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PhD thesis

Energy carriers and other co-products from microalgae

Sustainability aspects and feasibility of different production pathways

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Abstract

The cultivation and conversion of algae for biofuels emerged as one silver bullet technological solution over the last few years, in order to decrease our dependency from fossil fuels.

This thesis is based on an extensive literature review started in 2008 in order to put some clarity in the algae-to-energy sector, to discern overstatements about algae productivity and possible uses and to assess how this technology could contribute to sustainable development. The aim of the thesis is to identify promising technological solutions and algae-based production options, and to assess the viability of different pathways for energy production.

The main findings of the review are summarized in the first part of this thesis together with a characterization of promising algae strains.

A special focus is given to thermochemical conversion and biorefinery processes, as well as to sustainability impacts.

A second part of this thesis is focused on applying this knowledge to a specific case study: the Austrian context. Two promising algae species have been identified and some results of a project comparing different energy production pathways from algae in Austria are reported. Scenarios are drawn for 2020 and 2050.

Hydrothermal processes applied to algal biomass such as Scenedesmus obliquus *grown in wastewater appears to be a viable solution in the Austrian context, able to achieve a positive energy balance. The main products of the process would be bio-coal and heat or, alternatively, a syngas rich in methane and hydrogen.*

The research highlights that, although a promising solution, the use of algae for large-scale production of biofuels is still unpractical given some major technological bottlenecks especially at the cultivation and separation phases. The co-production of non-energy products together with bioenergy can improve significantly the overall viability and sustainability of the process but, to this end, their production scales and market potentials must be compatible.

Background and Acknowledgements

This dissertation builds upon the work I did on the Algae-to-biofuels topic since 2008, at a time when microalgae production was seen as a solution to the energy challenges, providing an endless source to be used as a feedstock for energy purposes. Algae would have also avoided the drawbacks of traditional biofuel feedstocks such as mais, rapeseed or palm oil, limiting the food vs. fuel competition and impact on natural resources. A lot of research, development as well as important public and private investments started flowing into algae for energy and, since then, a much more balanced and evidence-based understanding has been developed at the international level. In 2008 I developed and launched an inter-departmental working group within the Food and Agriculture Organization of the United Nations: the Aquatic Biofuels Working Group, to research available technologies, and their impact on sustainability of biofuels production from algae and fish waste. Within this working group, I co-authored and coordinated the development of the first two FAO reports on algae-based biofuels. A first report "**Algae-based Biofuels: A review of challenges and opportunities for developing countries**" was published in 2009 (available at http://www.fao.org/docrep/012/i1199e/i1199e00.htm), addressing mainly technological aspects of algae cultivation and biofuel production, at a time when information on algal biofuels was very scattered and a lot of claims about algae potential and productivity still had to be proven. Sustainability issues specific to algae-based biofuels and how they compared to conventional biofuels were also addressed, as well as knowledge gaps. The report provided an overview of available cultivation and harvesting concepts.

Since the economic and energy viability seemed to be very hard to be met, it was decided to develop a second report about the possible co-products of algal biofuels, looking at opportunities for integrated production to improve the overall sustainability. Possible co-products include energy products such as hydrogen and electricity but also non-energy products such as those for human consumption, livestock consumption, fish and shellfish consumption, chemicals, fertilizers, and fibers for paper.

The report "**Algae-based Biofuels: Applications and Co-products**" (available online at http://www.fao.org/docrep/012/i1704e/i1704e00.htm) was eventually published by FAO in 2010. The economic viability and environmental impacts improve as we move from the sole energy production to the so-called biorefinery concept, but also technology requirements and capital and skills requirements increase accordingly. The report highlighted how a trade-off would be always considered for these kinds of considerations. However, a number of case studies were reported, to show that integrated production of energy and non-energy products already exists in both developed and developing countries, associated to various degrees of complexity.

From January 2010 to June 2011 I also participated as resource person from FAO in the AquaFUELs project (http://www.aquafuels.eu/), focused on establishing the state of the art on research, technological development and demonstration activities regarding the exploitation of algae for biofuels production. This project was funded by the EC within the VII Framework Programme for Research and Development and brought together and coordinated existing knowledge on algal biofuels, to establish the state of the art for research, technological development and demonstration activities regarding the exploitation of algal biomass for 2nd generation biofuels production.

In 2010 I got in touch with the Chemical Engineering Department of the Vienna University of Technology (TU Wien) and I started a collaboration, joining a project funded by the Austrian Research Promotion Agency (FFG) to assess the potential of exploiting algae for energy production in Austria (http://www.klimafonds.gv.at/assets/Uploads/Bioenergie-2011.pdf#page=64). The project was aimed at identifying the most interesting combinations of technology pathways for microalgae-to energy production, evaluated technologically, economically and ecologically. As the potential depends further on the cost of production of microalgae and the fossil fuels, the assessment was coupled with an economic analysis, as well as an analysis of water requirements, nutrient requirements and the efficiency from the production of the energy source and the provision of energy services. Life Cycle Analysis (LCA) was undertaken to assess the environmental impacts and reduction of greenhouse gas emissions and fossil energy. The future of algae-to-energy in Austria was assessed drawing medium- and long-term scenarios. The project involved major Austrian research institutes such as Joanneum Research, Bioenergy 2020, IFA Tulln and the Vienna University of Technology. I joined the research team on behalf of TU Wien and concentrated on thermochemical conversion processes for algal biomass. A number of meetings (in Graz and Vienna) have been workshops organized and publications have been developed within this research activity. A final publication is currently under review. The work was presented to a number of international events (e.g. at the European Biomass Conference in 2011 – see http://www.joanneum.at/index.php?id=63&no_cache=1&tx_publicationlibrary_pi1[showUid]=6562&L=1 and in 2012 - see http://www.etaflorence.it/proceedings/?detail=7958).

This dissertation summarizes the work that I have been doing on algal biofuels over the last 4 years. This work was undertaken under the supervision of **Prof. Cristina Miceli** (University of Camerino), and of **Dr. Reinhard Rauch** (TU Wien) specifically for chapters 6, 7, 8 and 10.

1 Introduction

Fossil fuels are the largest contributor of greenhouse gases (GHGs) to the biosphere, and in 2010 associated CO_2 emissions were 30.6 Gt, increasing 5% since 2008 (IEA 2011). It is estimated that natural processes remove only about 12 Gt every year, therefore compatible mitigation strategies are needed to offset the remaining CO_2.

With the increase in anthropogenic GHG emissions, mainly due to large scale use of fossil fuels for transport, electricity and thermal energy generation, it has become increasingly important to develop abatement techniques and adopt policies to minimise impacts of global warming. The Kyoto Protocol of 1997 called for a 5.2% reduction in GHG emissions worldwide from 1990 values. To meet the agreed target, a range of effective technologies, including chemical and biological CO_2 mitigation possibilities, has been a focus of research. The use and valorisation of biomass, such as energy crops, forestry and agricultural residues, or aquatic resources has surely a fundamental role to play. Biomass contributes today for around 10% of the total primary energy supply (TPES), most of this being traditional biomass, which plays an important role in providing energy for cooking and heating, in particular to poor households in developing countries[1]. Its role as a contributor to fulfil energy needs is envisaged to increase sharply over the next decades and according to the IEA its share of TPES will reach 24% by 2050 (IEA 2012a).

In order to meet global objectives there is a need for enhancement of global strategies for energy security and mitigation of energy-related CO_2 emissions, for which the main strategies include the need for increasing energy efficiency (i.e. decreasing energy use per unit of product, process or service); increasing the use of clean fossil energy (i.e. use of fossil fuels coupled with CO_2 separation from flue gases and injection into underground reservoir for gradual release – carbon capture & storage); and increased use of renewable energy (i.e. development of low-CO_2 energy systems). Given the necessary CO_2 emission targets, and the potential of each of the outlined strategies to the timely reduction of CO_2 emissions to ‘safety levels’, it has been argued that the three strategies outlined above will have to be put in place at the same time in order to tackle the progression of climatic change.

Low-CO_2 energy solutions include biofuels, which are generally referred to solid, liquid or gaseous fuels produced from biomass. A variety of liquid fuels can be produced from biomass and these

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[1] Traditional biomass is usually used at very low energy efficiencies, typically between 10 and 20 %.

include ethanol, methanol[2], biodiesel, Fischer–Tropsch gas oil, syngas, biogas, biochar, hydrogen and methane among others. Liquid biofuels are primarily used for transportation, but can also be used into fuel engines or fuel cells for electricity and heat generation.

Biodiesel is usually produced by transesterification of edible and non-edible oils with methanol or ethanol in the presence of catalysts. Recently, an Ecofining process[3] by UOP reported the production of green biodiesel from both edible and non-edible oil in the presence of heterogeneous catalyst and hydrogen gas.

Ethanol, widely used for transportation in Brazil and United States, is usually produced from fermentation of sugar obtained from sugarcane or corn.

Bio-oils, produced from pyrolysis of biomass, can be further upgraded for different applications by hydrogenation and catalytic cracking processes, but they can hardly meet the quality required for transport fuels. Lipids rich bio-oils can also be obtained from algae through different processes and can then be upgraded to higher quality fuels.

Figure 1 shows some of the different routes for the production of liquid biofuels.

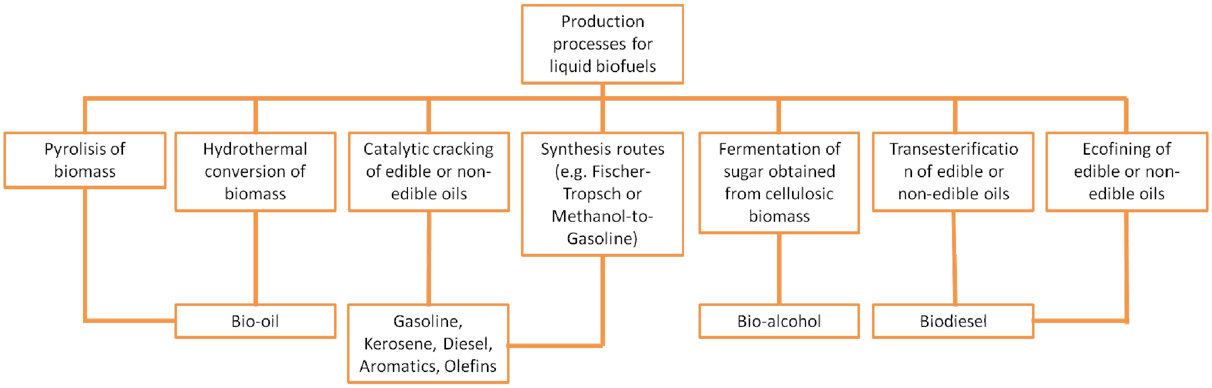

Figure 1 - Overview of different liquid biofuel production routes

In recent years, the use of liquid biofuels in the transport sector has shown globally a sharp growth, driven mostly by policies aimed at mitigating GHG emissions and at increasing national energy security (GBEP 2007).

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[2] Obtained from syngas by methanol synthesis

[3] In 2008, UOP LLC revealed its Ecofining process developed in collaboration with ENI which takes vegetable oils, or lipids, and converts them into replacements for diesel and jet fuels. The resultant fuels from this refining process are indistinguishable from existing fossil-based petro-diesels and jet fuels.

The so-called "*first-generation*" (or 1G) biofuels, which can already economically compete with their fossil fuel alternatives, are mainly produced from food crops such as rapeseed, sugarcane, sugar beet, and maize, as well as from vegetable oils and animal fats, using sugary or fatty material as a feedstock. It is expected that the growth in production and consumption of liquid biofuels will continue and increase in the coming years.

1G biofuels have some limiting characteristics such as the competition with food and feed production for the use of arable land, a typical lack of well managed agricultural practices for their production, high water and fertiliser requirements, and the detrimental effect they have on biodiversity.

This has raised questions over recent years about their potential to replace fossil fuels and the sustainability of their production. For example, apart from the risk that higher competition for food crops may have severe negative implications on global food security; the demand for biofuels could place substantial additional pressure on the natural resource base, with potentially harmful environmental and social consequences. Currently, about 1% (14 million hectares) of the world's available arable land is used for the production of biofuels, providing around 1% of global transport fuels but increasing sharply that share could owe to severe impacts on the world's food prices (IEA 2006) and to bad management of the large production land required.

With yields of less than 500-5,000 L of biodiesel per hectare (AquaFUELs 2010a), those crops require enormous areas of arable land, water and fertilizer and are generally highly work intensive. Life cycle assessments (LCA) indicate that low reductions in greenhouse gas emissions can be achieved using such biofuels (Zah et al 2007), and if they are being produced following conversion of natural ecosystems their GHG emissions surpass those of fossil fuels for years to come (Fargione et al. 2008). The major impact, land use, is often not adequately considered if the strategic implications of expanding biofuels production are taken into account.

On the other hand, *advanced biofuels*, such as those produced from lignocellulosic material or algae can potentially overcome some of the limits of first generation biofuels.

Lignocellulosic biofuels are produced from the whole plant matter of dedicated energy crops or agricultural residues, forest harvesting residues or wood processing waste, rather than from just the sugary or cellulosic part of the crop (e.g. the one normally used also for food production). However, the technology for conversion in the most part has not reached commercial scales which has so far inhibited their significant exploitation.

Conditions for unlocking the full potential of the biofuel resource are that the produced biofuel should:

- be competitive with their fossil fuel alternative;
- require low additional land;
- enable air quality improvement;
- mitigate atmospheric CO_2, and;
- require minimal water use.

Using microalgae as a feedstock for biofuel production could potentially meet these conditions and therefore make a significant contribution to fulfilling the demand for energy and other products, while simultaneously providing environmental benefits.

Algal biofuels have a number of advantages which underscore the potential applications of microalgae. Among the advantages of using microalgae to produce biofuels, one can surely include the fact that:

- nutrients for microalgae cultivation, especially nitrogen (N) and phosphorus (P), can be obtained directly from wastewater with a dual benefit, providing free growth medium while treating organic effluents from the agri-food industry;
- they can make direct use of flue gases as a CO_2 source for their growth (but these are unsuitable in high concentration owing to the presence of poisonous compounds such as NO_x and SO_x); and
- the fact that the biochemical composition of the algal biomass can be modulated by selecting the right algae strain[4] (or strains) and by varying growth conditions. This characteristic offers the possibility of adapting the algae composition to the specific product desired (not necessarily biofuel).

Despite its intrinsic potential as a biofuel resource, many challenges have hindered the development of algal biofuel technology to commercial exploitation that could allow for sustainable production and utilisation.

Challenges are not just at the algae cultivation stage but also at the stage of converting the algal biomass into biofuels. A positive energy balance and economic viability is key for algae exploitation as a future energy source.

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[4] The term has no official ranking status in botany; the term refers to the collective descendants produced from a common ancestor that share a uniform morphological or physiological character.

The ‘algae for energy’ industry, though presently in its infancy, has tremendous potential to provide future liquid transportation fuels that can improve national energy security by providing less dependence on fossil fuels. Microalgae offer significant advantages as “oil producing crops”. Microalgae are among the most efficient plants in terms of photosynthetic activity. During growth phases they actually can double their mass, converting atmospheric carbon dioxide into carbon neutral biomass in just a matter of 3–4 hours. Moreover, the production of microalgae does not require high quality, arable land and therefore does not compete with food crops. Several varieties actually grow very well in wastewater, thus providing another underutilized medium for the production of biomass.

Many microalgae can grow rapidly, and some studies describe them as considerably more productive than land plants and macroalgae (seaweed). However recent analyses (e.g. undertaken by the research group of Prof. Tredici from the University of Florence) indicate that C4 plants have a similar biomass productivity and photosynthetic efficiency under optimal conditions.

2 Algae biomass production

Algae are a group of organisms generally described as photoautotrophic unicellular or multicellular organisms, mainly water dwelling organisms lacking complex morphological organization. The prokaryotic blue-green algae (or cyanobacteria), are often included among microalgae, and indeed some cyanobacterial species hold a prominent position in the commercial uses of microalgae. A well-known example is the use of Spirulina for food (see section 4.1).

Several main groups of microalgae exist, each of them differing in biochemical components and life cycle. Traditionally algae can be classified on the basis of their photosynthetic pigments, nature of cell wall, presence of flagella and the number of membranes surrounding the chloroplast[5]. In recent times, classification has extended to comparisons of specific DNA sequences, leading by the way to major revisions in classification of many algae groups[6]. Their reproduction occurs primarily by vegetative (asexual) cell division, although sexual reproduction can occur in many species under appropriate growth conditions.

Microalgae, including the cyanobacteria Nostoc and Spirulina (or Arthrospira), have been part of the human diet for ages and were mainly harvested from natural blooms.

Today, more than 7,000 tons of algae biomass are produced annually mainly for use as human food supplements and animal feed. Table 1 shows the comparison of several algae production systems and the main application areas of microalgae (FAO 2010).

Microalgae biomass can either be harvested from natural blooms or from more or less controlled cultivation systems by means of open ponds, while commercial production in photobioreactors (PBR) is limited to a few hundreds of tons per year (see chapter 3 on cultivation technologies).

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[5] Chloroplasts are organelles found in eukaryotic organisms that conduct photosynthesis. They capture light energy, store it in energy storage molecules (ATP and NADPH) and use it in the process of photosynthesis to make organic molecules and free oxygen from carbon dioxide and water. Chloroplasts are observable as flat discs usually 2 to 10 micrometers in diameter and 1 micrometer thick. The chloroplast is contained by an envelope that consists of an inner and an outer phospholipid membrane.

[6] Recent genetic studies highlighted how photoautotrophic eukaryotes belong to several highly diverse groups of organisms and are the result of different and independent events of secondary endosymbioses. As a consequence, algae belong to genetically widely diverting groups of organisms often closer to non-photosynthetic organisms.

2.1 Algae biology and selection of algae strains

Microalgae are fast-growing photosynthetic organisms that can reach (short-term) productivities of 50-60 g/m^2/day. This productivity is reached for example in raceway ponds in Hawaii and California where CO_2 is added to the culture. This corresponds to an efficiency of transforming sun light to biomass energy of 5-6%. These characteristics and productivity data extrapolated from lab scale experiments have suggested that microalgae could be the silver bullet to easily produce enormous amounts of biomass for food, fodder or energy. However these results are very site and strain specific, and under long-term real conditions productivity is much lower. Many algal strains can also produce large amounts of oil or lipids that can easily be converted into biodiesel (Sheehan et al., 1998) that can reach 70-80% of the whole algae cell. Some studies combined the above mentioned maximal biomass productivity and maximal oil content, yielding very high oil productivity numbers[7]. In turn these claims attracted a lot of attention from privates and governments, leading to important resources channelled to funding research programmes on algal biofuels production. However, current productivity obtained in large scale operations can range from 40-60 t/ha/year of algal biomass. Conservative projections anticipate up to 100 t/ha/year of biomass, or 30 t/ha/year of biodiesel in subtropical or tropical regions (Scott et al 2010).

Nevertheless, algal strains containing higher amount of lipids are characterized by low growth rate. Slow growth increases the operational costs and demands cultivation (especially in closed bioreactors whose building is expensive).

Relevant microalgae for biofuel production can be classified as follows (US microalgal species program ASP, Sheehan et al. 1998):

- diatoms (Class Bacillariophyceae);
- green algae (Class Chlorophyceae);
- golden-brown algae (Class Chrysophyceae);
- prymnesiophytes or haptophytes (Class Prymnesiophyceae); and
- eustigmatophytes (Class Eustigmatophyceae)

To this we can add the prokaryotic blue-green algae, or cyanobacteria.

This classification doesn't include macroalgae and other aquatic biomass[8], which could emerge as a major bioenergy feedstock in the future, but their potential hasn't been as much studied.

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[7] Equivalent to oil productivities of over 100 tons/ha per year.

[8] Other aquatic biomass such as water lentils, water hyacinth, elodea and others have also been considered for potential biofuel production due to their usefulness in treating polluted nutrient rich water bodies and wastewater streams.

Algae strains have been reclassified several times in recent biology according to technical advances on the basis of differences in subcellular organization. Recent knowledge gained about genetics allowed more precise determination of evolutionary relationships between algae. As mentioned before, conventionally algae include also cyanobacteria, prokaryotic oxygenic phototrophs.

Recently a number of projects aimed at making some clarity on algae taxonomy, coming up with reference databases continuously updated over time. Two relevant exercises include the Tree of Life project[9] and the AlgaeBase project[10]. This chapter is largely based on the algae classification adopted by the AquaFUELs project[11], heavily relying on the AlgaeBase database (http://www.algaebase.org/).

For the purpose of energy production, a number of criteria can be identified that make microalgae strains particularly suitable. This mainly include the productivity, robustness of algae during the cultivation phase, the ease of harvesting algae and extract useful feedstocks from them, for the production of energy carriers or of other co-products[12]. In addition to this, for biochemical and thermochemical valorization of algae for energy, the composition of algal biomass is a key factor, together with the opportunities for co-producing non-energy products.

Productivity is intended as productivity of biomass or of specific biomass components (e.g. lipids for biodiesel production). Photosynthetic efficiency (i.e. percent of light energy converted into biomass energy) or experimental productivities could be used.

Robustness is mainly intended as resistance to extreme conditions such as variation of pH, of oxygen concentration, of temperatures, of O_2 concentration, of salinity or of contaminants. pH range is important as the correct pH reduces the risk of infections and improves CO_2 transfer to the cultivated alga. Temperature ranges are relevant especially in open systems since many algae strains die outside a certain temperature range and this is important when the culture is exposed to high variations between day and night as well as seasonal fluctuations. O_2 concentration is relevant for the design and operating conditions of closed systems such as photobioreactors as in these systems O_2 must be mechanically provided to the algae culture. Salinity influences the risk of infections and determines the ideal medium conditions for specific algae. Finally the capacity of adapting to

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[9] http://tolweb.org/tree/)

[10] http://www.algaebase.org/

[11] In scientific literature there is still no agreement whether certain microorganisms should be classified as algae, fungi or other. The classification is evolving over time, especially in light of new genetic discoveries.

[12] The criteria are intended for commercial scale production and not lab scale experiments.

contaminants allows the use of wastewater for example as growing medium or of flue gases as CO_2 source for the cultivated algae.

Harvestability and extractability of microalgae is basically determined by algae size and therefore their sedimentation rate, the possibility of flocculation, as well as the ease of mechanical harvesting. The thickness of the cell wall and the presence of fibers are also important to understand the ability of extracting liquids.

Eventually the final water content is a paramount parameter especially for thermochemical processes and it can determine the most suitable production pathway.

Algae biomass composition could be analyzed in terms of:

- Lipids content on dry weight and lipid composition. This is relevant especially for biodiesel production through transesterification.
- Starch content and carbohydrate composition, particularly relevant for biochemical ethanol production.
- Heating value of the biomass relevant for all thermochemical processes (see section 6.2).

Additionally, presence of heavy metals or toxins is relevant to foresee inhibition of catalytic processes and, together with protein content and composition, to have preliminary information on suitability of food/feed co-production. Co-products can be analyzed in terms of economic added value that would contribute to make energy production more economically viable.

2.1.a Cyanobacteria

Cyanobacteria are prokaryotic photoautotrophic microorganisms that can be found in almost every environment. They are sometimes referred as blue-green algae. These microorganisms are normally considered algae, even if they are bacteria *strictu sensu*. Aquatic cyanobacteria are probably best known for the extensive and highly visible blooms that can form in both freshwater and marine environments, which are sometimes toxic to humans and animals.

They can be traditionally classified by morphology into five orders[13]: Chroococcales, Pleurocapsales, Oscillatoriales, Nostocales and Stigonematales. The first two orders include unicellular cyanobacteria. The members of Chroococcales are unicellular cyanobacteria that reproduce by binary division. Cells can vary in length from 0.5 to 30 μm and cells can be single or

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[13] According to the International Code of Botanical Nomenclature.

in colonies. In Pleurocapsales, cyanobacteria reproduce by multiple divisions which generate small spherical cells. They can be motile or not. The remaining orders include filamentous cyanobacteria.

Generation times are usually longer than 24 h, although some strains can duplicate in 4 h. Cyanobacteria share the basic cell characteristics with other bacteria. The reserve carbohydrate is glycogen. They contain also cyanophycin, a nitrogen reserve polymer.

Most cyanobacteria are obligate photoautotrophs, but some species can grow as heterotrophs in the dark at the expense of glucose, fructose or sucrose. Under anaerobic conditions, some species can perform lactate fermentation.

Nitrogen fixation occurs both in heterocystous cyanobacteria and in some non-heterocystous cyanobacteria. Due to their ability to fix nitrogen in aerobic conditions they are often found as symbiotic with a number of other groups of organisms. The rice paddies of Asia for example rely on nitrogen-fixing cyanobacteria as fertilizers.

Some Arthrospira strains (commonly known as Spirulina) are famous food supplements especially in developing regions of the world including Asia, Africa, South and Central America. Spirulina is a microscopic spiral coil that can be found in both marine and fresh water and are sometimes referred as algae even if they are not eukaryotic organisms. Spirulina is also cultivated in aquaculture systems and is commercialized under different forms such as powder, drinks or tablets. Natural blooms can be found in tropical lakes with high pH and rich in carbonates and bicarbonates (used as a carbon source).

Commercial Spirulina is produced mainly in open raceway ponds (but also in photobioreactors) in the United States, Thailand, India, Taiwan, China, Pakistan and other countries.

It is characterized by an high amount of protein (55% - 77% by dry weight) and is a rich source of potassium, and also contains calcium, chromium, copper, iron, magnesium, manganese, phosphorus, selenium, sodium, and zinc (AquaFUELs 2010a).

Spirulina is cultivated without addition of CO_2 at elevated pH and relatively slow to grow.

Its cultivation does not include a stress phase and therefore it is mainly cultivated in semi continuous mode in natural open water bodies and in raceway cultivation using appropriate growth media (in terms of temperature, salinity and alkalinity).

Historically, Spirulina can be harvested easily using nets and filtered using fine cloth (usually by gravity) with mesh size of about 30 - 50 μm. Then the biomass can be dried and transformed to food tablets directly. Spirulina prefers temperatures above 30 °C, reduced temperatures during winter need to break the cultivation phase.

Cyanobacteria are interesting as they can be transformed genetically and have researched for enhancing their photosynthetic productivity, hydrogen production or other characteristics. For example Algenol engineered a strain of cyanobacteria transforming photosynthetically produced sugar into ethanol. This technology attracted investors' attention for a large pilot plant using ad-hoc designed bioreactors.

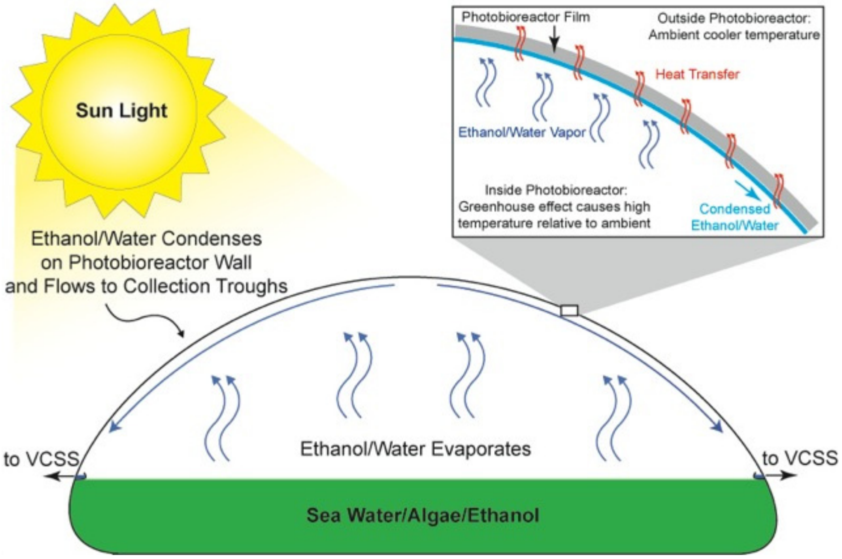

Figure 2 - Overview of the algae system developed by Algenol for ethanol production (Source: http://www.algenolbiofuels.com/overview.htm)

Recent researches have also hinted at their possible application to the generation of clean energy converting sunlight directly into electricity but this is still at an initial research stage.

A number of important advances have occurred in cyanobacterial biotechnology in the recent years but they seems to be particularly suitable to be used in the food, feed, fertilizer, colorant, nutraceuticals, pharmaceuticals products, rather than bioenergy. Further only a few strains (notably Spirulina) have been produced commercially so far.

2.1.b Green Algae

Green algae (Chlorophyta) include both green algae and embryophytes. They comprise unicellular and colonial flagellates as well as various colonial, coccoid, and filamentous forms. There are about 6,000 species of green algae and some of them can be found in symbiotic associations with fungi to form lichens. Prasinophyceae are a class of simple eukaryotic marine green algae with single, multiple or no flagellae. They are distinguished by their adaptation to light intensities. Chlorophyceae are another class of green algae.

Almost all forms have chloroplasts which contain chlorophylls (in addition to pigments such as beta carotene) giving them a bright green colour. Some have cells surrounded by a hard cellulose cell wall which also helps to prevent desiccation. They are eukaryotic organisms that can produce motile or non motile cells.

Chlorella is a genus of single-cell green algae, belonging to the phylum Chlorophyta. It includes a large and diverse genus of small unicellular green algae of highest relevance to multiple aspects of biotechnology. It is spherical in shape, about 2 to 10 μm in diameter, and is without flagella. *Chlorella* has a smooth rigid cellulosic cell wall and only asexual reproduction by autospores is known. Chlorella can be found in both freshwater and marine habitats. It contains the green photosynthetic pigments chlorophyll -a and -b (2-3%) and a variety of carothenoids in its chloroplast. Through photosynthesis, it multiplies rapidly. Its photosynthetic efficiency can, in theory, reach 8% (Zelitch 1971), comparable with other highly efficient terrestrial crops.

Chlorella are fast growing ($\mu_{max} = 0.20/h$) and have been reported to accumulate high concentration of oil under stress (Demirbas 2009) and are tolerant to a high temperature (e.g. 40°C).

Cultivation of *Chlorella* heterotrophically in fermenters using a solution containing acetate or glucose is also used and may provide a cost effective, large-scale alternative method for cultivation.

The commercial production of Chlorella is carried out today exclusively in open systems, apart from a large-scale cultivation in tubular bioreactor which started in Central Germany in 2000 and tubular reactors used to produce *Haematococcus* in Israel (AquaFUELs 2010a).

Speaking about large-scale commercial *Chlorella* cultures, only centrifugation by means of continuously operating self cleaning centrifuges, is used, which have the drawback of being a very energy intensive process, consuming a large part of total energy needed for the whole process. Typical harvest density is about 0.5 g l^{-1} and thickening can reach 150 g l^{-1} (Gudin and Thepenier, 1986).

The first commercial production of *Chlorella* started in Japan and Taiwan in the 1960's. Nowadays, large-scale production plants are located also in different regions of the world and its annual production is estimated to be about 5000 tons in the whole world. Most of the products have been used in human nutrition.

High growth rate, high photosynthetic efficiency, relatively high content of energy-rich chemicals on one side and available experience with large-scale culture and downstream processing raised increasing attention on *Chlorella* as a feedstock for both biodiesel and ethanol. Ethanol production used starch as feedstock material and relatively cheap biomass of high-yielded *Chlorella* cultures, containing good amount of starch grown in suitable open bioreactors is perspective solution but in order to be economically viable, those conditions for culturing starch-enriched algae in dense cultures must be attained. Using a thin layer algal suspension in outdoor cultures, linear growth continues up to very high biomass concentrations (about 40 g/L) enabling easy and cheap harvesting and processing (Doucha et al. 2006, 2009). However, the relative content of starch in the total biomass is low (15% of DW or less), but in S-limited cultures it can be brought up to 50 %. High starch algae can also be used for the production of H_2 but this pathway is still at an initial R&D stage.

Also *Scenedesmus*, *Tetraselmis*, *Botryococcus braunii*, *Clamydomonas reinhardtii*, *Haematococcus pluvialis*, and *Dunaliella* sp. are genus of Chlorophyceae. They are colonial and non-motile algae and they have all attracted the attention of the research sector as possible candidates for energy production.

Dunaliella sp. are motile, unicellular, algae typically 9 – 11 µm long and can be easily found in marine waters. It is characterized by a very wide pH tolerance. In particular *D. salina* is one of the most environmentally flexible eukaryotic organisms known and live in high salinity environments. It has two flagella of equal length and a single, cup-shaped chloroplast.

Dunaliella synthesizes different compounds in high concentrations such as glycerol up to 10% DW, that help it to continue its osmotic functions in high osmotic pressure (saline) environments, or beta-carotene up to 6% if it's dry weight to cope with high light intensities and to sore excess carbon. Proteins accumulate to 60% of the dry cell weight and contain most amino acids. Lipids accumulate to 6-18% DW depending on growth conditions.

For large scale production of *Dunaliella* there is the risk that low salinities protozoa can invade the culture and very rapidly decimate the algal production.

Dunaliella is used for producing β-carotene since the ‘60s, while the production of glycerol from *Dunaliella* is hardly economically viable and its cultivation is limited to the nutraceuticals market, reaching (low) productivity of about 2 g/m^2 per day, which are not competitive for the energy market.

Haematococcus pluvialis is a medium - large unicellular alga and its size can range from 10 to 100 µm. It has a large single chloroplast with two flagellae that loose mobility over time. Under stress conditions *Haematococcus pluvialis* accumulates carotenoids in the cytoplasm.

This alga is rich in protein and normally contains less than 10% as lipids containing significant amounts of polyunsaturated fatty acids (as per other green algae). Under stress conditions starch production is favoured (up to 50%) as well as triglycerides (up to 40%) (Boussiba et al. 1999).

Haematococcus is cultivated both in open ponds and in large closed bioreactors. Cultivation typically follows two stages, photobioreactor and then open ponds, in semicontinuous or batch cultivation. This configuration in Hawaii yields around 38 tons/hectare/year with 25% oil content over a long period (Huntley et al. 2007).

Haematococcus can settle spontaneously and be easily harvested in sedimentation ponds and then be centrifugated to increase its density. Algae are then dried in order to extract valuable oils for example by supercritical CO_2 extraction.

However *Haematococcus* is a slow growing alga and therefore not a good candidate for large scale algal biomass production. Further, this algae is very sensitive to contaminations, competitors, cold or heat stress that can significantly reduce productivity.

Chlamydomonas reinhardtii is a small unicellular alga (10 to 20 µm) with two flagellae and an "eyespot" that senses light. It can grow photoautotrophically or heterotrophically in the dark using feedstocks such as acetate.

The biochemical composition of this alga can vary a lot and can be mostly proteins during the early light period and then up to 50% starch. Recent studies revealed up to 20 % TAG under nitrogen starvation (AquaFUELs 2010a).

Clamydomonas can be cultivated in a large variety of synthetic growth media and the presence of acetate significantly enhances the growth rate.

This alga is currently not a candidate for mass cultivation. However the wide knowledge on its genetics and cell biology has allowed revealing numerous mechanisms of interest to biofuels production, such as biohydrogen production. This pathway has been investigated by NREL but only at lab scale.

In particular access to the numerous mutants and opportunities for genetic transformation technologies applied to this algae have made this alga an interesting target for current and future biofuels research. However this is still at an early R&D stage.

Tetraselmis are big marine green flagellate of around 80 µm and are usually encountered as solitary cells. They are very resistant to variation of pH, salinity and temperature and this characteristic make them particularly suitable for outdoor mass cultivation.

For example *Tetraselmis suecica* has high protein content (up to 40-50% DW), the rest being lipids (about 20% DW) and carbohydrate (about 20% DW) and the latter can be significantly increased under nutrient stress conditions. Ash content is relatively high (14-17%) as well as the percentage of polyunsaturated fatty acids over total (60%) (Renaud et al. 1999).

This alga offers a valuable source of protein, bioactive compounds, antioxidants, vitamins, sterols and polyunsaturated fatty acids for human and animal consumption and is therefore widely used as additive for animal and fish feed. Active ingredients extracted from this microalga are also used for production of cosmetics (Pertile et al., 2010).

In general *Tetraselmis* is cultivated under autotrophic conditions in both open raceway ponds and closed photobioreactors in batch, semi-continuous or continuous cultivation attaining a productivity of 15-20 g/m^2/day in PBR in locations like Hawaii, and of about 30 g/m^2/day in open ponds pilot plants in Southern Italy (Materassi et al., 1983).

Like other green algae, *Tetraselmis* settles spontaneously and can be harvested in sedimentation ponds and be followed by centrifugation, or be centrifuged directly for a faster process (but much more energy intensive).

An emerging use of *Tetraselmis* is for carbon biofixation in combination with biofuels production (Tredici, 2010) but for large scale operation this algae requires a lot of energy for culture mixing due to the high sedimentation rate, and this is necessary in order to reach high biomass productivities.

Scenedesmus sp. is a medium-large unicellular green alga, often appearing in groups of four connected cells, which can produce a range of oils and secondary metabolites. Multiple species produce different carotenoids up to 1% DW, protein up to 50%, and less than 10% lipids. Under stress conditions these algae can accumulate a large amount of triglycerides.

This algae can grow relatively fast, typically between 0.12 h^{-1} and 0.04 h^{-1} (this latter has been reported for *Scenedesmus obliquus* in particular). *Scenedesmus* is also very tolerant to high temperature (40 ºC) and grows particularly well at temperatures of 30-35 ºC with high light irradiance without showing signs of photoinhibition.

This great advantage of this algae is that it is one of the most resistant green algae which can compete very good with other algal species under high nutrient conditions such as in a wastewater medium; and can yield a relative high amount of oils (lipids) too, which can be significantly increase under nutrients (N and P) depletion conditions. The fast and vigorous growth of Scenedesmus can pose serious contamination problems when cultivating slower growing algae (such as *Haematococcus*) (AquaFUELs 2010a).

Scenedesmus is very robust and therefore very suitable for growing in wastewater outdoor using both open and closed photobioreactors, even at high pH. It can tolerate pH from 5 to 10 (although optimal pH is between 7.5 and 8.0). This is very important also for a possible application of *Scenedesmus* with (alkaline) flue gas from power plants or depuration. In open raceways ponds productivity is higher than 0.5 g/l/day and in closed photobioreactors can reach 1.2 g/l/day. (AquaFUELs 2010a).

Scenedesmus biomass composition is normally given by proteins (40-50 % DW) and carbohydrates (30-40 % DW) and lipids (lower than 15 % DW)[14], that can reach up to 30% under particular conditions. Still, this is a very good performance in terms of oil production.

2.1.c Red Algae

Red Algae (Rhodophyta) are a distinct eukaryotic lineage characterized by the accessory photosynthetic pigments phycoerythrin, phycocyanin and allophycocyanin arranged in phycobilisomes, and the absence of flagella and centrioles. This is a large assemblage of between 2,500 and 6,000 species in about 670 largely marine genera that predominate along the coastal and continental shelf areas of tropical, temperate and cold-water regions (AquaFUELs 2010a). They are common and widespread and are mostly free-living.

Red algae have a number of specific characteristics: absence of flagella and centrioles, starch as a storage product, accessory pigments, no chloroplast endoplasmic reticulum.

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[14] Normally no more than 2/3 are fatty acids.

They can be unicellular or multicellular and can achieve 1 m size and their cell walls are made of cellulose. Red algae can be divided into two classes: the Bangiophyceae and Florideophyceae.

Some of them are economically important as source of food additives such as agars and carrageenans but not for biofuel production. Commercial farming and natural harvest of red algae occurs worldwide for this purpose. Some companies are producing fibres for paper from red algae and some minor experiences exist to valorise the algal paper by-product for biogas production.

2.1.d Brownish algae

Heterokontophyta are characterized by a brown-yellow colour and are a major line of eukaryotes and can range from unicellular forms to large multicellular macroalgae. Flagellate cells possess two different shaped flagella. They are surrounded by several membranes and contain chlorophyll and usually accessory pigments, giving them a brownish colour.

These include the class of brown algae (or Phaeophyceae) which comprise mainly marine multicellular algae, including macroalgae living in colder Northern Hemisphere waters. There are about 1,500-2,000 species of brown algae. They play an important role in marine environments both as food, and for the habitats they form. Brown algae can be unicellular but can also be found as seaweed which can reach 60 m in length and forms underwater forests. Many brown algae can be commonly found along rocky seashores and some classes are used as human food. Some brown algae such as *Ascophyllum nodosum*, has been investigated extensively and cultivated at commercial scale. Brown algae have adapted to a wide variety of marine ecological niches but they are also important constituent of some brackish water ecosystems, and four species are restricted to life in fresh water. They are predominantly cool and cold water organisms that benefit from nutrients in up welling cold water currents and inflows from land (AquaFUELs 2010a).

Brownish algae (Heterokontophyta) include also Eustigmatophyceae, Xanthophyceae and Chrysophyceae. Eustigmatophyceae are a small group of eukaryotic algae that includes marine, freshwater and soil-living species. Most genera live in freshwater (Fawley, 2007) or in soil, although the *Nannochloropsis* genre includes species of picophytoplankton. They contain one or more yellow-green chloroplasts. Yellow-green algae or Xanthophyceae are an important group of heterokont algae. Most live in freshwater, but some are found in marine and soil habitats. They vary from single-celled flagellates to simple colonial and filamentous forms. Xanthophyceae chloroplasts contain the pigments chlorophyll a, chlorophyll c, β-Carotene. Finally golden algae or

Chrysophyceae are a large group of algae found mostly in freshwater and include unicellular flagellates. Most genera have no cell covering.

Among the microalgae the most important group is represented by the eustigmatophytes. *Nannochloropsis* is considered a promising alga for industrial applications because of its ability to accumulate high levels of polyunsaturated fatty acids. *Nannochloropsis* is also used as an ingredient in cosmetic products. *Nannochloropsis* has also been proposed as feedstocks for biodiesel production because of its ability to accumulate up to 60% lipid under nitrogen starvation (Rodolfi et al., 2009). It is considered a promising alga for industrial applications because of its ability to accumulate high levels of polyunsaturated fatty acids (eicosapentaenoic acid). It is mainly used as an energy-rich food source for fish larvae and rotifers and in cosmetic products (Tredici et al., 2009).

2.1.e Labyrinthulae

These unicellular eukaryotic protists are a common component of marine microbes. The Labyrinthulomycota are a group of microorganisms of uncertain taxonomic collocation. They were placed among fungi due to their functional ecology and morphology. They possess simple, asexual life cycles.

Thraustochytrids are a commercial source of polyunsaturated fatty acids and carotenoids (AquaFUELs 2010a), in particular doicosahexaenoic acid (DHA) which are produced through fermentation from specific classes of Labyrinthulae and used as nutritional supplements or as animal feeds. These algae grow normally on glucose substrate and their growth is typically characterized by a first phase where algal biomass grows and a second phase where lipid concentration increases.

2.1.f Diatoms

Only a few diatoms (Bacillariophyta) have been cultivated and studied although they are the most diversified (in species) and productive group of eukaryotic algae. They are extremely abundant in all aquatic ecosystems, occurring marine and fresh waters as well as in terrestrial environments.

They could probably provide 20-25% of global photosynthetic fixation of carbon and contribute up to 40% of the total oceanic primary production (Field et al. 1998, Falkowski et al. 1998). They are unicellular (10-200 µm) but can also be found in colonies.

Major pigments of diatoms are chlorophylls a and c, β-carotene, fucoxanthin, diatoxanthin and diadinoxanthin and they are mainly photosynthetic. Some are obligate heterotrophs, while others can live heterotrophically in the absence of light, provided an appropriate organic carbon source is available.

Diatoms are used for various biotechnological applications, including for commercial purposes such as silicon production, nanotechnologies, environmental remediation or as fish feed in aquaculture thanks to their high lipid and amino-acid content. They are also used for the production of pharmaceutical or cosmetic products, and for the production of pigments for fish or animal meat.

Nutritionally relevant biomolecules produced by diatoms include high quality polyunsaturated fatty acids (PUFAs) such as omega-3 fatty acids.

The average total lipid content of an oleaginous diatom is 22.7% DW under normal growth conditions, which could achieve 44.6% DW under stress conditions (Hu et al., 2008) such as N or P deficiency. Another important characteristics of this algae for energy production is that lipid synthesis (such as of TAG) can be modulated and made more suitable as feedstock for biodiesel production (Rodolfi et al. 2009).

It has been reported that high light alters fatty acid synthesis to produce more of the saturated and mono-unsaturated fatty acids and that the total lipid content of cells increases with age (Hu et al., 2008).

2.1.g Haptophyta

Haptophyta (or Haptophyceae) typically have two flagella. They include Coccolithophores, which have an exoskeleton of calcareous plates and are abundant marine phytoplankton, especially in the open ocean. Other planktonic haptophytes include *Chrysochromulina* and *Prymnesium*, which periodically form toxic marine algal blooms, and *Phaeocystis*, the blooms of which can produce unpleasant foam which often accumulates on beaches. This alga is commercially produced to be used as feed for shellfish and shrimp larvae but also for cosmetics (AquaFUELs 2010a).

The suitability of a genus of Haptophyta for producing oil to be further converted into biodiesel has been demonstrated in open ponds in Israel (Boussiba *et al.* 1988).

2.1.h Dinoflagellates

Dinoflagellates (or Dinophyta) are common in all types of aquatic ecosystems and can be photosynthetic exclusively heterotrophic. Most part are marine algae but can also live in freshwater. They can form toxic algal blooms (among the most potent biotoxins known) when cell densities reach high levels. Dinoflagellates are main marine primary producers.

Some species have been studied for lipid productivity, for production of oil, PUFA and biodiesel.

Today this alga is cultivated commercially for the production of oils rich in docosahexaenoic acid (DHA) for nutraceuticals or for the production of pharmaceutical products.

Other algal groups exist but these have been less studies or less useful for the scope of this work.

2.2 Selected strain

For the purpose of producing starch, oil or biomass for energy green algae species have been far more studied than other species given their vast metabolic capacity and there is a large but fragmented literature about lab experiments and properties of different genus. Green algae are also largely commercially exploited for production of pigments (for example *Dunaliella* or *Haematococcus*) or for biological remediation (for example *Chlorella* or *Scenedesmus*).

Most part of algal biomass produced today is given by *Chlorella*, *Dunaliella* and *Haematococcus* but not as bioenergy feedstock.

Since green algae species are very fast growing and are able to accumulate high concentrations of oil useful for biodiesel production, a significant number of species are being considered as bioenergy feedstock. For example about half the strains tested by Hu and Sommerfield as possible candidate for bioenergy production are green algae, as are 11 out of 30 tested in Italy at the University of Florence (Rodolfi et al. 2009). *Chlorella* has also been chosen by Solazyme as primary platform for custom made biofuels production via heterotrophic fermentation due to its relatively high lipid productivity.

Besides bioenergy there is a long experience with *Chlorella* cultivation both in open ponds and in photobioreactors[15] due to its protein, vitamin and mineral content as well as the capacity of producing glycerol or pigments. For this latter, facilities using green algae can be found in Asia, Australia and Hawaii, and Israel. But its applications are not limited to food additives but are extended to the health market. Several plants producing *Chlorella* and *Scenedesmus* have been running for decades so far and a significant experience has been gained.

Chlorella has desirable technological properties that make it very suitable for its use in photobioreactors such as its resistance to shear stress and low adhesion plastic surfaces as well as its low tendency to form aggregates. Further, its ability to grow under high CO_2 concentrations (up to 40% v/v) such as the one that could be supplied by flue gas is an important advantage (Douskova et al. 2009, 2010), and concentration and type of amino acids binding can be considerably modified.

Chlorella is a fast growing and some strains can accumulate very high concentrations of lipids under stress (Francisco et al. 2010) or high amount of starch (Doušková et al. 2010), depending on the species. *Chlorella vulgaris* and *Chlorella protothecoides* were tested in terms of oil production (e.g. Xu et al. 2006).

Typical characteristics and composition of *Chlorella* are reported in the table below, with oil content around 10%.

Chlorella holds a promise also as ethanol source from starch fermentation as high quantity of cheap starch biomass can be produced from cultures grown in suitable outdoor photobioreactors. The ability of coupling starch production with CO_2 capture makes this a very attractive option as it enhances the ecological and economic impact.

Together with *Chlorella* sp., also *Scenedesmus* sp. was selected as a suitable alga for the production of biofuels in wastewater due to its robustness and the capacity of living outdoor in open ponds. The literature review highlighted experience in cultivating *Scenedesmus* in wastewaters. Further, the high heating value of this particular algae makes it particularly suitable for thermochemical processes (see chapters 6 and 10, where *Scenedesmus* sp. is considered for a specific case study).

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[15] For instance in Taiwan (www.taiwanchlorella.com) or in Germany (www.algomed.de), as well as in Australia (www.nutrakol.com/pdf/Dunaliella.pdf) or in Israel (www.wondercare.co.in/nature.htm)

Item	% algal DW
Moisture	7-7
Proteins (N x 6.25)	55-58
Lipids[16]	8-12
Saccharides	10-15
Fibre	6-8
Mineral substances	6-8
Chlorophyll	2.5-3.5
Nucleic acids	3-4

Table 1 - Chemical biomass composition and main constituents of a production strain *Chlorella* sp. (strain P 12)

Many formulas are used for the cultivation of this genus and an optimized composition of nutrient solution for high-yielded production of *Chlorella* outdoors in distilled water was proposed for example by Doucha and Lívanský in 2006.

$(NH_2)_2CO$	1100
KH_2PO_4	237
$MgSO_4.7H_2O$	204
$C_{10}H_{12}O_8N_2NaFe$	40
$CaCl_2$	88
H_3BO_3	0.83
$CuSO_4.5H_2O$	0.95
$MnCl_2.4H_2O$	3.3
$(NH_4)_6Mo_7O_{24}.4H_2O$	0.17
$ZnSO_4.7H_2O$	2.7
$CoSO_4.7H_2O$	0.6
NH_4VO_3	0.014

Table 2 - Initial composition (mg/L) of nutrient solution for growing high-yielding *Chlorella* based on the mean content of P, N, K, Mg, and S in algal biomass

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[16] The proportion of essential unsaturated fatty acids (oleic, linoleic, linolenic) in the total fatty acids under optimum growth conditions is in the range of 40-60 %.

3 Cultivation technologies

Microalgae can be cultivated in batch, semi-continuous or continuous cultivation systems.

In batch cultivation fresh cultivation medium is inserted into a PBR. The algae grow rapidly and slow down once some components in the growing medium become scarce. For photoautotrophically growing algae this limiting factor is often the amount of light energy reaching the algae culture and the effects of cellular respiration of dense cultures during the night. During night this leads to a loss of net biomass accumulated during the day.

Some batch systems envisage also the addition of small amounts of nutrients over time leading the algae under stress conditions to increase productivity of one component (for example oil content) before they stop growing.

In semi-continuous cultivation, a certain percentage of algal biomass is removed every few day from the reactor, while the reactor is refilled with water and essential nutrients for a new algal growth cycle. This avoids to completely stop and restarting the operations with fresh algae and cultivation medium. There are also examples of semi-continuous cultivation of algae, followed by batch cultivation for handling the final stressing phase.

Continuous cultivation is used for cultivation of heterotrophic organisms. There is no need to stop the reactor or to vary its productivity over time but to this end all reactor parameters as well as cell density must be continuously monitored and adjusted. Algae are continuously harvested to maintain optimal growth conditions over long periods. This method can ensure the highest yields of biomass over time but it doesn’t allow bringing algae under stress conditions to increase concentration of particularly valuable components.

3.1 Open ponds

The simplest open air algae cultivation systems are open shallow, unstirred ponds. They have been the method of choice so far for producing relevant amounts of algal biomass with CO_2 inserted as required. The sizes range from a few m^2 to 250 ha (see Figure 3a and b) using CO_2 in the atmosphere as carbon source for algae.

Its natural dilution from air into water limits the growth rate, making the yield per hectare relatively low. Further, the slow diffusion of nutrients and flotation and sedimentation of dead and living algae heavily limit the usage of available sunlight. This can be improved by some form of agitation, sometimes done in circular ponds using a mechanical arm stirring in a circular motion (Centre-Pivot ponds, Figure 3c), or more commonly in the so-called raceway ponds (Figure 3d), in which a paddle wheel (Figure 3e) forces a circulating water flow through a long narrow pond. The circuit is built in concrete and may be lined with white plastic. Evaporation is significant as well as temperature fluctuations, and rainfalls can dilute the available nutrients.

Blowing gas bubbles through the medium can provide both agitation and CO_2. Air, compressed CO_2 (possibly in the form of CO_2-rich combustion gases) can be applied.

The major bottlenecks of these open systems are that there is almost no possibility for temperature control (unless a source of cheap surplus heat is available, for example from a power plant or a cement factory nearby) and that they are very susceptible to invasion of algal predators, parasitic or invasive algae, or other algal strains that grow better at the applied conditions and therefore compete with the desired species (Carlsson et al., 2007; Chisti, 2007; Pulz, 2001; Rodolfi et al., 2009). Only a limited amount of species is dominant enough to maintain itself in an open system. Examples are *Dunaliella salina* (high salinity) and *Spirulina* (high alkalinity).

Major producers of Spirulina and Dunaliella in California, Hawaii, Australia and Israel have been relying on this method for over 30 years, taking advantage of the fact that the growth media of those two algal species are unsuitable for competing algal species[17]. For example in open ponds *Scenedesmus* and other fast growing algae can overgrow *Haematococcus* cultures rapidly.

Currently, large cultivation of microalgae is limited to a few microalgal species that are cultivated in open (raceway) ponds as this is a very economic open system for microalgae cultivation[18]. Their simple design and relatively low building costs make them the most used technology for most products of microalgal mass cultivation with a 15-30 cm layer of algal suspension (Borowitzka, 1999).

Important drawbacks of this system are that due to thick layer of algal suspension, the culture must be grown at low densities (about 0.5 algal DW/l) and the slow flow of poorly mixed algal suspension (15-30 cm/s) leads to low utilization of light energy and to accumulation of oxygen dissolved in the suspension.

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[17] Too basic or saline respectively.

[18] The Algal Biofuels Program of the DOE also concluded that open raceway ponds would be the method of choice for algal biomass production to to their cheapness and simplicity to build and operate.

Figure 3 - Examples of open cultivation systems (FAO, 2010)

a. Small pond for *Spirulina* culture, Asia (Wikipedia, 2007)
b. *Dunaliella salina* ponds of Cognis, Western Australia (BEAM)
c. Centre-Pivot ponds for the culture of *Chlorella* in Taiwan (BEAM)
d. Open raceway-type culture ponds of Earthrise in California, US(Spirulina.org.uk)
e. Paddle wheel of a raceway pond (NMSU)

Figure 4 – Open raceway pond (courtesy of Wageningen UR, AlgaePARC, The Netherlands)

3.2 Photobioreactors

Photobioreactors relate to algal cultivation systems trying to increase growth yields by creating enhanced surfaces for better light utilization, while keeping algal biomass enclosed so to reduce contamination and evaporation.

Some of the problems illustrated above such as the need to control temperature, gas exchange and competition can be alleviated through closing open systems by covering them with transparent glass or plastic material or a greenhouse, but this can become very expensive for large surfaces. Another simple inexpensive example is using polyethylene bags or sleeves (Figure 6a) for batch culture. Sizes go up to 1000 liters, but sensitivity to environmental conditions and short life expectancy make this system inappropriate for outside use. Several more advanced systems have been developed based on more durable transparent materials such as glass, polyethylene and polycarbonate, and comprise tubular reactors with arrays of glass or plastic tubes circulating growth media and algae, panel systems where cultivation occurs in upright standing panels mixed by air bubbling, or any other array of enclosed growth media offering maximal exposure to light with minimal layers of growth media.

These reactors offer continuous operation, a high level of controllability and elevated biomass concentrations, which results in lower space requirements and lower harvesting costs per tonne of algae. One example is the bubble column (Figure 6b), a vertical tubular reactor[19]. The scalability of

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[19] Vertical reactors intercept sun rays at large angles and dilute light compared with horizontal ponds.

this system is limited since, when putting several systems close to each other, they will cast a shadow on each other (Figure 6c). Using a reactor consisting of long horizontal tubes eliminates this problem[20] (tubular reactor, Figure 6d-f). However, this has its own scaling problem: algae will consume nutrients and CO_2 while producing O_2 (which could inhibit[21] algal growth at elevated concentrations), so growth conditions deteriorate further along the tube. Up-scaling can be achieved by installing individual modules with optimized size vs. tube length ratios. To make optimal use of surface area receiving solar irradiation, a flat photobioreactor[22] can be applied (Figure 6g). This system can potentially yield a much higher biomass concentration, but is still under development[23]. Difficulties are the complicated flow regime inside the reactor and scalability, although the latter has been greatly improved by a design called the green wall panel (FAO 2009a). Figure 6h shows flat photobioreactors in a solar panel-like set-up. There are many variations and innovations on the previously described closed systems.

Figure 5 – Horizontal tubular photobioreactor (courtesy of Wageningen UR, AlgaePARC, The Netherlands)

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[20] It should not be easily concluded that simply replacing vertical tubes with horizontal tubes eliminates the problem of shadowing. Overcoming the problem in both instances is a function of their spacing.

[21] This will depend on the residence time of the algae in the tube.

[22] Flat Panel Reactors consist of a rectangular transparent box with a depth of only 1 to 5 cm. Accordingly, this reactor type allows growth of high cell densities.

[23] Like vertical or horizontal tubes, flat-pane reactors are not exempt from the problem of shadowing when arranged in arrays.

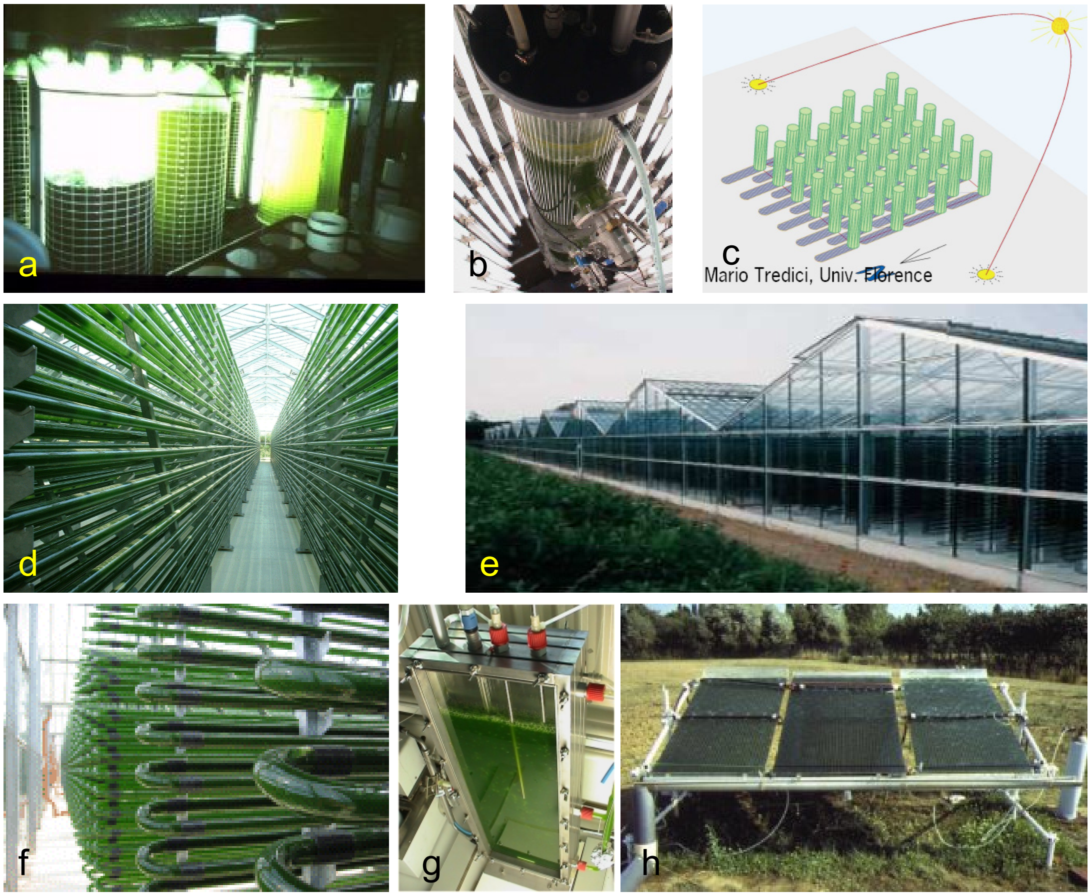


Figure 6 - Examples of closed cultivation systems

a. 'Big Bag' culture of microalgae (BEAM)
b. Bubble column reactor (Tredici in Wijffels, 2007)
c. Field of bubble columns induce shading (Wijffels, 2007)
d-f. Tubular reactor system (Bioprodukte-steinberg.de)
g. Experimental flat photobioreactor (Wijffels, 2007)
h. Experimental alveolar-panel photobioreactor (Tredici and Materassi, 1992)

PBR used for the cultivation of microalgae are either naturally or artificially illuminated to grow microalgae under photo-autotrophic conditions. Especially in lab experiments, they are artificially illuminated with fluorescent or other types of lamps.

All parameters of PBR (e.g. nutrients, light regime, gas exchange) are adjusted to realize optimal culture conditions. As already mentioned, costs of PBRs are much higher, but contamination is much lower compared to open systems. PBR design and engineering is still a very active field of research today, since closed culture systems are necessary to grow photosynthetic microbes and exploit them as a source of aquaculture feeds, food additives, specialty chemicals, cosmetics and are preferred by industry as research tools for biofuel production.

In air-bubbled plastic bags and annular columns the cost of operation (i.e. energy) may be very high due to the need of mixing to provide the necessary mass transfer. This operation requires more than 100 W/m^3 (or approximately 2000 MJ/ha/day) (AquaFUELs 2010b).

Within all the photobioreactor types described, tubular PBRs are the most popular type and their capital and operation costs are normally significantly higher than ponds.

As a way to decrease the final price of algal biomass production, the flue gas from various sources can be used as a cheap CO_2 source. For example, outdoor thin-layer bioreactor, built in a livestock farm, flue gas, after utilization of CH_4 anaerobically generated in biogas station, was used as a source of CO_2 for algal photosynthesis. Besides, minerals of liquid concentrate of the anaerobic digested livestock excrements can be used as a source of inorganic nutrients for algal growth, or flue gas, resulting from utilization of biogas produced from distillery stillage or from swine manure for electricity and heat production, was also successively applied as a cheap source of CO_2 for algae growth (AquaFUELs 2010b).

Further, there is the need for cooling PBR, which is generally provided by water (even seawater) spraying or by insertion of a cooling serpentine in the culture, but this requires pumping and can significantly increase the energy needed for algae growth.

PBRs have several advantages over open ponds. Being closed, it is easier to maintain an unialgal culture and reducing evaporation; due to a higher surface-to-volume ratio, they can attain higher volumetric productivities than ponds; they can reach higher cell concentrations significantly reducing costs for further concentrate the final algae paste; they provide a more accurate control of culture parameters (e.g. pH, temperature, pO_2), permitting in this way to cultivate species that couldn't survive in the open environment, and ensuring the predominance of the desired species.

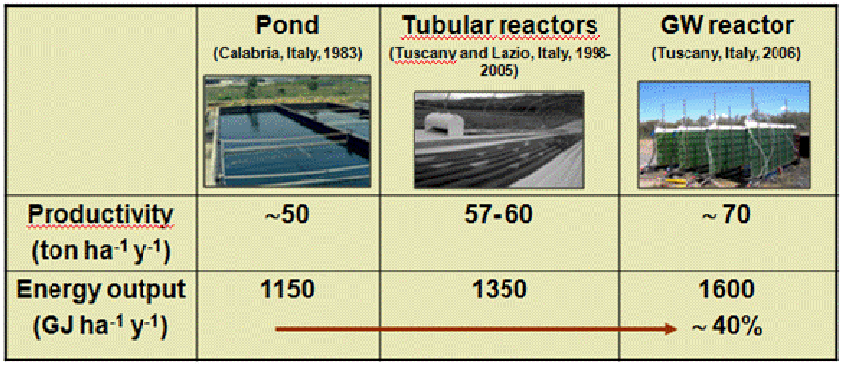
One of the main problems associated with PBRs culture is that the formation of biofilms of bacteria, oil or carbonate films, or the cultivated algae themselves, at the transparent walls of the tubes considerably reduce light penetration (they can be minimized e.g. by maintaining an highly turbulent flow in the reactor). In addition, they are much more expensive to build than ponds, but simple low-cost (and lower-efficient) systems can also be designed.

Main photobioreactors designs that have been discussed and identified during the AquaFUELs project include polyethylene bags, vertical columns, tubular PBR and flat PBR.

Polyethylene bags PBRs can be suspended or supported and those mixed by air bubbling are the most common cultivation devices for the production of algal biomass. From 50 to 500 L in volume, such reactors are mostly used indoors with artificial illumination. They are currently used by different companies (e.g. Ketura Kibbutz, Israel; GreenSea, France; NOVAgreen GmbH, Germany) for the cultivation of selected species for the cosmetic, food or pharmaceutical markets. Although sleeve reactors are inexpensive, their low surface-to-volume ratio (S/V), bio-fouling and the need of a very large number of units for large-scale production limit their applications.

Vertical column PBRs are made of rigid transparent cylinders (typically 2-2.5 m in height and 30-50 cm in diameter), with mixing achieved by air bubbling or by an airlift. They suffer from the same limitations of bags reactors. Vertical cylinders internally illuminated have been developed at the University of Florence and they can sustain algae culture with much higher S/V compared to completely filled columns. The small size and relatively high cost of this reactor limit its use for large scale production.

Tubular PBRs are commonly adopted in commercial plants. This category can be subdivided into: i) serpentine, ii) manifold and iii) helical PBR. Serpentine PBR consist of straight tubes connected by U-bends to form a flat loop that may be arranged either vertically or horizontally. Manifold PBR are made of parallel tubes connected at the ends by two manifolds. The main advantages of these systems over serpentine reactors are the reduction of head losses and lower oxygen concentrations, two factors that facilitate scale-up to industrial size. A horizontal manifold reactor is used by Algatechnologies Ltd (Israel) for the commercial production of *H. pluvialis*. Two small tubular units are currently used by ENI (Italy) to develop CO_2 abatement strategies with microalgae at their Gela refinery. Rather common, both at pilot scale and in commercial plants, are manifold photobioreactors arranged as to create a fence[24].



	Pond (Calabria, Italy, 1983)	**Tubular reactors** (Tuscany and Lazio, Italy, 1998-2005)	**GW reactor** (Tuscany, Italy, 2006)
Productivity ($ton\ ha^{-1}\ y^{-1}$)	~50	57-60	~ 70
Energy output ($GJ\ ha^{-1}\ y^{-1}$)	1150	1350	1600 ~ 40%

Figure 7 - Comparison between open ponds and PBR – productivity and energy output (Source: Prof Tredici, published in AquaFUELs 2010b)

Flat photobioreactors have not been used for mass cultivation of algae until recently. They are commercialized today by B Braun Biotech International (Germany) in sizes varying from 10 to 2000 L. Also glass panels exist (GW reactor, without alveoli), easy to clean and resistant to

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[24] The BioFence, developed by Applied Photosynthetics (UK) in the late 1990s, consists of an array of transparent tubes racked together in a fence-like structure in which the culture suspension is circulated by a centrifugal pump or by an airlift and industrial scale plants based on this design currently exist. More information on this PBR design and examples of current applications can be found in (AquaFUELs 2010b).

weathering. The drawback is their weight, fragility and high cost that prevent them to be used in large scale plants. A similar concept is being developed successfully in Austria by the company Ecoduna. More recently, a disposable panel has been developed, i.e. a flat reactor consisting of a plastic culture chamber enclosed in a rectangular metal frame.

The development of PBR is mainly driven by the fact that there is a demand for natural products to substitute those derived from synthetic ones as nutraceuticals but also for cosmetics for example. Therefore the need to produce always more algae biomass to be used as a feedstock for these industries. The choice between different cultivation systems and different bioreactors, which is inevitably linked to the final production costs, will necessarily consider the location of the production and the desired properties of the final algal biomass (e.g. optimization of production of pigments, triacylglycerols for biodiesel, or sugars for ethanol). According to the literature review and the outcomes of AquaFUELs project there is no best choice from both an economic and environmental perspective.

There is good experience in growing green algae in both open ponds and PBR.

At present, culture methods used in hatcheries for *Tetraselmis* production use mainly polyethylene bags and transparent glass-fibre cylinders (up to 500 L) usually kept indoors with artificial light (Fulks et al. 1991). For example during summer in Central Italy in a pilot experiment (reproducing a full scale plant), in 120-L annular columns at a daily dilution rate of 40%, *Tetraselmis suecica* attained an average volumetric productivity of 0.46 g/l/day, and an overall areal productivity of 36.3 g/m^2/day with a photosynthetic efficiency in the PAR region of 9.4% (Chini Zittelli et al., 2006). In table 5 for example a comparison of culture characteristics of Chlorella grown in raceway ponds and thin-layer PBR is reported, building on the information gathered during the AquaFUELs project.

LCA analyses of algal biofuels, including the work we did in the AquaFUELs project and the Algae&Energy Austria project agree on the fact that even under optimistic yield assumptions tubular photobioreactors require more energy to run than the algal biomass being produced, while in open ponds the overall energy balance could be positive (even if they can pay an higher energy cost to bring the algae slurry to the desired concentration). The main reason is the energy required for cooling and heating the growing medium.

Culture characteristics	Raceway ponds	Thin-layer
culture volume (l m^{-2})	150-300	6-8
culture layer thickness (mm)	150-300	6-8
biomass harvest density (g l^{-1})	0.5-1	35-50
harvest/downstream processing density multiply	150-300	3-4.3
surface/volume ratio (m^{-1})	5	100
photosynthetic efficiency (% of PAR)	2.5-4	5-8
areal productivity (g m^{-2} d^{-1})	10-20	20-40
volumetric productivity (g l^{-1} d^{-1})	0.05-0.1	2-5
efficiency of CO_2 utilization (%)	5-20	60-70

Table 6 - Typical culture characteristics of Chlorella sp. grown in raceway ponds and thin-layer PBR.

The situation can change significantly if the culture medium is provided by nutrient-rich wastewater, but in this case the cultivation would be restricted just to the most resistant algae species (e.g. *Scenedesmus sp.*).

Simpler panel reactors can have better performances in terms of energy balance, but still are unable to return all the direct and indirect energy required for their construction and operation.

In the case of CO_2 freely available at the cultivation site (including from waste incinerators, power stations, limekilns, cogeneration units, etc.), PBR have the advantage of being able of using it directly to grow algae. This could account towards the assignment of carbon credits with an economic value, and that could possibly be traded on the market or account towards the fulfillment of a carbon reduction mandate.

Cultivation system	Arrangement	Mixing system	CO_2 uptake	Temperature control	Suitability for monoculture	Suitability for scale-up	Cost (per m^2)
Raceway ponds	Horizontal	Paddle-wheel	Low	No	No	Yes	Low
Circular ponds	Horizontal	Rotating paddle	Low	No	No	No	Low / Medium
Vertical column PBR	Vertical	Air bubbling	Low / High	No	No (only under rare conditions)	No	High
Serpentine PBR	Horizontal / Vertical	Airlift / Pump mixing	Low / High	Yes	Yes	No	High
Manifold PBR	Horizontal / Vertical	Airlift / Pump mixing	Low / High	Yes	Yes	Yes	High
Helical PBR	Vertical	Airlift / Pump mixing	Low / High	Yes	Yes	No	High
Flat glass panel PBR	Inclined / Vertical	Airlift / Air bubbling	High	Yes	Yes	No	High
Flat disposable panel PBR	Inclined / Vertical	Air bubbling / pump mixing	High	Yes	Yes	Yes	Medium / High

Table 5 - Comparison of different algae cultivation systems (Adapted from Prof. Mario Tredici, Scientific Coordinator of the AquaFUELs project)

3.3 Offshore systems

Historically, seaweed cultivation techniques have been developed based on the local circumstances, often using shallow, protected coastal areas that are safe, easily accessible and allow for easy immobilization of the culture system to the seabed. Generally the techniques used are labor intensive and therefore are restricted to regions with the lowest incomes and where the quality of the final produced biomass is not fundamental. Harvesting natural macroalgae populations is also common practice in some areas such as South-East Asia.

For renewable energy production, macroalgae production is not based on harvesting natural populations and therefore focuses on growing seaweed species that can attach to underwater ropes or similar support structures. These locations shouldn't be intensively used for other purposes such as shipping routes, port areas, and recreation. Important examples of cultivation systems adaptable to these conditions are those based on vertical ropes, which allow the cultivated seaweed to catch all available light until the maximum light penetration depth; or systems based on horizontal lines, which minimizes the amount of rope material needed per unit of area, or hybrid systems combining horizontal and vertical lines. In all cases the systems can be floating, anchored to the sea or both. However important problems of damage to rope structures and washed off biomass have been reported (Chynoweth, 2002). During experiments at sea (Buck et al., 2004), using rings (diameter of 5 m, surface of 19.6 m^2 and 80-100 m substrate rope) with ropes as a base for seaweed to attach to, gave the best results, especially under high flow or heavy weather conditions. These rings can be attached to each other and/or the seabed and can include a slow-release fertilizer. The main problem of this system is that the rings need to be harvested individually, making cost-price reduction through economy of scale more difficult.

Offshore oil or gas platforms provide an anchoring point, boat and helicopter landing, personnel accommodation and in some cases pipes to shore that could be converted to pump seaweed or biogas to shore, or even CO_2 or nutrient rich waste water to the cultivation location. Also, offshore wind turbine parks contain a considerable amount of unused space between the turbines (distance between turbines is seven times the rotor blade length) which is restricted to maintenance vessels. Turbines provide anchoring points and have and individual boat landing, and in case seaweed is (partially) converted into electricity on-site, or if electricity is needed for a first processing step, a grid connection is available.

For seaweed cultivation on a large scale (1,000s ha), a cultivation system that is simple, low-cost, low maintenance, and has a high light capture, productivity, resilience to climatic conditions, durability and life expectancy, while allowing easy harvesting and replantation doesn't exist at present.

Offshore systems have been treated more extensively in (FAO, 2009a), but for the purpose of this research, trying to assess the best available option for energy production in Austria, offshore systems have been left aside.

3.4 Integration with wastewater treatment

Another possibility is the integration of algae cultivation in a wastewater treatment as the microalgae produce oxygen which is used by the bacteria and this in turn decompose waste materials with the release of CO_2, phosphates, ammonia, and other nutrients, which can be used by the algae. Furthermore, algae can decompose and remove chemical or organic pollutants, pathogens, or heavy metals. These processes are sometimes referred as Phycoremediation (Carlsson et al., 2007). Microalgae can be used for the treatment of municipal, industrial and agricultural effluents are (U.S. DOE, 2010). For cultivating open systems 'Stabilization Ponds' or 'High Rate Ponds' can be used. Stabilization Ponds consist of at least 2 ponds. In the first (4-5 m depth), the BOD reduction occurs by anaerobic digestion and sedimentation of solids. The second pond is a high surface area (2 m depth) in which the nitrification and oxidation of NH_4 occurs. The cleaning is carried out by aerobic bacteria, anaerobic bacteria and microalgae.

Through the combination of algae cultivation and wastewater treatment, the need for fresh water and nutrient requirements for algae production are reduced, the capital costs and operating costs are reduced, as well as the energy demand for oxygen to be blown in the aeration tank. Disadvantages are the large space requirements and long residence times, leading to very low productivities. Further if the microalgae are used for cleaning in municipal wastewaters, the biomass cannot be subsequently used for food or feed purposes.

Of course the potential for wastewater treatment and bioremediation is not limited to microalgae, but includes other aquatic species that can then be converted to energy through biochemical or thermochemical processes. Remediation efforts of polluted water bodies in general can provide significant amounts of free waste biomass from such water plant material (see for example Hartebeesport dam at http://www.dwa.gov.za/harties/) that may be utilized for fuels production.

3.5 Harvesting and water separation

When cultivating seaweed, every system requires a specific method of harvesting the biomass, but most commonly a specially developed harvesting vessel is used, which cuts the seaweed and hauls it inside.

When coming to microalgae, many methods are available for harvesting, and they consist in a first step towards concentration of algal biomass. Harvesting can be made trough (Richmond 1986):

- centrifugation,
- electroflotation,
- and chemical flocculation,

possibly followed by

- sedimentation or air flotation,

- continuous belt filtration,
- vibrating and stationary screens,
- sand bed filtration, and
- autoflocculation.

Sometimes it is also possible to proceed directly to sedimentation, without going through other harvesting processes. This improves significantly the energy balance but on the other hand make the harvesting process very long.

Microalgae concentrations always remain very low while growing (typically 0.02 - 0.05 percent dry matter in raceways ponds and 0.1 - 0.5 percent dry matter in tubular reactors (personal communication with Prof. Tredici, University of Florence), that is just 1 tonne dry biomass recovered from 200 m^3 to 5000 m^3 of water).

Harvesting can be responsible for 20–30 percent of the total cost of producing the biomass (Molina Grima et al., 2003).

The technically simplest option is the use of <u>sedimentation</u> in settling ponds. Once a day the settling pond is filled with a fully grown algae culture and drained at the end of that day, leaving a concentrated biomass volume at the bottom, which is stored for further processing (Benemann et al. 1996). This way generally 85 percent (and up to 95 percent) of the algal biomass was found to be concentrated in the bottom of the settler (Sheehan et al., 1998) at 3 percent dry matter (Sazdanoff, 2006) although this will depend on the species used. Sedimentation requires long residence times and therefore large areas. By the addition of flocculants, the process can be accelerated.

Another way of separating algae from water is <u>filtration</u>. During filtration, the suspension is passed through a permeable membrane or a screen, and separated based on the size. There are a variety of filtration systems such as microfiltration, ultrafiltration, pressure filtration, vacuum filtration and cross-flow filtration. Many options have been described, including vacuum, pressured and rotating filtering. Some acceptable results have been obtained for colonial microalgae, but not for unicellular species (Benemann et al. 1996; Molina Grima et al. 2003). Furthermore, filtration is a slow process and large capacity would be required to keep up with the production of a large algae production plants. Filtration could be the best option in terms of energy requirements and would significantly change the energy balance of algae production. New membranes are under development but no long term reliable solution has been demonstrated so far.

Membrane microfiltration and ultra-filtration are other possible alternatives to conventional filtration for recovering algal biomass, which are more suitable for fragile cells and small-scale production processes.

<u>Centrifugation</u> is often used for the concentration of high-value algae, and generally considered expensive because of its high energy (electricity) consumption. However it is the best known and deployed method to concentrate algae, especially small (unicellular) ones. Within the US Aquatic Species Program the cost of centrifugation were estimated at 40 percent of production cost (and 50

percent of investment cost considering open pond systems). It is possible to apply centrifugation as a secondary harvest method to concentrate from 1-5 percent dry matter to 15-20 percent and this would reduce centrifugation costs at least 50 times (Benemann et al. 1996). This two-step approach is the one that was chosen during the Algae&Energy project, for *Chlorella* and *Scenedesmus*. Green algae such as *Chlorella* and *Scenedesmus* are tolerant to impulsion using centrifugal pumps, in addition to aeration, no mechanical damage being reported by this phenomenon. This makes these algae suitable for centrifugation and this method could be considered the status of the art today for commercial exploitation of algae for energy.

Other options include flocculation that consumes a large amount of chemicals that need to be recuperated in a closed loop, and cells explosion with ultrasound (normally very energy intensive). Flocculation is currently applied in industry. A novel method of harvesting is the ultrasonic aggregation. By an ultrasonic field, the algae can be concentrated on a particular point, and they can be harvested by lowering. This type of harvesting is not suitable today for large-scale applications due to the high energy requirements and the necessity of cooling. However there are companies (e.g. Originoil in the US) that have patented very innovative solutions for cell explosions, extracting oil at high rates and at low cost. These are considered break-through technologies but they are still in the demonstration phase.

The harvesting and dewatering phases may account for 20-30% of the total production cost for algal biomass (Uduman et al., 2010). In order to remove large quantities of water and process large algal biomass volumes, a harvesting method involving several steps is preferred. The concentration of algal biomass is typically 0.5-1.0 g/L in open ponds and can reach 5-10 g/L in closed systems. At 1 g/L of algal biomass, 1000 kg of water must be processed to obtain 1 kg of dry biomass (AquaFUELs 2010b).

The choice of which harvesting technique to use depends very much on the species of microalgae and the final product desired.

Companies like BGU and Algatech have designed successful harvesting and processing procedures for Haematococcus biomass that are based on sedimentation and works without invested energy at over 90% efficiency, creating a concentrated cell slurry that can be further dewatered and dried. Flocculation of Nannochloropsis has also been successfully applied. Evodos Algae Technologies recently patented a technology that allows over 90% algae separation with a positive energy balance (AquaFUELs 2010b).

Dewatering process	Highest possible yield	Highest possible water removal concentration factor	Energy usage	Reliability	Limitations
Flocculation	>95% removal of microalgae	200-800 efficiencies of >80%	Low energy requirement for slow mixing: varies largely	Very good	Flocculants can be expensive and may cause contamination issues
Centrifugation	>22% TSS; 80-90% clarification; >95% cell harvesting efficiency; self-cleaning disk stack centrifuge: 12% TSS	Self-cleaning disk stack centrifuge: 120	Very high: 8 kWh/m^3	Very good	High energy input
Gravity sedimentation	0,5% - 1,5% TSS	Lamella separator: 16	Low lamella separator: 0,1 kWh/m^3	Poor	Process is slow
Filtration and screening (natural filtration)	1-6% TSS	15-50	Low vibrating screen filter: 0,4 kWh/m^3	Good	Filters and screens need to be replaced periodically
Filtration and screening (pressure filtration)	5-27% TSS	50-245	Moderate chamber filter press: 0,88 kWh	Very good	Filters and screens need to be replaced periodically
Tangential flow filtration	70-89% microalgal recovery	5-40	High: 2,06 kWh/m^3	Good to very good	High energy input; Filters need to be replaced

					periodically
Flocculation – Flotation	Dissolved air flotation: 1-6% TSS; Dispersed air flotation: 90% microalgae removal	n/a	High; Dissolved air flotation: 10-20 kWh/m^3	Good to very good	Electrodes need to be replaced periodically
Electrocoaugulation	95% microalgae removal	n/a	Medium-High: 0.8-1.5 kWh/m^3	Very good	Electrodes need to be replaced periodically
Electroflotation	3-5% TSS	300-600	Very high	Very good	Electrodes need to be replaced periodically
Electrolytic flocculation	>90% microalgae removal	n/a	Low-Medium: 0.33 kWh/m^3	Very good	Electrodes need to be replaced periodically

Table 6 – Microalgae harvesting techniques (Source: AquaFUELs 2010b)

3.6 Algae processing

After harvesting, the biomass must be processed quickly in order to prevent degradation by enzymes. In some process chains the algal biomass is processed immediately, prior to conversion into biofuels. It is normally processed in an intermediate product (oily slurry or powder) with higher energy density due to the higher dry matter content. This avoids transporting huge amounts of water making the overall process less expensive.

The treatment can consist in drying algae or in extracting a portion of the lipid contained in the cells. A more detailed description of algae processing methods can be found in Hingsamer et al. 2012.

For Chlorella, the next step after the thickening of algal biomass by sedimentation and centrifugation is the disruption of algal cells. The rigid cellulosic cell wall, one of the characteristics of *Chlorella*, causes a low utilization of cell content. The digestibility of ruptured *Chlorella* cells increases to 80 % (Doucha et al. 2008) compared to 15-25 % for unruptured cells for further biochemical conversion processes. To open the cells there are a number of methods available (freezing, alcalic and organic solvents, osmotic shocks, sonication, high-pressure homogenization and bead milling) but bead mills is most common method for large production. (Doucha et al. 2008). This process can be avoided when algae are further processed with thermochemical conversion. Similar considerations apply to *Scenedesmus*.

3.7 Biotechnology of Macroalgae

Although macroalgae are not dealt within the scope of this thesis, it would be good to mention them as a possible alternative to microalgae for energy purposes. Macroalgae are less suitable for the production of liquid biofuels[25], but hold a great promise as feedstock for fermentation processes or to be used directly in thermochemical processes. Current uses and biotechnology of Macroalgae far exceeds those of microalgae, with macroalgae being harvested for food, feed or biocompounds (e.g. agar, see chapter 4) all across the world, but mainly in South-East Asia. Three distinct algal classes, Chlorophyta, Rhodophyta, and Phaeophyta, have macroalgae representatives, and all classes are being exploited economically (AquaFUELs 2010a).

Culture systems are very different between macroalgae (seaweed) and microalgae (macroalgae and seaweeds have been treated more extensively by the author in FAO 2009a).

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[25] The most studied macroalgae for biofuels is *Chlorophyta sp.,* belonging to the genus of Ulva and Caulerpa.

The brown algae relevant to biofuel uses are mainly belonging to the order of Fucales (including representant of the following families: Alariaceae, Fucaceae, Himanthaliaceae, Sargasseae), Laminariales and Tilopteridales (AquaFUELs 2010a).

4 Algae non-energy products

Today algae are used by humans in many ways; for example, as fertilizers, soil conditioners[26] and livestock feed. They are cultured in clear tanks or ponds and are either harvested or used to treat effluents pumped through the ponds. Algaculture on a large scale is an important type of aquaculture in some places.

The number of products that can be made from algae is virtually unlimited, due to the large variety of species whose composition can be influenced by changing the cultivation conditions. With only a few commercial algae-based products deployed, this resource is largely untapped. This is due to a range of reasons: poor marketing (Edwards, 2008), the economic and bureaucratic barrier of getting new products approved by regulating authorities, insufficient experience with algae production, and the commercial barrier due to lack of investments in large-scale production facilities.

Today commercial production of microalgae is limited mainly to the genera Arthrospira, Chlorella and Dunaliella that, due to their high growth rate (or specific characteristics of the growth medium that limits contamination) can be grown in large open ponds. These systems are preferred as cheaper and easier to operate. However, this apply only to a small number of algae, which require a specific medium and cannot be cultivated for prolonged periods in open systems mainly because of contamination.

Still the bulk of commercial products from algae are derived from seaweed, produced for food and alginates[27] and partially harvested from natural populations, rather than cultivated. About 7000 tons dry weight of microalgae was produced commercially in 2004 (Brennan et al., 2010), compared to the 16 million tons fresh weight of seaweed production in 2007 (FAO, 2009b). The amount of commercially produced algae products is small if compared to the amount of known algal products.

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[26] For example Maerl is commonly used as a soil conditioner.

[27] Between 100,000 and 170,000 wet tons of *Macrocystis* are harvested annually in California for alginate extraction and abalone feed.

Microalga	**Annual production**	**Producer country**	**Application and product**	**Price**
Spirulina	3000 tons dry weight	China, India, USA, Myanmar, Japan	Human nutrition	36 €/kg
			Animal nutrition	
			Cosmetics	
			Phycobiliproteins	11 €/mg
Chlorella	2000 tons dry weight	Taiwan, Germany, Japan	Human nutrition	36 €/kg
			Cosmetics	
			Aquaculture	50 €/L
Dunaliella salina	1200 tons dry weight	Australia, Israel, USA, Japan	Human nutrition	
			Cosmetics	
			β-carotene	215-2150 €/kg
Aphanizomenon flos-aquae	500 tons dry weight	USA	Human nutrition	
Haematococcus pluvialis	300 tons dry weight	USA, India, Israel	Aquaculture	50 €/L
			Astaxanthin	7150 €/kg
Crypthecodinium cohnii	240 tons DHA oil	USA	DHA oil	43 €/g
Shizochytrium	10 tons DHA oil	USA	DHA oil	43 €/g

Table 1 - Commercially produced microalgae; amounts, locations, applications and market value (2004) (Brennan and Owende 2010, reported from FAO 2010)

Both commercial and yet-to-be-commercialized algal products can be interesting to co-produce with bioenergy. Depending on the microalgae species, various compounds can be extracted for industrial applications (biofuels, cosmetics, pharmaceuticals, nutrition and food additives, aquaculture, and pollution prevention): oil, fats, polyunsaturated fatty acids, natural dyes, pigments, antioxidants, sugar, high-value bioactive compounds, and other fine chemicals and biomass (Mata et al. 2010).

Algae carbohydrates include mono-sugars (glucose, lactose, mannose, xylose, ribose, rhamnose), di-sugars and 1,4 polysaccharides - glucosen and starch. The sugars, especially the poly-sugars can be used as stabilizers as they thicken and can give a smooth and gentle texture. They absorb large quantities of water and grant the product with moisturizing traits. Attached to the negative electrical charge of the poly-sugars are electrolytes, released in a controlled way to the skin cells.

For example the presence of polysaccharides in cosmetic products allows this controlled release of the active substances and offers an efficient treatment of skin diseases without side-effects.

4.1 Human food consumption

Algae use as food are present in Chinese literature as early as 2500 years ago (Tseng, 2004) and Chinese consumes more than 70 species, including fat choy[28]. In Japan, over 20 species are used; in Ireland the use of dulse is common; in Chile, the use of cochayuyo (AquaFUELs, 2010b). Several parts of Asia are well known for consuming algae directly and some indigenous people in Africa, South America and Mexico consume small quantities of naturally occurring algae mostly because of the vitamins and nutrients they provide (Edwards, 2008). Laver is used to make "laver bread" in Wales where it is known as *bara lawr*; in Korea, gim; in Japan, nori and aonori. It is also used along the west coast of North America from California to British Columbia, in Hawaii and by the Māori of New Zealand. Sea lettuce and badderlocks are a salad ingredient in Scotland, Ireland, Greenland and Iceland (AquaFUELs, 2010b).

Much less known to the general public is the variety of algae-derived ingredients that is used in food processing. Mostly as subordinate ingredients such as emulsifiers, thickeners, emollients (Edwards 2008), fats, polyunsaturated fatty acids, oil, natural dyes, sugars, pigments, antioxidants, bioactive compounds (Mata et al., 2010).

Cultivated microalgae (including Cyanobacteria) such as Spirulina, Chlorella are considered nutritional supplements and Vitamin-C supplement; Dunaliella has very high content of beta-carotene. Microalgae for human nutrition can be found today in the market in different forms such as tablets, capsules and liquids. They can also be incorporated into snack foods, candy bars or gums, beverages, noodles, wine, beverages, breakfast cereals, nutrition bars, cookies (Lee 1997; Spolaore et al. 2006).

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[28] A cyanobacterium considered a vegetable.

Algae oils have typically high levels of unsaturated fatty acids. For example, Parietochloris *incisa* is very high in arachidonic acid, where it reaches up to 47% of the triglyceride pool (Wikipedia). Some varieties of Algae favored by vegetarians contain the long-chain, essential omega-3 fatty acids, Docosahexaenoic acid (DHA) and Eicosapentaenoic acid (EPA), in addition to vitamin B12. Fish oil contains good quantities of omega-3 fatty acids (derived from microalgae). Algae has actually emerged in recent years as a popular source of omega-3 fatty acids for vegetarians who cannot get long-chain EPA and DHA from other vegetarian sources.

Most algae cannot be used directly as a human food and the reason for this is that cell walls are not digestible. However, mechanical solutions, strain selection or bioengineering could overcome this problem.

Seaweed is produced for human consumption especially in Asia and its cultivation and harvesting is a labor intensive process. Once dried, seaweed is normally consumed entirely, leaving no option for co-production.

However, even if it is not possible to digest the whole algae, technological solutions exist to extract valuable nutritional products. Algae can provide vitamins and are rich in iodine, potassium, iron, magnesium and calcium.

Proteins for example are of major importance in human nutrition and the lack of them is one of the biggest factors in world malnutrition. Some algae contain up to 60% protein.

As also mentioned in chapter 2, a well-known alga currently cultivated for its protein content is the cyanobacterium species *Athrospira*, better known as *Spirulina*. Consumption of *Spirulina* by the Aztecs has been reported already in the sixteenth century A.D. in Mexico and at Lake Chad (FAO, 2010).

The reason why *Spirulina* is the most cultivated microalga is that it is easy to cultivate as a monoculture and therefore can be used as a low-cost source of proteins, vitamin A, B12, and nutritionally relevant acids (FAO, 2010). As already mentioned, this is because it is one of the few species that grows at a high pH and is bigger than single cell algae as it can form multicellular groups, therefore it is easier to harvest. Comprehensive reports on Spirulina have been published by organizations like the FAO.

Spirulina is reported to contain not only around 60% raw protein, but also vitamins, minerals and many biologically active substances. Its cell wall consists of polysaccharides, has a digestibility of 86 percent, and can be easily absorbed by the human body (Becker, 1994).

Other algae species are known to have high protein content as well as showed in the following table but the lack of texture and consistency of the dried biomass, its dark green color and its slight fishy smell are undesirable characteristics for the food industry (Becker, 2007).

Alga	Protein	Carbohydrates	Lipids
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
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

Table 2 - General composition of some common microalgae (% of dry matter) (Adapted from FAO 2010)

Co-production for bioenergy purposes is not an option if the complete cell mass is used as food; therefore this co-production option is less relevant for the purposes of this paper. However it is possible to use the remaining algal biomass for energy purposes, after nutrients extraction. For example the two main nutrients from *Spirulina* are phycobiliproteins (a blue food dye) and a tasteless, odorless yellow-white protein extract that can have several food applications (FAO, 2010). The biomass remaining after extraction could be used for example for the production of biogas or biocoal (see chapter 7).

Vitamins (especially beta-carotene) are much higher in Chlorella than in plants. Chlorella has also been analysed in terms of mineral substance contained. The table below comes from AquaFUELs 2010a and is relevant not only for the use of these algae as food complement but also for estimating its thermochemical properties (see chapter 5).

Element	mg/100 g DW
Phosphorus	1200
Potassium	879
Sulphur	600
Magnesium	300
Calcium	230
Iron	70
Manganese	14
Zinc	11
Copper	4
Cobalt	0.5

Table 3 - Proportion of mineral substances and important trace elements in the Chlorella dry weight

4.2 Health and pharmaceuticals

In addition to food, algae provide a wide variety of medicines, vitamins, vaccines, nutraceuticals[29] and nutrients that may be unavailable or too expensive to produce using plants or animals. Health food products currently dominate the microalgae market (Pulz et al., 2004). A wide variety of algae and algal products have shown medical or nutritional applications. In Japan alone the 1996 consumption of health food from microalgae amounted to 2400 tons (Lee, 1997).

An overview of the pharmaceutical products that can be produced from algae is given below (further details can be found in FAO, 2010).

4.2.a Pigments

Microalgae contain a multitude of pigments associated with light incidence such as chlorophyll, phycobiliproteins (which improve the efficiency utilization of light energy) and carotenoids (which protect them against negative effects of solar radiation). Algal pigments are widely used for

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[29] A nutraceutical is a food or food product that reportedly provides health and medical benefits, including the prevention and treatment of disease.

processed food as natural colorants as an alternative to chemical dyes and coloring agents. At present carotenoids from microalgae are already used as β-Carotene (mainly from *Dunaliella*) as a vitamin A precursor; lutein, zeaxantin and canthaxantin for chicken skin coloration, or for pharmaceutical purposes. Astaxanthin (produced from Haematococcus) is used in aquaculture to give to certain fish a typical red color. The phycobiliproteins phycocyanin and phycoerythrin are unique to algae and they are used for food and cosmetics applications (Pulz et al. 2004).

Carotenoids are also important for their antioxidant functionality that gives them an anti-cancer effect (Astaxanthin being the most powerful natural anti-oxidant known. Some algal pigments can also be used as natural colorants in orange juice, chewing gum, ice sorbets, candies, soft drinks, dairy products and wasabi (Spolaore et al. 2006).

4.2.b Polyunsaturated fatty acids (PUFAs)

PUFAs are important nutrients that must be supplied by external sources as they cannot be produced by the organism itself. Well-known PUFAs include omega-3 fatty acids, that can be found at high concentrations is fish oil. This is because fish accumulate them by eating algae or other algae eating organisms. Direct production of PUFA from algae has developed only recently and has the advantage of lacking unpleasant fish odor, and producing a higher quality product (FAO, 2010). PUFAs can reduce cardiovascular diseases and obesity[30].

4.2.c Other bioactive algal products

The most important compound in *Chlorella* sp., from a medical point of view is the immunostimulator β-1,3-glucan, a free radical scavenger and blood lipid reducer. Efficacy of this compound against gastric ulcers, wounds and constipation, preventive action against atherosclerosis and hypercholesterolemia, and antitumor action have also been reported (Spolaore et al., 2006).

Microalgae are also a valuable source of essential vitamins (e.g., A, B1, B2, B6, B12, C, E, nicotinate, biotin, folic acid and pantothenic acid) (Richmond, 2004). Furthermore, sulfated polysaccharides of microalgae can be used in anti-adhesive therapies against bacterial infections both in cold- and warm-blooded animals (Banerjee et al., 2002).

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[30] They can improve the regulation of membrane's fluidity, electron and oxygen transport, as well as thermal adaptation (FAO, 2010).

The Chlorella Growth Factor (CGF) is a water-extractable cell fraction containing free amino acids, peptides, glycoproteins, polyamines, some vitamins, minerals and other, as yet not exactly defined components and still at the R&D stage. CGF promotes tissue regeneration, cell growth and division. It stimulates the production of leukocytes and their phagocytic activity, i.e. the ability to eliminate foreign bacteria and also the production of lymphocytes responsible for the synthesis of antibodies - important factors in the immunity against infections. It is a suitable dietary supplement during the administration of probiotics, i.e. substances positively affecting the composition of intestinal microflora. It has been shown that, following an administration of the algal extract, the organism exhibits a better regeneration of damage caused by ionising radiation. *Chlorella* extracts have found their use in topical applications, e.g. in the treatment of chronic inflammations, eczemas, crural ulcers, burns and other badly healing wounds, which are healed by a fully functional tissue. Japanese laboratories have repeatedly published data on the anti-tumour activity of the algal extract (AquaFUELs, 2010a).

Some beneficial stimulatory effect when used for watering freshly planted fruit or forest trees or vegetables are also attributable to the medium (the nutrient solution) used for *Chlorella* cultivation. It stimulates plant root-taking and growth.

4.3 Ingredients for processed foods

The most valuable algae products are the macroalgal polysaccharides, like agar[31], alginates and carrageenans, especially due to their rheological gelling or thickening properties. An increase in R&D related to new products from transgenic microalgae or protoplast fusion[32] has been observed recently.

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[31] Agar, a gelatinous substance derived from red algae, has a number of commercial uses. E406 when listed as ingredient in the EU.

[32] Protoplast fusion is a type of genetic modification in plants by which two distinct species of plants are fused together to form a new hybrid plant with the characteristics of both, a somatic hybrid.

4.3.a Agar

Agar made from seaweed is used in a wide range of applications: for food products such as frozen foods, bakery icings, meringues, dessert gels, candies and fruit juices; for industry uses like paper sizing/coating, adhesives, textile printing/dyeing, castings, impressions; for biological culture media, in molecular biology (more specifically agarose, used for separation methods) and for pharmaceutical products to produce bulking agents, laxatives, suppositories, capsules, tablets and anticoagulants (Cardozo et al. 2007 and FAO 2010).

4.3.b Carrageenan

Carrageenan is a water soluble group of polysaccharides that are more widely used than agar as emulsifiers and stabilizers especially in dairy products[33]. κ- and ι-carrageenans are especially used in chocolate milk, ice cream, evaporated milk, puddings, jellies, jams, salad dressings, dessert gels, meat products and pet foods, due to their thickening and suspension properties. Several potential pharmaceutical uses of carrageenans (like antitumor, antiviral, anticoagulant and immunomodulation activities (Cardozo, Guaratini et al. 2007)) have also been explored.

4.3.c Alginate

Alginate[34] (or alginic acid) is produced by brown seaweed and is used chiefly in the textile industry for sizing cotton yarn. It is widely used in the food and pharmaceutical industries due to its gelling and chelating ability and its capability to form a highly viscous solution (Cardozo et al. 2007).

4.4 Algae for livestock consumption

The use of algal biomass as feedstock for animals after oil extraction has an enormous market potential. Most algae have a natural high protein content while a high oil content is mostly achieved though manipulation of cultivation conditions. If recent soy meal prices (2008) are taken as a reference, the value of algae after oil extraction would be at least €230/t (Steiner 2008).

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[33] For example it can be extracted from the red alga *Chondrus crispus*. E407 when listed as ingredient in the EU.

[34] When used in the EU, it is normally reported as E400 to E405 among ingredients.

The use of micro-algae as animal feed is mainly limited to poultry, as it improves the color of the skin, shanks and egg yolks. Multiple nutritional and toxicological evaluations demonstrated the suitability of algae biomass as a valuable feed substitute for conventional protein sources such as soybean or fish meal (FAO 2010).

Besides its protein content, there are additional health benefits for livestock as well, such as improved immune response, improved fertility, better weight control, healthier skin and a lustrous coat (Pulz et al. 2004). Adding algae to the diet of cows resulted in a lower natural breakdown of unsaturated fatty acids and a higher concentration of these beneficial compounds in meat and milk. Another important example is the feeding of poultry with algae rich in omega-3 fatty acids, which flows through the food chain, placing this cholesterol-lowering compound in eggs.

The use of algae in food for cats, dogs, aquarium fish, ornamental birds, horses, cows and breeding bulls has also been reported (Spolaore et al. 2006).

4.5 Algae for fish and shellfish consumption

Microalgae are essential for cultivating bivalves, shrimp, and some finfish cultures. Microalgae are also used to produce zooplankton, typically rotifers, which are fed to the freshly hatched carnivorous fish (Benemann et al. 1996).

The use of microalgae in aquaculture can be divided as around 3/5 for mollusks, 1/5 for shrimps, and 1/5 for fish and in this case they are normally used fresh. Alternatives have been developed, like preserved, microencapsulated and frozen algae, as well as a concentrated algae paste (Spolaore et al. 2006).

Wild salmon and trout acquire their characteristic red color by eating algae with red pigments but cultured species lack this color, resulting in a lower market value. This can be corrected by adding astaxanthin to fish feed, mostly produced synthetically, but there is a growing market for algae-based astaxanthin (mainly from *Haematococcus pluvialis*).

Abalone cultivation is a booming industry in Chile, requiring an estimated 100 tons of fresh seaweed for the production of each ton of abalone. The current harvesting of natural populations cannot support this, so the switch to cultivation has to be made. (Vásquez 2008)

Zooplankton can be a major threat for algae cultivation systems (especially for open systems) lowering dramatically final algae productivity. Co-cultivating zooplankton-eating fish can be an option to avoid zooplankton invasion, co-producing valuable products during the cultivation phase rather than the processing phase.

4.6 Cosmetics

The use of some microalgal species, especially *Arthrospira* and *Chlorella,* is well established in the skin care market and some cosmeticians such as LVMH (France) and Daniel Jouvance (France) have even invested in their own microalgal production system. Their extracts are found in anti-aging cream, regenerating care products, emollient and as an anti-irritant in peelers and also in sun protection and hair care products (FAO 2010). For lipid-based cosmetics, ethanol or supercritical CO_2-extracts are gaining commercial importance. Glyco- and phospholipids from microalgae are also becoming increasingly interesting.

Mycosporine-like amino acids[35] are efficient natural UV blocker and microalgae use in sunscreen is becoming commercially attractive (Cardozo et al. 2007)

4.7 Fertilizer

Macroalgae have been used as a fertilizer for centuries in coastal regions worldwide, mainly for its mineral content and as a way to increase the water retention capacity of the soil, but also for their capacity to fix nitrogen (especially in rice cultivation). Both macro- and microalgae can contain compounds that promote germination, leaf or stem growth, flowering or can be used as a biological protection agent against plant diseases (Pulz et al. 2004).

Indeed after the extraction of oil or carbohydrates from both seaweed and microalgae, most of the nutrients are still present in the left-over biomass, which makes fertilizers an ideal co-production option for biofuels. Further the market would be compatible both in terms of large market volume and low market value. Part of these nutrients could be anyway reused for algae cultivation.

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[35] Mycosporine-like amino acids are small secondary metabolites produced by organisms that live in environments with high volumes of sunlight, usually marine environments.

Whether left-over biomass is used as fertilizer or algaculture nutrient source, anaerobic digestion is a valuable option. With this technology, the biomass can be directly fed into the anaerobic digester where a large part of the remaining organic carbon is converted into biogas, and the nutrients are further concentrated in the liquid and solid effluents. These effluents can in turn be used as input for cultivation.

Another option is the production of organic fertilizer, processing the effluents so that when applied into the field, the nutrients are released slowly which both benefits plant growth and reduces the microbial production of GHG emissions. This would avoid the energy intensive production of fossil-based chemical fertilizers, whose demand is anyway expected to increase in the coming years (FAO 2011).

4.8 Fibres for paper

Cell walls of most plants consist of cellulose, while algal cell walls can be very diverse. Some algae species have intracellular walls, or scaly cell walls made of deposits of calcium carbonate or silica, but most algae derive structural strength from continuous sulphated polysaccharides; other possibilities being cellulose, carrageenan, alginate and chitin (Okuda 2002). Algal cellulose can potentially be used as a renewable feedstock for paper production but in general the strong green colour of algae is more difficult to bleach than wood fibres. Although algae have normally a low cellulose and hemicellulose content, there are a few examples where algae are used as fibre source successfully (see FAO 2010 for more details).

Also seaweed can be used for fibre production as they can have very high productivities, may be grown on waste streams, and have high fibre contents. The table below shows the relative good content of cellulose, compared with lignin and ash of different aquatic plants. Water hyacinth for example gives good folding and tearing resistance to the paper. Goswami et al. (1994) reported that 75% water hyacinth pulp and 25% bamboo pulp paper gives high strength and good greaseproof properties to the paper.

	Cellulose	**Lignin**	**Ash**
Stem water hyacinth	58%	9%	22%
Leaf water hyacinth	49%	24%	15%
Torpedo grass	62%	21%	7%
Giant bulrush	62%	26	11%

Table 7: Cellulose content of aquatic plants (FAO 2010, adapted from Joedodibroto 1983)

5 Algae energy products

There are a number of pathways to produce bioenergy from algae, and the main routes to produce liquid biofuels have already been presented in Figure 1. If we look at the broader bioenergy picture, including also solid and gaseous biofuels, and bioelectricity, it is evident that the possible pathways are even more, and algae provide a more flexible feedstock than common land-based energy crops (see Figure 8). All these options have been treated in more detail in FAO (2009), and some of these thermochemical options will be further discussed in chapter 7. This chapter intends to briefly discuss characteristics of algal biomass and its suitability for producing main bioenergy carriers, as reported in FAO (2010).

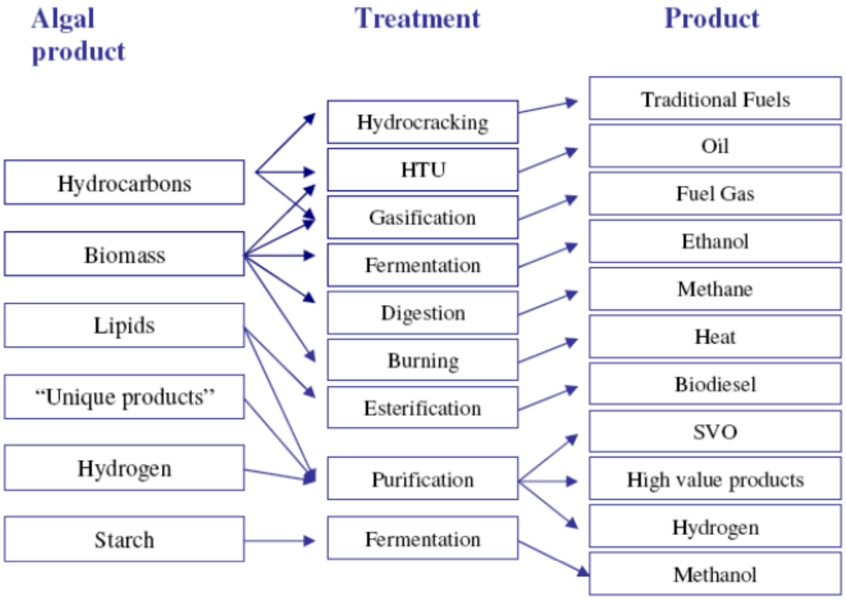

Figure 8 - Overview of major algae-to-energy options (FAO, 2010)

5.1 Ethanol

Ethanol is commonly produced from starch-containing feedstocks and some algae have been reported to contain over 50% of starch. Algal cell walls consist of polysaccharides which can be used as a feedstock in a process similar to cellulosic ethanol production, with the added advantage that algae rarely contain lignin and their polysaccharides, are generally more easily broken down than woody biomass. Co-products can potentially be derived from the non-carbohydrate part of the algal biomass.

In green algae, the conditions under which starch content increases to a level that would be viable for bioethanol production can be achieved if the processes and events during which starch is extensively degraded are slowed down, or stopped completely, while the factors supporting starch synthesis (i.e. light intensity) remain sustainable (Brányiková et al 2010). The freshwater alga Chlorella is a highly productive source of starch, and would be a good candidate to substitute starch-rich terrestrial plants in bioethanol production.

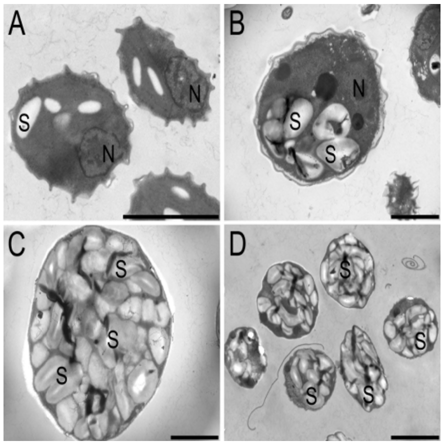

Figure 9 - Electron microscopic photographs of daughter (A) and mother (B) cells of Chlorella grown in complete mineral medium, in the presence of cycloheximide (1 mg/L) (C), and in sulfur limiting medium (D). N nucleus, S starch granules. Bars: panels A, B, C = 2 µm; bar panel D = 5 µm. (Source: AquaFUELs 2010a)

An increase in the production of starch in sulphur-limited culture up to a maximum of 50% starch content of algal biomass (DW) was demonstrated under field conditions using the outdoor scale up, thin-layer solar photobioreactor (AquaFUELs 2010b) and despite the relatively unfavourable climatic conditions in Czech Republic, a total yield of starch calculated per ha over a season of 150 days was 7 tonnes (Doušková et al. 2010). In optimum locations for photoautotrophic production of algae[36], the overall harvest might be increased by a factor of 10 (Doucha et al. 2006). The remaining parts of the cells, containing largely proteins, can be used as a feed supplement in order to further decrease the overall cost of starch production.

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[36] i.e. with a season lasting approximately 250 days.

5.2 Biodiesel

Biodiesel production from algal oils has received most attention since algae can contain theoretically over 80% of total lipids (this can be compared with rapeseed for instance, containing about 6% of lipids). Under normal growth conditions the lipid concentration is lower (<40%) and high oil content is always associated with very low yields. The various lipids production can be stimulated under stress conditions, e.g. insufficient nitrogen availability. Under such conditions, biomass production is not optimal though, reducing the non-lipid part of the biomass that can be further used as a source for co-products.

Similarly to starch for bioethanol, oil-producing Chlorophyta can be treated similarly in order to markedly increase their oil content.

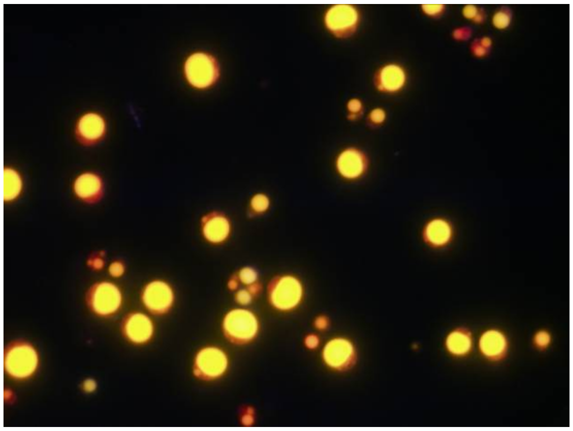

Figure 10 - Fluorescent microphotography of Chlorella cells with enriched content of oil (yellow spots oil stained by Nile Red, Source: AquaFUELs 2010a)

5.3 Hydrocarbons

One genus of algae, Botryococcus, does not produce the lipids, but long hydrocarbon chains, which are not suitable for biodiesel production. Instead, they can be converted in a process similar to the production of conventional fuels from fossil oil. Botryococcus is a freshwater species but can also grow in saline water and it can produce certain carotenoids (Banerjee, Sharma et al. 2002). Its drawback is the relatively slow growth speed. This genus is being extensively studied by the group of Prof. Tredici at the University of Florence.

5.4 Biogas

Anaerobic digestion converts organic material into biogas which is rich in methane (60-70 %), while the rest is mainly CO_2, which can be fed back to the algae reactor. A main advantage is that anaerobic digestion can use wet biomass, reducing the need for concentrating and drying the algae paste. Another advantage is that the nutrients contained in the digested biomass can be recovered from the liquid and solid phase and fed into the growing medium again. Anaerobic digestion can be applied to any left-over biomass after extraction of a co-product.

In fact agricultural waste fermentation could be coupled with algae cultivation. In this process, suitable agricultural waste is fermented first, and then the obtained biogas is used for cogeneration and growth of microalgae consuming the CO_2 (from biogas or flue gas). This concept was verified under field conditions in a pilot-scale photobioreactor, and analyses of the produced microalgae confirmed that it meets the strict EU criteria for relevant contaminants level in foodstuffs (Doušková et al. 2009; 2010a; Kaštánek et al 2010).

5.5 Bio-coal

The biological treatment of algal organic material has a non-biological counterpart, with the advantage that no live organisms are involved and therefore more varied and extreme process conditions can be used. The biomass undergoes a chemical conversion under high temperature and pressure conditions. Depending on the water content and how extreme these conditions are, the biomass carbon ends up in a raw gaseous, liquid or solid phase which can be further upgraded for usage as a biofuel. Thermochemical routes leading to the formation of bio-coal is discussed in section 7.4.

5.6 Hydrogen

Some algae can be manipulated (bioengineered) to produce hydrogen. Currently this process is at an early stage of development and yields are very low.

While use of algae with enriched starch content is conventional for bioethanol production, another attractive exploitation of starch from algae might be the production of hydrogen, which may be realized at commercial scale in the near future, using dark fermenters. Sulphur limitation could be one of the ways to support hydrogen production (Melis et al. 2000).

Recently it has also been reported that some strains of *Chlorella* can produce and accumulate significant volume of hydrogen gas under anaerobic conditions and sulphur deprivation (see for example Chader et al. 2009 with *C. reinhardtii*).

5.7 Bioelectricity

Algal biomass can also be co-combusted in a power plant. For this, the biomass needs to be dried first, which implies a significant amount of energy. This process is thus only interesting if the biomass is supposed to be dried anyway (for example in order to extract a certain co-product). Electricity can be produced starting from different forms of energy carrier. Assuming that the purpose is to producing electricity using co-firing technology in an existing power plant, its viability will be given by very basic parameters such as the cost if the input feedstock, its water content and its heating value (see section on combustion in chapter 7).

6 Relevant characteristics of algae for thermochemical conversion

Thermochemical processes applied to biomass are processes which make use of chemical energy stored into the biomass feedstock to transform it into heat, electricity, or other solid, gaseous or liquid bio-products.

The main parameters needed to characterize the process and the desired end-products are:

- Chemical and physical characteristics of the input feedstock material
- Reaction conditions (such as technology used, reaction speed, residency time, reaction means, process variables such as P and T)

6.1 Particle size and density of fuel

The fuel size is important when characterizing a potential source of energy, as it is relevant for the choice of the thermochemical process and in all those processes that make use of an injector and in gasification as it affects the pressure drop across the reactor and power that must be supplied to draw the feedstock through it. In gasifiers for example, large pressure drops will lead to reduction of the gas load (in downdraft gasifier), resulting in low temperature and tar production. Small size biomass feedstock such as algae biomass also favors the reactivity of fuel an increase the reaction surface, while excessively large sizes of particles would give rise to reduced reactivity of fuel, resulting in the need of long residence time inside the reactor. Acceptable fuel sizes depend to certain extent on the type of process chosen and design of the reactor or combustion chamber.

Algal cells size is in the order of micrometers. As already anticipated in chapter 2, freshwater Chlorella can vary between 3 µm and 10 µm (*C. vulgaris*), while *Scenedesmus sp.* is slightly bigger.

The bulk density is also important and is defined as the weight per unit of volume of loosely tipped fuel. Bulk density varies significantly with moisture content and particle size of fuel. It is also recognized that bulk density has considerable impact in combustion chambers, as it influences the fuel residence time, fuel velocity and flow rate.

6.2 Heating value

The calorific value is the amount of heat released during the combustion of one mass unit of biomass at standard temperature and pressure. In particular, we can refer to lower heating value (LHV) or higher heating value (HHV), namely if the heat of condensation of water contained in the products of combustion in gaseous form is accounted for or not. The water contained in the biomass consists mainly of biomass moisture and water resulting from the reaction between hydrogen and oxygen in the air. Between the two the following relation exists:

$$LHV = HHV - 581\,(H + 9\,W) \qquad [\mathrm{Kcal} / \mathrm{Kg}^{37}]$$

where W is the moisture content of the fuel [Kg_{H2O}/Kg], and H is the hydrogen present in the fuel [Kg_{H2}/Kg].

The actual calorific value can be measured experimentally using for example a bomb calorimeter[38]. The resulting measured heating value is considered high (or gross) heating value at constant volume because the biomass combustion in the container has taken place inside the fixed volume of the container. The resulting gross heating value can be expressed based on dry mass content of the sample biomass:

$$HHV_d = HHV / (1-M)$$

where HHV_d is the gross heating value of the biomass in MJ/kg of bone dry biomass, HHV is the gross heating value determined by the calorimeter. M is the moisture content of the biomass in decimal wet mass fraction.

The high heating value can be estimated from the composition of the fuel (Gaur and Reed 1995) as:

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[37] kcal/kg = MJ/kg * 238.846

[38] The device burns a small mass of biomass in the presence of oxygen inside a sealed container (or bomb). The heat released from combustion is transferred to a mass of fluid (air or water) that surrounds the container. The heating value is calculated from the product of (mass) x (specific heat) x (net temperature increase). The calculated heating value must be corrected for heat losses of the container. In modern calorimeters the corrections are made automatically using sensors and controllers.

$$HHV_d = 0.35\ X_C + 1.18\ X_H + 0.10\ X_S - 0.02\ X_N - 0.10\ X_O - 0.02\ X_{ash}$$

where X is the mass fractions (percent mass dry basis) of Carbon (C), Hydrogen (H), Sulfur (S), Nitrogen (N), Oxygen (O), and ash content (ash); or using the Milne formula:

$$HHV_{Milne} = 0.341 \cdot C + 1.322 \cdot H - 0.12 \cdot O - 0.12 \cdot N + 0.0686 \cdot S - 0.0153 \cdot ash$$

HHV should be measured in MJ/kg dry mass. The equation shows that the elements C, H, S increase the heating value whereas the elements N, O, and ash decrease it.

The experimental HHV of wood is around 20 MJ/kg dry mass basis, for herbaceous biomass it is around 19 MJ/kg dry mass basis and for algae it can range from 13 to 23 MJ/kg dry mass. For a moist fuel, the heating value decreases because a portion of the combustion heat is used to evaporate water in the biomass and this is not condensed to return to heat back to the system. An estimate of the LHV (or net heating value) is obtained from the measured HHV by subtracting the heat of vaporization of water in the products.

$$LHV = HHV(1-M) - 2.447M$$

where LHV is the lower heating value, M is the wet basis moisture content. The constant 2.447 is the latent heat of vaporization of water in MJ/kg at 25 °C[39].

The situation changes when the gases evolving from combustion of biomass cannot expand without constraints. Without pressure constraints, like in a boiler combustion chamber with unrestricted exhaust system, the equation below also applies (heating value at constant pressure):

$$HHV_p = HHV - 0.212X_H - 0.0008\ (X_O + X_N)$$

where HHV_p is the high heating value at constant pressure for dry biomass. X_H, X_O, and X_N are the mass fraction (percent dry mass) of the biomass.

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[39] A more accurate estimate of the net heating value can be obtained by including the heat released by the combustion of the hydrogen contained in the biomass.

Fuel type	Typical LHV [MJ/Kg]
Coke coal	31.4
Steam coal	21
Green wood	9.6
Oil	41.9
Heavy oil	39.8
Gasoil	44
Natural gas	34.8
Urban waste	8.4 – 12.6
Refuse Derived Fuel (RDF)	14,7
Algal biomass (Chlorella sp.)	14 – 17.2
Algal biomass (Chlorella vulgaris)	13.5 – 15
Algal biomass (Scenedesmus)	25.8
Algal biomass (Clamy reinhardi)	18
Algal oil	37.3

Table 4 - Indicative values of LHV for different fossil fuels and biomass products (based on Syngen figures available at www.syngen.it/home/gassificazione_tecnologie_biomassa.asp, and other sources)

6.3 Algae composition

The heating value of algae biomass, as well as other parameters important for algae characterization as fuel, can vary significantly between species and also for the same species due to different cultivation conditions. Nutrient concentration can play an important role in determining the protein, lipid and carbohydrate content of the cultivated algae, hence the heating value. For example high and low N input in outdoor mass cultures of *Tetraselmis sp.* can lead to the following differences (Tredici et al. 1987):

Constituent (%)	High N input (2.4 g/m2/day)	Low N input (0.34 g/m2/day)
Protein	48	14
Lipid	30	27
Carbohydrate	22	58
Total N	7.7	2.3

Table 5 - Constituents of algae Tetraselmis sp. under different cultivation conditions

On the basis on information on the constituents present in the algae, it is possible to estimate its heating value with the following formula:

$$HV = \%C \cdot 34.835 + \%H \cdot 93.87 - \%O \cdot 10.8 + \%N \cdot 6.28 + \%S \cdot 10.465 - 2.44 \cdot \%W$$

Biomass may be lower or higher than coal in fuel nitrogen concentration (measured in kg/GJ) and they may be lower or higher than coal with respect to ash concentration (around 8 % for the algae we considered). Fuel sulphur is typically low or absent in algae biomass.

For the calculations, the following algae compositions have been assumed:

	Chlorella sp.	**Chlorella vulgaris**	**Scenedesmus obliquus**
w_C (kg/kg)	0.489	0.5495	0.503
w_H (kg/kg)	0.068	0.0807	0.077
w_O (kg/kg)	0.313	0.2583	0.342
w_N (kg/kg)	0.069	0.1065	0.065
w_S (kg/kg)	0.006	0.005	0

Table 6 – Algal composition assumed (weight basis) for Chlorella and Scenedesmus sp.

C	H	O	N	P	S	K	Mg	Ca	Na	Fe	Mn	Zn	Cu	Co	Cl	Source
				1200 mg/100 g	600	879	300	230		70	14	11	4	0.5		Aquafuels-Roundtable Report
48.9 %	6.8	31.3	6.9	1.2												
40 mol/kg DW			4-5	0.12-0.77	0.12-0.24	0.1-0.6	0.08-0.56	0.08	0.008-0.2						0.08	Advances in microbial physiology, Volume 21, John F. Wilkinson

Table 7 - Composition analysis of Chlorella sp. (dry-weight)

	P	S	K	Mg	Ca	Na	Si	Fe	Mn	Ash	Source
Chlorella sp. + Scenedesmus sp.	0.01-38.8 (15)	3.13-9.10 (5.75)	5.83-34 (10.10) mg/g	2.46-26 (5)	0.43-51.10 (3.30)	0.17-16 (0.45)	1.40-3.16 (1.50)	0.72-7.70 (1.93)	0.03-22 (0.11)		Dried biomass of green algae and its matrix matching with green parts of higher plants (P. Mader, I. Stejskalovfi, A. Slfimovfi)
Scenedesmus obliquus + Chlorella ellipsoida										3.62 %	Nutrient content of various algae and amino acyd adequacy for growth of rats and chicks, US army medical research and nutrition laboratory

Table 8 - Composition analysis of Chlorella and Scenedesmus species (dry-weight)

6.4 Ash content and melting behaviour

The ash content of the feedstock material doesn’t react and can be found at the end of the thermochemical process.

The exact chemical composition of ash found again at the end of the process varies depending on the particular type of fuel and combustion parameters, but generally consists of highly oxidized substances with low melting temperatures and very high evaporation temperatures, such as ionic compounds of metals (in particular carbonates and oxides), with low content of light elements. Ashes are made up predominantly of silica (SiO_2), alumina (Al_2O_3), oxides of Fe, Ca, Mg. They are therefore present in the inert materials that do not participate in the process of combustion of the organic waste.

Ashes cause a variety of well-defined problems such as:

- formation of slag, caused by ash melting and agglomeration. It can lead to an excessive formation of deposits and reduce the functionality of the reactor. However formation of the slag depends on a number of factors including the ash content in the fuel, the melting temperature characteristic of these, the presence of catalysts (alkali), and the temperature profile established in the reactor;

- areas with high temperatures, created in the empty zones of the fuel bed due to the formation of bridges, which could lead to slag containing clinker (with high ash fusion temperature).

In general, slag doesn’t create major problems for fuels having an ash content of less than 5-6%. Important slag formation can occur for a fuel having an ash content of more than 12% such as some biomass feedstock. Between 6 and 12% the formation of the slag highly depends on the melting temperature, which is influenced by the presence of traces of elements which raise the melting point of eutectic materials[40].

High potassium content lowers the ash sintering temperature sometimes to < 700°C. At combustion or gasification temperatures required for a fast fuel conversion, the ash becomes sticky and increases the risk of reactor slagging. Most of the chlorine is released as HCl into the gas phase. Consequences are corrosion in heat exchangers and hot gas ducts, poisoning of downstream catalysts or formation of toxic polychlorinated dioxins or furans at unsuitable combustion conditions. Alkali salts become volatile at temperatures > 650°C; deposition of alkali chlorides, hydroxides or low melting eutectics can cause serious corrosion and plugging of pipes.

Classes of elements that are generated during combustion include:

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[40] A mixture whose melting point is lower than that of any other mixture with the same components.

- items that do not vaporize during combustion;
- elements that vaporize and condense in the system;
- elements that vaporize and condense, are the gas phase and leaving the plant.

Ash composition of biomass is fundamentally different from ash composition of various coals for example: alkalinity is much higher; typical base/acid (B/A) ratios can exceed 1 and may exceed 2. B/A ratios for coal are typically well below 1. For algae, ash compositions are a function of harvest time, and culture regime (e.g. fertilizer applications). B/A ratios can range from 0.3 to 3.0 depending upon culture practices.

Of equal significance to the alkalinity itself is the reactivity of that alkalinity. The alkali in general (sodium and potassium in particular) are more available and reactive in biomass and biofuels than in the various deposits of coal. This ash reactivity can cause significant difficulties in algae biomass combustion.

In general there are a number of strategies to reduce the risk of slag formation. One is to try to change the ash composition so that they melt at higher temperatures. This can be achieved by adding CaO or MgO or by providing a fuel rich in SiO_2. Another strategy to decrease slag is to reduce the amount of alkali metals that can participate in the slag formation. One way is to mix with a fuel containing an alkali absorbent such as a for instance a clay mineral. Such minerals often brake down when heated and react with alkali to stable high-melting so called alumino-silicates. Their melting temperatures are relatively high and consequently the slag problems are lesser (this can be combined with the addition of CaO or MgO to strengthen the effect) (Boström et al. 2011).

In order to determine the ash content, a standard procedure as outlined by the DIN 51719 developed by the German Institute for Standardization can be followed. Alternatively, the following procedure can be followed.

Algae are dried at 100 ° C for 12 hours. The sample is weighed (1 g) and placed in a ceramic crucible which is exposed to flame for 2 hours. Then the crucible is placed so that the walls with condensed compounds are exposed to the flame. The crucible is removed and cooled in the presence of silica gel to prevent that ashes absorb air moisture. After cooling the sample is reweighed and the ash content determined.

Ash content of algae can vary considerably. Wassink et al. give 6% ash for *Chlorella sp.* strain, Geoghegan (1953) gives 7.4% for *Chlorella vulgaris,* Milner (1953) 3.45% for *Chlorella pyrenoidosa,* 6.5% and 11.24% for *Stichococcus bacillaris* and 4.74% for *Chlamydomonas sp.*

Pinevich et al. (1965) found in *Chlorella pyrenoidosa* grown in the open air 8.4% and 10.8% of ash content, and for *Chlorella vulgaris* also from the open air 8-9.5%.

As a reference, strain *Scenedesmus quadricauda* Bartosova and Konicek (1967) give 4.94% ash content, but Hrdlička and Pribil (1966) found 7.2-10% in an open-air cultivation.

Wassink et al. give 11.2-22.4% ash for *Chlorella sp.* from an open-air cultivation, Gummert, Meffert and Stratmann (1953) give 11.92-18.07% for *Chlorella pyrenoidosa* during an open air cultivating season. More recently, Xu (2006) reports ash content for *Chlorella protothecoides* of 6.36 ± 0.05 %.

The content of ash in filamentous algae is similar to that in the reference species *Scenedesmus quadricauda,* an exception being a *Hormidium* sp. with 2.94% ash.

This variability of data is mainly caused by different treatment of material before analysis, e g whether and in what way the material has been washed. The cultivation conditions also play a role, especially the concentration of the cultivation medium, as well as the intensity of culture growth (Hindak F. and Pribil S.). Some references found in the literature available are reported below:

Ash content	Source
9.09 – 10.9 %	Yield and chemical composition of Chlorella species cultivated in pig, poultry and cow dungs in southern Nigeria, s.e. Vaikosen, s.o. Nwokoro, a.m. Orheruata
5-7 %	Abeille d'Or Corporation
8.7 %	Dry biomass of fresh water algae of Chlorella genus in thecombined forages for laying hens, Svetlana Grigorova
8.25 %	http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2621.1963.tb00189.x/abstract

Table 9 – Ash content of Chlorella. From the literature review, a 5-10% ash content can be assumed

Ash content expressed in weight % on dry basis. Through the water content and the ash contents are related:

$$Ash\ content\ (wt\%_{dry}) = ash\ content\ (wt\%_{ar}) \cdot 100 / (100 - water\ content\ (wt\%))$$

By using the hydrogen and ash fractions (wt% $_{dry}$) and moisture fraction w (wt% $_{ar}$) the different HHV's and LHV's can be calculated:

$$HHV_{rb} = HHV_{dry} \cdot (1-w/100)$$

$$HHV_{dry} = HHV_{daf} \cdot (1-ash/100)$$

$$LHV_{dry} = HHV_{dry} - 2.442 \cdot 8.936\ H/100$$

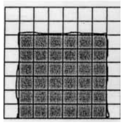
$$LHV_{rb} = LHV_{dry} \cdot (1-w/100) - 2.442 \cdot w/100$$

$$LHV_{rb} = HHV_{rb} - 2.442 \cdot \{8.936\ H/100\ (1-w/100) + w/100\}$$

[real biomass material considered (rb): weight percentage from the material in its original form (including ash and moisture); dry: weight percentage from the dry material (including ash); dry and ash free (daf): weight percentage from the dry and ash free material]

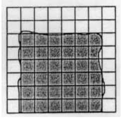
Ash from biomass and other inorganic compounds does not have a definite melting point but four steps can be identified in the melting process. Melting begins after sintering in a more or less large temperature range and before becoming liquid the ash goes through several plastic and viscous states. The determination of the ash thermal behavior is given in DIN 51730 (1976). The various stages of melting can be described as follows:

SIT: beginning of sintering



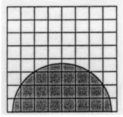
Sintering describes a process, where single ash particles stick together. During this process the sample may change its original dimension without showing characteristics typical at the softening point.

SOT: beginning of softening



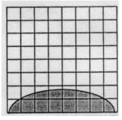
At the softening temperature the sample shows the first signs of softening, e.g. surface changes, the rounding of the edges are complete and the sample starts filling out the gas volume between the particles. If the edges are still sharp, a shrinkage of the sample should not be regarded as softening.

HT: hemispheric point



The hemispheric point gives the temperature, when the sample takes on the approximate form of a hemisphere. The height of the melted sample is approximate half the length of the base line.

FT: flowing point



At this temperature the sample has shrunk to one third of its original height.

Two technological properties should be taken into consideration to predict ash melting behaviour of biomass:

- the heating value[41],
- the softening temperature[42] of ash from biomass incineration

These can be modelled by the elemental compositions of the samples. TU Wien for example has proposed quite precise 4 components models to determine HHV and SOT (Friedl et al. 2004):

$$SOT\ [°C] = 1.81\ c(CaO) + 4.20\ c(Al_2O_3) - 2.41\ c(K_2O) + 5.31\ c(P_2O_5) + 1017$$

where c(x) are relative mass concentrations in ash, normalized to sum 100.

Indicative ash composition for *Chlorella sp.* is as follows[43]:

	F	Ca	K	Mg	Na	P
Chlorella sp.	53 mg/100g	94	1360	264	50	1680

Table 10 - Indicative ash composition for *Chlorella sp.*

The ash characteristics of the algae biomass can contribute positively to the performance of co-firing for example when sufficient biomass ash is added to the mix. Under such circumstances, the

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[41] As mentioned before, HHV, higher heating value (gross calorific value) is the enthalpy of combustion including the condensation enthalpy of water. It can be measured by bomb calorimeter.

[42] SOT, softening temperature (deformation temperature) is the temperature at which the first signs of rounding, due to melting, of the tip or edges occur. It can be measured by a heating microscope.

[43] Source: Abeille d'Or Corporation

B/*A* ratio of the total fuel mix can be increased, improving the viscosity of the slag formed in a cyclone boiler for example.

Melting behavior is observed experimentally but there is very little information publicly available in the literature about analysis of ash composition of different microalgae. If this information was available, it would have been possible to estimate the thermal behavior (at least flow temperature) of algae ash using the phase diagram of the system $SiO_2 \cdot K_2O \cdot CaO$ (see image below). At any rate these considerations are relevant only for those thermochemical processes that reach temperatures of 700° or above.

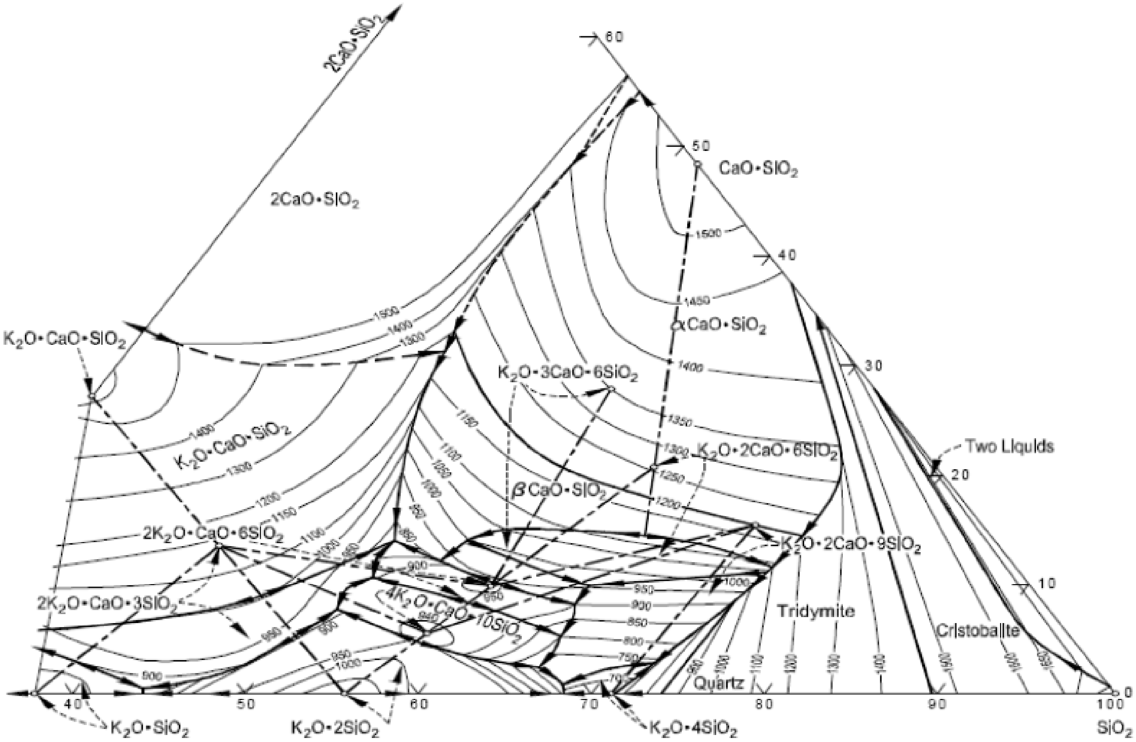

Figure 11 - Phase diagram of the system $SiO_2 \cdot K_2O \cdot CaO$ (Stahl et al. 2004)

6.5 Volatiles and fixed carbon

During combustion, the type of fuel can also influence the production of soot particles: first by inducing the formation of local zones richer in fuel and secondly by exerting a greater or lesser resistance to the formation of soot. In the first case the phenomenon is controlled by physical properties such as *viscosity* and *volatility* that have influence on the diameter of the droplets of fuel or its evaporation rate; in the second case depends on the molecular structure of the fuel.

Experimentally dependencies of particulate by the various classes of hydrocarbons can be obtained and, within each class, by the ratio C/H. These dependencies (especially the first) are in turn influenced by the type of fuel flow and, especially, the type of flame.

The combustion consequences of the biomass fuel composition — particularly the fuel volatility — involve adapting combustion within any device. The introduction of biomass and in particular algae biomass into a coal-fired or cyclone boiler adds a fuel where volatilization and gas-phase combustion is the dominant reaction sequence, rather than char formation and gas–solids oxidation as is the dominant combustion process for coal.

The volatile substance is the fraction of biomass fuel material that, when heated at high temperatures under air starvation conditions, evaporates (by reduction), while in the presence of air excess is oxidized. The amount of volatiles is expressed in weight % dry material and is determined by standardized methods. The amount of fixed carbon is calculated as the remaining part as determined by the above mentioned standardized method according to the following formulas:

dry biomass	*fixed C = 100 - ash (dry) - volatiles (dry)*
dry ash-free biomass	*fixed C = 100 - volatiles (daf)*
actual biomass	*fixed C = 100 - ash (actual) - water content - volatiles (actual)*

The process of volatile release is enhanced when using small particles such as dry algae. These characteristics are less relevant in hydrothermal processes as the algae biomass is processed only in a liquid medium.

The energy from biomass is a direct function of the percentage of volatile substances, and then the thermal characteristics of the biomass can be described by knowing the percentage of aggregates as shown in the diagram below. It shows that the LHV depends exclusively on the content of ash and moisture content of fuel.

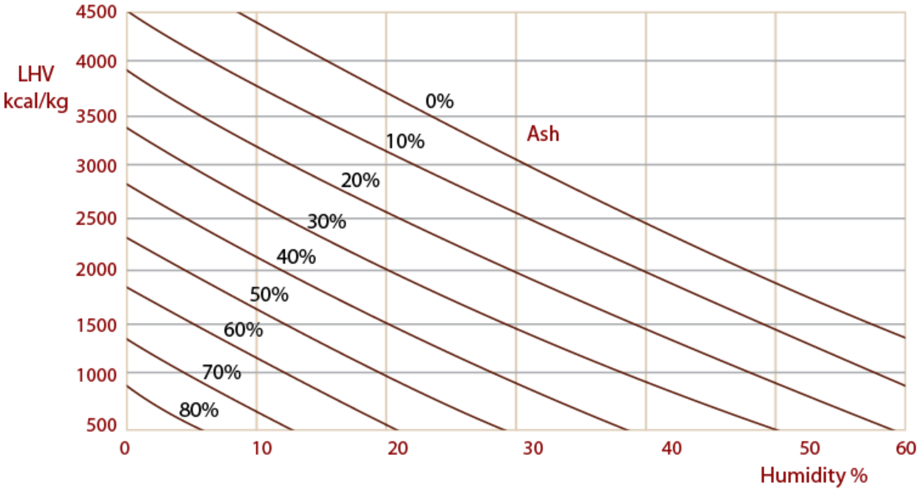

Figure 12 – Relation between Lower Heating Value, Humidity and Ash content of a fuel

LHV is related to humidity and ash content by the following formulas (ECN Phillis definitions, available at www.ecn.nl/phyllis/defs.asp):

$HHV_{real} = HHV_{dry} \cdot (1\text{-}w/100)$

$HHV_{dry} = HHV_{daf} \cdot (1\text{-}ash/100)$

and $LHV_{real} = HHV_{ar} \text{ -}2.442 \cdot \{8.936\ H/100\ (1\text{-}w/100) + w/100\}$

In order to sustain the flame without any external energy input, the percentage of inert and volatile substance must fall within an area where the percentage of volatile substance is capable of maintaining the temperature of ignition despite losses caused by heat absorption by the inert materials.

The Tanner graph in figure 13 shows the composition of biomass as a sum of a fuel component, moisture content and ash content and defines the range of autoignition.

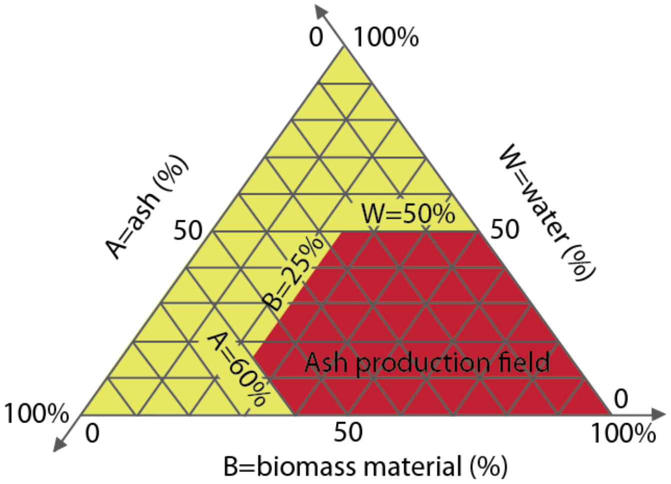

Figure 13 – Tanner graph, showing the relation between ash, biomass and water composition of a fuel

The biomass has a volatile/fixed carbon (V/FC) ratio typically >4.0 and frequently exceeding 5.0. The V/FC ratio for the coal counterpart is virtually always <1.0, while petroleum coke can have a V/FC ratio on the order of 0.2.

It is important to note that practical volatility can be influenced by two factors: (1) fuel particle size, and (2) combustion temperature. As mentioned, in some thermochemical processes the particle size and volatility of algae biomass can be not relevant and in general smaller particles release more volatiles, and more rapidly. Higher temperatures also cause a greater proportion of the combustible fraction of a fuel to be released as volatiles (as in the case of combustion or gasification), and lower temperatures will promote increased char formation.

The differences in fuel volatility are directly related to the algae considered. Algae are comprised of polysaccharides or holocellulose (cellulose and the hemicelluloses). Cellulose, the dominant polysaccharide, is composed of anhydroglucose units connected by 1→4-β-glucosidic linkages. The principal functional group is the — OH group. Upon oxidation, functional groups will include carbonyls, ketos, and carboxyls. Hemicelluloses are branched-chain polysaccharides. Functional groups associated with the hemicelluloses include carboxyls, methyls, and hydroxyls. There are no aromatic components in the holocellulose.

6.6 Impurities

Heteroatoms (e.g., N, Cl) are a function of living processes. Consequently, the nitrogen exists as a consequence of protein structures in the inner bark of biomass and in some lignin precursors, and is virtually always in amine structures ($-NH_{1-3}$) and can also be contained in pyridines, carboyoles, quinolines, and pyrroles.

Further impurities that can be found in fuel produced from microalgae or algal biomass due to culture conditions, depending on the type of microalgae strain employed in the process and the level of nutrients provided in the culture means. An indicative value of elements content in *Chlorella sp.* is showed in the table below:

Element	mg/100 g DW
Phosphorus	1200
Potassium	879
Sulphur	600
Magnesium	300
Calcium	230
Iron	70
Manganese	14
Zinc	11
Copper	4
Cobalt	0.5

Table 11 - Proportion of mineral substances and important trace elements in the Chlorella dry weight (source: EC AquaFUELs report)

Chlorella vulgaris however could not grow well using just the recovered solution, because of lack of nutrients. The optimal culture conditions for obtaining a high biomass production rate using the recovered solution with supplemented nutrients have been investigated by Tsukahara et al. (2001).

Algae can use a wide variety of nitrogen compounds, both inorganic and organic, as nitrogen sources for the synthesis of amino acids. *Chlorella vulgaris* can use ammonium as nitrogen source and grow well in media containing NH_4Cl at concentration ranging from 0.22 to 1.11 g/l, although NH4Cl becomes toxic for *Chlorella vulgaris* at concentration above 16.62 g/l. Minowa et al. (1999) found that the toxicity of ammonia can be avoided by diluting the recovered solution 30 fold although ammonia derived from the nitrogenous compounds of *Chlorella vulgaris* was found in high quantities (about 9000 mg/l) in the recovered solution.

Other studies, undertaken e.g. by the EPFL and PSI, were aimed at assessing the effect of metals such as nickel on the algae cultures. Nickel ions usually derive from reduced nickel catalyst and can be found in high quantities (240 mg/l according to Tsukahara et al. 2005) in the recovered media solution. Nickel ions inhibit *Chlorella vulgaris* growth on the basis of their concentration, likewise the toxicity of nickel ions can be reduced diluting 30 folds the recovered solution.

Phosphate and magnesium are important nutrient which have to be kept at a specific concentration in the culture medium as they are indispensible nutrients for algae growth. They have to be added anyway to the system. Experiments on recovered solution from gasification show that these are considered to be present in insufficient quantities in the recovered solution for the optimal growth of *Chlorella vulgaris*.

Chlorella vulgaris was considered to grow well in a 75-300 fold diluted recovered solution supplemented with P and Mg ions and micro-elements, although further research is needed to determine their optimum conditions (Tsukahara et al. 2005).

Microalgal system for fuel production with reuse of N and other substances have many advantages compared to open ones. Ammonium ions for example can be recovered after low temperature gasification process and the recovered solution can be used as nitrogen source, reducing in this way the energy requirement of the system. The energy input for N as fertilizer is proportional to the N content in the dry algal cells on the assumption that the specific energy unit for N, the organic content in the dry matter, the gas yield, and the efficiency of algal nitrogen consumption is constant.

6.7 Water content

For thermochemical processes, the input material needs to be relatively dry, and the moisture content as low as possible. Hydrothermal processes represent an exception as in these processes water itself is the reaction medium. Therefore usually the first steps consist in the drying and degassing and, subsequently, the conversion into energy carriers.

Thus the water content of the fuel for the characterization is important, in addition to the heating value, particle size and ash content.

As illustrated in section 6.2, water content has a direct impact on the lower heating value of a fuel that is the heat energy available after reducing the loss due to moisture. High water content levels can bring the heating value to zero.

To estimate the moisture content there are several formulas including the best known is the following:

Water content = (wet weight - dry weight) / total weight

Microalgae have a high moisture content (only 0.5 – 1 $g_{dry\text{-}cell}$ /l). If the biomass needs to be dried before use for energy production, this drying process would waste usually a relative large amount of energy.

In Minowa et al.'s experiment (1999), *Chlorella vulgaris* had 87.4 % moisture and a density as above, therefore the algal biomass had to be concentrated 126-252 times before whatever gasification process.

7 Thermochemical conversion routes for algae

The reasons for processing algal biomass or algal oil through conversion routes are multiple, but the main one is to increase their mass density[44] and their energy density to obtain a practical and efficient energy carrier.

The fuels that have high bulk density are advantageous because they have a high energy value per volume. The mass density varies significantly with moisture content and the type of fuel.

The conversion technologies for utilizing microalgae biomass can be separated into two basic categories: thermochemical and biochemical.

The main factors that influence the choice of conversion process include: the type and quantity of biomass feedstock available; economic and project specific considerations; and the desired form of the end product.

Further, thermochemical processes are typically used for biomass in which the C / N ratio is over 30 and the water content does not exceed 50%.

In this report, we will discuss technically viable conversion options specifically for algal biomass and algal oil. We will also provide information about the economic viability of processes under different circumstances.

Thermochemical processes used to convert algal biomass into energy are similar to those ordinarily used for conventional biomass (e.g. woody, crop residues, etc). Again the different options are usually dictated, to a large extent, on the types and sources of biomass available, conservation options and end-use demand.

In this context, thermochemical conversion is intended as the thermal decomposition of organic components in biomass to yield fuel products, and is achievable by different processes such as direct combustion, gasification, pyrolysis and hydrothermal processes.

The specific thermochemical conversion process (TCC) is defined on the basis of parameters such as temperature, pressure and reaction time and they can theoretically include also those processes that led to the formation of fossil fuels over ages. The logarithmic graph below illustrates this relationship:

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[44] The mass density is defined as the weight per unit volume of the generic type of fuel.

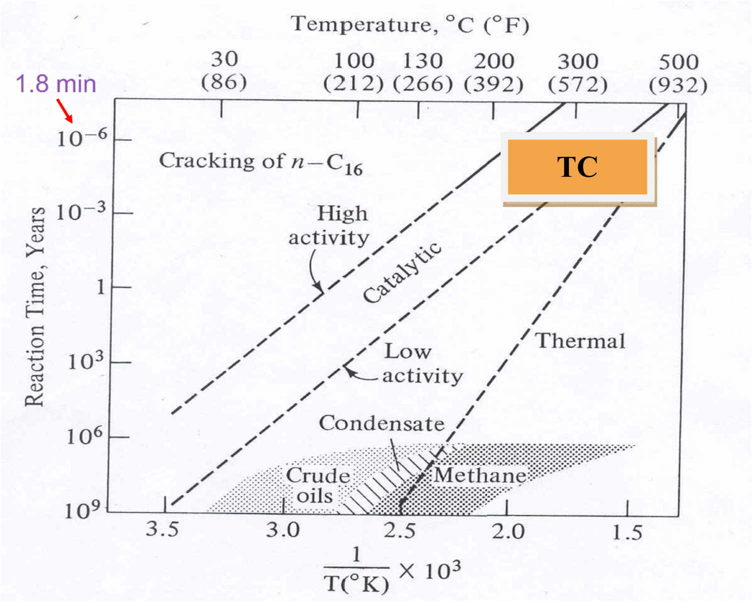

Figure 14 - Thermochemical conversion processes as a function of temperature, pressure and reaction time (adapted from John Hunt, 1979. Petroleum Geochemistry and Geology)

The table below is a compilation of thermochemical conversion processes considered for microalgae. It shows the range of oil yields achieved and their relevant HHV.

Conversion process	Microalga considered	Type of cultivation	Temperature [°C]	Pressure [MPa]	Liquid content [% dry wt.]	Liquid HHV [MJ/kg]	Gas content [% dry wt.]	Solid content [% dry wt.]
Gasification	Spirulina	n/a	1000	0.101	-	-	64	-
Hydrothermal liquefaction	Botryococcus braunii	n/a	300	3	64	45.9	-	-
Hydrothermal liquefaction	Dunaliella tertiolecta	n/a	300	3	42	34.9	-	-
Pyrolysis	Chlorella prothothecoides	Heterotrophic	450	0.101	57.9	41	32	10.1
Pyrolysis	Chlorella prothothecoides	Phototrophic	450	0.101	16.6	30	-	-
Pyrolysis	Chlorella prothothecoides	Phototrophic	500	0.101	18	30	-	-
Pyrolysis	Chlorella prothothecoides	n/a	500	0.101	55.3	39.7	36.3	8.4
Pyrolysis	Microcystis aeruginosa	Phototrophic	500	0.101	24	29	-	-

Table 12 - ***Comparison between thermochemical conversion technologies (adapted from Brennan et al. 2009)***

The understanding of reaction mechanisms and behavior of organic oils in combustion is not possible without a physical-chemical characterization of the same. Few studies have been undertaken with the aim of analyzing the chemistry of products of thermochemical conversion from algae and their molecular characterization as a function of different parameters. Most of them show the results of purely qualitative analysis, without going into details of its significant chemical complexity.

7.1 Combustion

In a direct combustion process, biomass is burnt in the presence of air to convert the chemical energy stored in biomass into hot gases, usually to be used in a boiler or steam turbine at temperatures above 800 °C. It is possible to burn any type of biomass, but combustion is feasible when the biomass has a water content <50%. As previously mentioned, water content reduces a fuel's LHV, therefore its usable energy. Theoretically fuels that contain high moisture content (more than 70-80%) are unable to burn, without auxiliary combustion fuels. The energy produced from combustion in the form of heat cannot be stored but must be used immediately as storage is not a viable option.

Therefore direct biomass combustion has the disadvantage of biomass generally requiring drying, often associated with other processes such as chopping and grinding, which incur significant additional energy demand, and therefore cost.

In general conversion efficiency in large biomass-to-energy plants may compare favourably to that of coal-fired power plants, but may also incur in much higher cost due to high moisture content of biomass. This is a major disadvantage in using algae biomass given the very high moisture content (up to 99%) after harvesting.

Generation of combined heat and power (CHP) is desirable to improve the overall plant efficiency but can hardly offset the energy wasted for drying extremely wet biomass.

Scale of biomass combustion for heat, power, and steam ranges from very small scale utilities up to large-scale industrial processes. Net energy conversion efficiencies for biomass combustion power plants range from 20% to 40%, with higher efficiencies obtained in larger systems (>100 MW) or when biomass is co-combusted in coal fired power plants (co-firing) (Demirbas 2001).

There is little evidence in literature of technically viable utilisation of algal biomass in direct combustion, but a life cycle assessment (LCA) of coal-algae co-firing (Kadam 2002) suggested that it could lead to lower GHG emissions and lower air pollution.

Even if algal biomass usually has high energy content if compared to woody biomass, their very high moisture content and high production cost (typical of an advanced feedstock that could undergo much more elaborated processes leading to higher value products) make the combustion option not economically viable.

Heating value of freeze-dried algae is around in the range of 14-25 MJ/kg and an indicative value can be 18 MJ/kg (this is the case for *Chlamydomonas reinhardtii*). With current technologies algae can be collected by centrifugation in an economic way up to 10% solids. This process is quite energy intensive and the result is that in 10 kg of collected alga paste centrifugate, there is about 1 kg of biomass and 9 kg of water. Without considering the energy needed for centrifugation, in order to obtain the dry 1 kg of algae needed for combustion, about 23 MJ are required to remove the water. Looking only at the energy balance, the process of drying and burning 1 kg of algae under ideal conditions would lead to a net energy loss of 23-18 = 5 MJ.

Therefore combustion will not be further discussed in this paper.

7.2 Gasification

Gasification describes a chemical process by which carbonaceous materials (hydrocarbons) are converted to a synthesis gas (or syngas) by means of a partial oxidation with excess air, oxygen and/or steam at high temperatures, typically in the range of 800-1500 °C. The syngas produced is a mixture of CO, H_2, CO_2, N_2, and CH_4. It is a low calorific gas (typical 4–6 MJ/m^3 by air as gasification agent and 10-14 MJ/m^3 with oxygen or steam as gasification agent) which can be burnt directly or used as a fuel in gas engines or gas turbines after impurities have been removed.

It can be seen as an interim step towards the complete oxidation of biomass. The external heat needed for the process can be supplied in different forms. A number of reactions take place which can happen only under high temperature and/or high pressure conditions. During primary gasification, the coke derived from the pyrolysis process is completely converted into combustible gases, subsequently, oxygen (brought to the process by a gasifying agent such as air, steam or O_2) is added to the system to complete the gasification of other compounds such as solid carbon (C). The coke is gradually broken down into gases such as CO, CO_2 and H_2 (from the steam reaction).

The gasification can happen in a pile of coke, a fixed bed, or e.g. in a fluid bed. Fixed bed gasification processes can be divided into two basically different process designs: counter-current ("up draft") and co-current ("down draft") gasification.

There are principally two approaches for gasification: 1) autothermal gasification, which provides the necessary heat-of-reaction by means of partial oxidation within the gasification reactor. This process applies commonly pure oxygen in order to avoid the dilution of the gas with nitrogen. 2) Allothermal or indirect gasification, which needs getting the required heat-of reaction from an external heat source into the gasifier. The main advantages of allothermal gasification systems are significantly higher H_2/CO ratios which are particularly favourable for the synthesis of any liquid or gaseous energy carrier. Allothermal gasification systems are usually bubbling or circulating fluidized bed gasification systems. The main technical challenge for allothermal gasifiers is the heat transfer into the fluidized bed[45].

The key advantage of gasification as a pathway to produce energy from biomass is that it can produce a syngas from a wide variety of potential feedstocks.

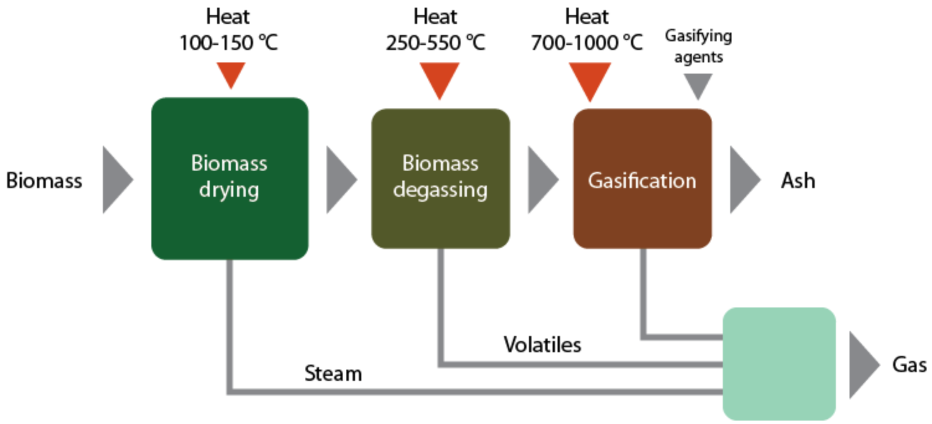

Figure 15 – Simplified scheme of biomass gasification process

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[45] Two concepts are discussed to solve the heat transfer problem: The first idea is to circulate hot solids (i.e. fluidized bed material) from a combustion zone to a gasifier zone. The most popular concept is the Güssing gasifier. It consists of two connected fluidized bed reactors - one for gasification and one for combustion. The bed material circulates between the combustion chamber and the gasifier to transfer the required heat into the gasifier.

A second concept suggests indirectly heated fluidized bed gasifier systems with integrated heat exchanger tubes. The main problem with indirect heating is the generation of sufficiently high heat fluxes from the heat carrier gas, i.e. flue gas, into the fluidized bed. The heat transfer between the fluidized bed and the heat exchanger tubes is excellent, but the inner heat transfer between tube wall and the gaseous heat carrier is normally quite poor.

Another concept comprises pulse combustors. The most effective technology for an indirectly heated gasification consist in the application of heat pipes to improve the heat transfer into the fluidized bed by magnitudes. First demonstration plants are currently under construction and in demonstration. The company AGNION is currently commercializing this concept for the production of syngas from biomass.

Hirano et al. partially oxidised *Spirulina* at temperature ranging from 850 to 1000 °C, and determined the gas composition required to generate theoretical yield of methanol. The highest theoretical yield would be 0.64 g methanol from 1 g of biomass in this case. They also estimated a ratio of methanol produced to the total required energy of 1.1, which show a marginal positive energy balance for algae gasification.

Reliable literature data for high temperature gasification of microalgae is very sparse.

The energy balance of drying the biomass for gasification seems to be the main bottleneck to make this thermochemical process viable and, although some experiences show good results (positive energy balances) under particular circumstances, more research is needed before drawing any definitive conclusion.

7.3 Pyrolysis

Pyrolysis is the conversion of biomass to bio-oil, gaseous fraction and charcoal in the absence of air at medium to high temperatures (around 500 °C and in the range 350–700 °C), or by heating in presence of a catalyst with short hot vapour residence time (about 1 s) to crack hydrocarbons into short chain molecules, then cooled to liquid rapidly (flash pyrolysis). It is an alternative to gasification for converting biomass into solid, liquid and gaseous fuels and is becoming increasingly popular as it is relatively simple and inexpensive to construct.

By varying the conditions of the process, three different types of pyrolysis can take place:

• Slow pyrolysis, characterized by a very low rate of heating fuel, with reaction temperatures also quite low (200 ° C -350 ° C) and very long residence times. This particular type of pyrolysis favors charcoal production (over 30%).

• Conventional pyrolysis, which takes place with moderate heating rate (≈ 20 ° C / s) and also moderate reaction temperatures (under 600 °C), with residence times varying from 10 seconds to 10 minutes. This second type of pyrolysis produces similar quantities of char, gas and liquid.

• Fast pyrolysis, characterized by very high heating rate (around 100 °C/s), which can be achieved by using biomass with a very thin size, by very short gas residence time (<2 s) and allows very low yields of char but rather tends to maximize the yield of liquid product. Liquids can be easily stored and transported, upgraded and refined to produce higher quality fuels. The product may also contain chemicals in economically recoverable amounts. Temperature reaches approximately 500 °C (Bridgwater, 2003).

The table below outlines the characteristics and expected yields of different modes of pyrolysis.

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Flash pyrolysis	Moderate temperature (500 °C), short hot vapour residence time (about 1 s)	75	2	13
Fast pyrolysis	Moderate temperature (500 °C), moderate hot vapour residence time (about 10–20 s)	50	20	30
Slow pyrolysis	Low temperature (400 8C), very long solids residence time	30	35	35

Table 13 - Operating parameters and expected yields for pyrolysis processes (adapted from IEA Bioenergy)

Flash pyrolysis yields up to 80 wt% liquid on dry feed (Bridgwater and Peacocke, 2000). The yields of gas and liquid depend on the type of biomass, residence time and temperature inside the reactor. One of the main drawbacks of this process is that the composition of pyrolytic oil is very similar to that of the original biomass, leading to important qualitative and quantitative differences associated with different biomass types. This depends mostly on biomass chemical composition rather than its structural characteristics. Physical properties of biomass (e.g. density) affect the heating rate and consequently the time of conversion (Di Blasi et al., 2001).

The residence time influences the degree of progress of secondary reactions that lead to a reduction in liquid yield, in favor of secondary volatile compounds and char.

As for the temperature dependence, the liquid yield follows a non-monotonic pattern characterized by a maximum at around 480-530 °C. The resulting liquid consists of water and an organic fraction, and the yield of the organic fraction reaches a maximum at about 430 °C (Aguado et al., 2000). The solid residue, however, decreases quickly to move to a value which remains constant at high temperatures. An increase in pyrolysis temperature leads to an increase in fixed carbon and ash content and a decrease of volatile matter in solid residues (Encinar et al., 1996). Finally, the yield of the gas phase tends to increase with temperature. This trend depends on the fact that initially there is some competition between the charring reactions and “devolatization” ones, which prevail at high temperatures. Therefore, yields of liquid and gas increases with temperature, while char decreases. At temperatures close to 480 °C the secondary degradation reactions of tar vapors start with associated production of gaseous compounds. This explains the constant evolution of char yield with high temperatures.

Three reaction zones can be identified in a pyrolysis process: primary, secondary and tertiary. Changes in temperature and residence time show a smooth transition between the four classes of products (Evans and Milne, 1997):

1. Primary products resulting from the degradation of cellulose, hemicellulose and lignin.

2. Secondary products, mainly phenols and olefins.

3.a Alkyl tertiary products that include methyl derivatives of aromatic compounds[46].

3.b Condensed tertiary products such as benzene, naphthalene, acenaftilene, anthracene and pyrene.

The cracking of primary compounds results in an increase in the yield of secondary and tertiary alkyl products. As the temperature increases, condensation reactions lead to the formation of condensates that, under more extreme reaction conditions, tend to produce heavier compounds, particulate precursors. The formation of primary products is followed by a second phase characterized by primary cracking of the vapors. Co-products of lignin are essentially aromatic low molecular weight resulting from the cracking of methoxyphenols at higher molecular weight (Evans and Milne, 1997).

Finally, commercial products (heavy aromatics) are the result of polymerization reactions of unsaturated compounds derived from aromatic or light holocellulose present among the primary products of lignin (Evans and Milne, 1997).

A detailed study of the dependence of fluid composition from the pyrolysis reaction temperature is included in the work of Branca et al. (2003). In this study trends in yields was observed as a function of reaction temperature of about 40 compounds among the 300 identified that, together with water, make up 62-65% of total liquid. These compounds were grouped into six classes: main carbohydrates, secondary carbohydrates and furans deriving from the degradation of holocellulose, guaiacol, and phenol siringoli produced by lignin degradation.

Even if liquids derive from different technologies, the most influential parameter is the type of biomass input.

During the manufacturing process, the lower heating rate, typical of conventional pyrolysis, which results in lower reaction temperatures, favors the reactions of dehydration. Longer residence times

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[46] Aromatics consist in hydrocarbons having one or more unsaturated ring structures such as benzene or unsaturated polycyclic ring structures such as naphthalene or phenanthrene, any of which may also have one or more side-chain paraffins.

can cause the secondary cracking of primary products, reducing yields and affecting adversely biofuels properties. Usually long residence time also require higher energy input. Recently, flash pyrolysis processes have attracted more attention for maximizing liquid yields, hence for the production of transport biofuels.

Flash pyrolysis is deemed to be a viable technique for future replacement of fossil fuels with biomass derived liquid fuels mainly because it can directly produce a liquid fuel and because of the high biomass-to-liquid conversion ratio (95.5%) (Demirbas 2006) and a possible efficiency up to 80% (Amin 2008).

Figure 16 reports a conceptualized fluidized bed fast pyrolysis system from Bridgwater et al.:

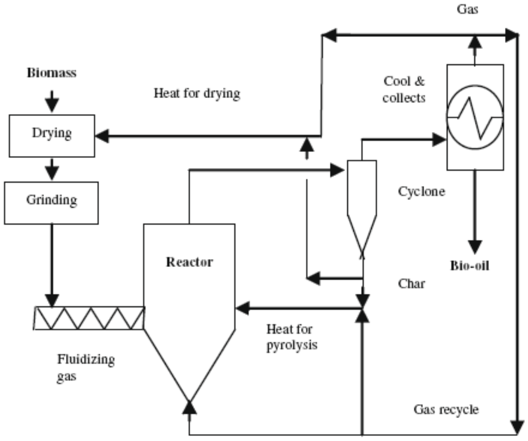

Figure 16 - Scheme of a typical fast pyrolysis process plant

A disadvantage of using pyrolytic oil for transport is the low HHV which is approximately 40% less than fossil oil, its pH value of 2-3, viscosity and its substantial solid content (Bridgwater, 2003). A secondary disadvantage is the relatively high water content in the final bio oil (up to 25 wt%) that cannot be readily separated and can cause miscibility problems with conventional liquid fuels.

Miao and Wu used fast pyrolysis to enhance oil yield from microalgae *Chlorella protothecoides* after manipulating its metabolic pathway towards heterotrophic growth. The recorded oil yield of 57.9% dry wt. basis from heterotrophic cultivation (HHV of 41 MJ/kg) was 3.4 times higher than achieved by phototrophic cultivation and the results suggest that pyrolysis has potential in algal BTL conversion. Miao et al. achieved bio-oil yields of 18% (HHV of 30 MJ/kg) with fast pyrolysis of *Chlorella protothecoides* grown phototrophically.

Demirbas, experimenting with *Chlorella protothecoides*, showed that bio-oil yield increased in line with temperature up to a point and then decreased at higher temperatures. For example, the yield rose from 5.7% to 55.3% with an increase from 254 to 502 °C, and subsequently decreased to 51.8% at 602 °C. They recorded a HHV from microalgae of 39.7 MJ/kg obtained at temperatures ranging from 502 to 552 °C (Brennan et al. 2009).

Results indicate that bio-oils from microalgae are of a higher quality than those extracted from lignocellulosic materials.

Properties	**Typical values of bio-oils from**		**Fossil oil**
	Wood	Microalgae	
C (%)	56.4	62.07	83-87
H (%)	6.2	8.76	10-14
O (%)	37.3	11.24	0.05-1.5
N (%)	0.1	9.74	0.01-0.7
Density (kg/l)	1.2	1.06	0.75-1
Viscosity (Pa*s)	0.04-0.2 (at 40°C)	0.1 (at 40°C)	2-1000
HHV (MJ/kg)	21	29-45.9	42

Table 14 - Comparison of typical properties of fossil (petroleum) oil and bio-oils from fast pyrolysis of wood and microalgae (Brennan et al. 2009)

Research on biomass pyrolysis is relatively advanced and there has been significant process development. Many fast pyrolysis plants are operating on a pilot or commercial scales (Bridgewater, 2003) however it appears unlikely that a dry pyrolysis process can be driven economically for the conversion of feed with a water content above 50–70%. Such a process would only be capable of producing charred material and an insignificant amount of additional energy and/or product gas. The lower the water content of the feed, the more heat can be produced and used for other purposes (Roberts et al. 2010). By contrast, hydrothermal processes (discussed in the following section) typically run with 'water content' of 75–90% or even higher. The amount of external heat necessary depends on the process design, but it is substantially lower than for the dry pyrolysis of such slurry.

Research on pyrolysis of algal biomass is already quite extensive and it still expanding, especially on flash pyrolysis, and it has achieved promising outcomes that could potentially lead to commercial exploitation.

Pyrolysis is in general a promising technique since it can use very different types of feedstock, can produce a liquid fuel which can be easily stored and transported, but the resulting oil has a relative low quality. There are still important technical challenges as resulting oils are acidic, unstable, viscous, and contain water traces. Therefore, the process oil will require upgrading (hydroprocessing such as hydrogenation) and catalytic cracking to lower oxygen content and remove alkalis.

At present the energy balance and quality of bio-oils obtained are the main barriers for using algae biomass in pyrolysis processes and therefore this process will not be investigated further in this paper.

7.4 Hydrothermal conversion

Among the main limitations of using algae for energy one can surely list the fact that it requires high-oil content oil species, which is usually associated with low yield, and requires drying. Both of these limitations can be overcome by hydrothermal processes.

After harvest, algae have a typical water content higher than 99%, which can go down to 75% after treatment in energy intensive centrifuges. The wt% of the slurry can be further increased with other pretreatment processes but at the expenses of the overall energy balance.

For fuels with such high water content like algae slurry, it is therefore appropriate to investigate hydrothermal processes to convert the wet biomass into biofuels. All enjoy the significant advantage that the starting biomass does not need to be dry, and the significant energy input required to remove water by evaporation is eliminated. In the hydrothermal (HT) process, biomass feedstock with a moisture content of preferably between 55 and 85 % is exposed to high pressure and moderate temperature in a liquid water environment. Hydrothermal conversion is a thermochemical conversion technique which uses liquid sub-critical or super-critical water as a reaction medium for conversion of wet biomass and waste streams.

Hydrothermal processes can be classified into three categories:

- Hydrothermal carbonization: to convert wet biomass into a kind of coal (or bio-char), at high temperature and pressure. The mildest reaction conditions in terms of temperature and pressure are employed. Lignocellulosic substrates have been extensively examined as reactants at temperatures from 170 to 250 °C over a period of a few hours to a day.
- Hydrothermal liquefaction: to convert wet biomass into liquid hydrocarbons in the presence of CO. It is generally conducted at 250–450 °C and provides liquid bio-oils (as well as some gaseous and liquid products).
- Hydrothermal gasification: to gasify wet biomass in supercritical water conditions. Hydrothermal gasification is the most thermally severe and can be conducted both without catalyst at 400–800 °C and in the presence of Ni and Ru catalysts at 350–400 °C. Gaseous products include hydrogen, methane, and carbon dioxide.

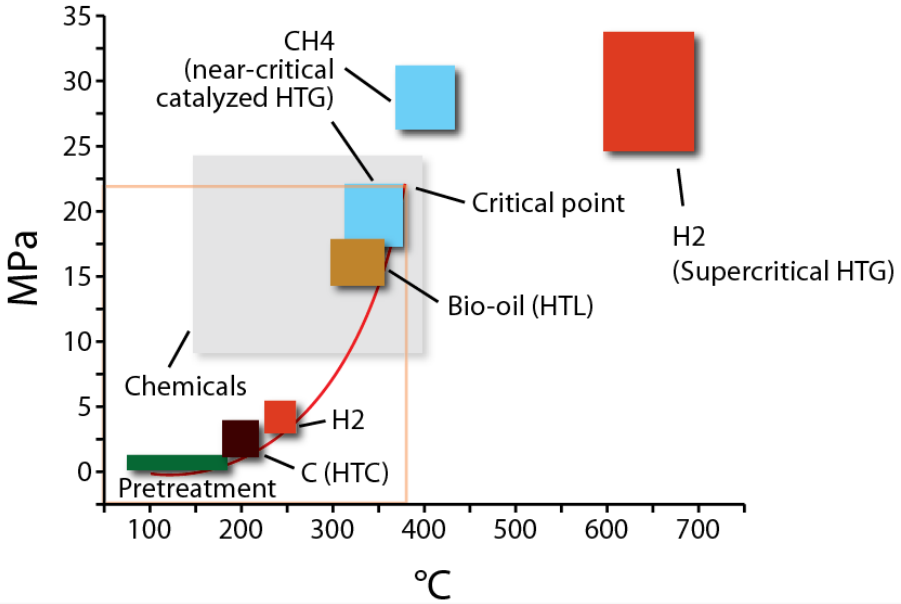

Figure 17 – Different hydrothermal processes and their products as a function of temperature and pressure

All of these hydrothermal processes have in common the fact that they work with relatively higher pressure and lower temperature if compared with biomass gasification. The advantage is that mostly pumpable liquid fuels can be used as a feedstock. Since the efficiency of liquid pumps is very high, a high efficiency is obtained with this method using feedstock with high water content (> 70%). Research in all these three hydrothermal processes has been extended to microalgae.

Another common feature of these methods is that they are all in the stage of research and development with only few commercial experiences.

Hydrothermal processes can lead to several products which can be used for different purposes such as:

- direct combustion as a liquid (to replace fossil fuels),
- combustion as a solid fuel (co-firing with coal),
- emulsified fuel (type "Orimulsion"[47])
- replacement of charcoal
- upgraded fuel products
- valuable gases, such as hydrogen or methane.

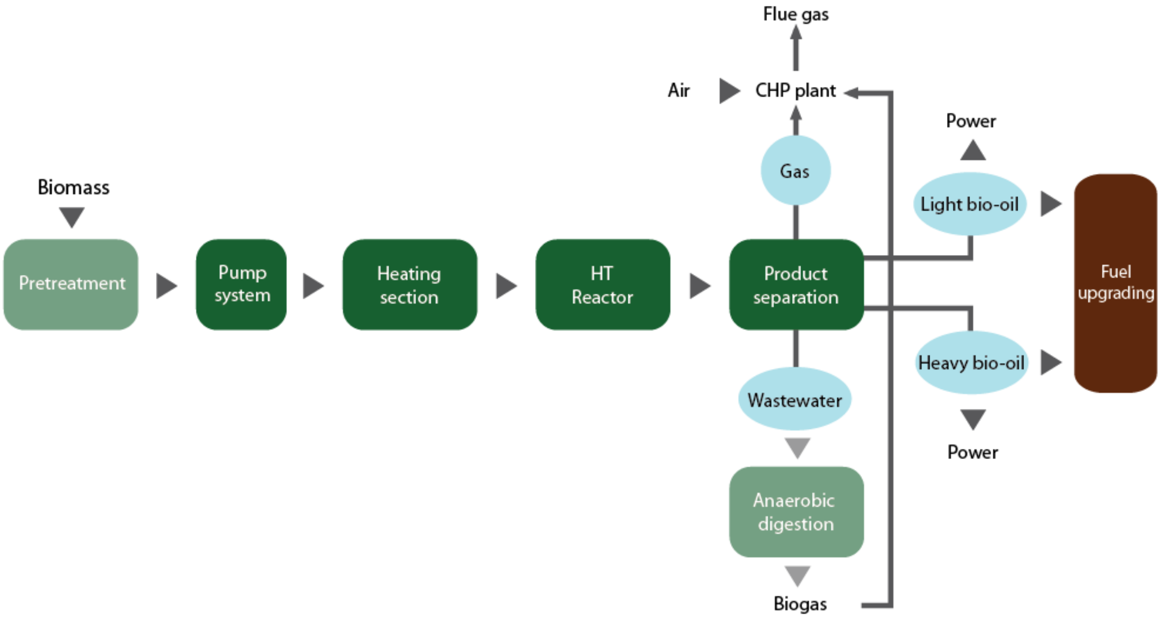

Figure 18 - Example of HT processing system. Effluents from the HT process can be further processed in an anaerobic digestor. Main products are electricity, heat and fuels

As shown below, HT conversion can be performed with various purposes and different products can be aimed for. In a catalytic version of the process almost complete conversion of biomass to methane rich gas is realized (Hydrothermal gasification).

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[47] Orimulsion is a registered trademark name for a bitumen-based fuel that was developed for industrial use by Intevep.

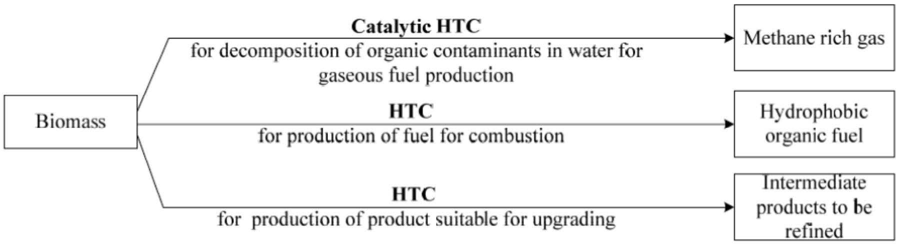


Figure 19 - Different HT conversion options (Knezevic 2009)

In simple terms, the hydrothermal process is a chemical reaction in which the hydroxide anions (OH^-) and hydrogen cations (H^+) are split off from organic molecules and water is separated. Subsequently, the dehydrated organic molecules (re)combine to form a variety of carbon-rich polymers.

This process is very similar to natural coalification. Since water is a very stable molecule, it is released from the cleavage of the organic molecules of biomass energy. The HTC-reaction is therefore an exothermic process.

The HTC-reaction so it works best with input materials such as sugars and starches, cellulose and hemicellulose, whose molecular structure has a number of hydroxide anions. Less suitable are input materials such as proteins or lignin with less content of hydroxide anions.

Besides the chemical composition also the physical structure of a particular biomass can affect the suitability for HTC. This is especially true for high lignin content, which typically gives the wood its structural strength. Slow reacting lignin layers slow down the faster cellulose reaction and considerably the overall HT process.

Basically biomass rich in cellulose and hemicellulose, and poor in lignin is the ideal raw material. Also biomass with high protein content (e.g. grain) is suitable and generally results in products of higher quality.

A scheme of a typical HT process is presented below. Prior to feeding into the process, biomass is pre-treated to ensure that the feedstock has the desired properties: rheological properties, water content, degree of fragmentation of biomass components etc.

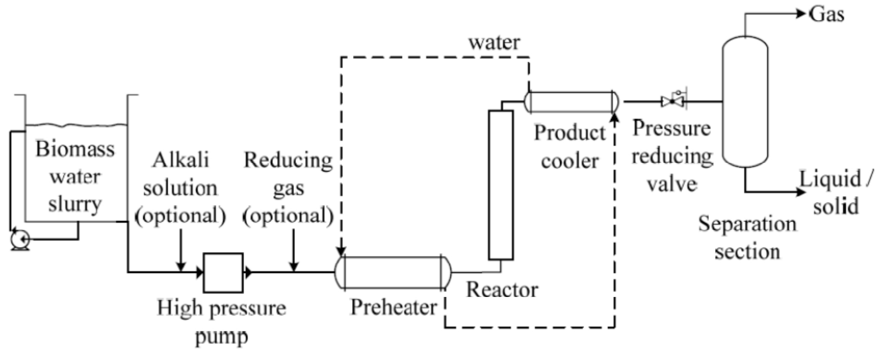


Figure 20 - Typical HTC system layout

In the feeding section, feedstock is pressurized and heated to the desired temperature, while being transported to the reactor. Feeding biomass-rich water and slurries is a common challenge due to the problems of biomass settling and filtering and blocking of the process lines, particularly for relatively high biomass/water ratios.

Hydrothermal carbonization (HTC) takes place effectively only in water, is an exothermic process, and proceeds spontaneously. Two product streams are created that are isolated by filtration: 1) an insoluble, char product and 2) water soluble products.

In general, the desired objective of increasing the carbon-to-oxygen ratio (commonly referred to as "carbonization") has been accomplished by endeavoring to split off carbon dioxide. This mechanism is undesirable because, with loss of carbon dioxide, carbon is depleted as well as oxygen, and creation of gaseous products causes even greater reaction pressures that increase complexity (hence cost) of reaction equipment.

In HTC, the input material is heated to the desired temperature in the range of 300 to 370 ºC while water is kept in liquid phase by pressure regulation. In most cases tubular reactors have been used for continuous installations.

Typically, residence times of 5-90 minutes have been applied. Upon cooling the reactor effluent of HTC, three different products, being also three different phases at room temperature, can be identified: a hydrophobic organic phase, an aqueous phase with organic compounds dissolved in it, and a gas phase, consisting mainly of CO_2 (Knežević 2009).

Ferrous ion and iron oxide nanoparticles have been found effective catalysts in HTC of insoluble biomass (Cui et al. 2006) and an acidic pH had been reported to provide less carbon dioxide product (Titirici et al. 2007).

A result of HT conversion using *Chlorella* as algal input material obtained by Heilman et al. (2006) is reported below:

	HTC conditions	**%C**	**%H**	**%N**	**Yield**	**% Carbon recovered in char product**
Starting Chlorella sp.	-	50.8	7.2	10.1	-	-
Algal Char	12.5% solids 200 °C 3h	65.3	8.5	7.2	39.5	51

Table 15 - Analysis of Chlorella sp. feedstock and its char from hydrothermal conversion

The table below, always by Heilman et al. (2006), shows that the %C values for two different algal chars and the natural coal material were comparable and in the 66–73% range, while only 62% C was observed with the lignocellulosic char, despite an extended reaction period of 17 hours. It also shows how nitrogen compounds, necessary for algae growth, can be inevitably found in algal biomass and subsequently in the final fuel products, in higher concentrations than their fossil fuel alternatives:

Sample	**%C**	**%H**	**%N**	**%S**	**Heat of combustion [MJ/kg]**	**Wt.% ash**
Natural coal	69.6	5.7	0.9	0.6	28.59	5.60
Lignocellulosic char	62.3	5.6	<0.5	<0.5	24.38	n/a
Algal char (from HTC of C. reinhardtii)	72.7	9.7	5.2	<0.5	31.58	n/a
Algal char (from HTC of Dunaliella salina)	66.3	7.9	7.3	0.5	30.51	0.33

Table 16 – Comparison of quality of different algal chars with lignocellulosic char and natural coal

Heats of combustion were higher with the algal chars that indicated the importance not only of carbon but also hydrogen for energy content, since the algal chars possessed significantly higher amounts of hydrogen than natural coal or lignocellulosic char.

In the algal chars also higher levels of nitrogen were observed and may have a negative effect as combustion conditions favor formation of oxides of nitrogen. However N concentration is heavily dependent on the growing medium as discussed before.

Some strains of cyanobacteria also provide high quality chars but yields are only half those obtained with green microalgae (Heilman et al. 2006).

Algae species leading to very low ash value of char, such as the one derived from *Dunaliella salina,* may be a significant attribute if the chars are utilized as a carbon source for conversion into synthesis gas.

Considering the most basic use for algal char, i.e. burning it for energy purposes, a comparison of energy outputs for burning *Chlamydomonas reinhardtii* itself and the char derived from it are reported below (Heilman et al. 2006). The starting point for each material was the centrifugate at 10 wt% concentration.

As previously mentioned, one major issue with any industrial process involving the combustion of algae is removal of water. In the experiment, to obtain 1 kg of dry alga from a centrifugate at 10% solids, 23.31 MJ were required and this resulted in a net energy input into the system of 5.27 MJ. In contrast with the HTC process, the 10% solids concentration was the desired HTC reaction medium and no energy input was initially required.

To heat the system from ambient to 203 °C, 7.31 MJ were required, and with proper insulation and temperature control, no significant additional energy was needed to maintain reaction temperature for 2 h. The char product isolated by filtration was moist and required 0.52 MJ to obtain 0.4 kg of dry char. The overall net result was that the process liberated 12.01 MJ/kg which was an improvement of 17.28 MJ over burning the starting alga.

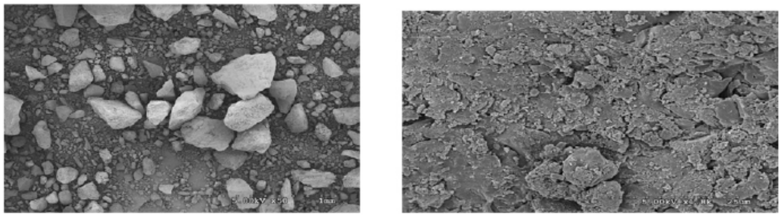
It should also be mentioned that no recovered heat was considered in this hypothetical process, and heat conservation measures would most certainly be employed in any industrial process resulting in additional energy improvement.

Another important result of Heilman et al. was that, under the experimental conditions, carbonization was not achieved by loss of carbon dioxide.

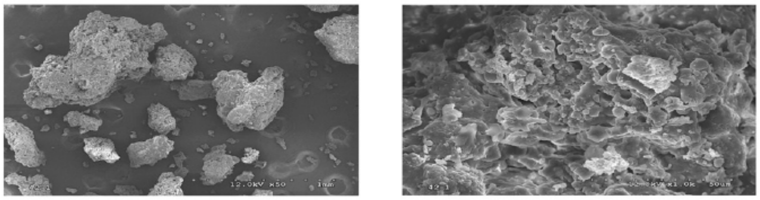
At the end of the process carbon was distributed as follows: 55% in the algal char, 45% in freeze-dried solutes in the aqueous filtrate, and 8% as carbon dioxide present in the headspace of the reactor (assuming all the gas was carbon dioxide) and dissolved in the filtrate. A significant amount of carbon was present in the solutes in the filtrates.

Also, a proper tally of carbon dioxide was obtained. Even assuming that all the gaseous products in the headspace of the reactor and dissolved in the aqueous filtrate were carbon dioxide, the level of that product was less than 10% of the total products. A reasonable explanation, though not directly proven, was that the predominant mechanistic pathway for carbonization was dehydration. Clarification of reaction mechanism awaits further investigation.

Natural coal



Algal Char



Lignocellulosic char from prairie grass

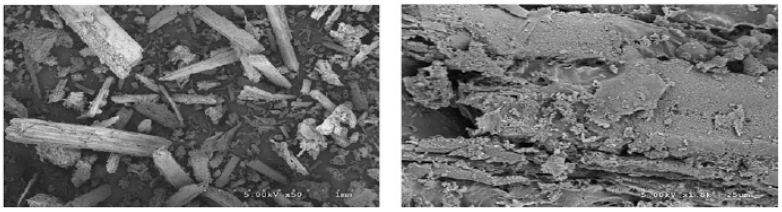


Figure 21 - SEM[48] pictures of natural coal, algal char and char from a lignocellulosic material

The final biochar can be obtained in different forms according to the use envisaged. A biochar powder can be obtained, similar to dry brown coal powder and can be used for coal powder firing or in entrained flow gasifiers. Alternatively it can be recovered in the form of powder-free granulate, being the simplest product form derived which can be burned directly in biomass firing or in power plants. Biochar can also be obtained as pellets, which have an especially high energy density and

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[48] Scanning electron microscope

can be used in pellet firing for heat generation, or co-fired in a power plant. Because of the high abrasion resistance and the hydrophobic characteristics, the pellets can be optimally stored and transported, similar to fossil coal.

Biochar powder

Biochar granulate

Biochar pellets

Figure 22 - Different forms of HTC biochar

Biochar obtained from HT conversion presents many advantages in comparison to wood chips and pellets. For example, as its hydrophobic characteristics allow pellets to be openly packed and transported, reducing handling costs, differently from wood chips and pellets.

Using this biochar in existing coal power plant does not require any significant additional investment, since the existing infrastructure. It can also be readily used in entrained flow gasifiers (as opposed to wood chips and pellets).

The HT process, in addition to the relatively low refinement costs, allows other biomass materials such as algae to be added to wood fuel for power application.

The costs of HTC are comparable to those of torrefaction. But taking into account that it can potentially use organic waste of existing processes (algae from wastewater treatment for example) and agriculture, the base costs can be actually much lower.

The final energy balance of a HT plant where the combustion or gasification of the biochar is done on-site is considerably better than that when the HTC coal must be transported to another location. This is because the waste heat from the biochar combustion on-site can be used to cover the total heat requirement for the HTC process. In addition, suitable re-cycling of the heat generated in the HTC process can cover a large part of the energy required for the separation and drying processes. Furthermore waste heat from the HTC process water (typically warm water at 70-80 ° C for carbonization but higher temperatures for HTL and HTG) can be used for other external processes such as pre-warming of water, heating for green houses, etc.

Hydrothermal carbonization is today pursued in Germany by SunCoal (carboREN technology) and AVA-CO_2.

AVA-CO_2 is operating a commercial HTC plant on an industrial scale since October 2010 in Germany, processing biomass into HTC coal. The exothermic process has a very high efficiency (close to 100%) and enables processing of wet and dry biomass. The processing water can to a large extent be reused in the closed system. The amount of process water recycled depends on the type of biomass used in the process. For biomass with high water content like algae only small amounts of process water can be recycled within the system. The closed circuit system means that almost no fresh water in the form of steam needs to be added.

The HT reaction in the AVA plant takes place at 220 °C under pressure and the transformation of wet biomass to end products takes a few hours. An overview of AVA plant is provided below:

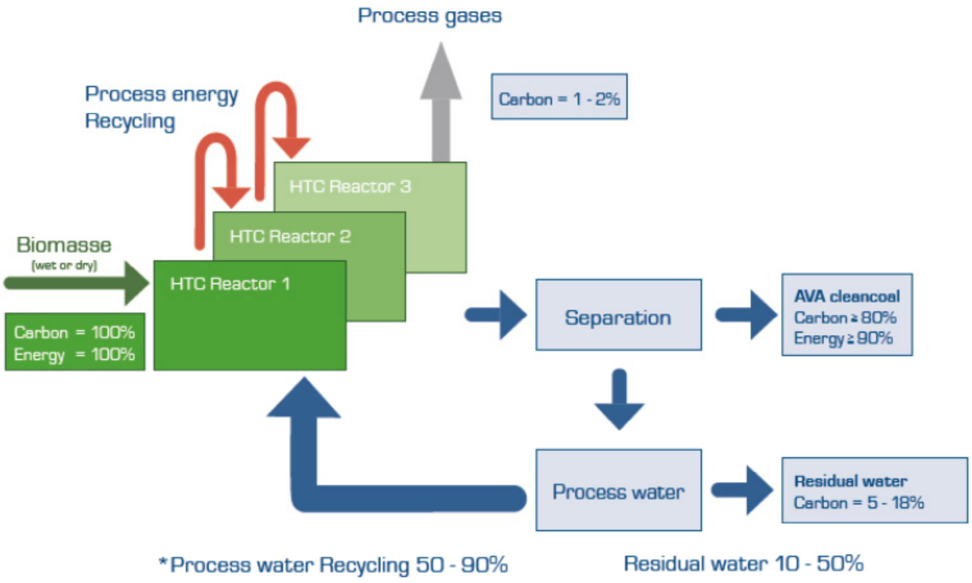

Figure 23 - Scheme illustrating the AVA process, with information on mass and energy balance

The product of the HT process depends very much on the input material. For example using brewers spent grain as input feedstock, it is possible to produce a biochar with 65% carbon content and an heating value of 25 MJ/kg hw (DIN), corresponding to 2.4 kg of CO2 emitted if combusted[49]. The biochar produced has a particle size smaller than 300 µm, sulphur content between 0.1 and 0.5 % and an ash melting point of 1400° C (higher than lignite), all maintaining heavy metals and toxic substances within the limits applying to foodstuff.

At the heart of every AVA-CO_2 HTC plant is the HTC module formed by up to 6 reactors which can be served by 1 mixing tank. Once the HTC process is completed the reactors are emptied into an outlet buffer tank and an evaporation tank. From there the slurry containing the carbon is transferred into the separation and drying system. Some technical data of the HTC module are reported in the table below.

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[49] The carbon content in one kilogram of AVA biochar is approx. 65 %, i.e. 650 g. In the combustion process, each carbon (C) atom combines with two oxygen (O) atoms to form CO_2. Carbon atoms have a specific weight of 12, while the specific weight of oxygen is 16. Consequently, a CO_2 molecule will have a specific weight of 44 (2 x 16+12). The weight of the CO_2 generated in the combustion process is therefore 3.666 (44/12) times higher than that of the burnt carbon. Accordingly, the weight of the CO_2 fixed in 1 kg of AVA biochar is approx. 2.4 kg (650 g x 3.666).

Yearly throughput of biomass (at 30% DMC)	8,000 t/reactor
Yearly production capacity of biochar	1,600 t/reactor
Heat requirement for carbonization	3 GJ/t biochar
Fresh water requirement	1,300 l/t biochar
Waste water	4,600 l/t biochar

Table 17 – Input requirements and outputs of a plant with AVA CO_2 HTC technology

A complete AVA-CO_2 HTC plant consists of one or more HTC modules but also other different upstream and downstream modules. A typical plant with two modules and upstream and downstream modules would have the following space requirements.

Modules	Space requirement
Biomass reception and storage	100-200 m^2
Steam generation	40-50 m^2
Separation and drying	150 m^2
Post-treatment and logistics	150 m^2
Process water treatment	25 m^2
Two HTC modules	270 m^2

Table 18 – Technical characteristics of AVA CO_2 HTC modules

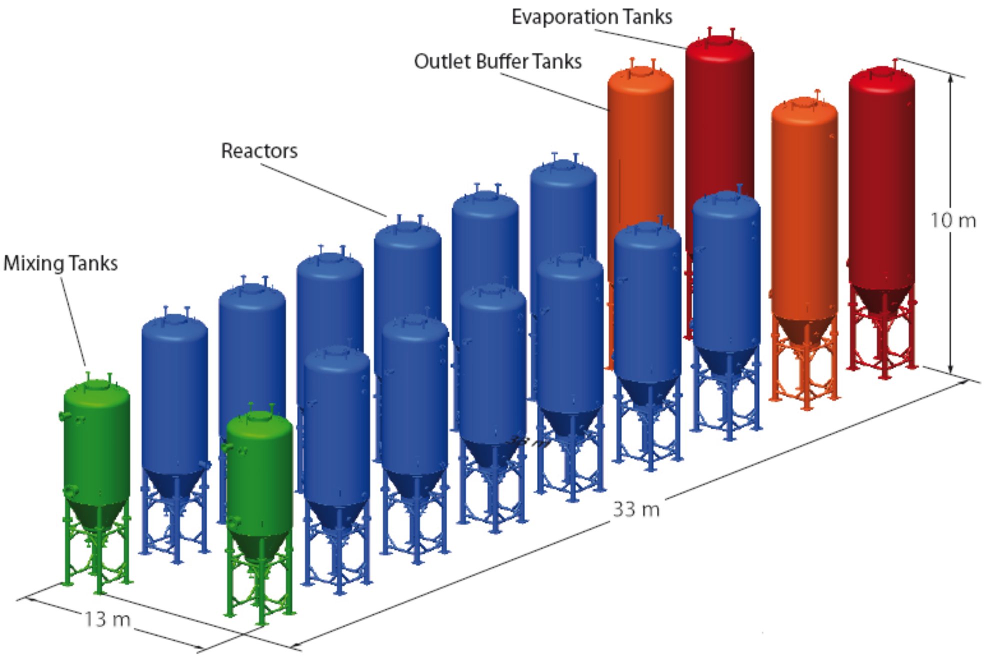

Figure 24 - Scheme illustrating two AVA-CO_2 HTC modules

Also SunCoal Biofuel has developed a quite mature technology for hydrothermal carbonization of organic waste with heterogeneous characteristics and the pilot plant that they have been running for years has been converted in 2011 for customer testing purposes. It is located in Ludwigsfelde, Brandenburg and can process 200 kg of biomass per hour.

SunCoal Industries makes use of its patented CarboREN technology. With this HT technology, damp biomass with 20–75% water content and a low heating value is converted to biochar which has similar characteristics to fossil coal. The process requires only a minimal amount of energy (7% of the energy of the produced biochar) and is designed in modular units to be constructed according to the needs.

During refinement, impurities and unwanted elements (sulfur, chlorine, nitrogen) are removed or reduced. The biochar obtained because of the high product quality achieved during refinement, can be used in all types of power plants as biofuel. The dry and hygienic biochar can be stored at length, and the high energy density (the LHV is much higher than that of the input biomass and the energy density would be double than wood chips) allows it to be easily transported.

In the SunCoal plant, the input wet biomass is crushed and reduced to a grain size of 60 mm and filtered to remove impurities. Then, in just a few hours, temperatures of 200°C and pressure of 20 bars completely breaks down the structure of the biomass and separates out the water. The resulting HTC-slurry is then removed from the cooker, brought to ambient pressure and cooled. The water content of the HTC-slurry is then reduced by 50% by a mechanical press. The separated water is mostly reused in the process. The HTC-cake is finally dried, reducing the water content to less than 5%. Wastewater produced by the process can either be directed to a treatment plant or treated in the plant itself. The resulting biochar can be processed into powder, granules or pellets, to be stored, further refined (for example, into gaseous fuel or syngas), or used directly as fuel.

The following diagrams show the material balance and energy efficiency of a CarboREN plant for 60,000 tons of material input per year (mixed green waste and grass cuttings) containing around 55% of water and 15% of ash.

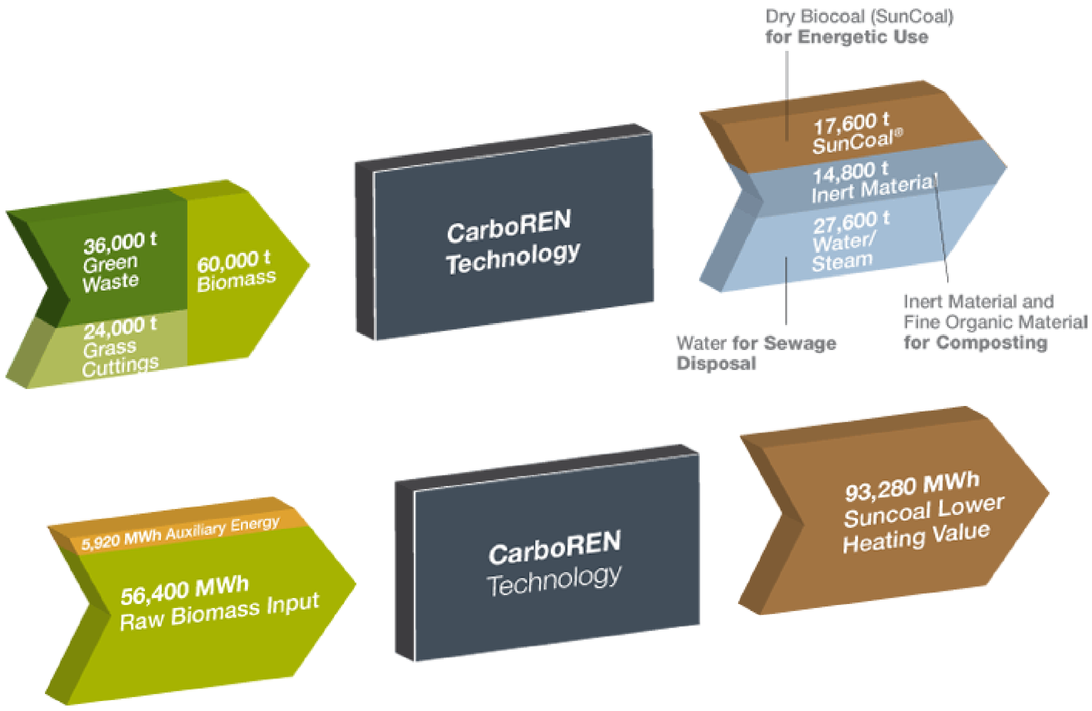

Figure 25 - Mass and energy balances of SunCoal CarboREN conversion plant

For each ton of biomass, auxiliary energy in the form of electricity and gas must be used, equal to around 7% of the energy stored in the biochar needs to be used in order to initiate and maintain the process. Per ton of biomass input only 99 KWh of electricity and gas in total are needed.

According to SunCoal Industries, the costs of organic waste refinement in a CarboREN plant of mid-size capacity (60,000 t/a) are similar to those in a composting plant, but at reduced carbon emission levels.

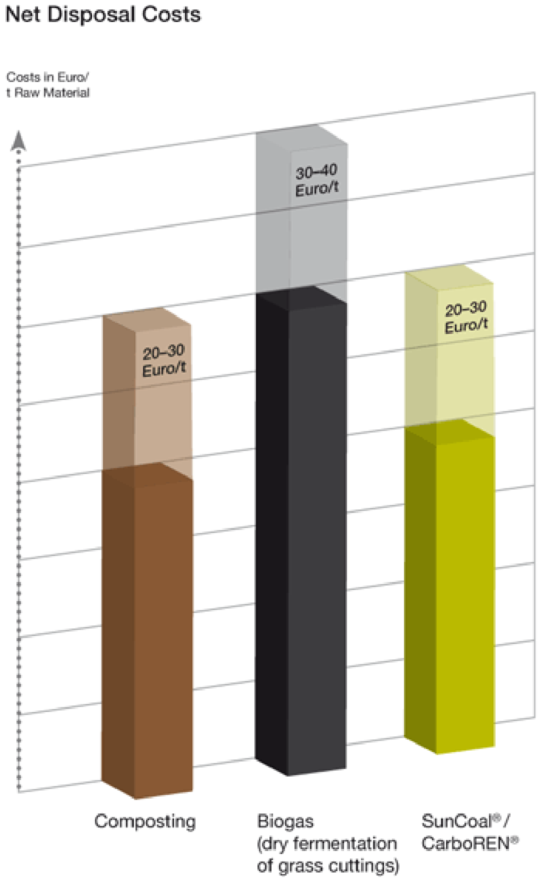

Figure 26 - Net disposal costs. In a mid-capacity CarboREN Plant (60,000 t/a), organic waste can be refined at a cost similar to that of composting.

Characteristics of a CarboREN plant for biochar production from organic waste are reported in table 19.

Input Quantity [Tons p.a.]	60000
Biochar produced [Tons p.a.]	17600
CO2-Reduction by Coal Substitution [Tons $CO_{2\text{-eq}}$ p.a.]	32000
Process duration [hours]	6-12
Plant surface [m^2]	6000
Energy output [MM kWh p.a.]	92,8
Equivalent Resulting Heat Supply [2 person households]	10200
Separated Material for Composting [Tons p.a.]	14800
Wastewater [m^3 p.a.]	27600

Table 19 - Input requirements and outputs of a plant with CarboREN technology

Comparison of algal char and natural coal (adapted from Heilman et al. 2006))

Global Warming Impact: The burning of natural coal, a fossil fuel, releases new carbon dioxide into the atmosphere. Based on projected growth in coal-fired electricity generating capacity by 2030, an estimated 2.7 billion tons of new carbon dioxide will be produced annually. Combustion of algal char derived from biomass creates no new carbon dioxide in the atmosphere.

Carbon Formation: The conversion of aqueous algal slurries into algal char occurs at a relatively moderate thermal condition in less than an hour under batch processing conditions. Natural bituminous coal, on the other hand, is non-renewable, requiring formation conditions of millions of years of heat and pressure.

Carbon Isolation: Algal char is isolated by filtration and obtained as a free-flowing powder. Natural coal is mined thousands of meters below the earth's surface and must be pulverized and powdered before use.

Carbon Contaminants: Most natural coal is contaminated with Cl, S, Hg, Pb, Cd, U, Br, Cr, Cu, Fe and Zn, some of which contribute to serious health problems when released into the environment. In contrast, algal char has only trace quantities (ppm levels) of environmentally benign S, Cu and Fe.

Carbon Fuel Quality: Both products are of bituminous level quality in terms of percentage of carbon and energy content.

An important area for future work will be to define utility for the aqueous filtrate by-products. These complex solutions contain considerable quantities of nitrogen containing solutes and are currently being examined as nutrient materials for both higher plants and algae (possibly in a closed loop system).

Heilmann et al. (2010b) also investigated this option with promising results. The filtrate of HTC of *Chlamydomonas reinhardtii* from the experiment illustrated above had the following characteristics:

% Solids	3.55
pH	6.13
Ash	4.65%

Table 20 - HTC filtrate of Chlamydomonas reinhardtii from Heilmann et al. (2010b)

%C	%H	%N	%S	%P
46.0	7.1	13.1	2.0	4.4

Table 21 - Elemental Composition of Chlamydomonas reinhardtii from Heilmann et al. (2010b)

Hydrothermal liquefaction is a process that can be employed to convert wet algal biomass material into liquid fuels and it basically consist in the reaction of the wet biomass with CO to produce liquids hydrocarbons.

Thermochemical liquefaction is a low-temperature (300–350 °C), high pressure (5–20 MPa) process aided by a catalyst in the presence of hydrogen to yield bio-oil. Reactors for thermochemical liquefaction and fuel-feed systems are complex (in comparison to other thermochemical processes) and therefore expensive. The process utilises the high water activity in sub-critical conditions to decompose biomass materials down to shorter and smaller molecular materials with a higher energy density.

In this process, HT conversion yields hydrophobic organic products (sometimes called biocrude) which are easy to separate from the water phase and can be burned directly as fuel in furnaces or boilers, or further upgraded. They can be further fractionated by means of extraction with polar organic solvent(s). The solvent-soluble fraction is then the desired product, part of which can be upgraded to transportation fuel quality by catalytic hydro-deoxygenation. The production of an intermediate suitable for refining and upgrading into transportation fuel is the preferred aim of HTL. Therefore this option is intensively studied and seems to be a promising option for producing liquid fuels from algal biomass. The focus of current research is on minimizing the yields of the reaction by-products and on separation of the products.

Several studies have investigated the characteristics of algal biomass as a feedstock for hydrothermal liquefaction (see table Table 12 - Comparison between thermochemical conversion technologies (adapted from Brennan et al. 2009).

Dote et al. (1999) successfully used thermochemical liquefaction at 300 °C on *B. braunii* to achieve a maximum yield of 64% dry weight basis of oil with HHV of 45.9 MJ/kg and also declared a positive energy balance for the process (output/input ratio of 6.67:1). Minowa et al. (1999) report that oil recovered from *B. braunii* has 1.6 fold the heating value (45.9 MJ/kg) of coal (28 MJ/kg). In a similar study, an oil yield of 42% dry wt. was obtained from *Dunaliella tertiolecta* giving a HHV of 34.9 MJ/kg and positive energy balance of 2.94:1 (Minowa et al. 1995).

The results of energy balance are highly influenced by the algae species involved. Algae cells which contain smaller amounts of N and P on an organic basis, require a lower energy input for fertilizers. This is generally true for all conversion processes. Microalgae that require relatively small amounts of nutrients are more suitable for energy production.

Dote et al. (1996) measured that 80% of the N was distributed in the aqueous phase resulting from the thermochemical liquefaction of albumin and roughly half of the N in the aqueous phase was ammonium. Therefore there is the possibility of reusing inorganic nutrients in the aqueous phase produced by liquefaction as a part of the growth medium for microalgae.

These results indicate that thermochemical liquefaction is a viable option for the conversion of algal biomass-to-liquid fuel and the relatively brief reaction time in batch processing suggests that a continuous process might be developed for the HTC processing of algae.

Tsukahara et al. (2005) highlighted that a 100 MW thermal plant using coal consumes 3.5 x 10^5 t/year of coal (2.28 x 10^5 t_C/year) and emits 8.3 x 105 t/year of CO_2 (2.28 x 10^5 t_C/year). If this thermal plant using coal is replaced by liquid fuel produced from microalgae (*B. braunii* in their example), the quantity of CO_2 mitigation would be 1.5 x 10^5 t/year. On the other hand, 8.4 x 10^3 ha of microalgal cultivation area would be necessary[50]. The two concepts are illustrated in the graph below:

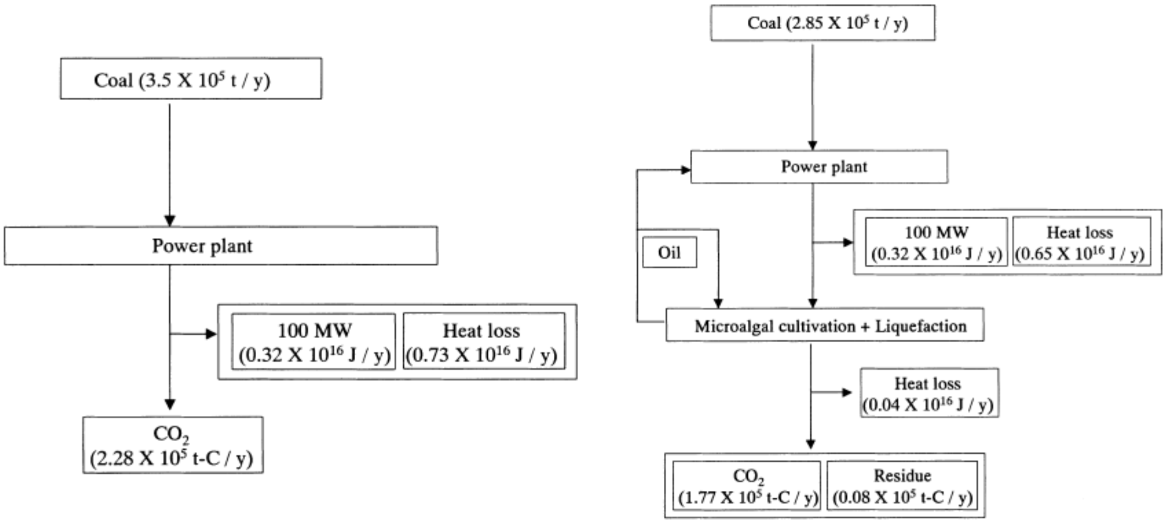

Figure 27 - Energy and carbon flow in a power generation plant using coal (left) and liquid fuel from *B. braunii* and coal (right)

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[50] They assumed an energy efficiency of the plant of 30%, heating value of coal of 28 MJ/kg, carbon content of coal of 65 wt%, 30% of the CO_2 in flue gas used for algae growth, heating energy for liquefaction supplied by the waste heat of the power plant, microalgal yield of 15 t dw /ha/year, a microalgal concentration of culture of 0.5 kg dw biomass /m^3.

In their calculation, 30.1 % of produced liquid fuel was consumed for microalgae cultivation. 2.85 x 10^5 t/year coal was needed to compensate carbon loss due to microalgae growth and gas and tar fractions resulting from HTL.

The main drawback of bio oil from HTL is the low quality of the final product which has been reported to be acidic, corrosive, polar, thermally unstable and highly oxygenated. Although HTL is a promising technology in the long term as it let envisage the possibility of producing biocrude from biomass with an overall positive energy balance, today the oil is not suitable for upgrading or catalytic conversion in commercial refineries. Therefore this process will not be investigated further in this paper.

Hydrothermal gasification is done normally in supercritical water to produce hydrogen or methane. Recently, a low-temperature catalytic method for gasification of biomass with a high moisture content was developed, by which biomass can be gasified directly into methane-rich fuel gas at moderate temperature (below 400 °C) and high pressure (around 20 MPa) using a metal catalyst. Nitrogenous compounds in the biomass are converted to ammonia at the same time (Elliot 1999).

The combination of fuel production from microalgae and the gasification of the rest of the microalgal biomass is also promising for effective energy production.

Low temperature catalytic gasification has been considered very suitable for energy recovery from microalgae, since the energy consumption ratio (energy for gasification / energy of produced gas) for *C. vulgaris* is 0.33. Further energy production systems using microalgae with associated nitrogen recycling combined with low-temperature catalytic gasification have been proposed. Gasification characteristics of microalgae biomass have been studied by several researchers and a flow diagram of a possible microalgae system is shown in the figure 28:

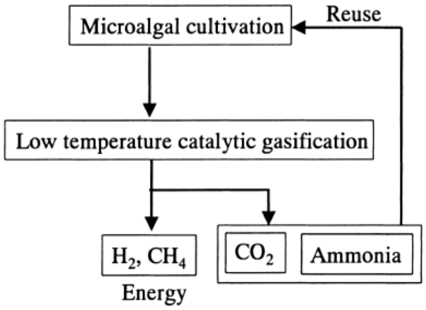

Figure 28 - Conceptual diagram of a microalgal system for fuel production by low temperature catalytic gasification with ammonia reuse (Tsukahara et al. 2005)

In the literature, different innovative production systems using microalgae have been proposed, such as Minowa and Sawayama who proposed a nitrous cycling combined with low temperature catalytic gasification of the algal biomass, or Elliot who developed a low temperature catalytic gasification of biomass with high moisture content. Minowa and Sawayama gasified the microalgae *Chlorella vulgaris* in a novel system with nitrogen cycling to obtain a fuel rich in CH_4 with all the nitrogen component of the microalgae converted into fertilizer quality ammonia. Both Elliot and Minowa and Sawayama experiences indicates that biomass with high moisture content can be gasified directly into methane rich fuel gas without drying and that nitrogen present in the algae can be directly converted into ammonia during the reaction.

Compared with complete combustion, the increase in the energy obtained after HTG (6.68 MJ/kg dry-cell) is higher than the heating energy needed for the gasification process (5.95 MJ/kg dry-cell) (Minowa et al. 1999), outlining this process as a net energy producer.

For environmental remediation and/or energy recovery from organics in water, a special catalytic HTC process can be used. In this concept, organic streams (for example industrial or household wastewater) are completely converted into methane rich gas.

The hydrothermal gasification is currently investigated by several researchers and European research institutes such as the Paul Scherrer Institute (PSI) in Switzerland or the Karlsruhe Institute of Technology in Germany are among the European leaders in this field today. They are currently investigating catalytic and non-catalytic[51] hydrothermal gasification processes respectively. PSI already published some studies on the use of algae as an input material for HTG.

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[51] Performing a truly non-catalytic experiment in supercritical water media is complicated by a number of factors: reactor walls may act as heterogeneous catalysts; alkali salts present in real biomass may act as homogeneous catalysts, or corrosion products from the reactor (transition metal ions such as Ni, Fe, and Cr) may act as catalysts

8 Conversion of raw algal oil into biofuels

The thermochemical conversion processes illustrated before are based on the use of the whole algae as a feedstock, while the relevant biofuel could be produced either from the whole algae or from the rest of biochemical or mechanical processes.

Two main thermochemical processes can be identified to convert algal oil into the desired biofuel:

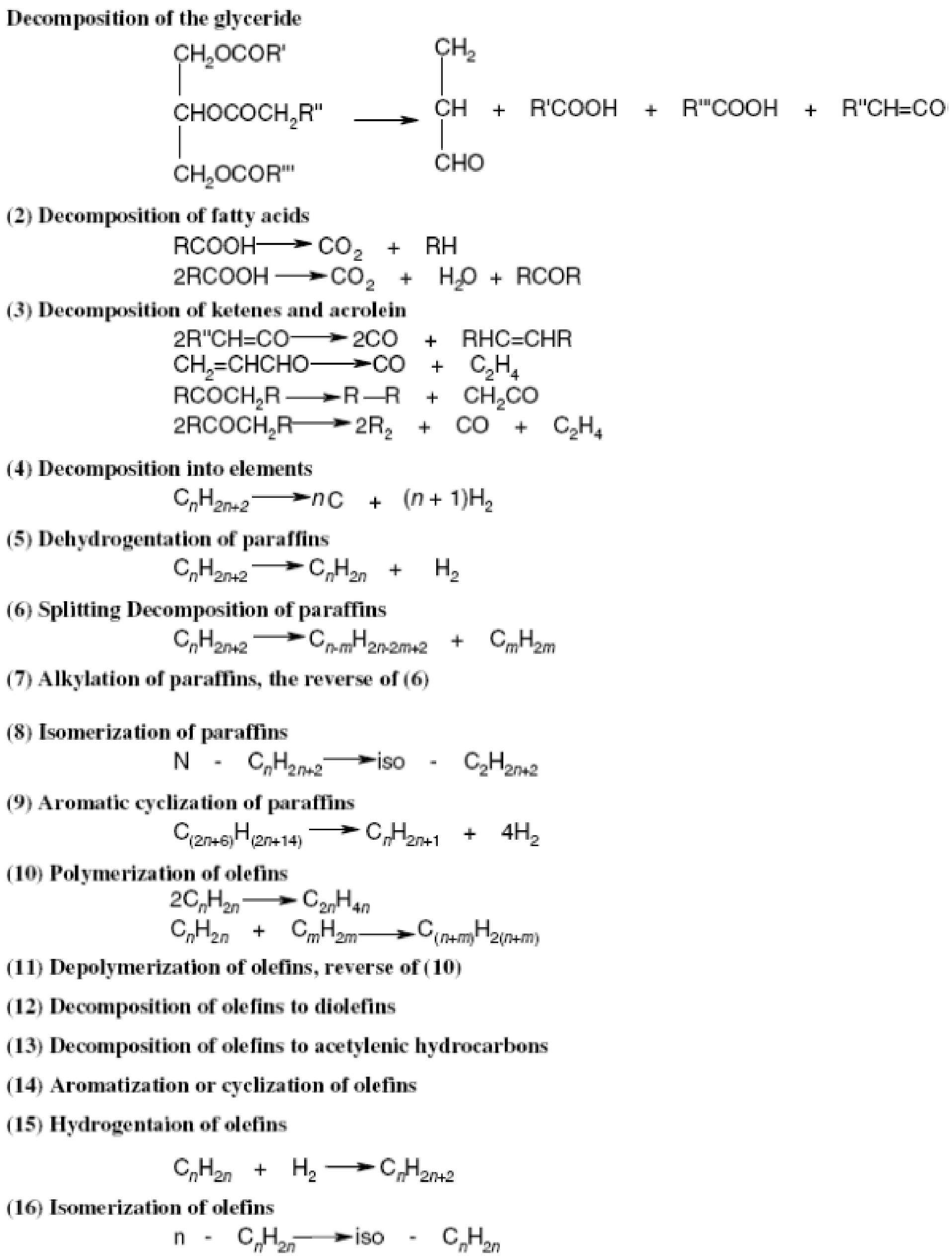
- hydroprocessing of bio-oil, and
- Fluid catalytic cracking (FCC).

The products are typically comparable to high grade gasoline (from FCC) or diesel (from hydroprocessing) and contain increased amounts of aromatics and decreased amounts of oxygen.

These processes apply not only to bio oils produced from biomass through techniques such as pyrolysis but also to vegetable oil (triglyceride based) fuels extracted from plants and algae. Advantages of using vegetable oils include their liquid nature, their high heat content (close to 90% of diesel fuel) (Karaosmanoglu, 1999), absence of water, and the fact that they are pH neutral and are relatively stable.

Several studies have investigated the thermal cracking of triglycerides. Model triglycerides including trilaurin, tripalmitin and tristearin have been subject to cracking to determine reaction products and elucidate decomposition pathways. Typical reaction products include hydrocarbons, carboxylic acids, ketones, esters and acrolein. Feeds included a range of plant and vegetable oils including tung oil, sunflower oil, safflower oil, canola oil, soybean oil, palm oil and others but only a few used algal oil. These studies are usually conducted in batch reactors for research purposes which are different from those for larger scale operations as they require clean-up and charging of the feed after each run and often experience low throughput and frequent interruptions. Therefore results in commercial plants could be significantly different.

Several studies have been investigating the decomposition process of both saturated and unsaturated triglycerides (less on cracking behavior of fatty acids) during the application of heat. It is well recognized that at 300 °C fats result in the formation of fatty acids and acrolein. At 400-500 °C cracking occurs, producing short chain hydrocarbons. The mechanisms involved have been studied and Chang and Wan (1947) proposed a reaction pathway for saturated triglycerides which includes 16 types of reactions as shown below:



Decomposition of the glyceride

$$\begin{array}{l}CH_2OCOR'\\ |\\ CHOCOCH_2R''\\ |\\ CH_2OCOR'''\end{array} \longrightarrow \begin{array}{l}CH_2\\ |\\ CH\\ |\\ CHO\end{array} + R'COOH + R'''COOH + R''CH{=}CO$$

(2) Decomposition of fatty acids

$$RCOOH \longrightarrow CO_2 + RH$$
$$2RCOOH \longrightarrow CO_2 + H_2O + RCOR$$

(3) Decomposition of ketenes and acrolein

$$2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR$$
$$CH_2{=}CHCHO \longrightarrow CO + C_2H_4$$
$$RCOCH_2R \longrightarrow R{-}R + CH_2CO$$
$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4$$

(4) Decomposition into elements

$$C_nH_{2n+2} \longrightarrow nC + (n+1)H_2$$

(5) Dehydrogentation of paraffins

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2$$

(6) Splitting Decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m}$$

(7) Alkylation of paraffins, the reverse of (6)

(8) Isomerization of paraffins

$$N - C_nH_{2n+2} \longrightarrow iso - C_2H_{2n+2}$$

(9) Aromatic cyclization of paraffins

$$C_{(2n+6)}H_{(2n+14)} \longrightarrow C_nH_{2n+1} + 4H_2$$

(10) Polymerization of olefins

$$2C_nH_{2n} \longrightarrow C_{2n}H_{4n}$$
$$C_nH_{2n} + C_mH_{2m} \longrightarrow C_{(n+m)}H_{2(n+m)}$$

(11) Depolymerization of olefins, reverse of (10)

(12) Decomposition of olefins to diolefins

(13) Decomposition of olefins to acetylenic hydrocarbons

(14) Aromatization or cyclization of olefins

(15) Hydrogentaion of olefins

$$C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2}$$

(16) Isomerization of olefins

$$n - C_nH_{2n} \longrightarrow iso - C_nH_{2n}$$

Figure 29 - Decomposition of triglycerides (Chang and Wan, 1947)

On this basis and results from Greensfelder et al. (1949), also a schema for cracking of unsaturated triglycerides was proposed by Alencar et al. (1983) as presented below:

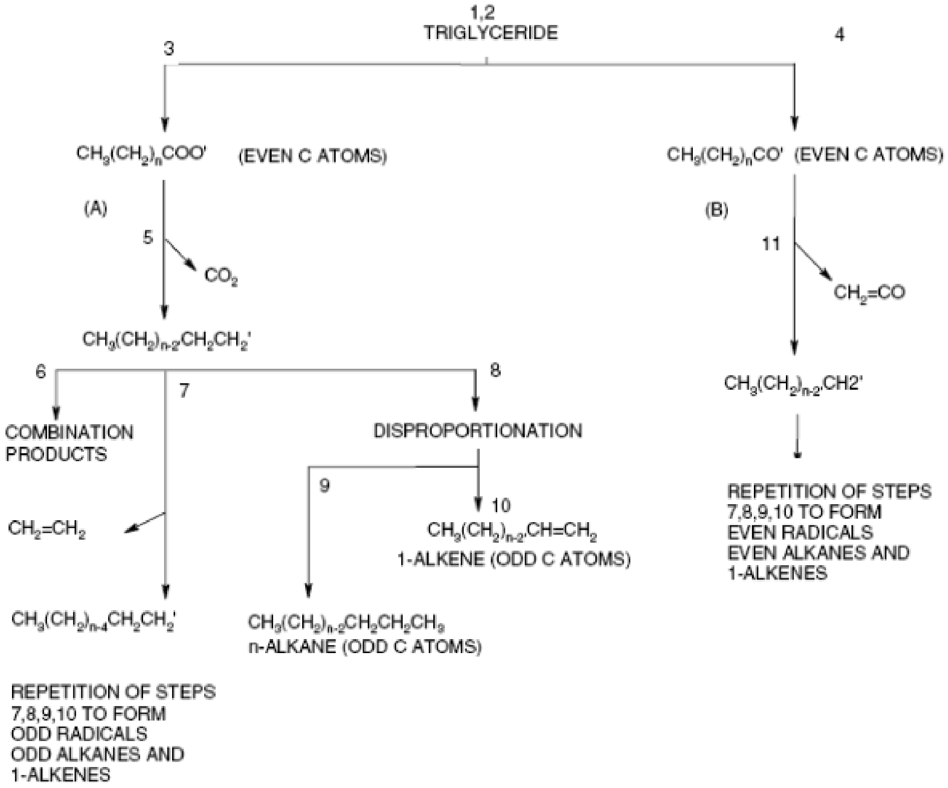


Figure 30 - Reaction mechanism for the pyrolysis of saturated triglycerides in 11 steps (Alencar et al., 1983)

The cracking of triglycerides produces free radicals (A) $RCOO^{\cdot}$ and (B) $RCH_2O^{\cdot}$. The odd n-alkanes and 1-alkanes are formed by decarboxylation of Radical (A) and then by subsequent disproportionation and ethylene elimination. The even series of alkanes[52] and alkenes[53] are

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[52] Hydrocarbons which contain only single bonds are called alkanes. They are called saturated hydrocarbons because there is a hydrogen in every possible location. This gives them a general formula C_nH_{2n+2}. The first four alkanes are methane, ethane, propane, and butane. Past this number of carbons, the -ane suffix is retained and the number prefixes penta-, hexa-, hept-, oct-, non-, dec-, etc are used. Alkyl groups are used as substituents, and alkane derivatives have many applications.
The alkanes are highly combustible and are valuable as clean fuels, burning to form water and carbon dioxide. Methane, ethane, propane and butane are gases and used directly as fuels. Alkanes from pentane up to around C17H36 are liquids. Gasoline is a mixture of alkanes from pentane up to about decane. Kerosene contains alkanes from about n=10 to n=16. Above n=17 they are solids at room temperature. Alkanes with higher values of n are found in diesel fuel, fuel oil, petroleum jelly, paraffin wax, motor oils, and for the highest values of n, asphalt. (http://hyperphysics.phy-astr.gsu.edu/hbase/organic/alkane.html#c1)

produced by the loss of a ketene from Radical (B) and followed again by disproportionation and ethylene elimination.

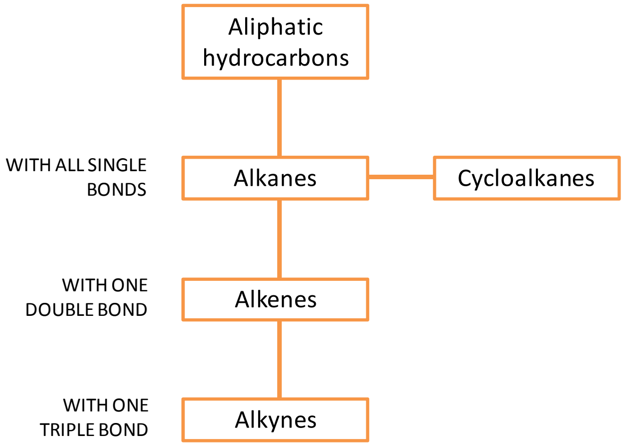

Figure 31 - Typologies of aliphatic hydrocarbons

Since plant oils also contain unsaturated components, it is useful to study the impact of heat on unsaturated fatty acids. In 1988, Schwab et al. proposed a mechanism to account for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from the pyrolysis of unsaturated triglycerides.

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[53] Alkenes are aliphatic hydrocarbons with one double bond between carbons are called alkenes. They follow the naming convention of the alkanes except that the suffix -ene is used instead of -ane. For alkenes above propene the position of the double bond must be specified in the name. Alkenes are unsaturated hydrocarbons and are generally very reactive. Typical reactions involve the addition of hydrogens or halogens. The double bond in alkenes can act to bond such molecules together in long chains and sheets. (http://hyperphysics.phy-astr.gsu.edu/hbase/organic/alkene.html#c1)

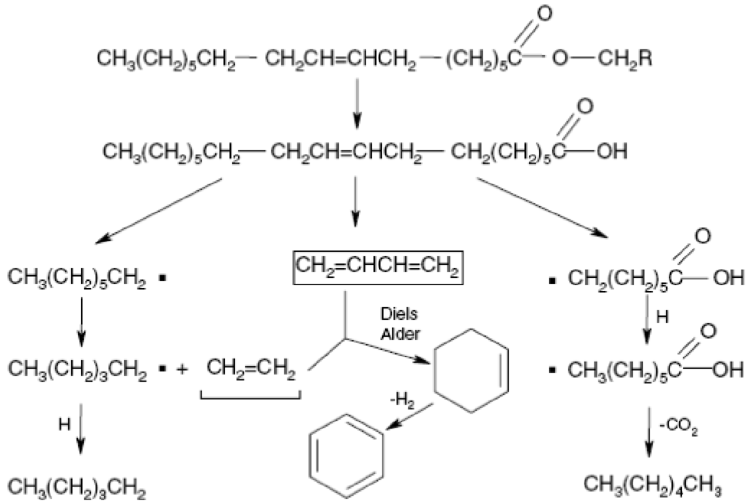

Figure 32 - Reaction mechanism for the pyrolysis of triglycerides (Schwab et al., 1988)

Generally, the thermal decomposition of these structures proceeds through either a free radical or carbonium ion mechanism. The formation of alkanes and alkenes can be attributed to the generation of an RCOO$^\cdot$ radical through triglyceride cleavage followed by decarboxylation. Unsaturated sites enhance cleavage at the C–C double bond, at a position a, b to the unsaturation and this cleavage is a dominant reaction. The formation of aromatics is supported by Diels–Alder ethylene addition[54] of a conjugated diene and carboxylic acids are most likely formed through cleavage of the glycerol moiety (as suggested by Nawar 1969). This also results in the formation of acrolein, which was also detected in the pyrolysis of sunflower oil.

In reality, vegetable and plant oils contain a complex mixture unsaturated and saturated triglycerides. Idem et al. (1996) studied the thermal cracking of canola oil in the presence and absence of steam and postulated a reaction scheme to account for the thermal cracking of both the unsaturated and saturated components. This scheme is more complex but builds on mechanisms previously proposed. The reaction scheme is shown in the scheme below and accounts for the formation of heavy oxygenated compounds including ketones, aldehydes and esters, carbon monoxide and carbon dioxide, C1–C5 straight and branched chain hydrocarbons, alcohols and

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[54] The Diels–Alder reaction is an organic chemical reaction (specifically, a cycloaddition) between a conjugated diene and a substituted alkene to form a substituted cyclohexene system. The reaction can proceed even if some of the atoms in the newly formed ring are not carbon.

dimethyl ether, diolefinic, cyclic and acetylenic hydrocarbon gases, C6+ aliphatic hydrocarbons[55], aromatics, heavy hydrocarbons, coke, and hydrogen during the cracking of canola oil in the absence of a catalyst.

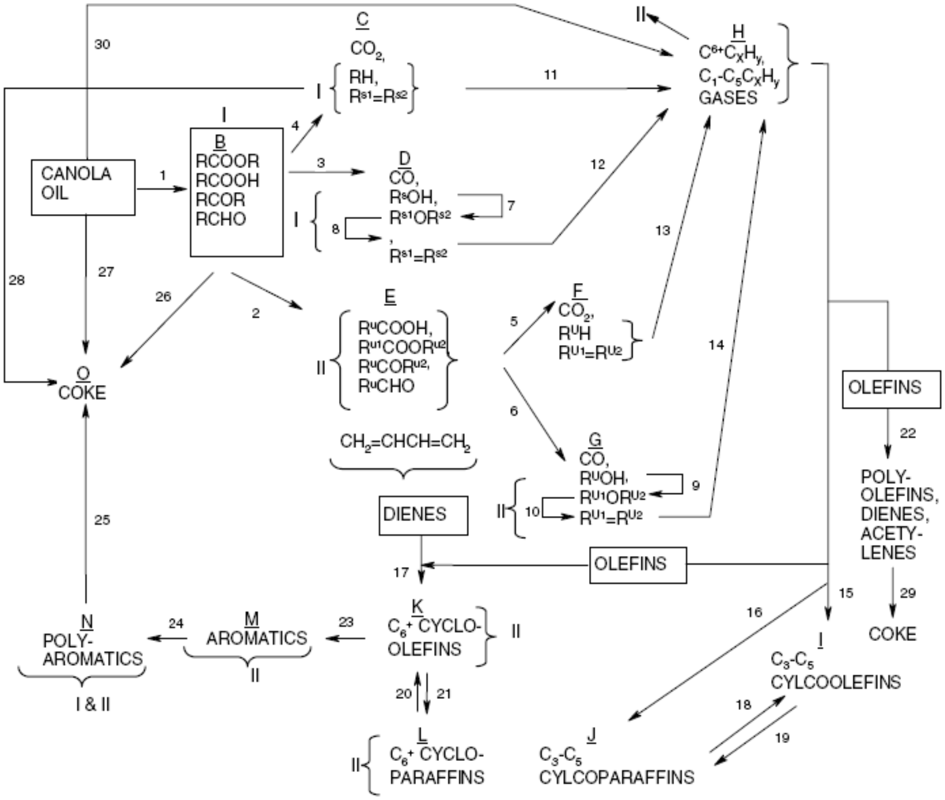

Figure 33 - Reaction mechanism for the pyrolysis of saturated and unsaturated triglycerides

The degree of unsaturation of triglycerides has a significant effect on the cracking behavior. For example, the radical intermediates that eventually react to form C1–C5 hydrocarbons can be produced via the decomposition of the heavily oxygenated compounds by different routes. Decarboxylation and decarbonylation can occur before or after the C–C bond cleavage. If the triglyceride is unsaturated, the cleavage most likely occurs before the decarboxylation and decarbonylation. It has also been shown that C–C bond cleavage for unsaturated and saturated molecules results in different products.

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[55] Aliphatic hydrocarbons are those which do not contain a benzene ring. Those which do contain benzine are called aromatic hydrocarbons.

These studies show the complexity of pyrolysis reactions and possible products. Cheng et al. (2004) recognized that historical studies have often neglected the possible control measures needed to form ideal products by selecting proper pyrolysis temperatures and conditions (Maher et al. 2006).

Catalytic cracking appear to be one of the most promising and investigated route at present to convert bio-oils into valuable fuels. Most routes involving the conversion of triglycerides into hydrocarbons at high temperature make use of catalysts.

Two major groups of catalysts can be identified:

- transition metal catalysts, commonly used in the hydroprocessing industry, and employed for diesel production under high hydrogen partial pressures; and
- molecular sieve type catalysts, employed for the production of highly aromatic products such as gasolines. This includes zeolite catalysts for conversion of triglycerides based oils to hydrocarbons. The highly crystalline and porous nature of this kind of catalysts allows them to be size selective.

Other groups of catalysers are pure insulator oxides (e.g. activated alumina) and sodium carbonate.

Trinolein, canola oil, coconut oil and other vegetable oils were tested over activated alumina with quite good results, yielding 65-79% hydrocarbon mixtures (n-alkanes and n-alkenes) at 450 °C under atmospheric pressure.

Also zeolites have been extensively studies for application to triglycerides, especially in fix bed reactors, with and without the addition of steam.

Hydroprocessing of biocrude and the use of mixtures of bio oils into commercial FCC plants are discussed in this section.

8.1 Hydroprocessing

With the term hydroprocessing is intended any of the several chemical engineering processes involving the use of hydrogen, and includes hydrotreating, hydrogenation and hydrocracking. These processes are clarified in the following pages.

This is recommended especially for pyrolytic bio oils as they are usually acidic, corrosive, polar, thermally unstable and highly oxygenated (Katikaneni et al., 1995). They can be subject to upgrading and deoxygenation techniques such as hydrotreating (and catalytic vapour cracking over zeolites) to produce high grade transportation fuels. Thermal cracking of triglyceride material is especially promising in areas where hydroprocessing industry is well established (for example in Austria) because the technology is similar to that of conventional oil refining.

With various hydroprocessing technologies used by refineries to catalytically remove impurities or reduce molecular weight, the algal oils could be made into diesel but also kerosene-like fuel, very similar to petroleum-derived jet fuels or into a fuel designed for multi-purpose use.

Here is how the process works:

1. The feedstock is separated into distillates and vacuum gas oils.
2. Waxy vacuum gas oil molecules flow to the hydrocracker to begin conversion.
3. Hydrogen is introduced to saturate the molecules and remove impurities such as nitrogen, sulphur, oxygen and heavy metals.
4. Hydrocracking, under conditions of extreme temperature and pressure in the presence of a catalyst, converts aromatic molecules into saturated paraffins.
5. The altered stock is noticeably lighter in colour due to the absence of contaminants.
6. Long waxy paraffin molecules are restructured into shorter, branched isoparaffins which resist gelling and improve low temperature pumpability.
7. Hydrogen is introduced again to remove any remaining aromatics and impurities, enhancing the oxidation and thermal stability of the now colourless oil.

The world’s first algal based jet fuel, refined with hydroprocessing, was produced by Solazyme in August 2008 and passed the most critical ASTM D1655 specification tests[56].

A number of flight companies have demonstrated the use of biofuels in aeroplanes since then, and some of them used algae-based fuels. At present, test flights using algal fuels have been undertaken by JetBlue Airways among others, following demonstrations by Air New Zealand (ANZ), Continental Airlines and Japan Airlines (JAL). Continental Airlines Inc. operated the flight with a biofuel blend of 50 percent biologically derived fuel (algal fuel) and 50 percent traditional jet fuel in one of the engines. It seems they have observed a slight difference in some of the readings indicating the energy from biofuel blend is higher than jet fuel.

100% blend biofuels for aviation have already been tested successfully (the first airline was Green Flight and a number of companies are following the example) and some companies are looking

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[56] ASTM International, known until 2001 as the American Society for Testing and Materials (ASTM), is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services.

specifically at hydroprocessing from algal oil. For example Boeing and Air New Zealand are collaborating with Aquaflow Bionomic on this hot topic[57].

Hydrotreating is a chemical engineering process in which reaction with hydrogen is used to remove impurities (usually sulphur, but also nitrogen for example).

In an industrial hydrodesulphurization unit (HDS), such as in an oil refinery, the hydrodesulphurization reaction takes place in a fixed-bed reactor at elevated temperatures ranging from 300 to 400 °C and elevated pressures ranging from 30 to 130 atmospheres of absolute pressure, typically in the presence of a CoMo catalyst (consisting of an alumina base impregnated with cobalt and molybdenum). Occasionally, a combination of nickel and molybdenum (NiMo) is used, in addition to the CoMo catalyst, for specific more difficult feedstocks, such as those containing a high level of chemically bound nitrogen.

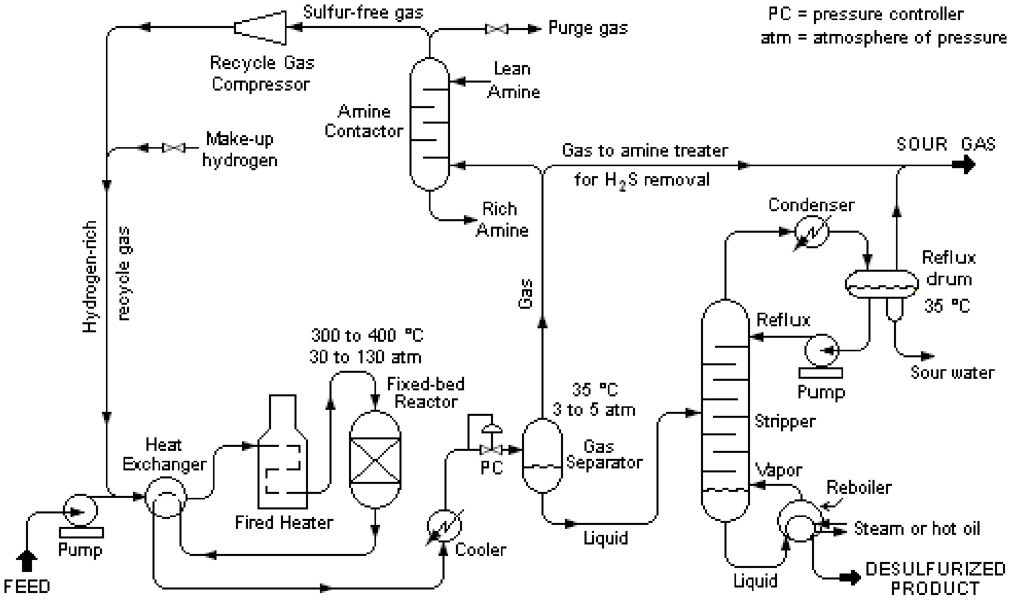

Figure 34 - Schematic description of the equipment and the process flow streams in a typical refinery HDS unit

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[57] Oil prices increased about fivefold from 2003 to 2008, raising fears that world petroleum production is becoming unable to keep up with demand. The fact that there are few alternatives to petroleum for aviation fuel adds urgency to the search for alternatives. Twenty-five airlines were bankrupted or stopped operations in the first six months of 2008, largely due to fuel costs. (More airlines fold as fuel prices soar: IATA, retrieved online in June 2012 - http://news.asiaone.com/News/Latest+News/Business/Story/A1Story20080708-75407.html)

The liquid feed (at the bottom left of the diagram) is pumped up to the required elevated pressure and is joined by a stream of hydrogen-rich recycle gas. The resulting liquid-gas mixture is preheated by flowing through a heat exchanger. The preheated feed then flows through a fired heater where the feed mixture is totally vaporized and heated to the required elevated temperature before entering the reactor and flowing through a fixed-bed of catalyst where the hydrodesulphurization reaction takes place. The hot reaction products are partially cooled by flowing through the heat exchanger where the reactor feed was preheated and then flows through a water-cooled heat exchanger before it flows through the pressure controller (PC) and undergoes a pressure reduction down to about 3 to 5 atmospheres. The resulting mixture of liquid and gas enters the gas separator vessel at about 35 °C and 3 to 5 atmospheres of absolute pressure.

Most of the hydrogen-rich gas from the gas separator vessel is recycle gas, which is routed through an amine contactor for removal of the reaction product H_2S that it contains. The H_2S-free hydrogen-rich gas is then recycled back for reuse in the reactor section. Any excess gas from the gas separator vessel joins the sour gas from the stripping of the reaction product liquid. The liquid from the gas separator vessel is routed through a reboiled stripper distillation tower. The bottoms product from the stripper is the final desulphurized liquid product from hydrodesulphurization unit.

The overhead sour gas from the stripper contains hydrogen, methane, ethane, hydrogen sulfide, propane, and, perhaps, some butane and heavier components. Sour gas is then sent to the refinery's central gas processing plant for removal of the hydrogen sulfide in the refinery's main amine gas treating unit and through a series of distillation towers for recovery of propane, butane and pentane or heavier components. The residual hydrogen, methane, ethane, and some propane are used as refinery fuel gas. The hydrogen sulfide removed and recovered by the amine gas treating unit is subsequently converted to elemental sulfur or to sulfuric acid.

Note that the above description assumes that the HDS unit feed contains no olefins. If the feed does contain olefins (for example, the feed is a naphtha derived from a refinery FCC unit), then the overhead gas from the HDS stripper may also contain some ethene, propene, butenes and pentenes, or heavier components.

The refinery HDS feedstocks (naphtha, kerosene, diesel oil, heavier oils, bio-oils) contain a wide range of organic sulfur compounds, including thiols, thiophenes, organic sulfides and disulfides, and many others. These organic sulfur compounds are products of the degradation of sulfur containing biological components, present during the natural formation of the fossil fuel or the bio-oil, such as algal oil.

Most metals catalyze HDS but those at the middle of the transition metal series are most active. Ruthenium disulfide appears to be the single most active catalyst, but binary combinations of cobalt and molybdenum are also highly active. Aside from the basic cobalt-modified MoS_2 catalyst, nickel and tungsten are also used, depending on the nature of the feed. For example, Ni-W catalysts are more effective for hydrodenitrification (HDN)[58].

Metal sulfides are "supported" on materials with high surface areas. A typical support for HDS catalyst is γ-alumina. The support allows the more expensive catalyst to be more widely distributed, giving rise to a larger fraction of the MoS_2 that is catalytically active.

Hydrogenation is a reductive chemical reaction that results in an addition of hydrogen, normally to saturate organic compounds, and usually under the influence of temperature, pressure and catalysts. The process consists of the addition of hydrogen atoms to the double bonds of a molecule through the use of a catalyst. It includes a class of chemical reactions in which the net result is the addition of hydrogen (H). Hydrogenolysis is a related reaction and results in the cleavage of the C-X chemical bond, where C is a carbon atom and X is a sulphur, nitrogen or oxygen atom. The net result of a hydrogenolysis reaction is the formation of C-H and H-X chemical bonds.

Thus, hydrodesulphurization for instance is also (includes) a hydrogenolysis reaction. Using ethanethiol (C_2H_5SH), a sulphur compound present in some petroleum products, as an example, the hydrodesulphurization reaction can be simply expressed as:

Ethanethiol + → Ethane + Hydrogen
Hydrogen sulphide

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$$

Likewise algae hydrogenation can be performed by using an autoclave under high temperature and pressure conditions in the presence of a catalyst and a solvent. It consist in a three-phase operation in which contact must be established between the gaseous phase (hydrogen and hydrocarbon phase), liquid phase (mixture of solvent and liquid product), and solid particle phase (algae and catalyst) in order to achieve algal conversion and to promote the transfer of momentum, heat and mass (Miyamoto 1997).

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[58] Hydrodenitrification is another hydrotreating process, not discussed in this paper.

Amin (2008) used a stirred slurry reactor to perform the three-phase operation: the gaseous reactant was bubbled through the liquid from a sparger at the bottom of the reactor, and the solid particles, slurred with the liquid, were fed to the reactor. The gaseous reactant and the solid reactant first dissolve in the liquid phase and diffuse with the liquid reactant towards the catalyst. All these reactants then interact at the surface of the catalyst. The liquid products, solid particles and unreacted materials were continuously drawn off to maintain a constant liquid level within the reactor, and a constant composition in the liquid phase. Gaseous products and unreacted gaseous reactant entered the space above the liquid surface and flowed out through a gas pipe.

Today the hydrogenation of vegetable oils is used in Europe by the Finnish Neste Oil refinery where it is operated commercially using the NExBTL technology. Neste Oil has been operating in Finland for several years two 170,000 t/a plants and also an 800,000 t/a plant in Singapore. A similar plant of about the same size is currently under construction in Rotterdam (The Netherlands). Whether as an admixture or in its pure form, NExBTL is able to supplement or partially replace diesel fuel without problems. Actually even unblended NExBTL meets the requirements set by the European fuel standard for vegetable oil refining process. The process entails direct catalytic hydrogenation of raw plant oils, which are rich in triglycerides, into the corresponding alkanes. The glycerol chain of the triglyceride is hydrogenated to the corresponding C3 alkane, propane (without glycerol side stream). This process removes oxygen from the oil; and the resulting biodiesel is not an oxygenate like traditional transesterified biodiesel. Unlike the yellow transesterified biodiesel, the product is a clear and colorless paraffin, with a good cetane number (85 to 99) and better properties than even fossil diesel. As it is chemically identical to conventional fossil diesel, it requires no modification or special precautions for the engine.

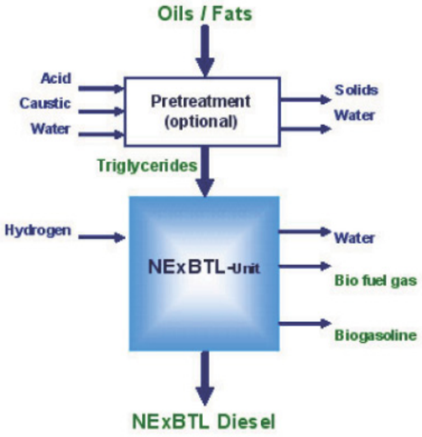

Figure 35 - Schematic NExBTL process (source: Neste Oil)

Below are reported the main reactions involved in the NExBTL conversion. All these reaction take place at temperatures below 320 °C. Side products include propane and gasoline.

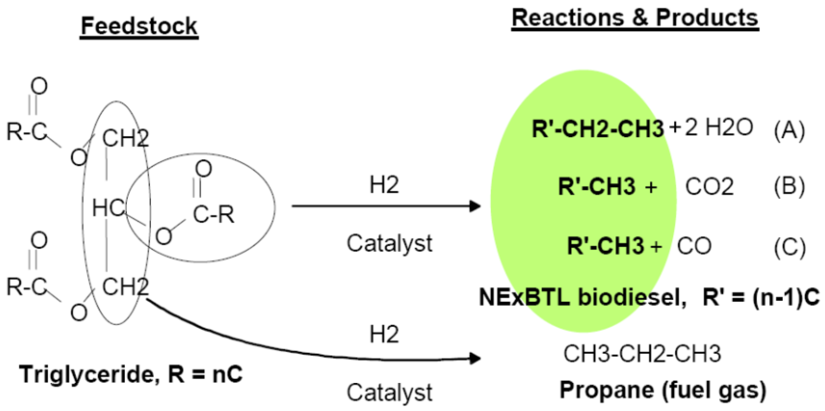

Figure 36 - Main reactions involved in the NExBTL conversion process

In these plants, mainly palm oil is currently being processed into a high-quality diesel (very high cetane, superior cold temperature performance, and reduced exhaust NOx, PM, HC, CO and toxic emissions) and pilot tests from algae and microbial oil are currently underway. The final product is a stable and pure paraffinic hydrocarbon. Based on the recent use of published materials for the NExBTL can be assumed that also algae oil can be processed without major problems.

The production of high-octane petroleum fuel and kerosene by hydrogenating large or complex hydrocarbons and then cracking them is referred as **hydrocracking**. Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydrotreater, the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms.

The products of this process are saturated hydrocarbons; depending on the reaction conditions (temperature, pressure, catalyst activity) these products range from ethane, LPG to heavier hydrocarbons consisting mostly of isoparaffins. Hydrocracking is normally facilitated by a bifunctional catalyst that is capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes.

Algal oil can undergo hydrocracking for the production of jet fuel and diesel, while also high octane rating gasoline fractions and LPG are produced. All these products have a very low content of sulfur and other contaminants.

8.2 Fluid Catalytic Cracking

The catalytic cracking process shows several clear advantages in comparison with the more conventional pyrolysis, fermentation or transesterification processes to treat raw organic oils. Firstly, the temperature of catalytic cracking process (450 °C) is lower than pyrolysis (500–850 °C). Secondly, the product quality derived from pyrolysis is strongly dependent on the type of feedstock used, while a catalytic cracking process is more independent. The use of a highly cellulosic feedstock will produce a liquid fraction that contains acids, alcohols, aldehydes, ketones and phenolic compounds.

This approach does not require added hydrogen and oxygen is eliminated in the form of water and CO_2. As compared to hydrotreating, cracking gives a higher value transport fuel product because of higher aromatic content.

FCC is today one of the most important conversion process used in refineries. It is widely used to convert high-boiling, high-molecular weight hydrocarbon fractions of crude oils to more valuable products. Today thermal oil cracking has been almost completely replaced by catalytic cracking as it produces more gasoline with a higher octane rating. It also produces by-product gases that are more olefinic, and hence more valuable.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340 °C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 °C or higher. This portion of crude oil is often referred to as vacuum gas oil (VGO). The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst.

However, also coke is generated during the reaction and deposited on the active sites of the catalysts, leading to catalyst deactivation. Therefore, regeneration of the deactivated catalyst is carried out continuously in a regenerator by burning the coke deposited on the catalyst in air to maintain its activity. In addition, the catalytic cracking reaction is endothermic while regeneration process is exothermic. Some cracking reactors are designed to use the heat from regeneration process to preheat the feed to reaction temperature.

The input feedstock for FCC processes, usually VGO, the top product from vacuum distillation, consists mainly of paraffins[59], naphtenes and aromatics with a typical boiling point of 350-650 °C. FCC is usually preceded by hydrotreating in order to reduce the sulphur content and extend the catalysts lifetime. In this case the input feedstock is algal oil, mainly consisting of triglycerides which are glycerine bodies (esters of fatty acids and glycerol) with three fatty acid chains of different lengths and degree of saturation (Bielansky et al., 2010). The main difference between VGO and algal oil is the oxygen bound in the carboxyl groups as the former contains only hydrocarbons.

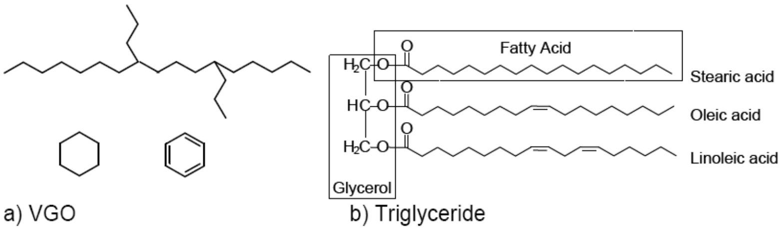

Figure 37 - Structure of VGO and triglycerides (Bielansky et al., 2010)

In order to increase gasoline yield and reduce the coking phenomenon, many researchers found that a short contact time between catalysts and oil vapours at moderate temperature was highly preferable. The same concept is applied in the production of biofuels especially bio-gasoline from vegetable oils. Triglyceride based feedstock is vaporized and brought in contact with catalysts in a riser reactor. The cracking reaction takes place on cracking catalysts with short residence time (20 seconds).

Basically, there are two different configurations for an FCC unit: the "stacked" type where the reactor and the catalyst regenerator are contained in a single vessel with the reactor above the catalyst regenerator and the "side-by-side" type where the reactor and catalyst regenerator are in two separate vessels.

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[59] Paraffins or alkanes are saturated straight-chain or branched hydrocarbons, without any ring structures

A schematic flow diagram of a typical modern FCC unit is shown below ("side-by-side" configuration):

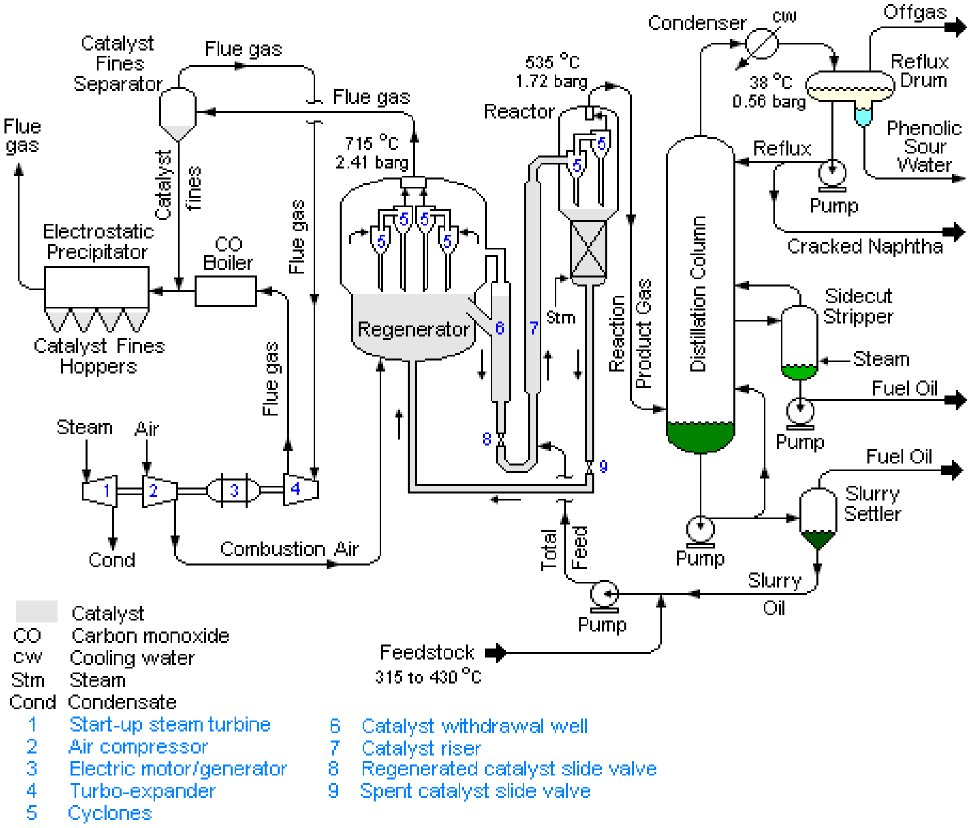

Figure 38 – System layout of a modern FCC plant

Basically the fluid catalytic cracking process breaks large hydrocarbon molecules into smaller molecules by contacting them with powdered catalyst at a high temperature and moderate pressure which first vaporizes the hydrocarbons and then breaks them. The cracking reactions occur in the vapor phase and start immediately when the feedstock is vaporized in the catalyst riser.

The process breaks high boiling, straight-chain alkane (paraffin) hydrocarbons into smaller straight-chain alkanes as well as branched-chain alkanes, branched alkenes (olefins) and cycloalkanes (naphthenes). The breaking of the large hydrocarbon molecules into smaller molecules is more technically referred to by organic chemists as scission of the carbon-to-carbon bonds. Some of the smaller alkanes are then broken and converted into even smaller alkenes and branched alkenes such as the gases ethylene, propylene, butylenes, and isobutylenes. Those olefinic gases are valuable for use as petrochemical feedstocks. The propylene, butylene and isobutylene are also valuable feedstocks for certain petroleum refining processes that convert them into high-octane gasoline blending components.

The cycloalkanes (naphthenes) formed by the initial breakup of the large molecules are further converted to aromatics such as benzene, toluene and xylenes which boil in the gasoline boiling range and have much higher octane ratings than alkanes.

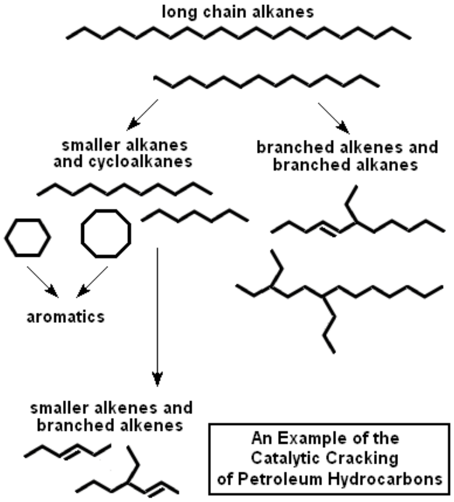

Figure 39 – Simplified scheme of petroleum cracking

Modern FCC catalysts are fine powders with an average particle size of 60 to 100 µm. The design and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst, which should meet the following properties:

- Good stability to high temperature and to steam
- High activity
- Large pore sizes
- Good resistance to attrition
- Low coke production

A modern FCC catalyst has four major components: crystalline zeolite, matrix, binder and filler. Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst. The zeolite used in FCC catalysts is composed of silica and alumina tetrahedra with each tetrahedron having either an aluminum or a silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice.

The catalytic sites in the zeolite are strong acids (equivalent to 90% sulfuric acid) and provide most of the catalytic activity. The acidic sites are provided by the alumina tetrahedra. The aluminum atom at the center of each alumina tetrahedra is at a +3 oxidation state surrounded by four oxygen atoms at the corners which are shared by the neighboring tetrahedra. Thus, the net charge of the alumina tetrahedra is -1 which is balanced by a sodium ion during the production of the catalyst. The sodium ion is later replaced by an ammonium ion which is vaporized when the catalyst is subsequently dried, resulting in the formation of Lewis and Brønsted acidic sites[60]. In some FCC catalysts, the Brønsted sites may be later replaced by rare earth metals such as cerium and lanthanum to provide alternative activity and stability levels.

The matrix component of an FCC catalyst contains amorphous alumina which also provides catalytic activity sites and in larger pores that allows entry for larger molecules than does the zeolite. That enables the cracking of higher-boiling, larger feedstock molecules than are cracked by the zeolite.

The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and the filler is usually clay.

Metal contaminants present in FCC feedstocks, all have detrimental effects on the catalyst activity and performance. Nickel and vanadium are particularly troublesome. There are a number of methods for mitigating the effects of the contaminant metals:

- Avoid feedstocks with high metals content: This seriously hampers a refinery's flexibility to process various algal oils produced in wastewater treatment plants or in contaminated growing mediums.

- Feedstock feed pretreatment: Hydrodesulfurization of the feedstock removes some of the metals and also reduces the sulfur content of the FCC products. However, this is quite a costly option.

- Increasing fresh catalyst addition: All FCC units withdraw some of the circulating equilibrium catalyst as spent catalyst and replaces it with fresh catalyst in order to maintain a desired level of

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[60] The term Lewis acid refers to a molecular entity (and the corresponding chemical species) that is an electron-pair acceptor and therefore able to react with a Lewis base to form a Lewis adduct, by sharing the electron pair furnished by the Lewis base. A Lewis base is any species that donates a pair of electrons to a Lewis acid to form a Lewis adduct. For example, OH^- and NH3 are Lewis bases, because they can donate a lone pair of electrons. Similarly Brønsted acids and Brønsted bases are defined, by which an acid is a molecule or ion that is able to lose a hydrogen cation (H+), and a base is a species with the ability to gain a hydrogen cation.

activity. Increasing the rate of such exchange lowers the level of metals in the circulating equilibrium catalyst, but this is also quite a costly option.

- Demetallization: Commercial processes exist to remove nickel and vanadium from the withdrawn spent catalyst. The nickel and vanadium are converted to chlorides which are then washed out of the catalyst. After drying, the demetallized catalyst is recycled into the circulating catalyst. Removals of about 95 percent nickel removal and 67 to 85 percent vanadium have been reported. Despite that, the use of these processes has not become widespread, perhaps because of the high capital expenditure required.

- Metals passivation: Certain materials can be used as additives which can be impregnated into the catalyst or added to the FCC feedstock in the form of metal-organic compounds. Such materials react with the metal contaminants and passivate the contaminants by forming less harmful compounds that remain on the catalyst. For example, antimony and bismuth are effective in passivating nickel and tin is effective in passivating vanadium. A number of proprietary passivation processes are available and fairly widely used.

FCC procedures are nowadays implemented in almost every refinery and then convert VGO into lighter hydrocarbons (gasoline, aromatics, olefins). As of 2006, FCC units were in operation at 400 petroleum refineries worldwide and about one-third of the crude oil refined in those refineries is processed in an FCC to produce high-octane gasoline and fuel oils. For example in 2007, the FCC units in the United States processed a total of 5,300,000 barrels per day of feedstock and FCC units worldwide processed about twice that amount.

Several studies of catalytic cracking of vegetable oils have been published, usually using fixed bed microreactors. Some investigated the cracking on fatty acids over zeolite catalysts, finding that the oxygen contained in the vegetable oils react to form H_2O and CO_2 (Adjaye et al., 1995). The two reactions that have been supposed are: the decarboxylation pathway (tryglicerides are converted to hydrocarbons and CO_2) and the deoxygenation pathway (leading to hydrocarbons, coke and H_2O).

Vegetable oil has been tested analyzing the impacts of different catalysts (more acid, basic or different shape selectivity) on the cracking process and it was found that the initial decomposition of triglycerides into long hydrocarbons was quite independent from these properties. The secondary cracking[61] though would be enhanced employing non-shape selective and amorphous catalysts with

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[61] It follows the primary cracking and converts heavier molecole into lighter molecole (gas or liquid).

higher gas yields (for canola oil). With high shape selective catalysts, the liquid products are higher in comparison and oxygen is mainly converted into H_2O, CO and CO_2 (Idem et al., 1997) as well as some short organic acids which can be found in the aqueous phase. Other studies (on rapeseed oil) found that the rate of aromatization is highly dependent on the olefinicity of the fatty acids processed and the reaction temperature (Dupain et al., 2007). Co-feeding H_2 with regular catalyst as well as the incorporation of Ni onto the catalyst would yield more gasoline with lower aromatics (for rapeseed oil) (Rao et al., 2010).

At the TU Vienna, various mixtures of VCO and vegetable oils to be co-processed with conventional feedstocks (up to 100%) in existing FCC plants were investigated using a pilot-scale FCC unit with an internal CFB[62]-design (Bielansky et al., 2011). It was found that all tested bio-oils with no problems in an FCC system can be converted to fuels as higher ratios of vegetable oils hardly affect the gasoline yields (although can cause a decrease in cracking gas). Thus, one can also assume that algae oil in an FCC system can be converted easily to liquid fuels and olefins.

Property	**VGO**	**Rapeseed oil**	**Soybean oil**	**Palm oil**
Viscosity (80 °C) [mm^2/s]	8.94	10.5	11.5	9.7
Energy content [MJ/Kg]	42.36	36.54	35.85	35.97
Boiling temperature [°C]	281-588	<350	<350	<350
S [ppm]	499	-	-	-
N [ppm]	29	-	-	-
O [wt%]	-	10.9	11	11.3
Paraffins O [wt%]	70.4	-	-	-
Aromatics O [wt%]	23.4	-	-	-
Saturated O [wt%]	-	7.6	15.4	50.3
Mono-unsaturated O [wt%]	-	64.3	26	39.9
Poly-unsaturated O [wt%]	-	28.1	58.6	9.8

Table 22 - Typical properties of VGO and vegetable oils (Bielansky et al., 2011)

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[62] Circulating Fluidized Bed

Gasoline composition (wt%)	VGO	Rapeseed oil	Soybean oil	Palm oil
High boiling components	0.6	0.7	1	0.7
Aromatics	54	63.8	60.5	53.3
Polynaphthenes	0.2	0.3	0.4	0.1
Cyclo-olefins	4.5	8.7	9.1	5.9
Naphthenes	6.4	3.5	4.3	5
Iso-Olefins	12.7	12.4	7.9	8.2
n-Olefins	7	4.6	3.1	3.2
i-Paraffines	12.4	3.8	9.3	17.4
n-Paraffines	2.2	2.4	4.4	6.1

Table 23 - Gasoline composition from VGO and vegetable oils (Bielansky et al., 2011)

The effects of vegetable oil mixtures on the product yields according to the TU Wien study are summarized in the figure below:

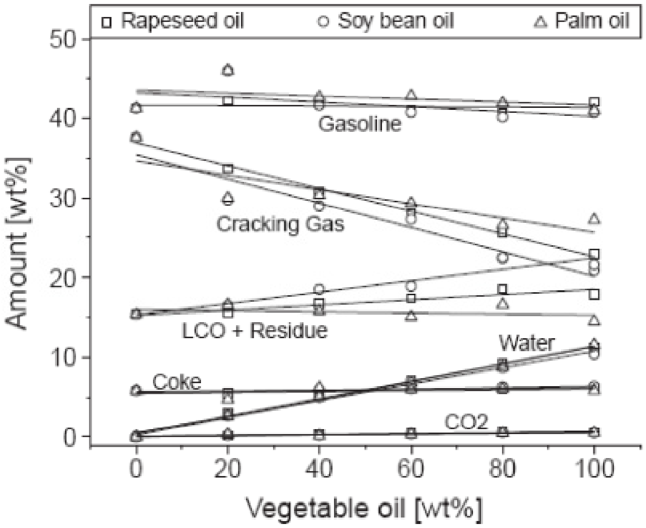

Figure 40 - Effect of vegetable oil admixture on the product yields (Bielansky et al., 2011)

It confirms that the yield of gasoline produced is quite constant at increasing mixtures of vegetable oils, while the cracking gas decreases at the advantages of water mixing higher amounts of vegetable oils. This shows that the oxygen contained in the feed, around 11 wt% for vegetable oils, is almost entirely converted into H_2O as it cannot be converted to hydrocarbons. The increase of CO_2 and H_2O is almost linear but with a factor 20. Oxygen content in algae biomass is in the order of 25-35 wt% but is significantly lower in algal pyrolytic bio-oil for example. From microalgae fast pyrolysis is possible to produce oil at temperature of 500°C with a heating rate of 600°C/s and the sweep gas (N_2) flow rate of 0.4 m^3/h and a vapor residence time of 2–3 seconds. The bio-oil yields vary from 17.5 to 23.7%. The contents of carbon and hydrogen of this bio-oil are higher than those of oil from wood, and are characterized by low oxygen contents with higher H/C ratios than the bio-oil from wood, sunflower bagasse and cotton straw and stalk. The lower oxygen content of bio-oils from micro algae compared to the bio-oil from higher plants such as wood is important as it makes algal oil more suitable for FCC. It also makes the algal oil more stable than the bio-oil from wood.

Analysis of primary oil produced through direct thermochemical liquefaction of *Botryococcus braunii* indicates very low oxygen concentration, as low as 2.6 wt% at 300 °C (Dote et al. 1991). This means that higher yields and lower H_2O production than plant vegetable oil can be expected.

Fatty acids can be either saturated or unsaturated and are distinguished by their chain lengths in the range of C12 to C24. Fatty acid content and their degree of saturation can vary a lot between algae species and is in general a function of cultivation length and of light intensity (Bigogno et al. 2001).

Since the algae oil is free of aromatics, all aromatic species that show up in the products emerge during the process. A key role seems to play the number of double bounds in the fatty acids which enhance the number of alkylation, cyclization and dehydrogenation reactions. The circumstance that during water formation hydrogen is consumed and thus more olefinic compounds emerge further enhances aromatization.

The TU Wien experiments showed that with a higher unsaturation of the fatty acids in the triglycerides led to more high aromatic light cycle oil. Di-aromatics do not undergo further reactions to form products in gasoline or gas range. It is interesting to see that the different vegetable oils yield similar gasoline but differ in cracking gas.

Aromatics in the gasoline seem to be dependent upon the degree of unsaturation of the fatty acids (more fatty acids increase light cycle oil formation at the expenses of cracking gas). Aromatics in the gasoline increase the octane number but are undesired from an environmental point of view. Coke formation for all three vegetable oils seems to be unaffected by the degree of unsaturation.

Algal oils have been found to be very high in unsaturated fatty acids (McMichens 2009), mainly monounsaturated fatty acids (Bigogno et al. 2001).

However the content of saturated fatty acids in *Chlorella sp.* and *Scenedesmus* algae oil are higher than those of rapeseed oil as well as the contents of monounsaturated fatty acids are quite lower. Further, fat composition under logarithmic growth increases amounts of short polyunsaturated fatty acids (e.g. gamma linolenic and stearidonic acid). Under stress, TAG accumulates mostly C16 and C18 unsaturated and some monounsaturated fatty acids.

The contents of polyunsaturated fatty acids can be considered similar between algae oil and rapeseed oil (Makarevičienė et al. 2011).

Fatty acids	Chlorella sp.	Scenedesmus	Rapeseed
Saturated	48.9	51.9	5.4
Monounsaturated	20.9	17.5	58.3
Polyunsaturated	23.7	27.4	36.3
Trans isomers	4.9	2.1	
Omega-3	5.0	17.7	
Omega-6	12.5	9.3	
Linoleic	2.3	10.6	5.0 – 13.0

Table 24 - Composition (%), of total fatty acids (Makarevičienė et al. 2011)

It can be expected that biofuels produced from algae oil will meet the requirements concerning linolenic acid methyl ester content and also the requirements for oxidation stability and iodine value (Makarevičienė 2011).

These similarities suggest that algae oil (in particular oil produced from *Chlorella* and *Scenedesmus* sp.) can behave in FCC more similarly to rapeseed oil given the amounts of polyunsaturated fatty acids, rather than soybean or palm oil, especially if algae are grown under stress conditions. Therefore the composition of gasoline from algal oil is expected to have a low amount of paraffins if compared to VGO. On the other hand it can be expected that the amount of aromatic compounds can be similar or higher than VGO (but also of other oils like soybean or palm oil).

The energy contents of feed and FCC products for VGO and pure vegetable oil experiments are given below. All feedstocks lead to similar coke yields. Energy efficiency is slighter lower for the plant bio-oils experimented than for VGO but, since the oxygen content is lower for algae oil than these plant oils, it can be expected that the energy efficiency of VGO is maintained.

	VGO	**Rapeseed oil**	**Soybean oil**	**Palm oil**
Feed [kW in]	29.83	27.01	26.59	26.27
Out [kW out]				
Cracking gas	11.65	7.11	6.48	8.44
Gasoline	12.83	13.07	12.68	12.75
LCO	2.78	4.44	5,22	3.64
Residue	1.55	0.87	1.15	0.65
Sum	28.82	25.48	25.53	25.48
Energy efficiency [%]	97	94	96	97

Table 25 - Energy contents of feed and products for VGO and pure vegetable oil experiments (Bielansky et al., 2011)

However conversion rates for vegetable oils in FCC is not easy to calculate as higher blending of vegetable oils lead to different relative conversion factors. In the TU Wien experiment, these (considering only the convertible part of the oil, i.e. excluding water and CO_2) decreased for rapeseed and soybean oil but showed a slight increase for palm oil. Probably this can be explained by the fact that vegetable oils do not contain aromatics, and these short molecules are not reactive in FCC as only molecules with more than three C atoms undergo dealkylation reactions. Mono-aromatics compounds such as benzene and xylene end up in gasoline, longer compounds in light cycle oil[63] or residues but do not take part in the process. Olefins can end up in gasoline or cracking gas but can proceed with other reactions as well (Bielansky et al., 2011).

The triglycerides decompose in a fast thermal cracking step to free fatty acids which can enter the catalyst pores and undergo further reactions.

The nearly linear trends for the lumps with different blends of vegetable oils and VGO lead to the assumption that the reaction rate of both feeds is similar and that the oxygen content is the main cause of decrease in conversion rate. From experimental results it seems also that there are no synergetic effects between VGO and vegetable oils and no quicker deactivation of the catalyst occurs. In light of this and the data and literature available, for the calculation of mass and energy

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[63] Cycle oil is an unwanted liquid residue produced when using catalytic cracking to convert heavy hydrocarbon fractions from earlier stages of refining into more valuable lighter products. Catalytic cracking produces gasoline, liquid petroleum gas (LPG), unsaturated olefin compounds, cracked gas oils, cycle oil, light gases and a solid coke residue. Cycle oil may be processed further to break it down into more useful products; in particular it may be mixed with heavier products and put through the refining process again.

balance of FCC of algal oil it can be assumed that *Chlorella sp.* and *Scenedesmus* oil can behave similarly to rapeseed oil, and the experimental conversion rates for rapeseed oil in FCC facility can be used with minimal adaptation.

9 Sustainability aspects of different production pathways

Microalgae have advantages over traditional energy crops, such as the potential for high-yield biomass production on marginal land or in seawater, thus, biofuel production avoiding land-use competition becomes possible. Another advantage of microalgae is their ability to capture CO_2 from power or industrial plants. Overall microalgal based biofuel is claimed to reduce environmental impact (Chisti, 2007). Thus worldwide there is great hope that the cultivation of microalgae for energy generation can contribute to sustainable energy supply of the future[64].

Preliminary assessments are indicating that with present technologies the energetic inputs of microalgae production could exceed the energetic output. In closed simple-build reactors more than 3 W/m^2 of electrical energy are used for operating the cultivation. This comes close to the amount actually harvested at the end.

LCA and sensitivity analysis are very location specific and should always be contextualized. This is what we tried to do within the Algae&Energy project in Austria (see chapter 10), highlighting at which points of the production chain technological progress is needed in order to make this option sustainable.

However, it has to be taken into account, that in nowadays commercial algae cultivation, a positive energy-balance is not targeted due to the high-prices of the common algal products.

Energy on the other hand is a low-value product. This means that alga cultivation should be as cheap as possible in order to make conversion into energy carriers economically feasible.

As for open systems, raceway ponds provide a higher yield than more extensive systems, while keeping capital investment generally low. An important factor is which microalga can remain dominant year-round (and how much energy can it yield?). In case of unsuitable climatic

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[64] Additional advantages of algal biofuels include the following (from FAO 2009):

Algae can contain large concentrations of the desired product, whereas in plants this is often concentrated in the seeds, as in corn, soy and rapeseed.

Algae are much more uniform than higher plants. Algae lack roots and leaves, microalgae are in many cases unicellular thus completely uniform, while seaweed may have very basic structural differentiation but all without hard, cellulosic material, therefore easily pumpable. This way the entire biomass can be processed, rather than just parts like seeds or roots.

Algae growth is dependent on climatic conditions, and thus on the seasons, but does not have the annual growth cycle of sprouting in the spring and harvest in autumn.

conditions, high contamination by local algae, or costly land, a horizontal tubular system may have the best characteristics. Although much more expensive, it offers a much higher yield per hectare and controllability, while up-scaling is easier than with other closed systems. A few large-scale commercial raceway examples exist, while closed systems are limited to a few hectares.

In recent years, many claims have been made on possible productivities and oil yields that even exceed the theoretical maximum. Often these are the result of extrapolation of preliminary lab results, while commercially yields would be much lower.

An overview of environmental impacts of algal biofuel production is reported below. The same issues are discussed in more details in FAO 2009a, and partially in FAO 2010.

9.1 Land use

Direct land use changes (LUC) are caused when new areas (e.g. forest areas or degraded land) are taken into production to directly cover the additional feedstock demand. An indirect land-use change (ILUC) is caused when new land is used to cover the agricultural demand, previously displaced by bioenergy feedstock production. LUC and ILUC can have both positive and negative consequences on aspects such as biodiversity, carbon stocks and livelihoods (Dehue et al. 2009).

Since algae are grown in water, the cultivation systems have no land quality requirements and soil fertility is not an issue. Land needs to be relatively leveled and sufficiently solid to build the cultivation systems, which still allows a huge area of land to be used, such as deserts, infertile saline soils, polluted land and other land with low economic (and ecologic) value. As an example, Glenn et al. (1998) indicate that 43 percent of the earth's total land surface is arid or semi-arid and estimate that 15 percent of undeveloped land has sufficient access seawater (max 100 km), which amounts to 130 million ha. Bai et al. (2008) estimated that 24 percent of the earth's total land (about 3,500 million ha) has been degrading over the last 25 years. Part of the world's deserts further away from the sea may have saline ground water that could be used, or access to wastewater or sufficient fresh water. There is an enormous amount of land suitable for algae production without competing with agricultural land and avoiding conversion of land with high carbon stocks.

One of the possible problems of production on land could arise from the enormous size of envisaged commercial production systems, with facilities in the order of 1,000 ha having been proposed (Wijffels, 2008). Plots of this size with low current economic and ecologic value can be scarce. Large-scale open systems can cause fog blankets and other local climatic changes. During heavy rain, closed systems built on hard surface may result in water disposal problems (BCIC, 2009) and in open systems this may lead to high nutrient, high biomass excess water. Small-scale systems may be possible from an economic point of view especially when considering co-production of bioenergy and higher value products.

Considering cultivation at sea, it is well known that two thirds of the planet is covered by water but clearly, not all this surface is equally suitable for seaweed culture. They would provide a safe place for young fish to grow up, which can contribute to the recovery of fish populations (Florentinus et al., 2008).

An important synergy with offshore infrastructure is also possible. The potential area for offshore wind turbines is estimated in 550 million ha (considering water depths, shipping routes etc.) (Hoogwijk, 2004) and the space between wind turbines could be used for seaweed culture, as it is off limits for shipping and supplies anchoring point and other possible advantages. Gas and oil platforms provide anchoring points as well. Further the area "behind" wave energy facilities could be exploited as it has milder sea conditions (Florentinus et al., 2008).

Near shore high nutrient areas and open ocean biological deserts are options that could be considered in the future for algal biofuels production (see FAO 2009a). The design of sea-based cultivation systems should guarantee that sea mammals and other wildlife don't get entangled.

9.2 Greenhouse gases

CO_2 is the carbon source for photosynthesis for algae and plants alike. The amount of CO_2 captured by algae varies per species, but in general about 1.8 tonne CO_2 is integrated in 1 tonne algal biomass (Chisti, 2007) but algae have a few advantages over plant based CO_2 capture.

Indeed algae can grow directly on combustion gas (typically containing 4-15 percent CO_2) in closed systems, whereas plants take up CO_2 from the atmosphere.

Extra CO_2 from combustion gas could be a cheap source. However, gas cleaning is often necessary to remove components which are toxic to algae, the CO_2 (-containing gas) has to be transported and dissolved into the water phase, which will lower the pH, so energy input, chemicals, control equipment and gas cleaning facilities may be needed. Although the potential for CO_2 capture is huge, achieving an overall positive CO_2 balance is very challenging.

Combustion gas contains also other gases like NO_x and often SO_2 and both have indirect greenhouse effects. Algae cultivation using these pollutants as nutrients, with high removal efficiencies, has been reported in literature.

Further risks may arise if algae cultures establishment causes direct and indirect land use changes in high carbon stock areas.

In a global LCA also GHG emission of algae production waste streams should be taken into account. Also, when cultivation conditions become toxic, mass algae death can occur, which in turn can result in GHG emissions.

According to the IEA, the cultivation and the drying phase are extremely relevant when the production of algal biodiesel production is analyzed with respect to life-cycle emissions. The cultivation is affected by the need to provide nutrients (chemicals) to the microalgae, and by the energy requirements and emissions related to their manufacturing. Drying is characterized by high energy requirements. Specific GHG and pollutant emissions depend on the type of fuel used for the provision of the heat needed in the drying process but the graph below shows the energy ratio (MJ of primary energy needed per MJ of biodiesel produced) for each step of the production chain of biodiesel from algae. The first two bars show the energy ratio of growing microalgae in photobioreactor (PBR) and in open ponds.

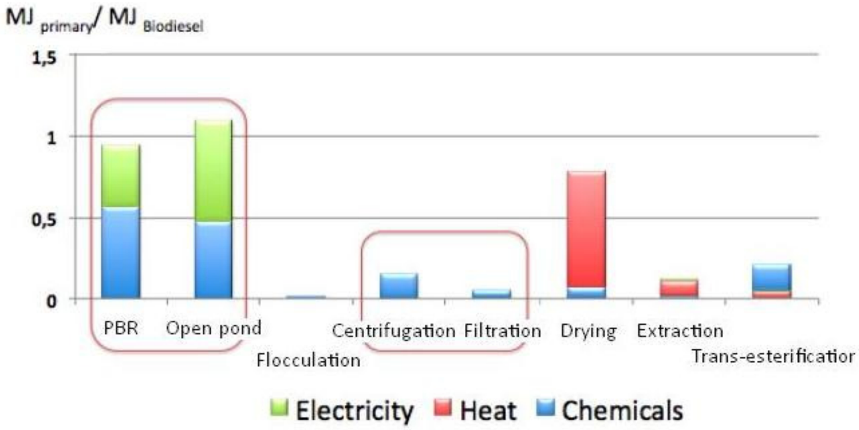

Figure 41 – Graph illustrating primary energy required to produce biodiesel through esterification (Courtesy of Pierpaolo Cazzolla, IEA, 2009)

9.3 Nutrients

The amount and kind of nutrients needed for algal growth depends very heavily on the species, but as an indication for the most important nutrients, about 5 percent (typically is 7-8 percent) of algal dry matter consists of nitrogen (N) and 1 percent of phosphorus (P).

The most convenient form to supply nutrients is through chemical fertilizer, but from sustainability point of view this is undesirable since nitrate production is very energy intensive and phosphorus is mined (thus a fossil resource that will be depleted). Properly planned algal biomass production facilities may recover and reuse most of the nutrients applied, minimizing eutrophication impact, and this in contrast to intensive agriculture where nutrient runoff and escaping nitric oxide pose serious problems.

A second option commonly used in agriculture is manure. This source is also applicable to algae. Wastewater is often too diluted and polluted with pathogens to be used in agriculture, but application in algaculture is certainly possible. Algae cultivation systems are watery systems that produce oxygen (O_2) during daylight, therefore there is a lower chance of ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4) emissions than with land application. Per tonne of manure, algae systems are likely to have lower over GHG emissions than agriculture. However, the fact that not all components in manure and wastewater are easily biodegradable, can contain heavy metals and other micropollutants and introduces a high concentration of microorganisms that may compete with target algae, limits significantly these concepts.

Another unique nutrient source is nitrogen oxides (NO_x) and to a lesser extent sulphur dioxide (SO_2, has a large pH effect) from combustion gas. The gasses dissolve into the water phase where they are used for algae as a nutrient source.

As already mentioned in section 3.4, also sewage can be treated with algae, reducing the need for greater amounts of toxic chemicals than are already used. Algae can be used to capture fertilizers in runoff from farms and, when subsequently harvested, the enriched algae itself can be used as fertilizer.

Agricultural Research Service scientists found that 60-90% of nitrogen runoff and 70-100% of phosphorus runoff can be captured from manure effluents using an algal turf scrubber (ATS). Scientists developed the ATS, which are shallow, 100-foot raceways of nylon netting where algae colonies can form, and studied its efficacy for three years. They found that algae can readily be used to reduce the nutrient runoff from agricultural fields and increase the quality of water flowing into rivers, streams, and oceans. The enriched algae itself also can be used as a fertilizer. Researchers collected and dried the nutrient-rich algae from the ATS and studied its potential as an organic fertilizer. They found that cucumber and corn seedlings grew just as well using ATS organic fertilizer as they did with commercial fertilizers (AquaFUELs 2010b).

9.4 Water consumption

One major advantage of algae cultivation over fuel crops and agriculture in general, is the ability of many algae to tolerate saline water. Fresh water is scarce in many parts of the world, and agriculture uses 70% of the total global fresh water consumption. This characteristic of algae allows a much greater area to be potentially utilized for algaculture. Besides seawater, other sources of salt water are saline aquifers and certain wastewaters.

In land-based cultivation systems water consumption can be a concern. The water resulting from algae separation contains organic components due to imperfect separation and leaked algal cell content. Ideally, this water is (at least partially) recycled, which may require additional treatment, therefore additional energy. Possible problems are the accumulation of unwanted compounds and proliferation of micro-organisms. Non-recycled water should be disposed of properly, which can be more difficult due to the high salt content.

Open cultivation systems (land-based) suffer of significant water loss due to evaporation. During this process, water is removed but the salts are left in the system, which need therefore to be replenished with low salt water, even in systems running at high salt concentration. Alternative options are batch culture without water recycling.

Interestingly, even under desert conditions the water footprint of algal biomass production is lower than that of irrigated maize ethanol production, calculated on the water input per unit of energy created. AquaFUELs 2010 suggests that it requires about 0.5 million liters of water to produce on 1 dry ton of algal biomass (It can take about 3 million liters of water to produce 1 T of rice and about 2 million liters to produce one T of soybeans.

9.5 Genetically modified organisms

A lot of biotechnological research aimed at improving genetically algae characteristics is currently going on and will probably even increase in the next future. Two possible improvements have already received significant attention:

- Reduction of antenna size. Under natural conditions, algae have to compete for light with surrounding photosynthetic organisms. Therefore the so-called antenna part of chlorophyll which receive light has evolved to catch more light than can be photosynthetically processed under optimal lighting conditions, wasting up to 60 percent of the received light energy (Melis et al., 2001). Reducing the chlorophyll antenna size would result in more efficient use of light.
- Triggering of lipid production. The exact biochemical process for accumulating lipids has received significant attention, in order to find out what triggers it.

9.6 Strains of local origin

The use of locally selected strains may be of significance both for ease of management and sustainability considerations. For example, based on criteria of the 'Roundtable on Sustainable Biofuels' non-native potentially invasive biofuels crops should not be used in open cultivation systems, and adherence to this rule will require the identification and use of locally isolated algal strains. Furthermore such strains may have unique adaptations to the local climate, water and possible parasites that imported or laboratory grown strains may not have.

9.7 Economic viability

Realistic estimates for dry microalgal biomass yield vary from 40 to 80 tons per year per hectare depending on the technology used and the location of production, despite common claims of higher yields (Wijffels et al. 2010). The location of the production system is also of importance for the economics, as it determines the costs of land, labour, CO_2, nutrients supply and other factors that have a major influence on the process.

Current microalgae production is based on relatively small systems, producing high-value products for special niche markets. Because of these high value products, the market price of microalgae is on the average €250/kg dry biomass (Pulz et al. 2004), which is 1,000 times too high for producing biofuel, with a 50% oil content (see table 26). Biomass prices between €0.5 and €5 /kg are regularly calculated for large systems. For biofuel, the technology needs to develop from a small scale activity to an industrial scale technology. During this development, production costs will decrease and, with every step in reduction, new markets will open. Most likely, initially the production of edible oils for food and fish feed will become economically viable and only later the production of bulk chemicals, biomaterials and biofuels can become feasible (FAO 2010).

By assessing the viability of algae projects from a market perspective, it is clear that total installation, operation and maintenance costs will be a major barrier to future commercialization but technologies are being developed to further reduce costs and increase yields.

The production cost of algal biomass, and consequently of algae-based biofuel or any other product, can only be determined by running a commercial scale production facility. Extrapolation from test scale or current operations is inaccurate and risky.

Product	**Microalgae**	**Price (USD)**	**Producer**
β-Carotene	Dunaliella	300-3000 /kg	AquaCarotene (Washington, USA) Cognis Nutrition & Health (Australia) Cyanotech (Hawaii, USA) Nikken Sohonsha Corporation (Japan) Tianjin Lantai Biotechnology (China) Parry Pharmaceuticals (India)
Astaxanthin	Haematococcus	10000 /kg	AlgaTechnologies (Israel) Bioreal (Hawaii, USA) Cyanotech (Hawaii, USA) Mera Pharmaceuticals (Hawaii, USA) Parry Pharmaceuticals (India)
Whole-cell dietary supplements	Spirulina Chlorella Chlamydomonas	50 /kg	BlueBiotech International GmbH (Germany) Cyanotech (Hawaii, USA) Earthrise Nutritionals (California, USA) Phycotransgenics (Ohio, USA)

Product	Microalgae	Price (USD)	Producer
Whole-cell aquaculture feed	Tetraselmis	70 /L	Aquatic Eco-Systems (Florida, USA)
	Nannochloropsis		BlueBiotech International GmbH (Germany)
	Isochrysis		Coastal BioMarine (Connecticut, USA)
	Nitzschia		Reed Mariculture (California, USA)
Polyunsaturated fatty acids	Crypthecodinium	60 /g	BlueBiotech International GmbH (Germany)
	Schizochytrium		Spectra Stable Isotopes (Maryland, USA)
			Martek Biosciences (Maryland, USA)
Heavy isotope labelled metabolites	N/A	1000-20000 /g	Spectra Stable Isotopes (Maryland, USA)
Phycoerythrin (fluorescent label)	Red Algae	15 /mg	BlueBiotech International GmbH (Germany)
	Cyanobacteria		Cyanotech (Hawaii, USA)
Anticancer drugs	N/A	N/A	PharmaMar (Spain)
Pharmaceutical proteins	Chlamydomonas	N/A	Rincon Pharmaceuticals (California, USA)
Biofuels	Botryococcus	N/A	Cellana (Hawaii, USA)
	Chlamydomonas		GreenFuel Technologies (Massachusetts, USA)
	Chlorella		LiveFuels, Inc. (California, USA)
	Dunaliella		PetroAlgae (Florida, USA)
	Neochloris		Sapphire Energy (California, USA)
			Solazyme, Inc. (California, USA)
			Solix Biofuels (Colorado, USA)

Table 26 - Marktet values of some of the main algae based products
(FAO 2010, adapted from Rosenberg et al. 2008)

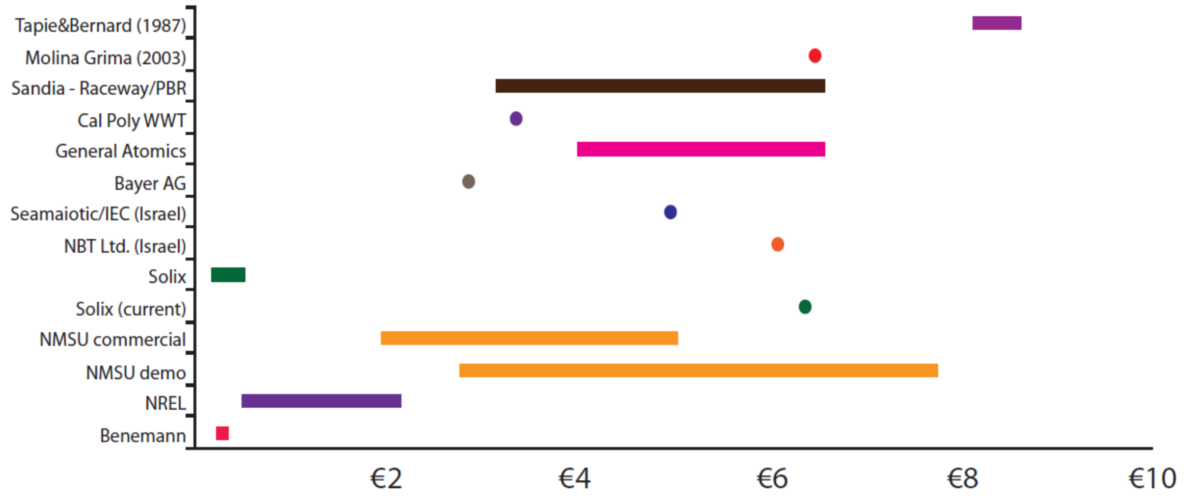

Figure 42 - Production costs (current, demo and estimates) of algae biomass from different private companies and research centers (Source: adapted from FAO 2011)

Today, after many years of R&D, there is not yet an algal strain or reactor or combination of both able to achieve large scale (hundreds of hectares) yields comparable to C4 plants (e.g. sugarcane) and no company has, at present, a mature technology to be on the market and compete with fossil fuels (Tredici 2010).

Cascading of algae chains with other higher-value products is key to make the process economically viable today.

While algal biomass production may never achieve the low production costs of other agricultural commodities, full accounting of additional environmental services may result in a balance favouring the algal fuels. This point requires intensive investigation progressing far beyond currently used LCA models, starting with defining those production parameters and system boundaries that will actually deliver the above mentioned environmental advantages.

Further, since algae use sunlight as main energy source, the potential yield is highest in warm countries close to the equator[65] as shown in Figure 43. Typically these high yield areas have also lower costs for land and labor. While this applies to fertile, tropical zones for plants, algae can be cultivated on even cheaper unfertile land in dry climate zones.

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[65] It is interesting to note that, with few exceptions, the measured productivities of microalgal cultures are not higher than the short-term yields reported for C3 and C4 plants (Tredici 2010).

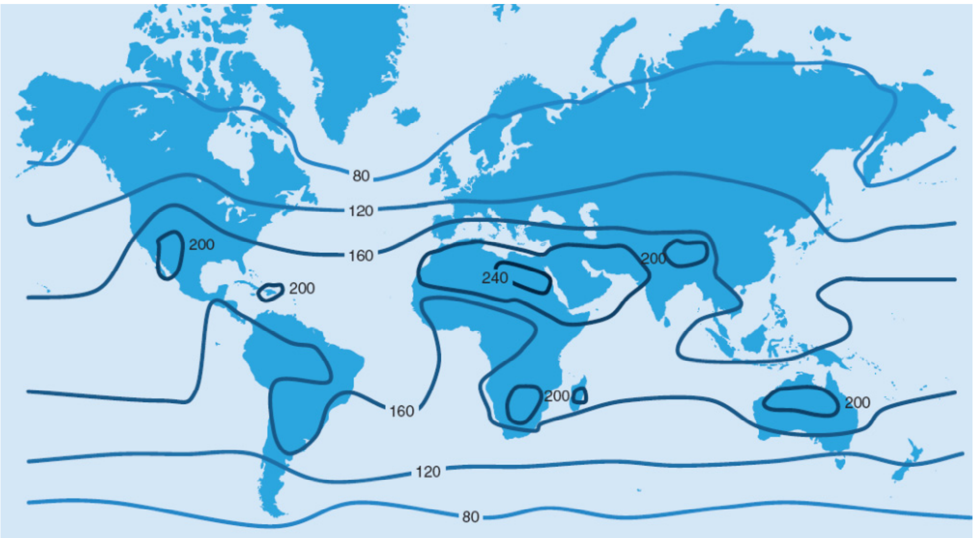

Figure 43 - World map of algae biomass productivity (tons/ha/year) at 5% photosynthetic efficiency considering an energy content of 20 MJ/kg dry biomass (Tredici 2010)

9.8 Co-production options

There is increasing competition of land for energy crop production, feed, and fibre and production systems may be designed in a way to respond to multiple product demands at the same time, thus improving the economics. It is possible to design cultivation systems that co-produce algae, seaweed, fish or shellfish, thereby providing possible feedstock for bioenergy.

Many of the algal products, especially those used for food, such as proteins, omega-3-fatty acids and some carbohydrates cannot be subjected to high temperatures, high or low pH, toxic chemicals and/or high oxygen concentrations, as this would decrease their functionality. Usually these extreme conditions are used to speed up or improve the processing of algal biomass. If only mild conditions can be used, the preparation processes will be more difficult on a large scale, because they are slower and more expensive.

The use of different waste streams acting as a nutrient source for algae cultivation is preferential over the use of expensive and energy intensive fertilizers. However, these waste streams most likely contain more contaminants than nutrients, which, can be reabsorbed by the algae, and in some cases reduce their growth. Most of the algal products are food or food-related, therefore cannot be contaminated by toxic compounds, while for biofuels this problem is less severe. Only certain wastewaters can be used and depending on the type of wastewater used, the algae product may require further purification in order to remove contaminants. This is the case for several algal products, independently of the nutrient source. Further optimizing the production of the desired compounds in algae is often dictated by available nutrients. Controlling nutrient concentrations is more difficult with waste streams than with artificial fertilizers.

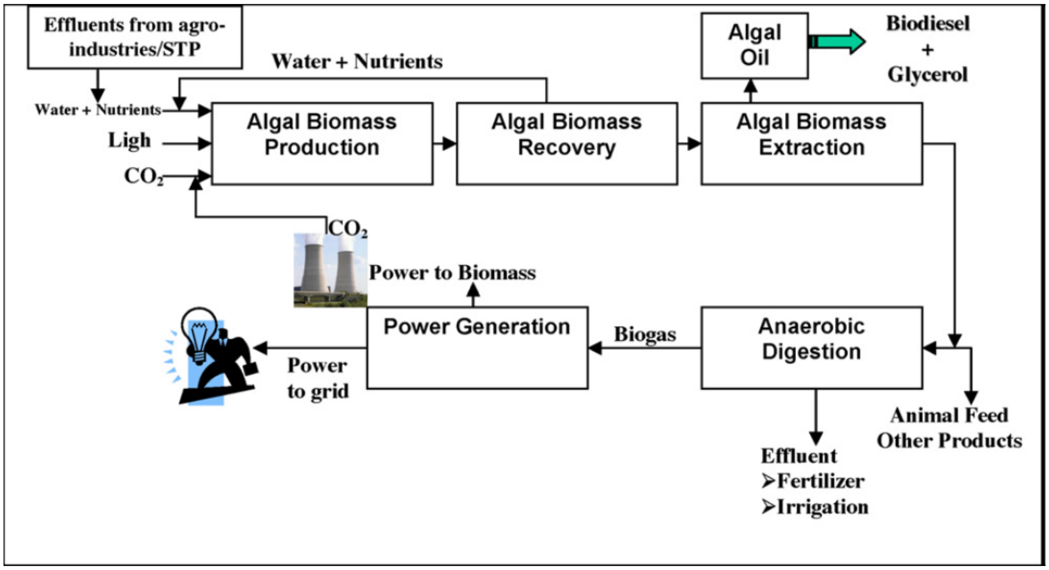

Figure 44 - Integrated algal production concept with various co-products (Khan et al. 2009)

Figure 44 shows a concept with algae cultivation for biodiesel production if the left-over biomass after oil extraction cannot be sold for high enough price (e.g. as animal feed) it is anaerobically digested to produce biogas. Burning this biogas leads electricity and CO_2, which are again used for algae cultivation.

In order to assess the economic viability of the co-production of bioenergy and other products, Wijffels et al. (2010) have chosen a combination of microalgal products that have a bulk-scale market, through biorefinery. Assuming 40% lipids, 50% proteins and 10% carbohydrates, a quarter of the lipids is sold to the food and chemical industry for €2/kg, the rest for biodiesel at €0.50/kg, soluble proteins (20%) for food at €5/kg, the rest (80%) for feed at €0.75/kg. The carbohydrates (sugars), used as chemical building blocks, at €1/kg. Furthermore, nitrogen removal is assumed, which conventionally costs €2/kg removed, and the oxygen that is produced during cultivation is captured and sold (to fish culture) at €0.16/kg oxygen. This “biorefinery” yields €1.65/kg algal biomass (not including costs for biorefinery), relying solely on products with a low market value but a very large market size. They conclude that this type of biorefinery is required to make algae-based biofuel economically viable, although the development of such an integrated concept will take many years (Wijffels et al. 2010).

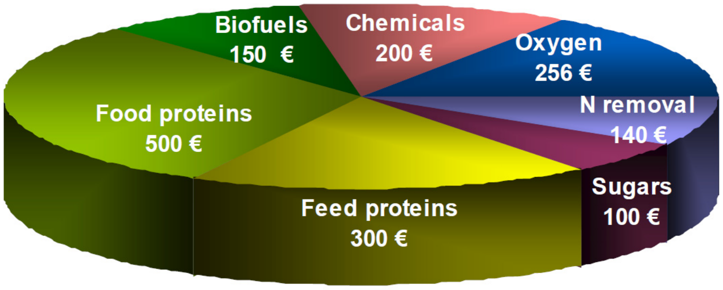

Figure 45 - Market value distribution of 1000kg algae after biorefinery (Wijffels et al. 2010)

If the entire algal biomass is consumed as food or feed, no co-production options are available. Co-cultivation with different animals might be possible, and large algae culture system can occasionally produce batches that are inferior to the quality standards, surpass the processing capacity or have other operational problems. This surplus biomass can be used for energy production using one of the technologies that can be applied to wet biomass. Anaerobic digestion of hydrothermal treatment appears to be good candidates, as they can handle surplus algae and a variety of other organic wastes.

If the primary product is a lipid like PUFA, it will be removed from the oil content, leaving few opportunities for co-producing biodiesel for example. Remaining polysaccharides and carbohydrates can be good feedstock for bioethanol production. An extra pre-treatment step will be needed for some, but not all algal compounds. Anaerobic digestion and thermochemical treatment can be applied even if the surplus biomass is not dry, although anaerobic digestion may be susceptible to toxicity of chemicals used in the extraction of the primary compound. If the surplus biomass is dry enough, it might be directly gasified.

The market value of different algal products differs greatly and the products with the highest value typically have the lowest market size. Therefore production of high-value products in niche markets is incompatible with that of biofuels, because the latter have a potentially much larger market. For example omega-3-fatty acids and other PUFAs have roughly a 10 times lower concentration in algae than lipids for biodiesel. Co-producing these two products at a scale to replace a few percent of the total diesel consumption would produce much more PUFAs than needed. This would make their price drop under economically feasible levels[66].

To be able to use extracted fatty acids and pigments from algae biomass, mild ways of breaking the cell wall and extraction techniques based on the "food-grade" solvents ethanol and water are required. Subsequently the extracted products need to be stabilized for storage by concentrating them, using a carrier material and/or removing proteases and microbial contamination.

Compound	Total market size (USD x 10^6 year^{-1})	Volume of product (tons year^{-1})	Microalgal part of volume (%)	Volume of microalgal product (tons year^{-1})	Product prize Non-algal (USD/kg)	Product prize (algal product) (USD/kg)
Astaxanthin	250	100	~1	0.3 – 0.5	2000	> 6000
ß-Carotene	200	300	25[a]	60	600	>1200
lutein	25				30 - 800	
Lycopene	35				40- 400	
Notes:	a: based on an average ß-carotene content of 5 % dw.					

Table 27 - Market sizes and prices of caotenoids and their algal share (FAO 2010)

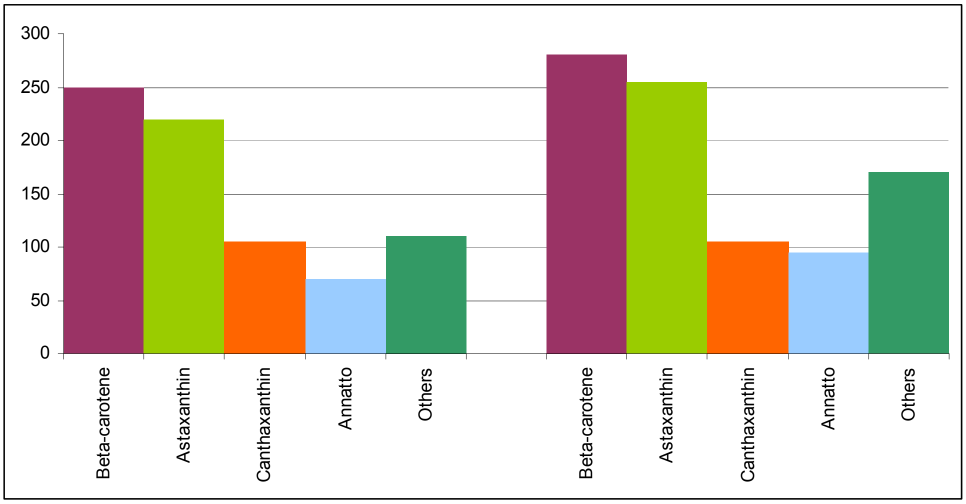

Figure 46 - Global Carotenoid market and future outlook in millions of USD (Source: author's elaboration on BBC Research data July 2010)

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[66] See FAO 2010 for more details.

If the algal biomass is used for nutrition purposes, its proteins will be the main interest, which, in most cultivated algae, commonly represent more than half of the dry biomass. The remaining biomass will consist of carbohydrates (mainly cell walls and other membranes) and, possibly, lipids or carbohydrates (for energy storage). Generally the lipid content will be too low for viable extraction for biodiesel production. The carbohydrates may be a good source for bioethanol production, or else thermochemical treatment or anaerobic digestion can be used, depending on the toxicity and biodegradability of the remaining biomass. If recent soy meal prices are taken as a reference, the value of algae after oil extraction would be at least €300 /ton with a very large potential market (FAO 2010).

The option of algae-based paper production is still at an initial stage. Information on the waste stream after fiber extraction is not available, so energy co-production options are unclear. For the inverse process, after the extraction of valuable compounds and/or biofuel feedstock, the remaining biomass will most likely still contain the fibers, which could be channeled into paper production.

Algae cultivation requires nutrients and these could be partially supplied by a waste stream (which can vary from a highly concentrated stream like manure or industrial waste to very dilute streams like effluent of a wastewater treatment plant that still contains some nutrients, of eutrophicated surface water) is not only cheaper than using artificial fertilizer, but it may generate additional income for the service of water purification and can significantly improve the economic viability of the algae production. After lipids and/or carbohydrates extraction, the leftover biomass contains most of the nutrients, and can be re-used as organic fertilizer. This may displace part of the energy for production (and transport) of synthetic fertilizer.

Seaweed cultivated for food consumption doesn’t allow co-production because the whole biomass is used for food and dietary supplements production, unless a cultivation system that co-cultivates seaweed with fish or shellfish can be devised. The same holds for the use of seaweed for abalone production. Bioenergy co-production options from seaweed appear limited, as the products available from seaweed are far less versatile and controllable than in microalgae.

Besides the development of new algae concepts, making additions and innovations to existing algae production systems can be a viable pathway to co-producing energy. Some of these options such as HTC or biogas fermentation are applicable to developing countries as well, both to microalgae and seaweed. During the preparation of FAO 2010 we did an extensive literature review and internet search to identify and report commercial algae production in developing countries. The full list is available in FAO 2010. For microalgae, most commercial operations were located in China, Taiwan and India and, in 1997, around 110 commercial producers of microalgae were identified just in the Asia Pacific region, with capacities ranging from 3 to 500 tons /year (Lee 1997).

9.9 Scale of operations

Through economies of scale, large-scale algae facilities can achieve a lower production price per kilogram biomass. In fact, Um 2009 suggests that the smallest viable size for an algal biodiesel plant would be 1,000 ha, pumping about 1 billion litres of salt water a day.

For developing countries, two scenarios are foreseeable, one where these kinds of scales are achieved, and one where the concepts are reduced to the community level of the rural poor.

The large scale scenario requires large investment and market for inputs and outputs, as well as sufficient skilled personnel for construction, operation and management. This means such a concept will be more viable in an urban setting with substantial industrial development. Current commercial examples of algae cultivation in developing countries fit in this category.

Algae farming on a very large scale may result in alienation and lack of integration between the environment and people. These projects should be analyzed thoroughly for their possible environmental and social impacts. They risk forcing human populations into migration, and undervalue cultural and religious attachment to the land that contributes to well-being, destroys or disrupts entire ecosystems and their inhabitants and animals. If such large projects are envisioned, a strong effort needs to be made to integrate them into the existing ecosystem and social system (UNESCO 2009). The larger the system, the higher the risk if the technology doesn't perform as expected. Obviously, these risks are common to large-scale land-based biofuel production as well. Note that positive impacts can be expected as well (e.g. employment creation), if projects are well designed.

Furthermore, harvesting requires significant investment in technology, which can therefore be a barrier. An option to avoid the need for expensive harvesting technologies is the cultivation of filamentous algae species.

For small systems, it is possible to dry harvested algae naturally in the sun, while large operations will focus on using all available land to capture sunlight for algae cultivation. Oil can be relatively easily extracted from the dry biomass using an oil press similar to the ones used in manual soybean oil extraction, and left-over biomass would make good animal feed, or alternatively the algal biomass could be easily processed into biogas.

9.10 Socio-economic aspects

Looking only at energy from algae, commercially viable production may still be several years to come. The availability of energy is of crucial importance to economic growth. In the coming decades, fossil fuel prices will most likely continue to increase, which impacts the rural poor through their use of fossil fuels for cooking, transportation, electricity, lighting, heating, petroleum-based fertilizers, and some agricultural products. A 74% increase in price overall household energy needs between 2002-2005 was reported (UNESCO 2009). Accessibility of energy is reduced at higher fuel prices. Forced decrease in energy use can result in cuts on many basic rights such as lighting and transportation, direct and indirect effects to health and education, and increase food insecurity.

The profitability of algal biofuel investments will also depend on expected fossil fuel and carbon prices. Today it is plausible that ABB will become a successful technology, but of course there is no guarantee. As for other renewable energy alternatives, under-investment leads to slower development which prolongs the dependence on fossil fuels, together with its multiple environmental and economical risks, that are costly to prevent or mitigate (UNESCO 2009).

On a macro-scale, it is clear that significant investments are justified, but within certain economical limits. The main benefits of co-producing energy and other products from algae are improved economic feasibility and short-term gain in practical experience with algae cultivation and processing. Both of these would accelerate the development of algae for bioenergy and attract investments.

9.11 Sustainability requirements and standards

In recent years, several initiatives have been developed to guarantee the sustainability of bioenergy, and of liquid biofuels in particular. Firstly, the deployment of algae co-production projects should consider and comply with the basic safeguards of biodiversity such as described in the international, legally binding Convention on Biological Diversity (CBD). It addresses strategies for sustainable use of biodiversity, meaning that human kind can use land (or water) and the ecosystems, flora and fauna it harbors, but in a way that prevents long-term damage.

Sustainability criteria for biofuels include the UK Renewable Transport Fuel Obligation (RTFO), the EU Renewable Energy Directive (RED), the Roundtable of Sustainable Biofuels (RSB), the Algal Biomass Organization standard and the US Renewable Fuel Standard (RFS). All these certification systems have a different scope, e.g. internationally, nationally or state level, or address only certain feedstocks, only certain biofuels or only limited criteria (e.g. only social or environmental), in various stages of implementation and some are voluntary, some binding. Among other criteria, the biofuels are required to use less energy for their production or release less GHGs than conventional fuels (on a LCA basis).

When co-producing biofuel and other products, the energy and GHG balances have to be calculated including the co-products and subsequently spread over these, on the basis of the energy content of the final products or other allocation methods. In general, co-production of biofuels would need little energy increase, since the algae need to be cultivated, harvested and processed in any case for other purposes. The total energy used in the process and therefore the associated GHGs are usually divided over the co-products based on their energy content and, in this way, the biofuel would account for the vast majority of the total GHG emissions in the chain. This calculation method would penalize co-produced biofuel. The problem arises for example when a producer of non-energy products from algae (e.g. nutraceuticals, pigments) decides to co-produce bioenergy (e.g. biogas from fermentation of processing residues). The co-production of biogas would require a minor increase of the total energy requirement. If the producer wants to use this biogas in the transport sector he has to comply with the minimum GHG reduction. In this case, since the co-products have a lower energy content than the biofuel produced, the application of the allocation method would show that the biofuel product is responsible for the vast majority of GHG emissions, whereas the additional biogas production actually only causes a minor increase in the overall energy consumption of the system. If the producer is not going to be able to use the biofuel for transportation he won't be motivated to shift towards integrated bioenergy production (FAO 2010). Therefore it is important that GHG emission allocation methods are designed in a way that does not discourage integrated production.

Even if the discussion on the sustainability of biofuels has focused so far on land-based biofuels, driven by the sustainability concerns arising from large-scale feedstock production, existing sustainability standards may be easily extended to algal biofuels. In general, all of the issues addressed are to some degree relevant to algal biofuels.

At present only the EU RED mentions algae as part of a list of possible future second generation biofuel options.

Impact studies on the sustainability performance of algae based bioenergy chains are still limited and more information is needed to gain more insight about the key sustainability concerns for algae based bioenergy chains, as developed in different geographical regions (dry or tropical areas, saline or fresh water) and under different management systems (large scale vs. small scale). An important attempt to assess the environmental impacts of algae production using LCA was undertaken within the AquaFUELs project. The exercise examined the current production methods and future possibilities of using algae to produce biofuels, the current status of LCA of algae derived fuels that are available in the academic literature, and the environmental impacts from micro-algae and macro-algae cultivation. A detailed report of the work can be found in AquaFUELs 2010c.

10 Algae-to-energy: an applied research in the Austrian context

This chapter summarizes the main findings of the Algae&Energy: Austria project, to which I contributed as team member on behalf of the Vienna University of Technology during the period November 2010 – March 2012.

The project was aimed at identifying the most interesting combinations of technology pathways for microalgae-to energy production, evaluated technologically, economically and ecologically. As the potential depends further on the cost of production of microalgae and the fossil fuels, the assessment was coupled with an economic analysis, as well as an analysis of water requirements, nutrient requirements and the efficiency from the production of the energy source and the provision of energy services. Life Cycle Analysis (LCA) was undertaken to assess the environmental impacts and reduction of greenhouse gas emissions and fossil energy. The future of algae-to-energy in Austria was assessed drawing medium- and long-term scenarios.

Based on the possible cultivation, harvesting, processing and conversion technologies for Austria from today's perspective, a number of energy production pathways for bioenergy from microalgae have been identified. Several stakeholders were involved in the selection process also by means of two workshops. Pathways were chosen with the aim of maximizing the energy use of the algal biomass, not of co-products. The selected conversion pathways were evaluated for their development prospects for technological, economic, environmental and energy-related criteria for a medium-and long-term.

The selected nine utilization pathways for bioenergy from microalgae are:

For oil utilization:

- Biodiesel (algae oil about 50 Kt/a, energy from 1.5 to 1.7 PJ/a)
- Biogasoline (algae oil about 50 Kt/a, energy from 1.3 to 1.5 PJ/a)

For starch utilization:

- Bioethanol (algal biomass KTTS about 200 / a, energy about 2.7 PJ / a)

For use of the whole alga cells:

- Biomethane (algal biomass 20-70 KTTS / a, energy from 0.2 to 0.9 PJ / a)
- HTC-coal (algal biomass approximately 70 KTTS / a, energy from 1.0 to 1.1 PJ / a)
- Biohydrogen, biomethane (algal biomass approximately 70 tDS / a, energy from 1.1 to 1.2 PJ / a)

For cultivation in wastewater:

- Biomethane (algal biomass KTTS about 2 / a, energy <0.5 PJ / a)
- HTC-coal (algal biomass KTTS about 2 / a, energy <0.5 PJ / a)
- Biohydrogen, biomethane (algal biomass KTTS about 2 / a, energy <0.5 PJ / a)

10.1 Selection of algae strain

The distribution of triglycerides in different fatty acids (with different chain length and number of double bonds) essentially determines the properties of the final oil or biomass. The fatty acid composition varies with the cultivated species of algae, and in the project was found that *Scenedesmus obliquus* is particularly suitable for the production of biodiesel, while in *Chlorella vulgaris* the proportion of linoleic acid (18:3) appears too high (according to EN 14214 limit ≤ 12% and would therefore not qualify for the fuel quality standards set by the EU). Another special feature of microalgae-derived oil that should be considered is that they have usually relatively high concentrations of unsaponifiable oil components. This unsaponifiables fats are stored in the form of polar molecules, especially in the cell membranes. Since the unsaponifiable can be converted either by base transesterification even by acid esterification to biodiesel, they reduce the yield of product from the oil. On the basis of these considerations and the amount of available experience and information available on a number of microalgae (as also illustrated in chapters 2 and 3), *Chlorella sp.* and *Scenedesmus obliquus* were chosen as suitable algae strains for Austria, to be grown in closed photobioreactor systems using freshwater, and open ponds using wastewater respectively. Also the scenarios were developed on the basis.

For the selection of algae strains, four main groups of algae were identified on the basis of their main valuable extractable product:

Oil producing microalgae:

In this group the use of algae oil to produce energy is in the foreground. The algal oil is extracted and used as raw material for the production of energy products. In the pathway "biodiesel" algal oil is transformed into biodiesel and transesterified. In pathway Fluid Catalytic Cracking algal oil is processed into biogasoline, light cycle oil, fuel gas and ethylene and propylene (and the extraction residue used as feed). For this group, an oil content of microalgae of 30% and an increase in the oil content to 45% in long-term period has been adopted. A species with high oil content is *Nannochloropsis sp.*

Starch producing microalgae:

This group of algae is intended for the production of starch for bioethanol production. Starch in algal biomass is fermented into ethanol, and the by-product slurry is further processed in a biogas plant. For this group, a starch content of microalgae for the long-term period of 55% was assumed. An example of alga belonging to this group is *Chlorella vulgaris*.

Use of the whole alga cells:

Algae belonging to this group are suitable for the use of the whole algal biomass (in thermochemical processes or methane fermentation) without any further treatment step after the harvest. In the pathway biomethane, the biomass is fermented into methane and upgraded into biogas. In other production pathways, algae undergo hydrothermal carbonization to obtain HTC-coal and hydrothermal gasification to obtain a synthesis gas formed of biohydrogen and biomethane. An example of alga belonging to this group is *Chlorella sp*.

Cultivation if wastewater:

This group differs from the previous ones since instead of fresh water used in closed systems, wastewater is used in an open system for the cultivation of microalgae. The conversion technologies are the same of those of the ‘use of whole algae cells’ pathways. The whole algae are converted to HTC-coal, biohydrogen and biomethane. An example of algae belonging to this group is the *Scenedesmus obliquus*.

10.2 Cultivation and processing technologies considered

Due to the conditions in Austria, photobioreactors are preferred over open ponds for the cultivation of oil and starch rich microalgae. The reason for this are:

- Austrian climate: due to the climatic conditions in Austria the cultivation in open ponds would be more problematic than in photobioreactors and might need to be stopped during winter. For biogas plants this is particularly unconvenient as it requires approximately one month for the start-up to be fully operative.
- Space needs for open ponds: the space requirement for open ponds is significantly higher than in photobioreactors. As in Austria no marginal land is available, agricultural land should be used for algae cultivation, leading to a conflict with food production.

- Land prices in Austria: Land prices are high for large-scale cultivation of algae, especially in the vicinity of sources of CO_2. Therefore the amount of land used is an important constraint in Austria.
- Contamination by external organisms: the processing of algal biomass is more difficult in the presence of impurities or different types of algae or organisms. This is particularly important for processing into quality biodiesel, and less important for thermochemical processes.

For using wastewater, open ponds are the best option. Growing algae in photobioreactors in combination with wastewater has been discussed and discarded. All these choices have been discussed with stakeholders and endorsed during the first workshop.

For harvest of algae, a two-stage harvesting method has been selected. This includes flocculation with flotation and then centrifugation of the algal biomass. Through this two-stage process, a dry matter content of the algal biomass of about 25% can be reached (30% in the long-term scenario). For methane fermentation, only harvest by flocculation with flotation was considered (dry matter content of 5% in the medium term, 7.5% in the long term).

The filtration technology has not been chosen (even if very energy efficient) has not been included because for the selected species of microalgae special micro filter would be needed, which are mainly still under development and would be very expensive and complex to operate.

Likewise ultrasonic aggregation has not been considered as this is a relatively new and not mature process, not been tested outside the lab. It is also very energy intensive.

With regard to treatment technologies a number of thermal drying and oil extraction technologies have been considered (also in terms of sustainability). For alcohol fermentation, drying of the harvested algal biomass is necessary. The dry matter content after drying can be about 90%. On the other hand for oil extraction, biogas production, and for hydrothermal processes, a two-stage drying after harvesting was deemed not necessary.

The conversion technologies considered can be grouped into biochemical, thermochemical and mechanical-chemical.

Under biochemical conversion, the identified pathways consist of alcohol fermentation and methane fermentation. In this latter the methane contained in the biogas obtained by methane fermentation is upgraded into biomethane. No other uses of algal biomass are possible beside this transformation technology (e.g. esterification or alcohol fermentation). Alternatively it is possible to use by-products from other conversion technologies in a biogas plant, and the biogas obtained is then burned in a co-generation plant.

Among thermochemical processes, combustion, gasification and pyrolysis as pathways have not been selected due to either the high energy consumption for drying the algal biomass, or the too high water content of the algal biomass after harvest. Further there are problems associated with the composition of the algal biomass for the use of these processes such as the high chlorine content in the algal ash.

The use of algae oil in the refinery process is considered in the fluid catalytic cracking process. Hydrogenation has not been investigated in detail as no literature exists and no research operates in this area at present (at least in Austria).

Regarding hydrothermal processes, hydrothermal gasification and hydrothermal carbonization have been considered. Hydrothermal liquefaction has not been considered further as the product oil is of too low quality and would require substantial upgrading in order to be processed.

Under mechanical-chemical conversion processes, basically the esterification and transesterification of algae oil into biodiesel has been considered.

My research within the project focused on hydrothermal processes.

10.3 Hydrothermal conversion of algae biomass: the case for Austria

In order to estimate the potential for biofuel production from algae in Austria, only hydrothermal carbonization and hydrothermal gasification were considered among thermochemical processes, after due research and considerations. The reason is that the bio oil produced from hydrothermal liquefaction is usually of very low quality and therefore difficult to be further processed into transportation fuels. It would require filtration and upgrading, therefore increasing the production costs and making the process not economically viable today. As research continues and evidence is provided of a process that could produce good fuels from HTL directly, this conversion process would certainly need much attention.

The feedstock needed for the hydrothermal processes is supposed to come from two pathways:

- algae used for wastewater treatment (*Scenedesmus obliquus*) in a plant resulting in 9900 tons of wet algal biomass per year at 75% water content. The size of the feedstock supply has been estimated on the basis of a typical wastewater treatment plant size in Austria and the final 22.2% of dry biomass content in the input feedstock for the process has been considered as this level of concentration is achievable without much energy need through a centrifugation and flocculation process (2.8% of total wet mass is supposed to be flocculant).

These assumptions have been considered to be constant until 2020, while for a scenario to 2050 an increase in the condensation capacity up to 70% water content of the input feedstock has been assumed for a low energy intensive centrifugation (and flocculation) process and a wet biomass availability of 7563 tons per year (29.1% dry biomass and 0.9% flocculant). This hypothesis allows maintaining the dry algal biomass processed constant for 2020 and 2050, therefore easing a comparison. The rationale is that in 2050 less wet algal biomass, hence smaller algae production plants, will be needed to achieve the same energy output.

- algae cultivated ad-hoc for energy purposes in photobioreactors (*chlorella sp.*). For this pathway a feedstock availability of 272000 tons per year with a 75% water content has been considered as input up to 2020 (24.5% dry biomass), and feedstock availability of 223423 tons per year at 70% water content for the 2050 scenario (29.9% dry biomass), for the same reasons as above.

Specific reasons for the choices of dry biomass availability and technology used to separate the liquids can be found in the forthcoming publication Algae&Energy Austria (Hingsamer et al. 2012).

To estimate the performance of the HTG pathway using *chlorella sp.* as a feedstock, the energy balances of the Verena pilot plant developed by KIT in Karlsruhe was taken as a reference. This is one of the few HTG pilot plants existing and it was tested in 2010 using ethanol (glycerol) as input feedstock, reaching a max reaction temperature of 615 °C at 28 MPa. The experiment results and energy balance are shown in figure 47.

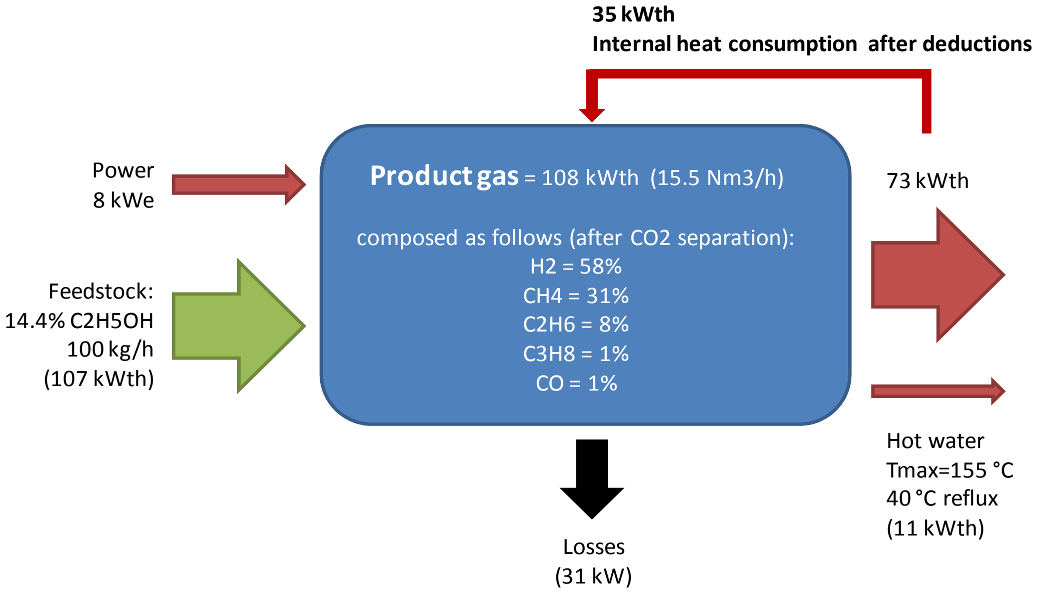
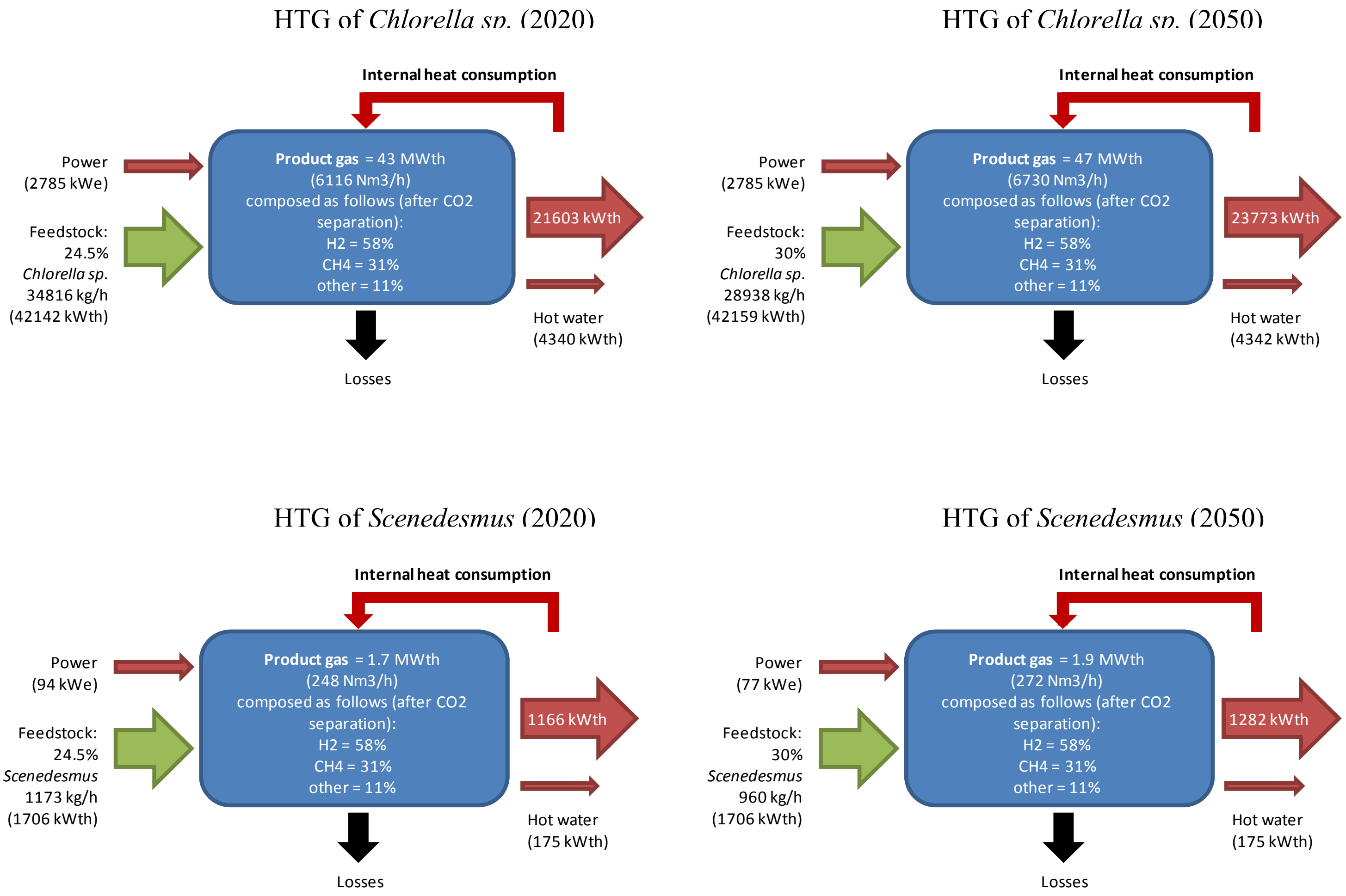


Figure 47 - Energy balance of the KIT Verena non-catalytic hydrothermal gasification plant

In the experiment reported, 100 kg per hour of a mixture of ethanol at 14.4% was used to feed the pilot plant. It has a heating value of 26.7 MJ/kg compared to 17.5 of *chlorella* biomass and 21.5 of *Scenedesmus* biomass. The difference in the heating value as well as the higher dilution of the input feed, and the difference in ash content (8% ash in chlorella and *Scenedesmus* biomass, 5 to 7% for the Verena feed) have all be considered to estimate the gas production associated to the two production pathways in our simulation.

To 2020 the efficiency of the commercial plant (272 Ktons/year) is supposed to be the same as in the small-scale Verena pilot plant, whereas for 2050, and an increase of 10% of the process (10% more product gas) is envisaged. The calculations leads to the following energy balances (assumes same composition of product gas).


HTG of *Chlorella sp.* (2020)

HTG of *Chlorella sp.* (2050)

HTG of *Scenedesmus* (2020)

HTG of *Scenedesmus* (2050)

Figure 48 - Energy and mass balances of the hydrothermal conversion processes considered. Chlorella sp. and Scenedesmus obliquus have been used as input feedstock

The study also assessed the overall energy balance of the two pathways, considering also the energy needed to grow algae ad-hoc in photobioreactors and the energy needed to grow algae in wastewater medium.

The analysis was then further coupled with an economic analysis to assess the viability of HTG of algae biomass in comparison with other non-thermochemical pathways such as transesterification for biodiesel production and fermentation for biogas production.

This analysis showed that algae cultivation is still the main bottle neck for economic exploitation of algae biomass and that HTG pathway is very promising as a technology to convert algae biomass into gaseous biofuels. It also showed that the wastewater pathway, using *Scenedesmus obliquus* leads to positive energy balance.

For the hydrothermal carbonization process, the foreseen energy balance is based mainly on a lab experiment by the University of Minnesota of 2010 (Heilmann et al. 2010a), where the principal objective was to focus on the char product of different feedstocks via HTC, aiming at obtaining a high level of carbonization and yield, while simultaneously minimizing processing time. The feedstocks tested included also algae biomass (*Chlamydomonas reinhardtii*) with the below characteristics.

%C	%H	%N	%S	Heat of combustion [MJ/kg]
51.6	7.9	9.8	0.6	18.04

Table 28 – Composition and heat of combustion of *Chlamydomonas reinhardtii* (Heilmann et al. 2010a)

10 kg of algae paste at 10 wt% were used directly in HTC. The suspension was heated from 22 °C to 203 °C using 7.31 MJ and then maintained at 203 °C for 2 hours withosut significant additional energy input. The products of reaction were cooled gradually after reaction and not allowed to flash; therefore there was no loss of energy due to vaporization. The conversion led to 0.63 kg of wet algae char with 63% of solids, which required additional 0.52 to dry it. Therefore for the 0.4 kg, 7.31 + 0.52 = 7.83 MJ were needed, which is equivalent to 19.57 MJ/kg. The overall net energy of the process was therefore a gain of 31.58 - 19.57 = +12.01 MJ.

A similar process has been applied to the chlorella biomass considered in 2020 and 2050. The following assumptions have been made:

- same rate of biochar production / quantity of dry algae biomass input[67];
- heating value of the final algae biochar proportional to the heating value of the dry biomass input;
- 5% less heating energy required to heat an algae paste with 24.5 wt% (instead of 10 wt% of Heilmann et al.(2010a)'s experiment)
- 10% more heating energy required to dry char in comparison to the laboratory conditions of Heilmann et al.(2010a)'s experiment.

	Chlorella 2020	Chlorella 2050
Algae paste input [kg]	272000000	223422667
wt % in the algae paste	24,5%	29,5%
dry biomass input [kg]	66666667	66693333
dry biomass input [MJ]	933333333	933706667
Heat for reaction [MJ]	462966667	509467039
Heat to dry char [MJ]	38133333	41963445
Biochar [kg]	42000000	46218480
Biochar production rate	0,63	0,69
Dry biochar [kg]	26.666.667	29.345.067
Biochar heating value [MJ/kg]	31	31
Biochar energy content [MJ]	831.788.402	904.575.361
Net energy production per year [MJ]	322.702.745	350.941.358

Table 29 – Energy and mass balance of the HTC conversion process of *Chlorella sp.* under different scenarios

In 2050 a higher concentration of algae paste (29.5% instead of 24.5%) is considered to be possible with similar energy need due to technological improvements. The results in terms of energy are reported below.

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[67] Although there is more biomass in the algae paste, which could lead to an increase of 6-7% on the biochar conversion rate, a similar decrease is expected in a commercial plant as opposed to lab conditions.

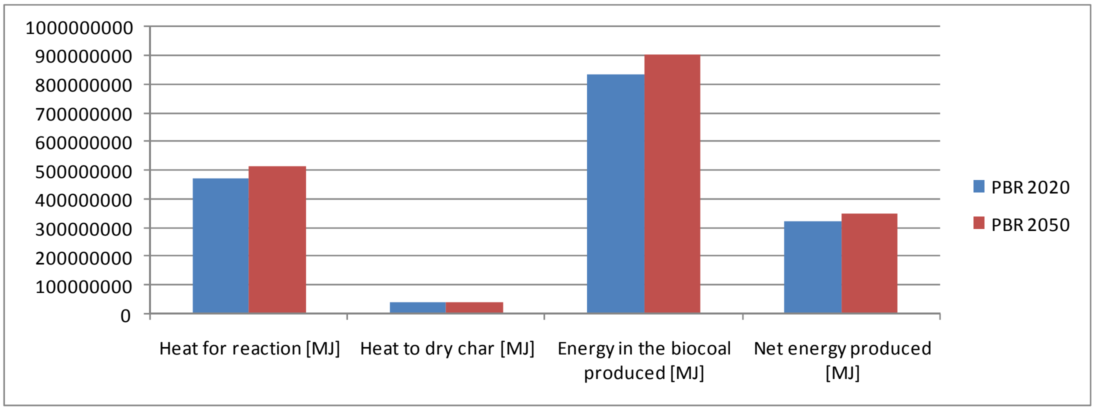

Figure 49 – Energy requirements and net energy produced in the post-harvest transformation on *Chlorella sp.* into HTC-coal under different scenarios

In the 2020 scenario, the assumptions above were made, while for the 2050 scenario an improvement of 10% of the efficiency of the biochar production was assumed.

Research is currently undergoing to further elaborate the concept of producing biochar from algae through HTC. Hydrothermal treatment of *Chlorella vulgaris* at temperatures of 225 °C and higher for 15–60 min in an unstirred condition (Levine et al. 2010) has been studied and the residual solids created, containing high levels (77–90%) of adsorbed fatty acids were not isolated per se but converted directly into biodiesel fuels by a high temperature transesterification process. This elaborates the approach illustrated here in which microalgae were converted into high energy char and nutrient-rich aqueous solution products.

A similar analysis has been done using *Scenedesmus obliquus* as algal biomass deriving from a wastewater treatment plant. Again, the experiment from Heilmann et al. (2010a) was taken as a model and different in heating value, ash content and dilution of the feed entering the system were taken into account.

In addition to this, the same assumptions as for the case of *Chlorella* have been made to account for the different scale of operation, technological improvements over time. The calculations lead to the following results:

	Scenedesmus o. 2020	Scenedesmus o. 2050
Algae paste input [kg]	9020000	7379167
wt % in the algae paste	24,5%	29,5%
dry biomass input [kg]	2200000	2200000
dry biomass input [MJ]	47222109	47222109
Heat for reaction [MJ]	15277900	16805690
Heat to dry char [MJ]	1258400	1384240
Biochar [kg]	1386000	1524600
Biochar production rate	0,63	0,69
Dry biochar [kg]	880.000	968.000
Biochar heating value [MJ/kg]	38	38
Biochar energy content [MJ]	33.139.427	36.453.369
Net energy production per year [MJ]	16.603.127	18.263.439

Table 30 - Energy and mass balance of the HTC conversion process of *Scenedesmus Obliquus* grown in wastewater under different scenarios

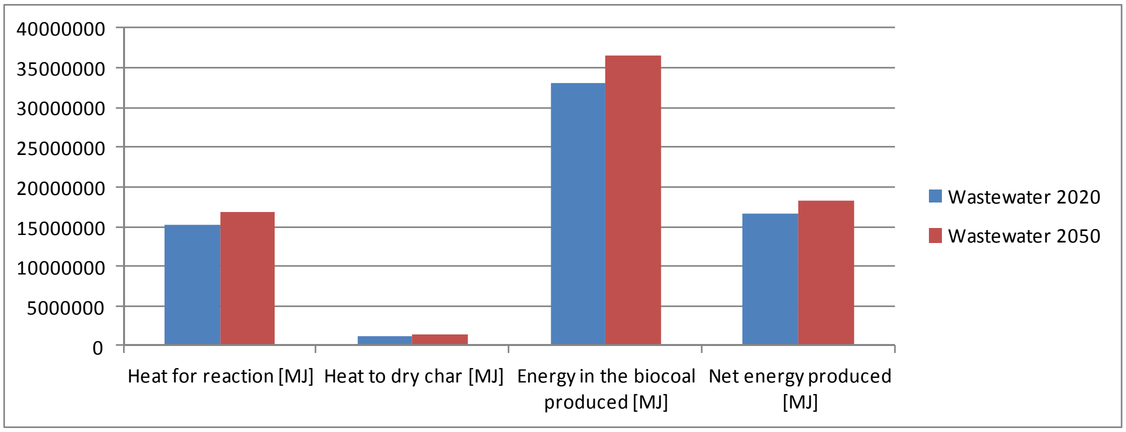

Figure 50 - Energy requirements and net energy produced in the post-harvest transformation on *Scenedesmus obliquus* grown in watewater into HTC-coal under different scenarios

As for the HTG pathway, the assessment went further assessing the overall energy balance of HTC of algae biomass both ad-hoc grown in photobioreactors and from wastewater treatment plants, considering also the energy needed to grow algae in such different mediums and conditions.

An economic analysis to assess the viability of HTC of algae biomass was undertaken, in comparison with other non-thermochemical pathways such as transesterification for biodiesel production and fermentation for biogas production (see graph below. Pathways leading to a negative energy balance are reported in red color).

This analysis showed that hydrothermal carbonization performs better than hydrothermal gasification with algae biomass in terms of energy performance. Of course the choice is also dictated by the final energy carrier desired, gas or biochar. Again the analysis highlight that algae cultivation is still the main bottle neck for economic exploitation of algae biomass and that the HTC pathway is very promising to convert algae biomass into biofuels and is already competitive with other thermochemical processes in treating wet algae biomass from an energy and economic point of view. It also showed that the wastewater pathway, using *Scenedesmus obliquus* is already viable, leading to positive energy balance and economics.

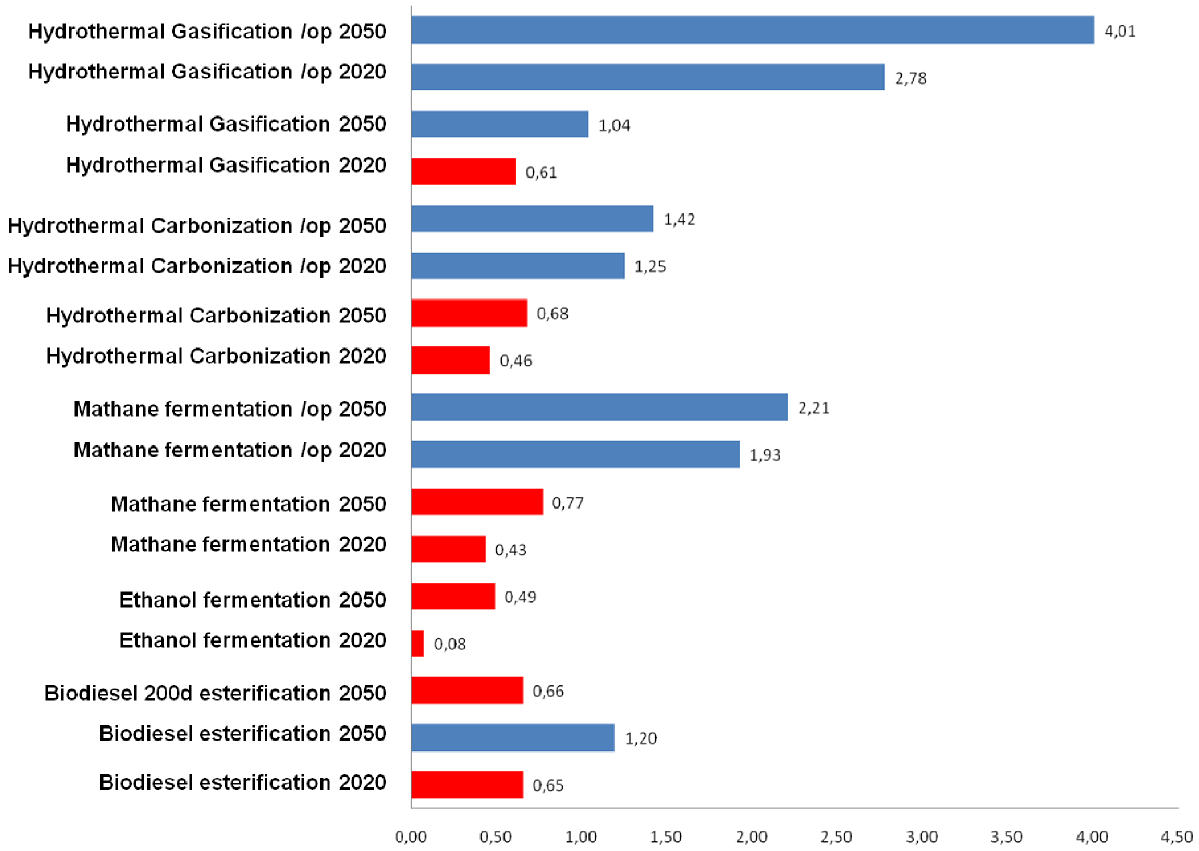

Figure 51 - Energy balance of hydrothermal conversion compared to other pathways for the production of algae-based energy carriers

10.4 Fluid catalytic cracking of algal oil: the case for Austria

The FCC process has been studied in more details as a possible thermochemical pathway to convert algal oil into valuable commercial products such as biogasoline, ethylene and propylene.

Given the very small quantities of algal oil achievable in the near future, if compared to the quantities of fossil fuels that are processed daily by a typical refinery, the algal oil is supposed to be blended with fossil oils and processed in an existing plant using the existing infrastructure.

The OMV refinery in Schwechat was used as a reference for the experimental values for efficiency and yields of the process. In this plant there is already some experience in processing vegetable oils for biodiesel production.

The envisaged quantity of algal oil to be treated is around 50,000 tons per year with a water content of 0.5% and 2,400 MWh per year are required to process such quantity.

Algal oil characteristics are supposed to be similar to other vegetable oil usually processed in the plant, and containing 15% of free fatty acids. As illustrated before, free fatty acids (and their degree of unsaturation) have detrimental effects on the catalyzer of an FCC plant.

Three main factors have been taken into account for the conversion rate into end products: experimental conversion rate of oil free from water and fatty acids, the amount of water and the effect of fatty acids on the FCC process. The input oil is assumed to contain 5% of water and the free fatty acid content reduces by 15% the conversion efficiency. Around 23% of the input feedstock can be found in gaseous form at the end of the process (ethylene, propylene and heating gas).

It is assumed that to 2050 free fatty acids won't pose a problem anymore to FCC processing due to technological improvements. The results of the analysis are reported below:

	2020	**2050**
Algae oil [tons/year]	50.000	50.000
Water content	0.5%	0.5%
Power consumption [MWh/year]	2400	2400
Biogasoline produced [tons/year]	17.554[68]	20.662

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[68] 41.5 % after accounting for water and free fatty acids present in the input oil (from experimental data)

LCO produced [tons/year]	7.783[69]	9.161
Ethylene produced [tons/year]	484[70]	570
Propylene produced [tons/year]	3.875[71]	4.560
Combustion gas produced [tons/year]	5.328[72]	6.271

Table 31 - Results of the estimated biofuels production through FCC of algal oil in the Algae&Energy Austria project

The FCC process is a very efficient conversion process for the production of gasoline, LCO as well as ethylene, propylene and heating gas. From experimental data, the process would need 2,400 MWh/year as electricity and would produce 210,651 MWh/year of gasoline, 91,840 MWh/year of LCO, 6,343 MWh/year of ethylene, 49,225 MWh/year of propylene, 62,111 MWh/year of heating gas.

Considering the energy needed to cultivate and harvest Chlorella, the energy balance is negative using today’s technology and is expected to become positive with some expected technological improvement by 2050. However, the production of gasoline and other valuable fuels from FCC can be comparable in terms of efficiency with biodiesel transesterification.

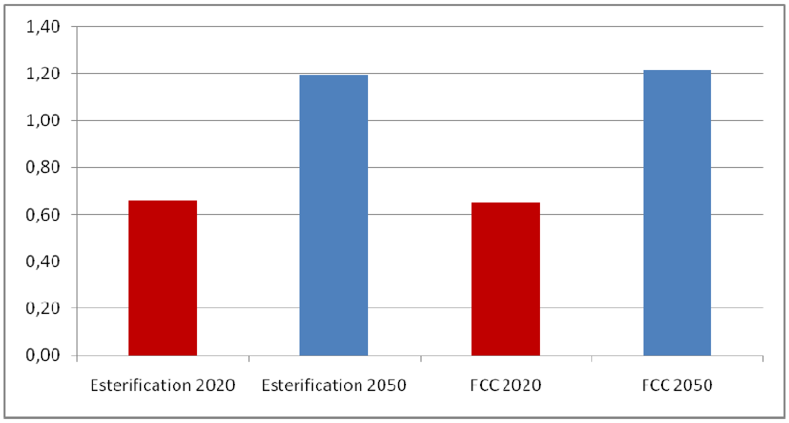

Figure 52 – Comparison of energy efficiency (percentage) of Fluid Catalytic Cracking compared to esterification of algal oil under different scenarios

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[69] 18.4 % after accounting for water and free fatty acids present in the input oil (from experimental data)
[70] 5% of the gas produced is ethylene (from experimental data)
[71] 40% of the gas produced is ethylene (from experimental data)
[72] 55% of the gas produced is ethylene (from experimental data)

Energy balance of biofuel production through FCC of extracted algae oil compared to transesterification process. Products of the transesterification process are biodiesel and glycerol, while products of FCC are gasoline, LCO and other valuable gases.

10.5 Main project's findings

Main conclusions of the project is that the production cost of fuels from microalgae is still much higher than for conventional systems (e.g. the production cost when using wastewater as culture medium is in the order of 35 - 50 € / GJ). Use of wastewater as growing medium is very interesting from an economical and energy balance point of view, further, synergies with wastewater treatment can be exploited. With successful technology developments significant cost reductions can be achieved (the production costs of all pathways in the long term can achieve 20 - 35 € / GJ). Approximately 35 - 50% of the production costs is determined by the cost of capital for the cultivation and harvesting phases.

The successful development of cheaper and more efficient cultivation and harvesting systems technologies is therefore a prerequisite for the commercial implementation. The reduction in the operating costs of cultivation and harvest (i.e. energy, nutrients) are a further challenge. Cultivation and harvest are responsible for approximately 55 - 75% of the total operating costs for the production of fuels from algae.

The ecological assessment based on the primary energy consumption and greenhouse gas emissions (performed in a life cycle analysis) shows that a significant reduction of greenhouse gas emissions and the cumulative fossil primary energy demand in the replacement of fossil fuels is only possible when the energy demand is optimized in the cultivation phase and can rely to a considerable extent on renewable energy and re-use of waste heat (for example from a nearby power plant).

If compared to the corresponding reference fossil energy systems, the reduction of greenhouse gas emissions from the pathways using freshwater is about 40 to 60%, and 70 to 90% in the long term. Also critical for greenhouse gas emissions is the amount of nutrients provided (such as nitrogen and phosphorus). Combining algae cultivation with wastewater treatment plants the need of mineral fertilizers and of freshwater can be reduced considerably. Indeed the highest greenhouse gas reduction can be achieved growing microalgae in wastewater, leading to about 90% GHG reduction (95% in the long term).

Fossil primary energy demand for all the pathways can be reduced between 60 and 95% (85 to about 95% in the long term).

One advantage of fuels from microalgae is the lower space requirements if compared with land-based energy crops. For example, currently the footprint of algae cultivation for biodiesel is about 0.005 m^2 / $MJ_{Biodiesel}$ (about 0.003 m^2 / $MJ_{Biodiesel}$ in the long term), while the footprint of biodiesel from rapeseed is about 0.12 m / $MJ_{Biodiesel}$ (or about 0.09 m / $MJ_{Biodiesel}$ in the long run).

Building on the economic and environmental considerations, scenarios for Austria have been developed. Pathways leading to biodiesel, biogasoline, biohydrogen and biomethane (via HTG) were considered. It was assumed that a commercial plant using wastewater could produce biohydrogen and biomethane for approximately 0.04 PJ / a in total). For the long-term scenarios the analysis was based on potential investment locations and two variants were defined: use of power plants and industrial sites (Steel, P & P, cement industry) as sources of CO_2 (CO_2 requirement of 0.5 to 1 million tonnes / year). In the long term scenario, about 20 - 50 PJ / a (from biodiesel, FCC products, biohydrogen or biomethane) would be produced and therefore greenhouse gas emissions reduced by about 1.2 -3.0 million t CO_{2-eq} /year.

In order to move to large-scale applications in Austria significant successful developments are still needed, in particular in relation to the auxiliary energy required for the cultivation of algae.

11 Conclusions

Algae have several characteristics that offer improvements in sustainability that are unique to this species in relation to other bio-based production systems:

- Algae are grown in water containing systems, do not require fertile agricultural land thus cultivation systems can be located on marginal land. Protection of the ecosystem, soil integrity and alternative uses of these lands has to be balanced against the alternatives of algae-based production, which often will require existing agricultural land or the conversion of productive ecosystems. Furthermore, seaweed can be cultivated without the use of land, but also here the ecological impact should not be neglected.
- Algae can capture CO_2 from combustion gas; in fact adequate CO_2 supply is essential for high productivity. Algae can even capture other pollutants from combustion gas, so whenever possible, algae cultivation could be co-located with CO_2 emitting industries.
- Many algae can be cultivated in saline water. Fresh water is the natural resource with the highest consumption, and increasingly scarce. Large scale concepts should only focus on salt water use, keeping in mind the disposal issues of wastewater and salts.
- While dilute nutrient sources like wastewater or eutrophic surface water are not suitable for agriculture, algae can make efficient use of these sources, while providing the service of pollutant removal and/or nutrient recycling.

These characteristics have led over the last years in an exponential growth of interest in the topic but also at times a negative perception surrounding commercial efforts. The fact is that no commercial algal energy producer exists yet, and high-yielding terrestrial crops like sugarcane in Brazil will not easily be overtaken by algae in terms of energy balance, that a positive energy balance of energy output versus energy input for operation and the production of the cultivation system, and the subsequent financial returns to cover the process costs and the initial investment for the cultivation system are very challenging. At present, economy of scale differences between the algal oil industry and the petrochemical industry are significant and will require important investment for liquid algal biofuels production. The present microalgae manufacturing industry is very small at only 5000 tons/year and is almost completely devoted to synthesizing high value nutraceutical products and not extensively engaged in the mass production of high oil-containing microalgae.

However the algae for energy industry is moving very fast and investing a lot in R&D for algae production and harvesting, both in the so-called “upstream” side and the “downstream” side, i.e. the transformation of algae into commercial energy carriers.

This thesis includes part of the work done within the project Algae&Energy Austria, where an extensive literature review of the state of the art of conversion of algae in energy carriers was undertaken. Although scarce, the data available suggests that a number of thermochemical processes are technically available and have been already tested for this end. Combustion, gasification, pyrolysis and hydrothermal processes have been analysed for the conversion of the whole algae into liquid, gaseous or solid biofuels. Further, hydroprocessing and fluid catalytic cracking of raw algal oil for the production of valuable commercial biofuels have been analyzed.

Although combustion and co-firing of microalgae is possible, their very high water content, and the need to dry them before combustion, make this process unattractive from an energy balance point of view and from an economic point of view. Other low-value biomass feedstocks would be preferable for combustion, while, given the high cost of algae production and their uniqueness make them more suitable for other conversion processes, possibly associated with the production of fertilizers, food, feed, nutraceuticals or bio-materials.

Similarly to combustion, gasification of microalgae is technically possible but the need of drying algae before the process and the subsequent negative energy balance that may result is the main bottleneck of this pathway. Gasification is a quite flexible technology as it can process very different biomass types. It would be more suitable to apply it to more low-value bioenergy feedstocks like wood or other residues to transform these into heating gas. The very high temperatures and pressures required for gasification make the process particularly energy intensive and hardly viable from an energy point of view. For the production of gaseous fuels, hydrothermal gasification at relatively lower pressures would make more sense for treating small sized humid feedstock like microalgae.

A lot of R&D is still underway regarding the pyrolysis of biomass and several lab-scale test plants exist. Pyrolysis of algae has also been investigated with good results from an energy and economic point of view for the production of bio-oil. However, as well as for other feedstocks, the quality of the final oil obtained is still too low to be used as liquid biofuel commercially. Pyrolytic bio-oils are acidic, unstable, viscous, and contain traces of toxic contaminants produced during the process. Similarly to gasification, hydrothermal processes, more suitable for processing very wet biomass, seem more appropriate for the production of liquid bio-oil. This latter pathway has been fairly investigated for processing wet algae, but the low quality of the final oil which is unstable and contains traces of water, is hardly usable. These low-quality oils would necessarily need upgrading in order to be used commercially as energy carriers but research on hydroprocessing of pyrolytic oil is at an early stage of development.

Among the thermochemical processes analysed for the conversion of the whole algae into energy carriers, hydrothermal gasification and hydrothermal carbonization appear to be the most suitable and promising. These processes are very suitable to process wet biomass with up to 85% of water content, as the water itself at high temperatures and pressure facilitate the cracking and conversion of biomass into gaseous, liquid or solid biofuels. Varying pressure, temperature and residence time of the biomass, it is possible to maximize gaseous or solid fuel production. The resulting gas is rich in methane and hydrogen and these can be further separated and sold to the market. Recently a number of research centres and private companies around the world are piloting hydrothermal carbonization and the resulting biochar seems to have good properties, comparable and sometimes superior to conventional charcoal. Effluents resulting from hydrothermal processes are very rich in nutrients and can be re-used as fertilizers, for example of the algae cultivation medium itself. Together with biofuel production, the process results in a large quantity of warm water to be disposed. This relatively low temperature water (ranging from 70 to 200 degree, depending on the hydrothermal process) can be used for district heating, space heating, aquaculture heating or similar uses. While hydrothermal gasification plants still exist at the piloting stage, some commercial hydrothermal carbonization plants are already running in Europe.

In the context of the research project Algae&Energy Austria, hydrothermal processes have been analysed with the algae species *Chlorella* and *Scenedesmus* and the energy balances and other environmental and economic performance have been compared with other non-thermochemical processes for the valorisation of algal biomass. The result of this study, briefly explained and reported in this paper, highlight how hydrothermal processes favourably compare with others, and how some technological improvements that can be expected in the medium-long term could improve the (already positive) performance. Hydrothermal conversion is an exothermic process meaning that the energy output of the system is higher than the usable energy that enters the system.

Alternatively to the conversion of the whole algae to energy, it is possible to extract the raw oil from algae through mechanic or other methods, and then upgrade it to commercial high quality biofuels. Plant oils can already be upgraded today in commercial refineries through hydroprocessing or FCC. Bio-oils are normally processed together with conventional fuels for the production of diesel, gasoline and other valuable liquid and gaseous fuels because upgrading plants are costly and in order to be economically viable it makes sense to make use of the existing facilities available at refineries. Hydroprocessing of plant oils is already a commercial reality and R&D is currently underway to extend it to algal oil. The initial results seem to confirm its suitability. Plant oils can also be refined in conventional FCC plants and a number of successful pilot tests have been undertaken by the Vienna University of Technology using different plant oils. The comparison of the characteristics of *Chlorella* and *Scenedesmus* raw oil with common plant oils, suggests that their composition (e.g. in terms of saturation of fatty acids) is similar to rapeseed oil (rather than palm oil or soybean oil) and, therefore, a high quality gasoline rich in aromatics can be expected from FCC of algal oil.

Common to all algae-to-energy pathways, a major bottleneck remains the energy and economic cost at the cultivation stage, which could be significantly improved with smart harvesting and biomass separation technologies, and which makes algae-to-energy hardly viable from an economic point of view. Hydrothermal processes and the use of raw algal oil in refinery facilities seem to be a promising thermochemical conversion pathway for the production of commercial fuels and other energy carriers. The characteristics of harvested algae *Chlorella* and *Scenedesmus* and their high water content after (conventional low energy intensive) separation phase make hydrothermal gasification and carbonization particularly suitable if compared with other thermochemical, biochemical and mechanic conversion processes as well, as demonstrated within the Alga&Energy Austria project. Hydrothermal processes perform better from an economic and energy balance point of view, and the utilization of waste heat in the form of warm water resulting from the process can even improve the overall performance.

FCC of algal raw oil, possibly blended with conventional fuels, is also a very promising route for the production of gasoline and other valuable fuels, although this was never tried in practice according to the literature available. The quality of fatty acids and some characteristics of the oil extracted from *Chlorella* and *Scenedesmus* make FCC a suitable route for the valorisation of algal raw oil.

The research highlighted that important bottlenecks exist and high yields and large scale production can only be successfully achieved through a comprehensive and well-funded RD&D programme which promotes business models that look not only at the potential of algae for energy production to displace the transportation fuels market, but also consider the cascading of algae chains with other higher-value products in order to make the economic viability achievable. Research and development is required in all areas of the process chain, from the raw materials (e.g. algal biology, species selection, optimization of growth) to cultivation (e.g. optimization of productivity, energy, water, nutrient requirements), harvest (e.g. optimization of technologies), transformation (e.g. selection of suitable technologies) to integration into the existing infrastructure and production systems (e.g. for CO_2 supply, water supply, co-production).

Global efforts to develop the production of algae biomass as a raw material for the industry and energy sector and development of efficient, economical, ecological, sustainable production technologies for algae-to- energy can be effective in the medium to long term. Essential for a commercial-scale implementation is to optimize the cultivation and processing of algal biomass reducing the auxiliary energy demand and the cost of growing algae. Under these conditions it is currently expected that cost of algae bioenergy would be produced competitively in Austria. Likewise these considerations can apply to other industrialized countries under similar conditions.

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