Chitosan (480 mg/m^3, Divakaran & Pillai 2002) is selected as a flocculant due to its biodegradability

in anaerobic digestion. For secondary harvesting filtration is selected. 20 % solid content is assumed after filtering.

Algal biomass slurry is perishable and must be processed rapidly after harvest. Dehydration or drying is a commonly used method. Drying the biomass after harvesting is a crucial step from techno-economic viewpoint, partially because it is a very energy intensive unit operation. Different drying methods utilized in algal biomass drying include sun drying, low-pressure shelf drying, spray drying, drum drying, fluidized bed drying, rotary drying and freeze drying (Brennan & Owende 2010; Ryan 2009). Little research has been done on evaluating the best possible methods of drying algae on large scale with biodiesel production in mind. When trying to isolate high value products, spray drying is often the method of choice; however, there is the risk of causing deterioration of pigments or other components. In laboratories, freeze-drying is commonly used, but it is too expensive to be used in large scale (Molina Grima et al., 2003). According to Ryan (2009) current drying practices appear to favour drum dryers over solar or freeze drying. In addition, rotary drying and other emerging methods may soon outperform conventional ones, due to drum dryer's considerably high energy consumption (Ryan 2009).

Low energy and high capacity rotary drying is selected as the final drying method, with thermal efficiency of 80 %.

7.2.4 Cell wall disruption

The selected technology includes cell wall disruption to recover intracellular products before wet extraction and also before anaerobic digestion. High pressure homogenization is selected. The specific energy consumption of disruption processes found in literature varies from 0.2 to 147 kWh/kg (Günerken et al. 2015; ANL NREL PNNL 2012; Milledge & Heaven 2011). Here the specific energy consumption is selected based on the ANL, NREL, PNNL 2012 report; 0.2 kWh/kg disrupted dry algae.

7.2.5 Lipid extraction

In lipid extraction the main question is whether algal oil is extracted from dry or wet algae. With wet extraction of algal oil, the energy consuming drying step is avoided. According to Lundquist et al. (2010) algae oil has not been extracted in full scale, and based on ANL, NREL, PNNL (2012) there is also only some experimental data available to support the solvent selection for wet extraction. In this study hexane is selected as a common solvent for both types of extractions. Hexane is seen to offer many processing advantages (ANL, NREL, PNNL 2012), such as a low boiling point (thus less heat demands for solvent stripping and recovery) and low water miscibility (thus low loss of solvent into the water phase during separation). Selected wet and dry extraction processes include hexane as solvent, with extraction to solvent ratio of

5 (solvent / dry biomass, ANL, NREL, PNNL report 2012). Solvent loss in circulation is estimated to be 0.3 % of the total solvent amount. Heat consumption of the extraction process is calculated based on the evaporation heat of the solvent.

7.2.6 Anaerobic digestion

Anaerobic digestion is performed for the whole algal biomass (BIOGAS concept) or the residual biomass after lipid extraction (BIOGAS – LIPID concept). The process is performed with 5% solid content. The residual liquid from AD is recirculated back to the algal cultivation to provide nutrients, solid residual is dried to be utilized as biofertilizer. Cell disruption with high pressure homogenization is performed before digestion to increase the methane production.

Methane yield in anaerobic digestion (AD) is calculated from the theoretical yield as described earlier in chapter 5.2.1. 70 % degradation of organic matter is assumed, implying efficient pre-treatment to disrupt the algal cell walls.

7.2.7 Electricity consumption and yields

Electricity consumption and yields, with literature references, are shown in Table 8 and Table 9.

Table 8. Specific energy consumptions of unit operations.

Unit operations		Unit	Estimate reference
Cultivation (Mixing)	1.875	kW/ha	ANL, NREL, PNNL 2012; Lundquist et al. 2010
CO_2 distribution	1	kW/ha	Lundquist et al. 2010
Settling & DAF	0.1	kWh/m3	Udom et al. 2013; Zamalloa et al. 2011
Filtration	0.5	kWh/m3	Wiley et al. 2011
Cell disruption	0.2	kWh/kg dry biomass	ANL, NREL, PNNL 2012
Thermal drying	0.032	kW/kg evaporated	Estimate
Extraction, dry	0.012	kWh/kg dry biomass	Lundquist et al. 2010
Extraction, wet	0.276	kWh/kg dry biomass	ANL, NREL, PNNL 2012
Pumping	0.045	kWh/m3	approximated from ANL, NREL, PNNL 2012
Anaerobic digestion, electric	0.085	kWh/kg-TS	ANL, NREL, PNNL 2012; Delrue 2012
Anaerobic digestion, heat	0.22	kWh/kg-TS	ANL, NREL, PNNL 2012

Table 9. Yields in unit operations in biological CO_2 capture.

Yields in unit processes		
	%	Reference / comments
Primary harvesting	96	ANL, NREL, PNNL 2012, harvesting tot 95 %
Secondary harvesting	99	ANL, NREL, PNNL 2012, harvesting tot 95 %
Drying of algal cell mass	99	Estimate
Separation of algae oil from cell mass	85.5	ANL, NREL, PNNL 2012, Disruption 90 % and extraction 95 %
Dissimilation of organic matter in AD	70	Lundquist et al. 2010
Dewatering of solid digestate	97	Estimate
Drying of solid digestate	99	Estimate

7.2.8 Unit prices

Estimates of lipids and biogas prices are based on crude oil and natural gas prices. The biogas price estimate is based on its methane content and the natural gas price. Between years 2010 and 2015 the natural gas price (Finish tax-free energy price) has ranged from 20 to 34 €/MWh (https://www.energiavirasto.fi/tilastot). For produced biogas a price of 25 €/MWh was chosen. Lipid or crude algal oil price is estimated from the crude oil price between years 2010-2015, the price has been 280-700 €/t. In this study we used the 5 year average 400 €/t. Biofertilizer price estimate is based on its nitrogen content and urea price; 730 € / t nitrogen. Similar nitrogen basis price estimates can be found in literature (730 €/t in Delrue et al 2012; 500€/t in Lundquist et al. 2010). Other operating cost assumptions are listed in Table 10. The assumed nearby power plant, which provides CO_2 to algae facility is assumed also to provide electricity in the own cost price of 45 €/MWh. Electricity price, that we used, is low compared to Eurostat price (for example Finland, year 2014: 72 €/MWh) (http://ec.europa.eu/Eurostat/statistics-explained/index.php/Electricity_and_natural_gas_price_statistics#Electricity_prices_for_industrial_consumers). The effect of possible higher electricity price is taken into account in sensitivity analysis.

Table 10. Unit costs assumption used in calculations.

	Price	**Reference**
Electricity	45 €/MWh	von Weymarn et al. 2007
Steam	35 €/MWh	estimate
Chitosan	8 500 €/t	Davis et al. 2011
Hexane	1000 €/t	Alibaba.com
Urea	260 €/t	www.indexmundi.com
DAP	390 €/t	www.indexmundi.com

7.2.9 Capital investment

Capital investment estimate of microalgal mass production in open raceway ponds is largely based on the techno-economic analysis carried out by Benemann and Oswald (1996). Unit operations which were not included in that work are estimated based on works by Davis et al (2011), ANL, NREL, PNNL 2012, Delrue et al. 2012 and Wrigth et al. 2010. All prices have been updated to 2014 euros. Equipment cost estimates taken from literature are installed equipment costs. Lang's method for approximation of total capital investment is used. In that method total capital investment (*TCI*) is calculated from the equation below (Peters et al. 2003).

$$TCI = F_l \sum C_e \quad (2)$$

In the equation F_l is Lang factor and C_E is purchased equipment cost. In our case installed equipment costs are used instead of purchased costs. This has been taken into account when estimating the value for Lang factor, which is based on ratio factors of capital investment items presented by Peters et al. (2003). Value of 3 is used.

The production capacity we use is large compared to capacities considered in literature studies. For example capacity in techno-economic analysis of Beneman & Oswald's (1996) is one tenth of that used here. Scaling up the equipment costs equation (3) is commonly used with the scaling factor (F) ranging from 0.2 to 1 depending on the equipment, being on average 0.6 (Peters et al. 2003).

$$C_E = C_B \left(\frac{Q}{Q_B}\right)^F \quad (3)$$

In the equation C_E is equipment cost with capacity Q and C_B is known base cost for equipment with capacity Q_B. The process evaluated here is very large and it is assumed that to build up such a large system several smaller sites are required. We assume that ten smaller plants are built next to each other, thus scaling factor 1 is used for upscaling most of the units. Extraction process makes an exception and 0.6 scaling factor is used there as the data is scaled down from typical large utility.

Capital cost estimate basis is shown in Table 11.

Table 11. Capital cost estimates in € 2014 for installed equipment.

		Unit	Source
Cultivation	13 372	€/ha	Benemann & Oswald 1996
CO2 sumps, diffusers	6 078	€/ha	Benemann & Oswald 1996
CO2 supply	6 078	€/ha	Benemann & Oswald 1996
Settling	8 509	€/ha	Benemann & Oswald 1996
DAF	2 431	€/ha	Benemann & Oswald 1996
Belt press	0.50	€ / (t water removed / year)	Delrue et al. 2012
Drying	40	€ / (t water evaporated/year)	Wrigth et al. 2010
Cell wall disruption	4 900	€/ha	ANL, NREL, PNNL 2012
Oil separation	2 670	€/ha	Lundquist et al. 2010
Anaerobic digestion	65	€ / (t dry residue year)	Davis et al. 2011; Delrue et al 2012
Water & nutrient delivery	6 321	€/ha	Benemann & Oswald 1996
Digestate drying	40	€ / (t water evaporated/year)	Wrigth et al. 2010

7.3 Results and discussions

All studied concepts produce 41 t/hour biomass (ash free dry weight). The water evaporation from the open ponds is 1000 m^3/h. Volumetric liquid flow from cultivation is 41 666 m^3/ hour, which corresponds 1.6 times the average flow in river Aura in Finland. Annual end-product production rates can be seen in Figure 8.

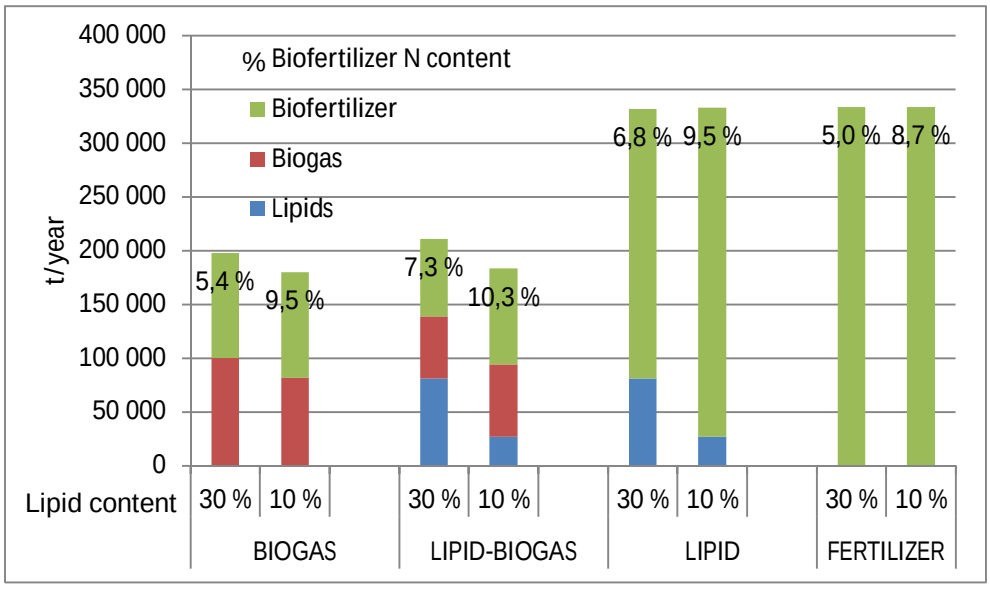

Figure 8. Biogas, lipids and fertilizer production in all four concepts. Fertilizer nitrogen content shown as percentages.

7.3.1 Capital investment

Total capital investment does not vary significantly between the different concepts (Table 12). It is highest (about € 585 million) in concept LIPID (emphasis on dry lipid extraction), and lowest in the BIOGAS concept being about € 550 million. Installed equipment cost breakdown for all concepts is shown in Figure 9. The share of cultivation with CO_2 supply and delivery technology is high, about 44 % of total investment costs. Investment cost of drying is also significant having a share of about 20 %.

Table 12. Total capital investment for all concepts.

	BIOGAS	LIPID-BIOGAS	LIPID	FERTILIZER
TOT M€	550	559	585	559
TOT k€/ha	138	140	146	140

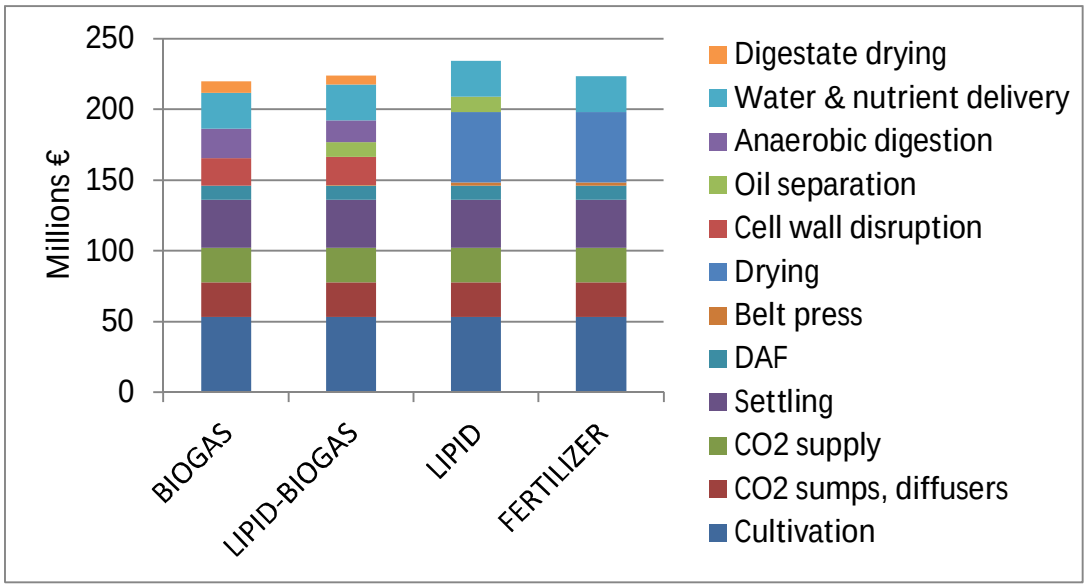

Figure 9. Installed equipment costs.

7.3.2 Revenues

Annual revenues are summarised in Figure 10. They are highest in co-production of lipids and biogas (concept LIPID-BIOGAS) and lowest in fertilizer (concept FERTILIZER) production. Altogether, biofuel production seems more profitable than fertilizer production. However the prize of fertilizer is estimated based on its nitrogen content only and this might underestimate its value as it also contains phosphorous and might have potential as a high value biofertilizer.

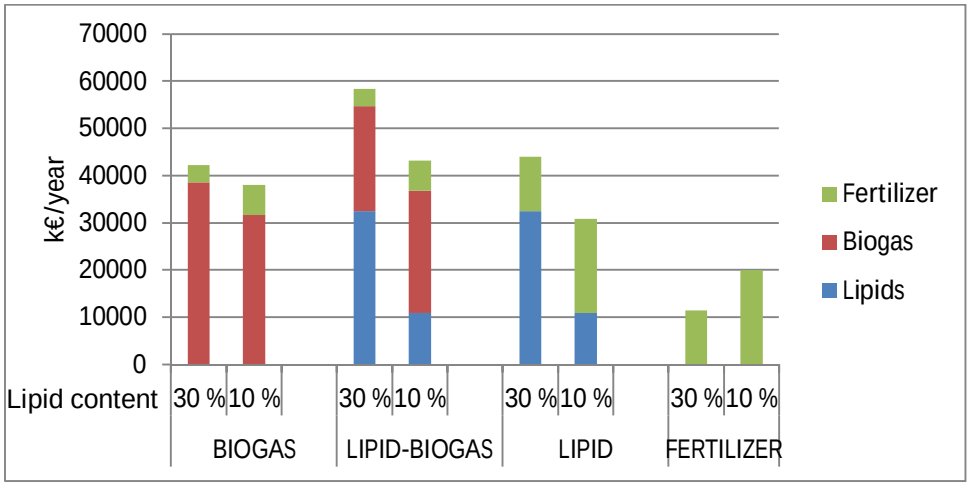

Figure 10. Revenues.

7.3.3 Production costs

Figure 11 compares the cost components and total revenues in all concepts. It shows that all evaluated concepts are unprofitable. Fixed costs (operating labour cost, capital charge and other fixed cost) dominate in all concepts. Variable costs

compared to the total revenues are shown in Figure 12. In the concept (LIPID, FERTILIZER) with biomass drying the heat consumption is the major cost contributor to the variable costs. Nutrient costs are high in concepts without AD, as in these concepts there is no recycling for nutrients. Actually already the nutrient costs in the FERTILIZER concepts are as high as or higher than total revenues.

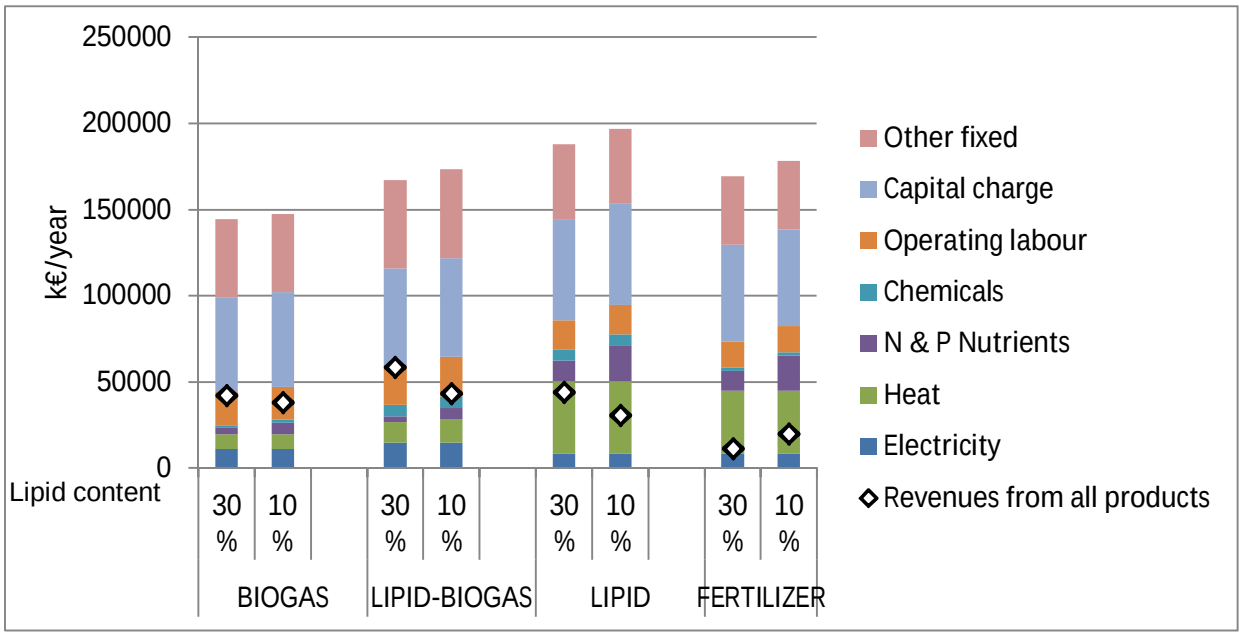

Figure 11. Cost components of evaluated concepts.

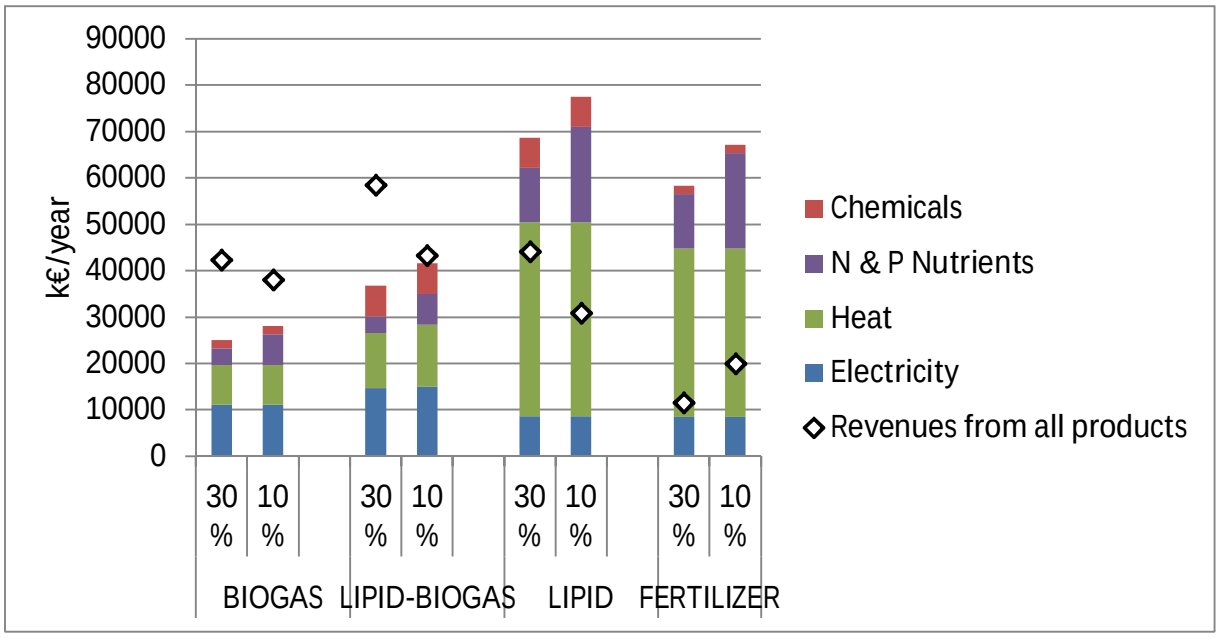

Figure 12. Variable costs for all concepts.

Electricity and heat consumptions are broken down in Figure 13 and Figure 14. Selected cell wall disruption and wet oil extraction technologies have high electricity

consumption. Cultivation with CO_2 feeding also has high electricity consumption. Harvesting (without drying) represents 10 to 20 % of whole electricity consumption. As expected drying the algal biomass consumes a lot of heat.

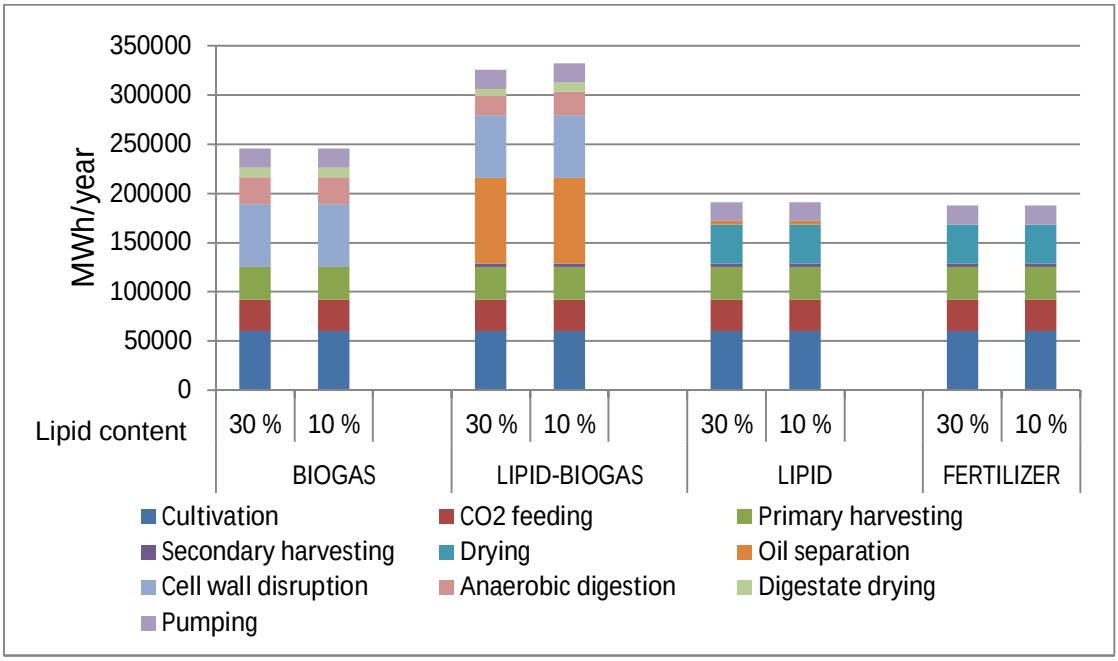

Figure 13. Electricity consumption

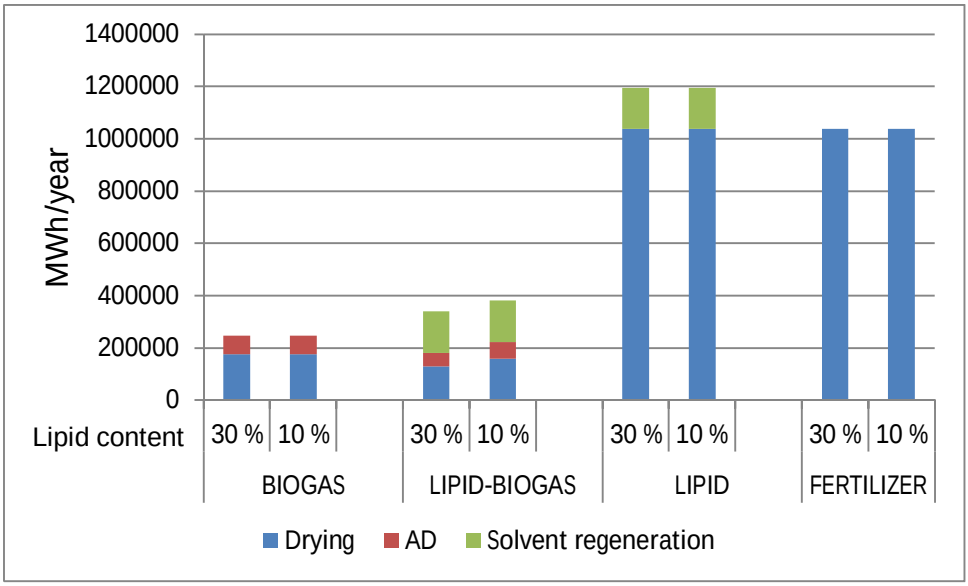

Figure 14. Heat consumption

Comparing the two scenarios with different cell lipid content, the scenario with higher lipid content shows more potential. The biofuel yields, both for lipids and for biogas are higher with higher lipid content. In the current evaluation the growth rate was assumed to be same and not dependent on the lipid content. However the

productivity of microalgal biomass may decrease while aiming for high lipid content as discussed earlier in chapter 5.1.

7.3.4 CO_2 fixation potential

The CO_2 fixation capacity of each concept depends on the product and its use, see Figure 15. Biogas production releases CO_2, thus lowering the CO_2 fixation capacity. Between two biogas concepts the released amount is naturally larger when the whole biomass is digested. 20-30% of captured CO_2 is released in anaerobic digestion. The CO_2 fixation capacity depends also on the scenario (i.e. the lipid content). The amount of CO_2 captured is 10-18 % higher in the scenarios with higher lipid content. The composition of algae causes this difference. The higher the carbon content of the algae, the higher is its potential to fix carbon dioxide. As lipids contain more carbon than proteins and carbohydrates the lipid rich scenario has a better fixation potential.

It should be noted here that, as the power plant providing electricity and steam was not included into the study, neither were CO_2 emissions from electricity or heat production evaluated in our study.

In addition to CO_2 in flue gas carbon is available in make-up waste water. This has a minor effect on the carbon balance, as over 99% of carbon comes from flue gas.

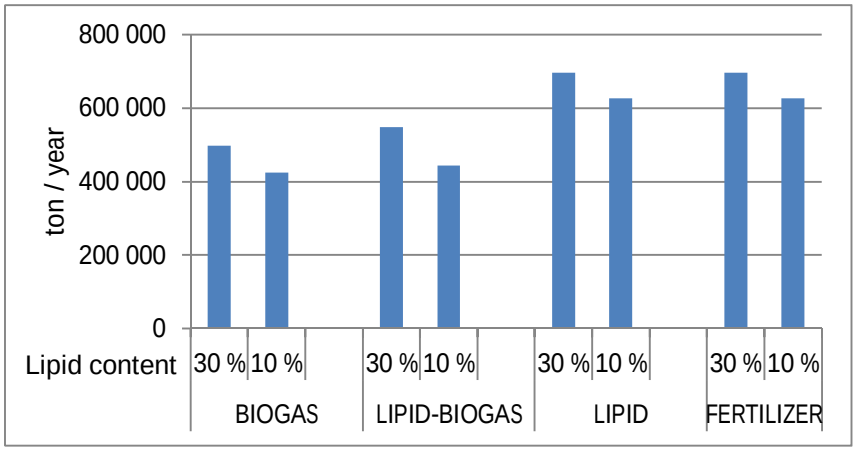

Figure 15. CO_2 fixation potential between different concepts.

7.3.5 Sensitivity analysis

Sensitivity analysis was performed on scenario 2, in which the algae were assumed to have 30 % lipid content. Figure 16 to Figure 19 summarize these analyses. In the figures sensitivity parameters are presented as a fraction of the base value on the x-axis. The Y-axis represents the profit of each concept.

As indicated in the figures profit is the most sensitive to the product (LIPID, BIOGAS) prices. Quite naturally revenues are higher with higher product prices. Also, capital

charge was one of the largest cost contributors in all concepts, so it is not surprising that the profit is very sensitive to plant life time.

All concepts are also quite sensitive to productivity. In the two first concepts (BIOGAS and LIPID-BIOGAS), profit increases with productivity, but in two last concepts (LIPID and FERTILIZER) the effect is opposite. This indicates that the variable costs of these two latter concepts are higher than revenues, causing the higher costs when there is more biomass to be processed.

The figures also indicate some sensitivity of the profit with respect to the degree of water circulation. The utilised water was assumed to be free of charge as it is waste water and similarly, the waste water from the algal process was free of charge. Sensitivity analysis indicates that the lower the water circulation degree the higher the profit. In addition to function as water supply, the waste water serves also as nutrient source, meaning lower nutrient costs when more waste water is used.

The profits of the two latter concepts (LIPID and FERTILIZER) are very sensitive to the price of heat, while the two former concepts (BIOGAS and LIPID-BIOGAS) are not. The difference between the concepts is caused by the heat amount needed for the drying process in the two latter concepts.

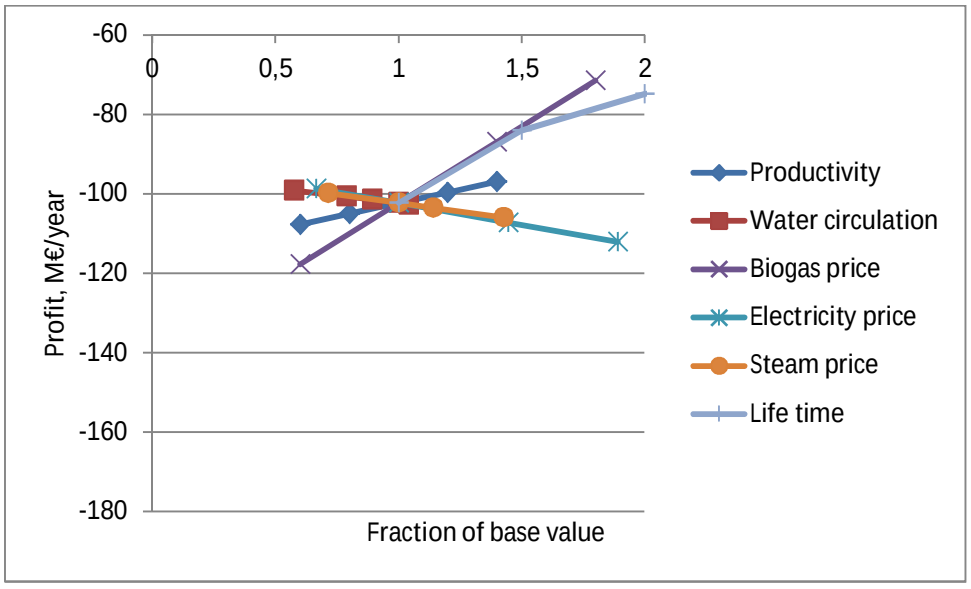

Figure 16. Sensitivity analysis for concepts BIOGAS. Profit as a function of the fraction of base value.

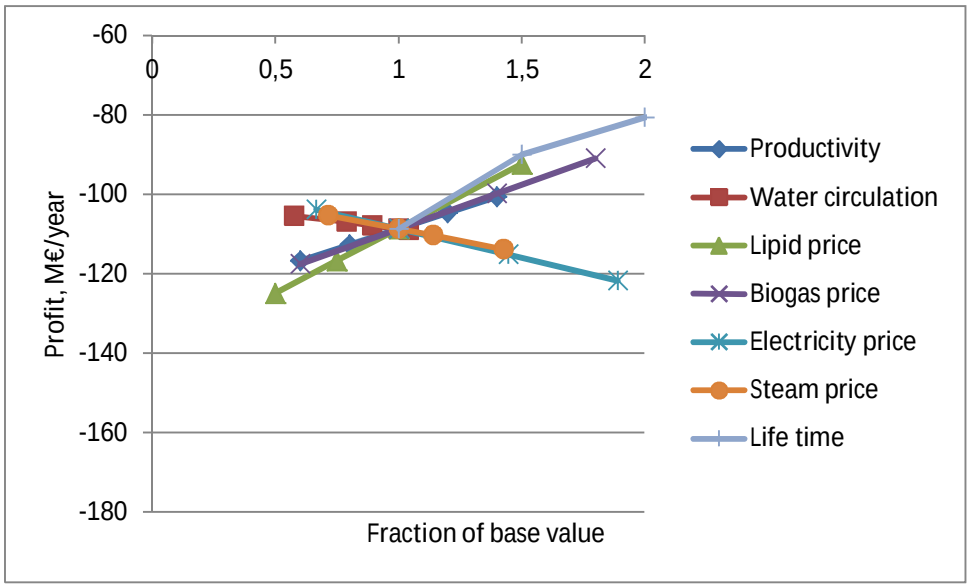

Figure 17. Sensitivity analysis for concepts LIPID-BIOGAS. Profit as a function of the fraction of base value.

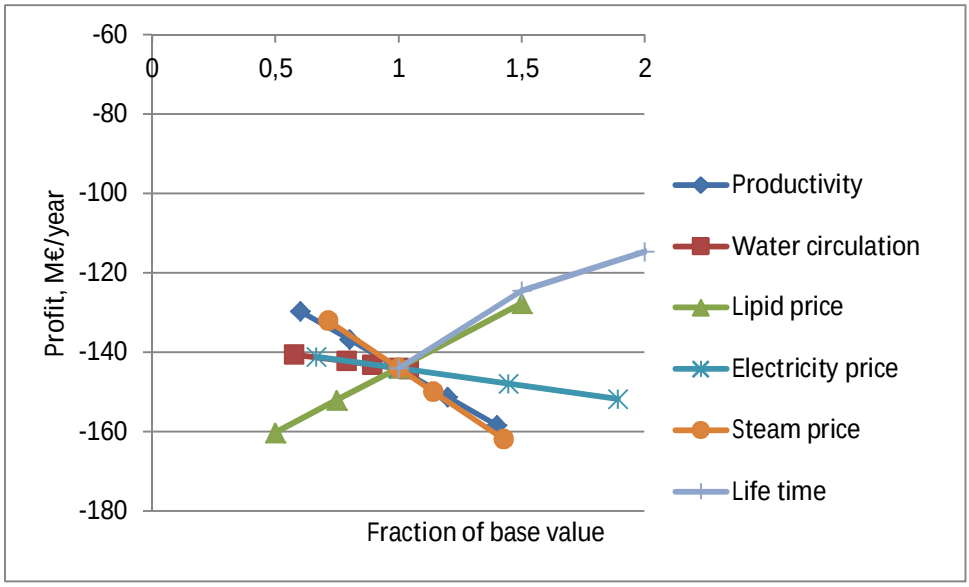

Figure 18. Sensitivity analysis for concept LIPID. Profit as a function of the fraction of base value.

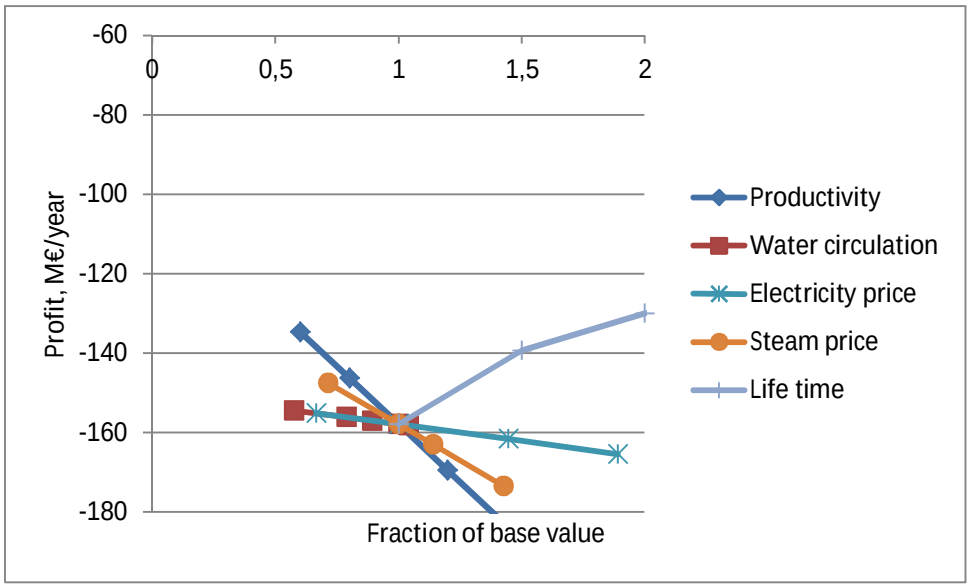

Figure 19. Sensitivity analysis for concept FERTILIZER. Profit as a function of the fraction of base value.

7.4 Maturity of the concepts

The maturity of each processing unit shown in Figure 7 was evaluated separately using Technology Readiness Level (TRL) based approach. European Commission [1] and the United States Department of Energy DOE [2] guidelines were used. The obtained maturity of each concept equals to that of the separate unit operation with the lowest TRL in the system. Part of the technologies used are proven technologies and already utilized in full-scale operation (TRL 9). However, some of the selected technologies are well understood and industrially used, but their utilisation in algae production has not been proven, or has only been proven in laboratory studies. In these cases TRL level 4 to 6 were selected.

Open pond cultivation is a mature technology and is used in many places, mainly to produce high value algal products.

Harvesting with the three selected technologies (settling, dissolved air flotation, filtration) one after another is a rarely used combined harvesting concept and therefore low TRL is given to that. Filtration is highly dependent on the algal specie and best suited to large algal cells. Clogging or fouling may also be an issue and therefore centrifugation is more utilised method as a secondary harvesting method. However the capital and operational costs of filtration are lower compared to centrifugation (Milledge & Heaven 2011).

Another unit operation with low technology readiness level is extraction using hexane. The extraction process itself is again well known and widely used technology, however in case of algae oil it is not used in full scale and studies are limited to laboratory scale (Mubarak et al. 2015; Lundquist et 2010). Reported studies

1 "Technology readiness levels (TRL)" (PDF). European Commission, G. Technology readiness levels (TRL), HORIZON 2020 – WORK PROGRAMME 2014-2015 General Annexes, Extract from Part 19 - Commission Decision C(2014)4995. Available at: http://ec.europa.eu/research/participants/data/ref/h2020/wp/2014_2015/annexes/h2020-wp1415-annex-g-trl_en.pdf
2. http://en.wikipedia.org/wiki/Technology_readiness_level#Other_definitions_and_uses

on wet extraction with hexane were not found in the literature; however the technology is used in techno-economic and environmental assessments, for example in the report by ANL, NREL, PNNL 2012.

High pressure homogenization is used widely in industry, for example in the dairy industry, and it seems to work well for algae as well (Günerken et al. 2015). However its specific electricity consumption depends highly on the species and can be more than an order of magnitude larger than the value selected here.

Anaerobic digestion of algae may also present challenges. For example the C/N ratio of the digestion is not readily in the desired range when digesting only algal biomass and this may cause collapse of the system. Co-digestion is an easy solution, if there are suitable co-digestion feedstocks available.

The majority of the selected technologies are proven in industrial processes but not necessarily proven in the field of producing large scale (usually low cost) products from microalgae. Harvesting algae growing in very low concentration as well as the extraction of large quantities of algal lipids are the largest question marks of the studied concepts. The BIOGAS concept got the highest TRL: 6-7, the TRL of other concepts were lower (4-6) mainly because of the secondary harvesting steps and wet extraction of lipids. In general, innovations are still needed for the development of technologies and to reduce costs while increasing the yields.

8 Conclusions and further research

Based on the literature reviewed here and also the results of our techno-economic evaluation the key challenge of microalgal based carbon capture targeting primarily bulk products is its poor economic feasibility resulting mainly from high capital and operating costs of biomass cultivation and downstream processing. In addition, many techniques, for example for harvesting and extraction, are available but the best available technique is yet to be determined. Therefore many different aspects need to be considered simultaneously in order to be able to lower the unit production costs. Moreover, the combined production system of microalgae based low value commodities (biofuels, fertilizers) and high value co-products, with CO_2 capture and waste water utilisation is an important topic for the future development efforts.

The profit of all evaluated concepts is negative with the used assumptions, the capital charge being the largest cost contributor. Comparing selected product portfolios, the co-production of lipids and biogas is the most promising. That concept benefits from wet extraction, and nutrient recycling from anaerobic digestion compared to other concepts.

Biological mitigation of CO_2 from flue gas combined with microalgal biofuel production does not provide permanent CO_2 sequestration because carbon taken up

during photosynthesis is released during biofuel combustion. However the carbon has been used twice: once for energy generation in a power plant and secondly to grow algae for fuels. In that sense fertilizer is a good product as fixed CO_2 in agriculture is estimated to have a retention time of 50–100 years.

In the future, the study can further be updated and continued by reviewing the assumptions and data used and examining the effect of other co-products. Interesting future updates from a CO_2 point of view would be introducing different technologies for efficient CO_2 transfer to cultivation media and recycling CO_2 from anaerobic digestion to cultivation. The other interesting aspect for future research is the examination of different lipid levels and their effect on productivity in general to find out how this affects the economic feasibility. In the current study we assumed the same productivity in all concepts and scenarios. Also, an interesting continuation for the study would be a real case study based on measured/local data of the inputs (fluegas, waste water, climate conditions), including realistic estimates of the algal specie and its productivity in the case study conditions, and specific power consumptions of all unit operations.

9 References

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