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Modeling and integration of a closed loop system for production of SNG from microalgae

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Modeling and integration of a closed loop system for production of SNG from microalgae

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A 30 ECTS credit units Master´s thesis

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ABSTRACT

In recent years 3rd generation of biofuels are recognized as one of the most promising pathways for the reduction of greenhouse gases and the production of renewable energy.

SunChem is integrated biological and thermal process in which main aim is to obtain methane, and also electricity and heat (1). Biological part is performed in photobioreactors (open or closed) and thermochemical process is in fixed bed catalytic gasification (HTG). SunChem system is developed in terms of thermochemical performance (laboratory scale HTG plant in Paul Scherrer Institute premises) on wet feedstock (15-30% dw. biomass), but there is not mastered biological part. Lab scale experiments of closed PBRs are just starting on EPFL.

I concentrated on closed loop system, which means that nutrients, water and carbon dioxide is looped in SunChem system with potentially low environmental impact (relation to open ponds).

In my master thesis was performed analysis of microalgae strain characteristics. Next was developed biological part of microalgae engineering, where was analyzed two types of closed PBR cultivation. Microalgae cultivation was performed in terms of scenarios, which aims were set up as carbon dioxide utilization and bulk biomass production for feedstock purposes. Obtained results of high productivity scenario, was integrated in thermochemical process of HTG and modeled by Martin Gassner. There was also performed economical estimation of investment motivation in terms of biological part and thermochemical part of SunChem system.

The main challenge in SunChem system is to increase its efficiency and decrease the cost of production and conversion into useful energy carrier.

Proposed system SunChem is very promising for Poland as it is combing possibilities of multiple system performance in field of biological, carbon dioxide mitigation and energy carrier production.

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1 INTRODUCTION

Renewable energy and fuels during last few decades gain support in environmental protection subject and energy production, as sustainable use of earth sources is step towards sustainable growth of civilization.

1.1 Motivation

Motivation of development is based on possibility of shortage of conventional energy sources but also, environmental pollutions especially GHG negative influence. In the picture is presented percentage share of greenhouse gases in global scale (without influence of water vapor).

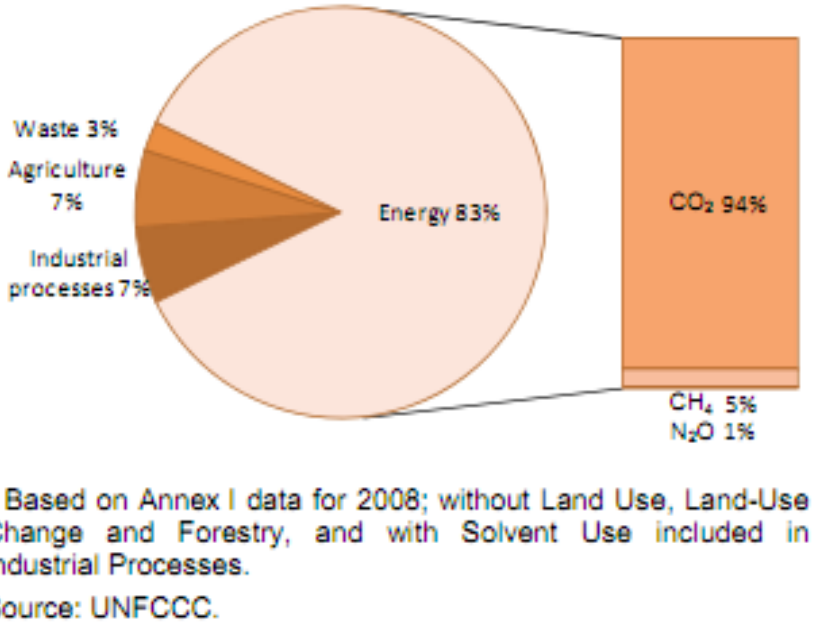


Figure 1 Shares of anthropogenic greenhouse-gas emissions in Annex I countries, 2008

(3)

Highest share of GHG is on carbon dioxide part, which is rapidly growing since industrial revolution in 18th to 19th century (IPPC reports). Methods of overcoming these problems are to capture and store CO2 in ground or in deep water or to biofix it in plant.

According to Kyoto protocol (1998) counties which signed documents (only USA not intendant to) are obligated to aim at '*stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system*'. There were introduced many schemes (Joint Implementation, Clean Development Mechanism) which are supporting this issue.

European countries set up climate – energy packet in other words - „3x20", which was approved by Council of Europe in march 2007 and presented in last version in 23rd of January 2008 r. by European Commission. Documents contain four major regulations such as:

- Directive EU ETS 2009/29/EC - to improve and extend the greenhouse gas emission allowance trading scheme of the Community
- NON ETS decision - to reduce their greenhouse gas emissions to meet the Community's greenhouse gas emission reduction commitments up to 2020
- Directive RES 2009/28/EC - on the promotion of the use of energy from renewable sources
- Directive CCS 2009/31/EC - on the geological storage of carbon dioxide

All of them got aim to:

- lower use of energy in UE by 20% till 2020 in accordance to 2005 as a base year
- lower emission of GHG by o 20%
- 20% of renewable energy share in overall end use of energy till 2020 r.
- 10% of biofuel share in transportation fuels by 2020 r.

Obstacles which are connected with production of renewable energy and biofuels can be differing in terms of environmental and technological. Environmental issues in general view are based on problems with food vs. fuel competition, sustainability issues, land use profile (displacement of cultivation, soil erosion, deforestation, biodiversity related problems), surplus water use, impact on natural reservoirs, irrigation concerns and most commonly discussed problem – use of genetic engineering. Technical concerns which need to be evaluated are corresponding to carbon emissions, energy efficiency/balance level, related cost and infrastructure. Biomass is additionally characterized by zero net carbon cycle addition, low sulphure dioxide and ash content level than conventional energy carriers.

There is a need to find and perform on technology which is addressing all these points.

As an answer to mentioned concerns there is waste or microalgae biomass. Wastes are commonly available sources and if not landfilled, they need to be specially pre-treated which is economically and energy absorbing (e.g. MSW - sorting, grinding, drying etc.).

Second possibility is microalgae, which is promising biomass source as they are highly productive (most photosynthetically efficient organisms) and thanks to closed loop PBR system production are giving possibility of cultivation with low consumption of water, nutrients and land use requirement. Additionally thanks to ability of biofixation of carbon dioxide they are also serving as natural carbon sinks.

Microalgae can be converted into energy or energy sources as they are characterized by various biomass characteristics (high level of lipids/ carbohydrates) which varies by each strain. However, methane is most interesting energy product as it can be easily fitted into existing infrastructure and it is on mature level of use. Energy and energy products from microalgae can be obtain by biochemical (anaerobic digestion with 25-35% thermal efficiency) or thermochemical processes (4). Among the thermochemical routes, hydrothermal gasification is a promising technology, because it allows effective conversion of wet biomass without drying.

Conversion of microalgae into energy or energy products in path of HTG can be compared with other processes which are presented in table 1.

Table 1 Conversion of microalgae into energy or energy products

Characteristic	Conventional gasification & methanation	Anaerobic digestion	Hydrothermal gasification
Feed type	Wood, grass (w_{water} < 15%)	Manure, household residues, sewage sludge, marine algae	Most wet types (w_{water} > 60%)
Thermal efficiency (biomass to SNG)	54–58%[b] (absolutely dry wood)	25–35%[c] (<8 wt % DM manure)	62–71%[d] (manure, wood)
Residence time[a]	<10 min.	20–33 days[c,e]	<30 min.
Technological readiness	Good (PDU 1 MW_{SNG} in Güssing 2008)	Very good (commercially available)	R&D (PDU planned 2010)
Advantages	High efficiency for dry biomass, close to commercialization	Established commercialized, fertilizer by-product	Full conversion, high efficiency, fertilizer by-product
Drawbacks	Low efficiency for wet biomass	Residues, low efficiency, plant size, requirement of co-substrates	Technical barriers to be solved

(4)

Thermo conversion of microalgae in process of hydrogasification got several advantages such as: ability to perform on highly moisture biomass, no char formation during process and also extremely high productivity in comparison to terrestrial plants. Direct conversion of microalgae into methane in process of HTG is achieved in process of

- Hydrolyzing biomass into liquid aqueous phase at high pressure (250-350 bar, 200-380C)
- Precipitation and recovery of inorganics as salts (supercritical water conditions 400-550C)
- Gasification and hydrolysis of product over catalyst - Ni and Ru (400C)

SunChem is a project in which two Swiss companies - Paul Scherrer Institute (PSI) and Ecole Polytechnique Fédérale de Lausanne (LENI-EPFL) are cooperating in. Paul Scherrer Institute (PSI) experimentally develops catalytic hydrothermal gasification process. Industrial Energy Systems Laboratory of the Ecole Polytechnique Fédérale de Lausanne (LENI-EPFL) is working on thermo-economic model of process to investigate optimal process design. Project is set up and planned for next 5 years during which need to be fulfilled points such as (5)**:**

- construct and run a mobile plant (ca. 1 kg/h), which will be able to convert microalgae slurries to synthetic natural gas (Bio-SNG), via hydrothermal processing. This plant will be installed as a mobile unit (i.e. in a container) in order to perform methane production tests at different existing microalgae production facilities worldwide
- construct open ponds to test the performance of different algae strains in real scale at the same geological and meteorological conditions
- improve design and construction of bioreactors for optimal cultivation conditions
- realize the process system design and engineering on pilot scale and real scale
- perform, based on own data, a sound and comprehensive assessment and evaluation of the entire production system, including all production steps (from biomass production to fuel delivery)

Biotechnological approach towards production of energy and energy carriers is gaining more interest due its huge possibilities. In SunChem project biomass production is directly coupled with thermochemical process of hydrogasification to obtain grid quality methane. Concept is novel as till this point PBR and HTG were decupled and analyzed separately.

Microalgae are cultivated in closed PBR, next they are dewatered and directed towards preheater, salt separator to catalytic reactor they are converted into valuable energy carrier – methane. Process is novel and promising; however there are several issues which need to be developed. Most important is to tackle difficulties connected with efficient conversion of microalgae biomass to biofuel.

Major issues which need to be overcome are connected with mastering of biomass production part, in which is used closed PBR system type. Type of selected biomass strain and used bioreactor is crucial for overall performance of project. It got influence on productivity and therefore obtained methane yield and amount. Second crucial issue is coupling of PBR with HTG in order to obtain optimal process design.

SunChem project is not only attractive from renewable fuel/ energy source point of view but also from Kyoto protocol carbon dioxide mitigation site.

Thanks to use of bio methane origin from *SunChem* process as an energy carrier in Poland it is possible to decrease carbon dioxide by 0,24 tCO_2/capita (population of Poland 38,5mln) **(6).** Presented number of CO_2 saving can be higher when CO_2 sequestration at the end of the *SunChem* process would be performed.

Level of emission in Poland in 2008 was 323,83 million tons of CO_2 (7) which is 8,4tCO_2/capita. In conclusion SunChem process is promising technology which can lower carbon dioxide emission by 3,14%.

1.2 Critical view on the SunChem system

SunChem is a project which is based on microalgae biomass source cultivation in 1) open ponds or in 2) closed type of PBR. Second system is more sustainable as it giving possibility to lower demand of nutrients, waste water, water and higher level of uptake carbon dioxide (source).

System is characterized by several disadvantages which are considered as weak points. They need to be overcome and developed before commercial large scale introduction into industrial system.

One of most inhibiting points in commercial development is formation of salts, which are precipitating in process of salt separation before heating in catalytic reactor. Process of SunChem is on its first steps of development, there are so far no available experimental data concerning composition and amount of obtained salt brine (except stechiometry calculations, no real data performance). Additionally process itself of complete salt separation is not mastered. Small particles of salts got negative influence on catalysis in reactor HTG part of process. Low pH and organic material is also negatively influencing corrosion of reactor. Slats can plug or poison catalyst, so chemical reactors are defected. This got direct influence on methane conversion and its obtained yield.

Another withdrawn is high requirement of water, nutrients and energy for system performance. Even thought, there is closed loop type of process need of nutrients are need

in considerable amount. As an example based on chemical formula $CO_{0,48}H_{1,83}N_{0,11}P_{0,01}$ of microalgae, nitrogen requirement is estimated on 8 to 16 tons of nitrogen/hectare in a year time. Given number is extremely high it is 55 to 110 times higher than for estimated need of fertilizer for rapeseed **(8).** Proposed process of recycling of nutrients in a closed loop system is required to lower economic and environmental negative impact.

Next, there can be differed problems connected with microalgae selection. Characteristic of microalgae varies in terms of strain but also between cultivation type (continuous, PBR type etc.) in one strain. Several factors got influence on obtain biomass material such as biotic and abiotic factors. It is not easy to obtain same chemical formula (lipid and carbohydrate yield) of cultivated biomass as it varies in many terms. In conclusion chemical formula got influence on final product – methane yield. This part need to be developed as it is crucial for production purposes. In literature it is possible to find several characteristic (growth, carbon dioxide uptake) for one strain and all of them will be correct. It is also important to select microalgae that are resistance to harsh environmental conditions and most important is characterized by high productivity.

Harvesting and dewatering of biomass is high energy consuming. In terms of harvesting its type depends on density, size of microalgae, and value of the desired products. In all of possibilities process can be based on use of additional chemicals (fluctuation) and mechanical energy (collection after sedimentation). Small particles of microalgae are easier to coagulate and harvest, bigger ones need to be proceeding in sedimentation procedure which requires time and also additional reactor.

Dewatering of microalgae is based on mechanical performance without heat addition. This part needs high level of electric energy to perform.

In process of SunChem it is possible to add oil extraction process. This will positively influence economic benefits of project as price for high quality of products used as human nutrients, cosmetics can be as high as 215-2150 Euros per kg of algae (Dunalliela Salina) (look at table 10 chapter 2.5). However, circulated effluent from catalytic reactor to PBR, could have negative influence on growth performance of microalgae. Nickel (used catalyst) in considerable dose is toxic for microalgae a sit got negative impact on cell division which result in lower cell division. Issues which got influence on toxic character on microalgae are mentioned in chapter. Lethal dose for microalgae usually vary between species and also within one species in order of magnitude (4). In first phases should be provide optimal conditions to obtain maximal productivity of culture. Additionally products (oil for pharmacies and cosmetic companies) that would be obtained from biomass would have toxic performance on organisms. Heavy metals are accumulated by microalgae, in most cases they are not essential for growth. After treatment they are still existing and can be used only in production processes (not even as food for animals) **(9).** Growth rate is important for production and need to be as high as possible. Due to mentioned, there are several reasons to work on genetically modified biomass suited especially for process. However, GMO kind of biomass when released can have negative impact on bicenosis. Additionally products from GMO microalgae can also negatively influence organisms. Aim in SunChem process is to select strain which can fulfill most requirements.

Additionally what is most problematic for system is that so far considerable production of microalgae is not effective in terms of size of investment (ha) and required number of units. In Gattiker M.Sc. 2009 which considers open pond cultivation, highest production in year time was estimated as 51 870 tDW/year, where required number of units were 4731 and land requirements were 2020 ha. This got huge impact of project economics and LCA

in terms of benefit for environment. Produced energy product methane was estimated as 199 GWh.

1.3 Points to develop

Proposed drawbacks can be solved by reasonable solutions.

In my thesis I will propose solutions for closed type of PBR used in process which will provide highest productivity level. I will concentrate on closed type of PBR with selected strain of microalgae. Strain will be chosen based on its growth rate, pH, temperature and CO_2 uptake level requirement. It is also necessity to analyze possibilities of waste water treatment from industrial type of processes but in thesis it is not performed due to lack of data. Selected microalgae strain should be commercially available and be characterized by resistance to harsh environmental conditions.

There is a need of modeling an optimal separation device which would provide very high salt separation and removal level. In terms of catalyst deactivation there is proposed to used surplus amount of catalyst which will be efficient, robust and not fast deactivated. In this process should be used corrosion resistance materials as they can accumulate in effluent and negatively influence after recycling microalgae growth. There are performed experiments based on ruthenium (Ru) catalyst use which seems to be more suitable in HTG process.

In terms of heavy metals accumulation in microalgae, there is need of creating additional reactor in which would be performed separated growth. Mentioned reactor would serve as strain culture only for production of methane. Diversification of microalgae (one with and without contact with heavy metals) is essential in terms of impact on human health. Pharmaceutical or cosmetic companies will not be interested in product which is toxic for their customers. Microalgae oil is considerably interesting for these companies.

Additional reactor is also essential to provide optimal environmental conditions in first phase of growth in culture.

Nutrients and water requirements can be lowered if recycle and reused by culture. This is interesting in terms of technological, environmental and economic (LCA impact). Closed type of PBR is giving possibility to obtain high biomass yield per ha per year with very low precipitation (kg of water per m2). Requirement of water in relation to productivity in PBRs is presented in figure 2.

Right selection of system for harvesting and dewatering is essential for project. Proposed solution for harvesting can be based on flocculation and then sedimentation. Proposed system is mature and broadly applied in waste water treatment plants. Dewatering can be performed in mechanical type of bond with additional press to dry weight of 20% dw. Higher level of moisture is lowering efficiency of methane production by system but is favoring energy requirements (vice versa).

In my master thesis will be performed modeling of both elements PBR cultivation of microalgae and HTG process for methane production which is interesting for overall system performance.

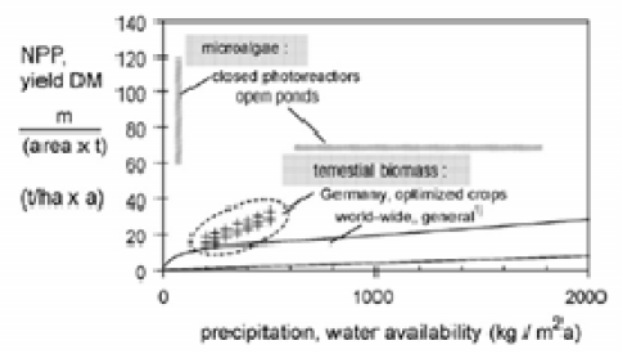


Figure 2 Effect of available water in relation to produced biomass yield

(10)

1.4 Advantages of SunChem

SunChem process can be applied to wide variety of biomass with high moisture yield e.g. manure or algae. This is considerably cheap biomass as it is not interesting for production of energy in most processes (apart fermentation and biomass degradation – biogas). Additionally microalgae are most photosynthetically efficient microorganism which is more productive than any of land plants or microalgae (4). It is characterized by high productivity of microalgae biomass, it can reach between 45-120 tons of dry biomass per hectare per year and an oil yield higher than 111 58’700 L/ha/a (30 wt. % oil content in biomass). It is described that in closed loop photo reactors productivity yield is – 150t/ha/yr. In open ponds in tropical areas productivity reach 25 - 30 t/ha/yr. There is no interference with land use for agriculture purposes as it was a problem in 1st generation of biofuels. There is also novelized problem with high need of water, as in case of open ponds evaporation. Closed loop system allows for recycling nutrients, water and gases with predicted low environmental impact. SunChem is a carbon-neutral process of producing SNG from renewables. It is possible to reduce carbon dioxide and other gas pollutants, process is separating its CO2, which can be reused for PBR or sequestered.
Process of HTG is providing no coke and tar formation as in catalytic reactor there is full mineralization of organic biomass. It is also providing higher yield of methane as final product as it is more efficient than classical methanisation process. System is suited to produce methane and electricity by combined cycle at the same time. Process is characterized by high efficiency of overall process (60-70%). Moreover, obtained product can be handled easily and used in existing gas infrastructure.
In the end it is worth to mention that coupling of biotechnological advantage with hydrothermal processing is a novel concept.

1.5 SunChem process – general sketch

The main challenge for algal biomass systems is to increase the efficiency and decrease the cost of production and its conversion into useful energy vectors. In recent years 3rd

generation of biofuels is recognized as one of the most promising pathways for the reduction of greenhouse gases and the production of renewable energy/fuels.

The dominating species of microalgae in commercial production includes strains such as Isochrysis, Chaetoceros, Chlorella, Arthrospira (Spirulina) and Dunaliella (Haiduc 2009).

The overall concept of SunChem process is presented on figure 3.

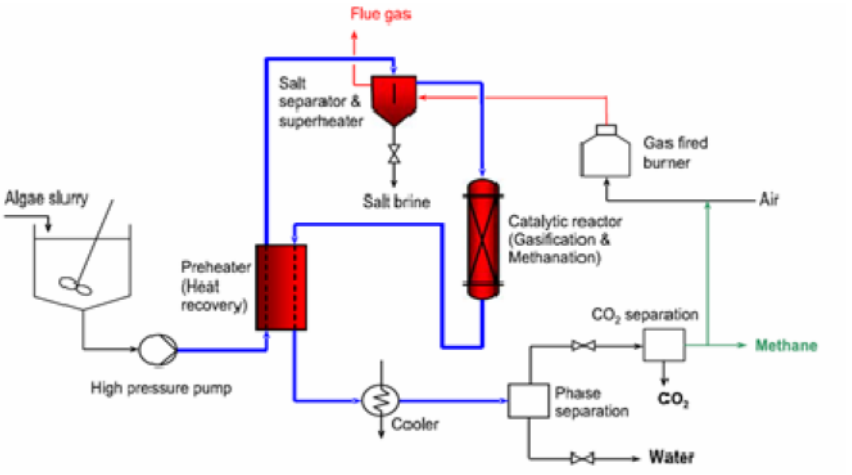


Figure 3 Process scheme SunChem

(4)

The process is based on steps as follows:

1. Production of biomass in photobioreactors (PBR)

Growth of microalgae is in optimal conditions to maximize possible growth rate. Microalgae fix CO2 and transform it into biomass and O2 by photosynthesis. Next biomass is harvested. In case of very intensive pumping its energy requirement starts to be very high and production of bio methane cannot compensate the electricity requirement (6).

2. Biomass dewatering

Water is removed mechanically from the biomass (ca. 20% wt. dry mass). Separated water is recycled to PBR. Microalgae slurry is pumped by high pressure pump (30 MPa) to preheater.

3. Hydrolysis

Slurry is preheated to just below critical point (a temp. 300–350 C) and kept above critical pressure of water (22.1 MPa), i.e. around 30 MPa. In consequence biomass is hydrolyzed and large molecules of biomass are broken ones which are accessible to catalytic reactor.

4. Salt separation

After hydrolysis biomass is heated above critical point to precipitate the salts to avoid catalyst poisoning and recycle the nutrients. Salts are thus precipitated in a separation

device, and then cooled and recycled as nutrients to the PBR. Separated supercritical fluid stream (organic fraction and water) is directed to catalytic reactor.

5. Gasification

The organic fraction of the stream is catalytically gasified under hydrothermal conditions to Bio-SNG. Main product from the reaction is methane, carbon dioxide and water.

6. Cooling and phase separation

After cooling and water condensing, carbon dioxide is separated from the methane. Carbon dioxide is separated as it is lowering LHV of obtained product and it is upgrating volume of biogas. This can be done by various technologies, e.g. Pressure swing absorption (PSA), physical absorption in a liquid solvent or at high pressure in water, and membrane separation. The separated carbon dioxide can be stored or recycled to PBR.

The depleted streams for the process can be used to cover the heating needs of the process and cogenerate electricity. The net production of methane is injected into the natural gas grid.

The overall process efficiency is estimated to 60-70% and defined by lower heating value of net produced methane and the lower heating value of the algae dry matter fed to the hydrothermal gasification [4].

1.6 Objective of work

Main objective of the study is to investigate the possibilities of combining two close systems, which are microalgae production, closed type PBR and its thermochemical conversion to synthetic natural gas (SNG) by catalytic HTG.

In thesis will be firstly analyzed available literature data on microalgae strain and modeling of its growth conditions based on obtained information. Next, there will be performed research on commercially available PBR with selection of most promising technology. Then there will be analysis of production performance based on selected microalgae and PBR. There will be performed thermo-economic modeling of a bioreactor system with respect to key design parameters. Next will be integration of the model with the process model of HTG. In the end will be performed evaluation and comparison with competing routes (e.g. open pond systems, conventional biofuel technologies).

Main assumptions that developed technology would fulfilled point which are characterizing sustainable development requirements in terms of considerable energy efficiency level and considerable economic evaluation.

The most important advantage of the master thesis is that the integrated design of the entire process is addressed, i.e. that the energy and mass balances from algae growth in bioreactor via hydrothermal catalytic gasification to carbon dioxide separation are simultaneously considered. System analysis and energy-integration will be done in a Matlab-based modeling framework OSMOSE developed at LENI-EPFL.

2 MICROALGAE BIOTECHNOLOGY – STATE OF ART

In this chapter will be discussed state of art of microalgae concerning its photosynthesis, kinetic growth and principles of cultivation.

2.1 Microalgae - introduction

Microalgae are unicellular and live unpaired or in short chains. For my master thesis most interesting are species of plankton and neustion which are characterized by size of 1 to 50µm **(11)** as they are characterized by highest productivity and photosynthesis performance in any type of plant – terrestrial or microalgae. Additionally they are able to bio fix high amount of carbon dioxide (1,9 of CO2 per 1kg of microalgae) with little requirement on purity and type of water and most important with low land use requirement. They can be differed in terms of group of photosynthesis organisms such as

- Prokaryote (e.g. Cyanophyta)
- Eukaryote (e.g. Chlorophyta, Diatomeae, Dinophyceae, Euglenophyta)

Microalgae can be differed by strains types which are near the surface of the water such as neuston and plankton. Neuston can be find on surface of water - phase between water and air (characteristic for open pond cultivation). Plankton can passively or actively move in water. This type of microalgae can be differ in terms of species such as: Chlorophyta, Coscinodiscophyceae (Bacillariophyceae), Dinophyta and Haptophyta.

In microorganism it is possible to differ ca. 28 different particles (C,H,O,N,S,P, CL, BR, I, F, B, Si, AS, CA, Mg, K, Na, Fe, CU, ZN, NI, CO, Mn, Al, SN, Mo, V, Ti) in which few of them are basic, building particles (C, H,O,N,S). **(12).**

Microorganism can be differed in terms of obtaining energy according to:

1)carbon uptake

autotrophs, heterotrophs and prototroph.

They growth is based on arability of carbon access. Autotrophs growth is depending on accesible of carbon dioxide.

2) energy uptake

phototrophs and chomotrofs

Phototrophs required in their growth sun energy.

3) donors of electrons

Litotrophs and organotrophs.

Litotrophs source of electrons are not organic type of source such as chemical compounds: CO, NH_3, H_2S etc.

Microalgae can be phototrophic, heterotrophic, mixotrophic and photoheterotrophic. Comparison of the characteristics of microalgae and their different cultivation conditions is listed in table 2.

Table 2 Comparison of the characteristics of microalgae and their different cultivation conditions

Cultivation condition	Energy source	Carbon source	Cell density	Reactor scale-up	Cost	Issues associated with scale-up
Phototrophic	Light	Inorganic	Low	Open pond or photobioreactor	Low	Low cell density High condensation cost
Heterotrophic	Organic	Organic	High	Conventional fermentor	Medium	Contamination High substrate cost
Mixotrophic	Light and organic	Inorganic and organic	Medium	Closed photobioreactor	High	Contamination High equipment cost High substrate cost
Photoheterotrophic	Light	Organic	Medium	Closed photobioreactor	High	Contamination High equipment cost High substrate cost

(13)

2.2 Photosynthesis in microalgae

Microalgae are phototrophic type of microorganism and their energy performances are based on process of photosynthesis. Photosynthesis is the process characteristic also for plants (and some bacteria's) during which light energy is converted into chemical energy and is stored in the bonds of sugar. Carbon dioxide is converted into sugars in a process called carbon fixation. In exemplary type of process is given in the picture 4.

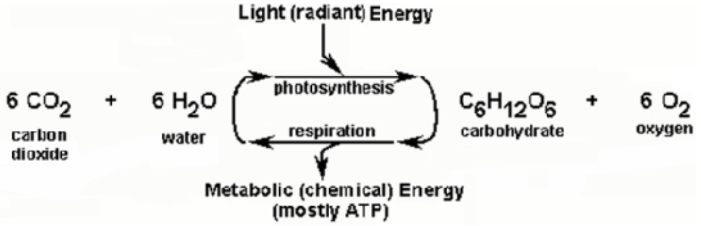


Figure 4 Photosynthesis

(14)

Photosynthesis is the opposite process to cellular respiration, where glucose and other compounds are oxidized to produce carbon dioxide, water, and release chemical energy. Photosynthesis process occurs in two stages, such as:

1) light stage

light-dependent reactions during which energy of light is captured and used to make the energy-storage (carbohydrates). During this stage microalgae is gaining sugar and release oxygen.

2) dark stage

called also light-independent reactions in which photons are not essential. During this stage carbon is captured and reduced from atmosphere thanks to enzyme RuBisCO (look figure

5). Process requires release of three-carbon sugars. In conclusion microalgae are lowering their weight but they are gaining carbon dioxide.

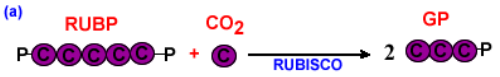


Figure 5 Photosynthesis

(15)

Microalgae are using much oxygen during this stage, in nature environment this time is deficit of oxygen in water.

Scheme of photosynthesis needs four photons for Photo-System I for water splitting to form a molecule of O_2 and additionally four photons are then required to Photo-System II to synthesize other four protons ($4H^+$) and CO_2 into algal biomass (CH_2O):

$2H_2O \rightarrow O_2 + 4H^+$ Photosystem I

$CO_2 + 4H^+ \rightarrow CH_2O + H_2O$ Photosystem II

(16)

In summary eight photons are required for completed process of photosynthesis.

Content of energy of one mole of 'CH2O' (ECH2O) is 468 kJ (Walker, 2009). Energy content of eight photons of red (680 nm) light (EP) is 1408 kJ. Photosynthetic solar conversion efficiency (npho) is 33%. However, 48% of solar energy is photosynthetically active radiation (PAR) and because 10–20% of the solar energy is lost by surface reflection, only 12.8–14.4% of solar energy (gtheo) can theoretically be converted into algal biomass (look table 3).

Table 3 Irradiation and photosynthesis balance

Symbol	Parameter	Value	Description
E_{CH_2O}	Energy required to produce algal biomass (CH_2O)	468 kJ/mol	One gram of glucose ($C_6H_{12}O_6$) releases 2813 kJ as heat. As glucose is made up of six molecules of CH_2O the energy content of CH_2O is at least 468 kJ $E_{CH_2O} = \frac{2813\ \text{kJ}(C_6H_{12}O_6\ \text{as heat})}{6\ \text{mol}\ CH_2O} = 468\ \text{kJ/mol}$
E_P	Energy value of a photon	~176 kJ/ photon	One photon of red light (680 nm) has an energy value of ~176 kJ. Eight photons (1408 kJ) are required for complete photosynthesis (PSI and PSII)
η_{pho}	Photosynthetic solar conversion efficiency	33.2%	$\eta_{pho} = \frac{E_{CH_2O}(468\ \text{kJ/mol})}{E_P \times 8\ \text{photons}\ (1408\ \text{kJ})} \times 100 = 33.2\%$
η_{par}	The fraction of photosynthetically available solar radiation (PAR)	~48%	The visible light spectrum (light wavelength of 400–700 nm) is only available for algal growth
L_r	Reflection loss	10–20%	Reflection loss at the pond water surface depending on solar angle and mixing conditions of the ponds
η_{theo}	Theoretical algal photosynthetic efficiency	12.8–14.4%	Solar energy 12.8–14.4% can be theoretically fixed by algae as chemical energy $\eta_{theo} = \eta_{par} \times L_r \times \eta_{pho}$
L_{sat}	Light saturation of algal photosystem	10–17%	Photosynthesis of most algal species is saturated at a solar radiation level of ~200 μmol/m^2/s, which is about 10–17% of summer/winter maximum outdoor light intensity
η_{max}	Maximum efficiency of photosynthetic solar energy conversion	1.3–2.4%	Maximum solar energy of 1.3–2.4% can be fixed by algae $\eta_{max} = \eta_{theo} \times L_{sat}$

Factor of light saturation level (Lsat) is dependent on algal strain and culture density. Growth of most algal species is inhibited by light levels above 200 lmol/m2/s, which is only about 10–17% of winter or summer solar PAR radiation.

Highest algal photosynthetic conversion efficiency (gmax) is only 1.3–2.4% of total solar radiation. **(16).**

Process of photosynthesis is taking place in organelles called chloroplasts (ca. 10 to 100 per cell). Chloroplast is pictured in the figure 6.

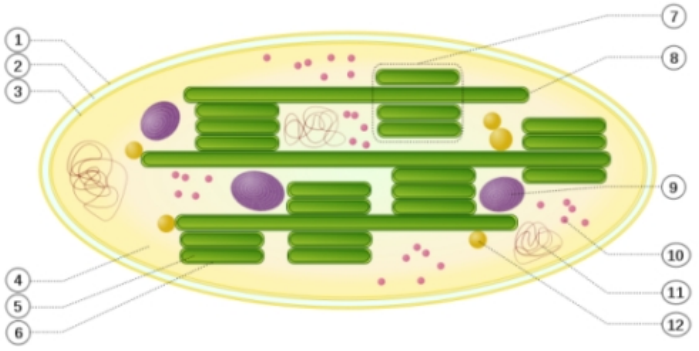


Figure 6 Chloroplast structure

1. outer membrane, 2. intermembrane space, 3. inner membrane (1+2+3: envelope), 4. stroma (aqueous fluid), 5. thylakoid lumen (inside of thylakoid), 6. thylakoid membrane, 7. granum (stack of thylakoids), 8. thylakoid (lamella), 9. Starch, 10. Ribosome, 11. plastidial DNA, 12. plastoglobule (drop of lipids) **(17)**

During photosynthesis microalgae use pigments to absorb the light by use of chlorophyll (green) or carotenes, phycocyanin, and xanthophylls which are all present in green algae. Phycoerythrin is in red algae and fucoxanthin is well recognized in brown algae and diatoms. Mentioned pigments are placed in antenna-proteins (light-harvesting complex).

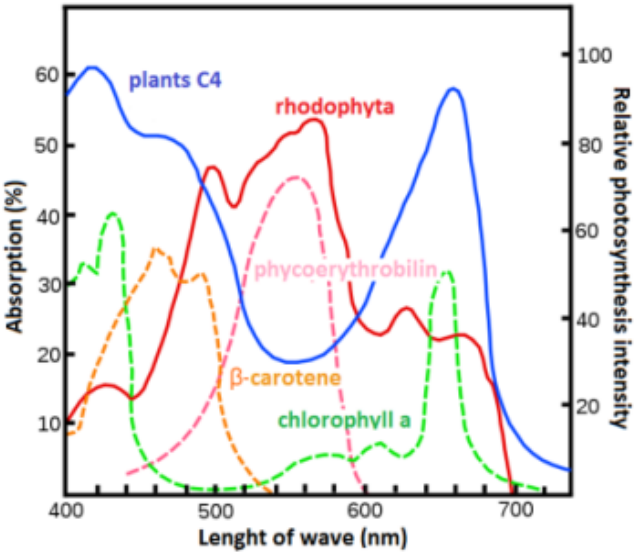


Figure 7 Light wave and photosynthesis intensity

Pigments are recognizing photosynthetic spectrum of wavelengths (picture 7). In green microalgae (Chlorophyceae) pigments are working on same basis as in plants (C3) - absorption spectrum for chlorophylls and carotenoids are peaking for violet-blue and red light. In terms of Cyanophyta mostly is used yellow light which is directed by pigments of Phycocyanin.

In red algae, the action spectrum overlaps with the absorption spectrum of phycobilins for blue-green light, which allows these algae to grow in deeper waters. Microalgae in not suitable light can chromatically adaptive **(17).**

Photosynthesis is related to many factors such as carbon uptake. Photosynthesis process is rising to point of light saturation.

Schematic photosynthesis in terms of plant of C4 and C3 is presented below.

1 – cell respiration (dark phase), 2 – light compensation point, 3 – point of photosynthesis saturation, 4 – start of photoinhibition

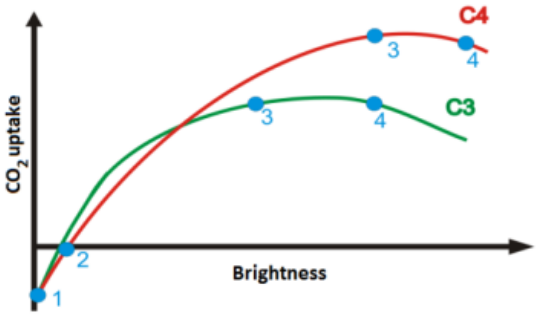


Figure 8 Process of photoinhibition

(17)

When sun radiation is not sufficient plants start to release carbon during cell respiration. Light compensation point (LCP) is when cells are up taking during photosynthesis and realizing during cell respiration same amount of carbon dioxide. When solar radiation is higher than LCP than photosynthesis intensity is much higher. Than point of photosynthesis saturation (PPS) can occur. If sun radiation is still present than photosynthesis system can be damage (picture 8) and carbon dioxide up taking will be lower. Photoinhibition is related to damage of photosynthesis system. Some of microalgae is accommodating to low level of light by accommodation by higher level of chlorophyll (Chlorella) or by reorganizing photosynthesis apparatus – speeding up photosynthesis process (diatom Cyclotella). Time for accommodation is estimated for ca. 3 weeks.

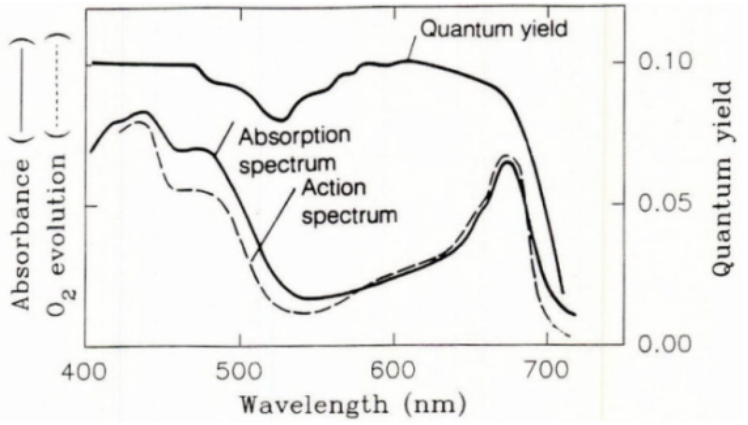


Figure 9 Absorption spectrum

Action spectrum and quantum yield (picture 9) for photosynthesis with the chloroplast (chlorophyll) absorption spectrum (quantum yield of photosynthesis is the moles of carbon fixed per mole of photons absorbed) (From Taiz and Zeiger, 1991 **(18)**.

In terms of plant performance atmospheric carbon dioxide on ca. 0,1% level is precursor of fair transformation of photosynthesis. When CO2 is too low respiration is releasing more CO2 than is assimilated in photosynthesis. Equilibrium of assimilation and releasing of CO2 is named compensation point of carbon dioxide (CPCO2). If CO2 level is too high it can be toxic for microalgae and photosynthesis can be much lowered.

Effect of carbon dioxide concentration on photosynthetic rate is shown on picture 10 for C3 and C4 crops (constant temperature).

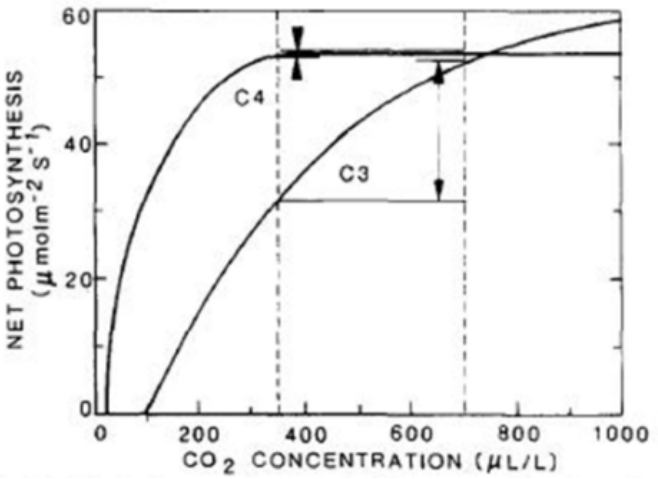


Figure 10 Photosynthesis and carbon dioxide uptake

Photosynthesis curves for plants C3 and C4 species (Taits & Zeiger, 1991). Dashed vertical lines at 350 and 700 µl/liter mark the current CO2 level and doubled predicted concentration (Houghton, 1990). Arrows indicate incremental rise in net photosynthesis due to the doubling of CO2 (Kimball, 1993**) (18)**.

In terms of microalgae in water carbon dioxide is dissolved in water can be in form of molecules or ions (HCO3- , CO32-). Microalgae got more complex interactions with dissolve carbon dioxide in water. Solubility of gas components as function of temperature can be presented as in picture 11.

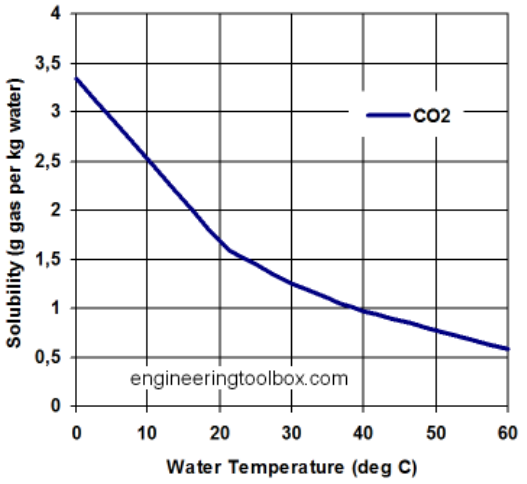


Figure 11 Solubility of carbon dioxide in water

(19)

Picture is showing how carbon dioxide is dissolved in given temperature. If pH of water will be lower than 6.35 there will be mainly carbonic acid accumulation and rest of products such as HCO3- and CO32- will not be sink and probably reveled to natural environment - atmosphere (can assumed that will be pushed into atmosphere – higher than 385 ppm of CO2).

$$CO_2+H_2O = H_2CO_3$$

Total inorganic carbon dissolved in water CT= [H2CO3] + [HCO3-] + [CO3--]

$$H_2CO_3 \leftrightarrow [H^+] + [HCO_3^-]$$

$$HCO_3 \leftrightarrow [H^+] + [CO_3^{2-}]$$

Concentration of dissolved inorganic carbon is presented on figure 12.

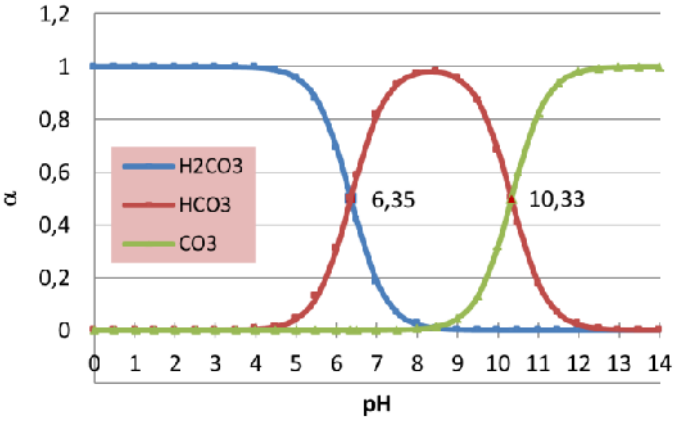


Figure 12 Concentration of dissolved inorganic carbon

Where: alpha represents fraction of carbon.

Photosynthesis organism can absorb (DIC) dissolved inorganic carbon on different rate. Most of them are capable of assimilation of not jet dissolved carbon dioxide (very low pH, caution of assimilation of nitrogen). However, only few are capable of assimilation of HCO3 (ca. pH 8,5) e.g. Chlorophyceae Hydrodictyon africanum, or some diatoms. Ability of assimilation of carbon in form of ion HCO3 is great because it is heightening level of carbon fixation in microorganism. HCO3 is not directly included in Calvin cycle but they are firstly dehydrated (carbonic anhydrase). Than in form of carbon dioxide they are used by RuBisCO. Microalgae cannot assimilate CO3 (pH higher than 9). However, microalgae which can assimilate HCO3 ion can also live for some time in waters which got pH 11. Temperature and level of CO2 got huge influence on photosynthesis rate of plants C3 and C4 as presented on schema in figure 13.

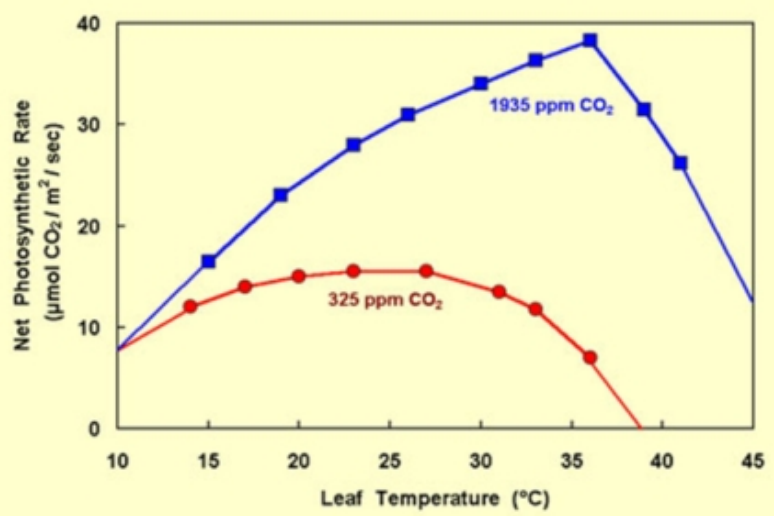


Figure 13 Schematic photosynthesis rate and influence of temperature for plants C3 and C4 in leaves.

2.3 Balance of microalgae kinetic growth parameters

To obtain optimal growth it is important to keep optimal length of stay in PBR, it is due to its specific growth conditions and metabolism of harmful complexes and substrates. In practice to describe growth performance of microorganism there is need to use generalization based on known data and relationships.

In biology microorganism growth can be described as growth of biomass and its volume, or as growth of its population.

Microorganism growth in my thesis is based on growth of population. Growth of population can be described as growth of biomass (g/dm3), as a difference between starting (X_o) and ending point of biomass growth (X) **(12)**

$$\Delta X = X - X_o \qquad \text{Equation 1}$$

Main attribute that should be described is specific growth rate (h^{-1}) which is describing growth of biomass in relation to overall growth of biomass s in related time.

$$\mu = \frac{1}{X} * \frac{dX}{dt} \qquad \text{Equation 2}$$

In terms of one cell biomass growth can be specified as cell number growth (h^{-1}).

$$\mu = \frac{1}{N} * \frac{dN}{dt} \qquad \text{Equation 3}$$

Very important is also efficiency of biomass factor which can be described as:

$$\frac{Yx}{S} = \frac{\Delta X}{\Delta S} \qquad \text{Equation 4}$$

Where delta ΔX is biomass growth and ΔS is substrate addition.

Other type of factor is biomass growth factor based on starting point of substrate addition.

$$YS_o = \frac{\Delta X}{S_o}$$ Equation 5

In terms of microorganism growth can be differ two types of growth which are unlimited growth or limited growth.

Unlimited growth of microorganisms is when there is no limitation of nutrients in PBR than growth of microorganisms itself, optimal parameters of cultivation are performed, and there is lack of inhibiting influence of external metabolism products from cells. Unlimited growth is an auto-catalyzing process in which speed of performance is based on auto catalyzing process – ability to self-reproduction. When cell number is N and biomass concentration is X than growth is presented as **(12):**

$$\frac{dN}{dt} = \mu max * N$$ Equation 6

or

$$\frac{dX}{dt} = \mu max * X$$ Equation 7

μ is specific growth rate which in these conditions is maximal specific growth rate – μmax. It can be also presented as:

$$N = N_{o*} \exp(\mu \max (t\text{-}t_o))$$ Equation 8

or

$$X = X_{o} * \exp(\mu \max (t\text{-}t_o))$$ Equation 9

So growth of population can be presented in function of time or mathematical interpretation.

When N – population growth is presented as biomass growth than time of generation can be described as where time of doubling of biomass production is t_d.

$$\mu max = \frac{ln2}{g}$$ Equation 10

or

$$\mu max = \frac{ln2}{t_d}$$ Equation 11

In terms of limited growth of microorganisms it can be characterized by state when there is limited concentration of fertilizer or when there is too much of metabolites or substrates. Lowering of substrates of basis is influencing growth of microorganisms in terms of Monod's law (which is coherent with equation of Michaelisa – Menten, which can be presented as:

$$\mu = \mu max * \frac{S}{S + K_s}$$ Equation 12

Where S concentration of substrate, Ks is constant of substrate saturation in which

$$\mu = \frac{1}{2} * \mu max$$ Equation 13

Mentioned relationship can be described as presented on figure 14.

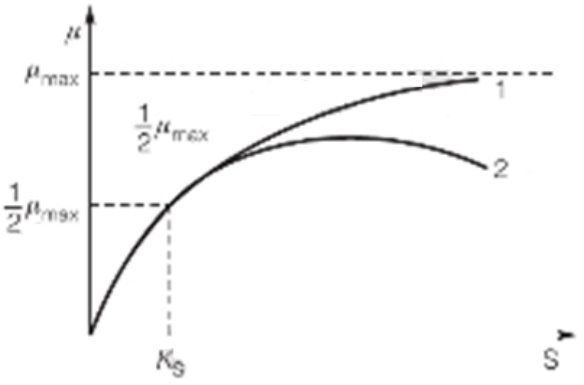


Figure 14 Dependency between specific growth rate and concentration of substrate (S)

1 – limiting substrate, 2 – limiting (small concentration) and inhibiting (high concentration) substrate

(12)

High substrate concentration is upgrading specific growth, but also some of substrates are inhibiting growth. In case of influence of inhibition (metabolites of microorganisms) it can be written in form of kinetic equation:

$$\mu = \mu max * \frac{K_p}{P + K_p}$$ Equation 14

P is concentration of products and Kp is inhibiting constant in which (Equation 13)

$$\mu = \frac{1}{2} * \mu max$$

In case when there are several inhibiting substances they can be described as resultant of them based on each of inhibiting factors. Substrates can be described as ones which are essential (source of carbon, oxygen and nitrogen) and ones promoting growth (mineral particles). This can be presented by Tsao-Hansen equation:

$$\mu = \left(1 + \sum_j \frac{k_j \cdot S_{E,i}}{K_{E,j} + S_{E,i}}\right) \prod_i \frac{\mu_{m,i} \cdot S_{S,i}}{K_{S,i} + S_{S,i}}$$ Equation 15

Where S_{si} is concentration of substrate which are essential to growth of microorganisms, S_{Eo} is concentration of substrate which are promoting growth.

When growth is limited by carbon and oxygen it can be described as combination of two equations e.g. Monods equation

$$\mu = \mu_{max} \frac{S_S}{K_S + S_S} \cdot \frac{S_{O_2}}{K_{O_2} + S_{O_2}}$$ Equation 16

Where so is concentration of oxygen in environment and Ko is constant saturation of oxygen.

Presented basic equation is commonly used due to their simplicity in description of microalgae growth. There are many more possibilities to describe specific growth but there will not be evaluated as there will be no sophisticated model performance. In table 4 is presented other possibilities of presentation of mentioned issues.

Table 4 Specific growth rate kinetics

Relation	Application	Mathematical formula
Monod kinetics substrate inhibition relation	Substrate at high concentration becomes limiting	$\mu = \frac{\mu_m S}{(K_s + S + S^2/K_I)}$
Monod Diauxic	Substrate 1 inhibit substrate 2	$\mu - \mu_{m,1}\frac{S_1}{K_1 - S_1} + \mu_{m,2}\frac{S_2}{K_2 + S_2 + S_1^2/K_I}$
Monod kinetics Multiple substrate	More than one substrate which is limiting	$\mu = \mu_m \prod_{i=1}\left(\frac{S_i}{K_i + S_i}\right)$
Monod kinetics Double substrate	Two possible parallel reactions in relation to substrate	$\mu - \mu_m\left(\frac{k_1 S_1}{K_1 - S_1} - \frac{k_2 S_2}{K_2 + S_2}\right)\left(\frac{1}{k_1 + k_2}\right)$

(12)

Application of presented relation can be used in various PBR types. Most commonly used kinetics and their application are presented in table 5.

Table 5 Kinetics growth rate and their application

Kinetics	Batch tank	Continuous tanks tubular or in series	Single tank constant	Fed batch tank
Substrate inhibition	Minimal initial concentration	Minimal overall concentration	Best	Best
Product inhibition	Best	Best	Minimal conversion	Minimal conversion
Productivity dependent on environment	Temperature change, applicable	Possible	Not suitable	Best in concentration change

Kinetics	Batch tank	Continuous tanks tubular or in series	Single tank constant	Fed batch tank
Zero order	Applicable	Applicable	Applicable	Minimal conversion
First order	Best	Best	Minimal conversion	Best

(12)

2.4 Principles of microalgae cultivation

Influence on growth of microorganisms can be differ in terms of biotic, where got influence biological factors or abiotic where major influence origin from physical and chemical basis. Below are described issues which got highest influence eon cultivation of microalgae in PBR. On growth of microorganism got influence temperature which is most important environmental factor. It is influencing specific growth rate of microorganisms, its chemical composition and also enzyme activity. Moreover, it got influence on substrate fertilizer uptake. Each strain of microorganisms is characterized by three major temperature characteristics – min, optimal and max. Above minimal temp and in optimal temperature growth is the fastest, generation of biomass is maximized and its time is shortest. Below and above min and maximum temperature growth of microorganisms is not possible. Relation is presented on schema on picture 15.

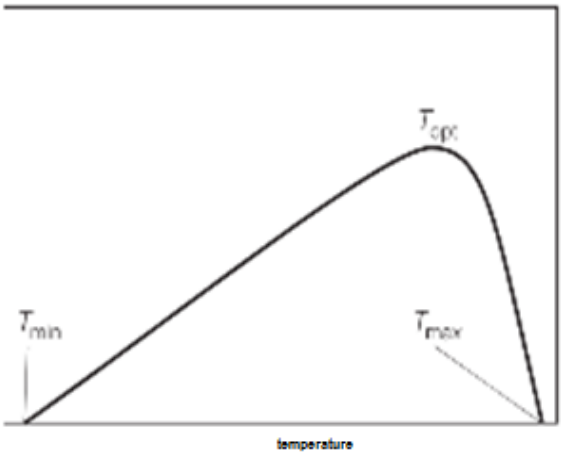


Figure 15 Influence of temperature on specific growth rate of microalgae

(12)

Most microorganisms can be differed in terms of temperature range:

- Psyhophiles – optimal temp range below 15 C,
- Psychrotofes -optimal temp is 20-25 C,
- Mezophiles – optimal temp range 20-45,
- Thermophiles- optimal temp growth above 60 C

and hipertermophiles.

Second most important influence got pH=-log(H+). Each microorganism is able to perform in characteristic range of temperature. Same as in term of temperature there is min, optimum and max pH. There is possibility to differ:

- Neurophiles – pH range to neutral 6,5 to 7
- Acidophilus – pH range below 4
- Alkilophilus – pH range pH above 8

Next factor is oxydoreductive potential of environment which is ability of releasing electrons or its receiving. This potential is important factor in microorganism specific growth rate. High oxydoreductive potential is characteristic for environment with influence of oxygen and low in anaerobic environment. There is possibility to differ:

- Obligated anaerobes
- Relative anaerobes
- Aerobes – microorganism which need to perform in presence of oxygen

One more factor that is worth to mention is activity of water in environment. Life performance of microorganism is based on level of available water. This factor can be described as pressure of given substance in relation to pressure of pure water, characterized by:

$$a_w = \frac{p}{p_o} = \frac{N_2}{N_1 + N_2}$$ Equation 17

Where p is described as pressure of substance, p_o is pressure of pure water and N_1 is number of moles of substance and N_2 is number of moles of water.

Irradiance is important in terms of photosynthesis influence. Low radiant of sun is shining is influencing low losses of reflection - when irradiance is on 90 degrees there is lowest losses yield of irradiance. In water some of irradiance is also loss in terms of small particles and suspension. Diffusion of irradiance can be 25 % of obtained irradiance absorbed by water. Intensity of light is inhibiting with depth of water. Microalgae's are photoautotrophs which are influenced by solar energy – for them depth of 0,5 till 2 meters is described as optimal.

Careful design in PBR of movement of water is influencing homogenous temperature, substrate and mineral particles.

PBR is not only serving as culture breeding reactor but also as a waste treatment plant for effluent origin from after processes. Waste water treatment with use of plants is used mostly in countries which are characterized by warm and average climate in summer time. Differences in profile of waste treatment in amount and type of accumulation of different plants are differing not only in terms of type of plant but also in terms of growth rate, yield of tolerance of different chemical compounds and also overall condition of plants. Abiotic conditions such as: temperature, pH, concentration of ions, synergic and antagonism influence of different particles and biotical influence which is mostly recognized in open ponds systems but not in closed PBR.

Accumulation time of particles such as heavy metals and others are not for infinity, time of accumulation differs in terms of plant basis and also biotic and abiotic terms. Heavy metals

are accumulated in plant cells in active or passive way. Accumulation can be differed by its type such as active accumulation where uptake is based on energy use of microorganism, they are metabolically active. Another possibility that can be differed chemical reaction type, such as oxidation and reduction reaction. Another possibility is to passively accumulate heavy metals, without use of energy; they are based on physiological processes. In terms of passive accumulation, mostly heavy metal absorption occurs in cases when metals such as: lead, molybdenum and nickel are uptake. They are mostly not essential for growth of plant so they are not needed. However, their concentration i plant cells can be very high.

Uptake of heavy metals is based on cell reactions which are not inside - thanks to reviled metal bio complexes and thanks to bio fixation of metals on cell wall (biofixation).

Heavy metal uptake depends on their environment interactions (degree of oxidation and type of chemical compound in which they are built in). There is also possibility to differ interactions between up taken heavy metals. Some heavy metals are taken in synergic way – they are supporting uptake but some are antagonism way - one metal can stop of up taking of other metal and can be precipitated. Heavy metal uptake from environment depends on its pH and temperature. Microalgae have possibility to uptake much more particles than C4 plants. There is general trend that less complicated and evaluated are plants (algae) than they have less complex physiological barriers and heavy metal uptake is passive. Heavy metals are returning to environment when they are decomposing. High heavy metal concentration in environment is mostly affecting microalgae photosynthesis, also it got negative influence on physiological performance and harms it. High influence and accumulation of heavy metals in plants cannot be used by humans but they can be used as feed for animals or as plant for fertilizers basis, substrate for biogas production – industrial purposes (Kowlaik 1997). Microalgae which treat after process effluent cannot be used by humans and should be separated by oil extraction process.

Inside accumulation of heavy metals is in terms of graduate process which is performed in steps. Heavy metal must be in form of easy accumulated particles. Plants are accumulating metals which are essential to perform but also additional not needed heavy metals. In first step heavy metals are absorbed by ligands of external cell membrane with which they are creating complexes. In second step external cell membrane is changing its permeability. In third last step, heavy metals are transported to center of cell by protein ligands.

Table 6 Biosorbents for heavy metals removal

Biomass	Pb (0.4)[a]	Cd (0.1)[a]	Ni (0.1)[a]	Zn (0.1)[a]
K. spiculiformis	0.71	0.34	0.28	0.42
V. dichotoma	0.7	0.28	0.37	0.42
S. maxima	0.49	0.27	0.12	0.23
C. vulgaris	0.46	0.29	0.31	0.18
S. platensis	0.38	0.29	0.4	0.27
P. tricornutum	0.36	0.23	0.19	0.37
C. species	0.23	0.2	0.17	0.16
A. cylindrica	0.22	0.14	0.14	0.1
D. salina	0.1	0.07	0.06	0.06

(20)

Process of transportation of heavy metals depends on abiotic conditions such as temp, pH, humus particles, concentration of metals in environment and also biotic conditions (growth rate, speed of division of cells). Inhibiting influence on process is mainly by low

temperature, low level of irradiance and also lack of carbon energy source (Brierley, 1990). Heavy metals in most cases are characterized by overall performance of heavy metal cleaning (usually 60-90%) and time essential for cleaning (usually 5 days). Typical values for bio sorbents for heavy metals are listed in table 6.

2.5 Advantages of microalgae as biomass source

Characteristic which are highly preferable for microalgae cultivation in PBR include features such as rapid growth rate, high required product content, ability to growth in extreme conditions, considerable large cell size, wide tolerance to environmental conditions, high CO2 tolerance and uptake, tolerance to shear force and also low auto inhibition in high cell culture densities. Mentioned features are listed in table 7.

Table 7 Microalgae biomass source

Characteristic	Advantages
Rapid growth rate	Competitive advantage over competing species; reduces culture area required
High product content	Higher value of biomass. (Note: use of metabolic energy to generate product usually leads to slower growth)
Growth in extreme environment	Reduces contamination and predation. (Note: Limited number of species can grow in extreme environments. Can be difficult to maintain conditions)
Large cell size, colonial or filamentous morphology	Reduces harvesting and downstream processing costs
Wide tolerance of environmental conditions	Less control of culture conditions required. Growth over range of seasons and ambient weather conditions
CO_2 tolerance and uptake	Greater potential for CO_2 sequestration and use of waste CO_2
Tolerance of shear force	Allows cheaper pumping and mixing methods to be used
Tolerance of contaminants	Potential growth in polluted water and on flue gases containing high CO_2, NO_x and SO_x
No excretion of autoinhibitors	Reduces autoinhibition of growth at high biomass densities

(8)

Microalgae are interesting source of biomass as they are characterized by **(21)** high per-acre productivity. They are easy to reproduce, as they are characterized by simple cell division cycle (apart from optimal conditions). Additionally in relation to 1st generation of biofuels they are not food based feedstock resources and they are use non-productive, non-arable land/space. There is no interference with agriculture and biodiversity type of land use. Thanks to their ability of utilization of a wide variety of water sources (fresh, brackish, saline, marine, produced, and wastewater treatment), (Round, 1984) **(21)** they are characterized by lower impact on scarcity of sweet water resource. Moreover, they are able to perform well both in production of biofuels and valuable co-products (natural pigments). Many species of algae can be induced and cultured in such a way in PBR (engineered) to produce particular products (table...), Additionally they are representing huge potential of recycling of CO2 and other nutrient from waste streams. Microalgae are **(22)** considered as very efficient biological system for harvesting solar energy for the production of organic compounds (ca. 10% PE). Algal biomass production systems can easily be adapted to various levels of operational or technological skills so control of maintenance and operation can be easily performed by limited number of workers.

Table 8 Potential high–value products from photosynthetic microorganisms

Product	Source organism[b]	Current or potential use
Amphidinolides and amphdinins	*Amphidinium* sp.	Antitumor agent
Astaxanthin	*Haematococcus pluvialis*, *Chlorella* sp.	Pigment
β-Carotene	*Dunaliella*	Colorant, food supplement
Docosahexaenoic acid	*Isochrysis galbana*	Essential fatty acid
γ-Linolenic acid	*Spirulina* sp.	Essential fatty acid
Other polyunsaturated fatty acids	*Phaeodactylum tricornutum*, *Isochrysis galbana*	Health care, food supplement
Fucoxanthin	*Phaeodactylum tricornutum*	Antioxidant
Goniodomins	*Alexandrium hiranoi*	Antifungal agent
Oscillapeptin	*Oscillatoria agardhii*	Elastase inhibitor
Phycobiliproteins	Red algae, cyanobacteria	Colorants
Phycocyanin	*Spirulina platensis*	Colorant

a) based on Yamaguchi (1997) and Baseman (1989) b) Only representative examples are listed.

(23)

Microalgae can be cultivated according to their high value products (listed above) or according to desirable yield of oil (cosmetics), proteins (nutrients) or other type of valuable products. Possibility of use of microalgae as biomass source is very broad and promising for commercial companies as listed in table 9

Table 9 Gross composition of several microalgae species

Species	Proteins (%)	Lipids (%)	Carbohydrates (%)
Euglena gracilis	39–61	14–20	14–18
Chlamydomonas reinhardtii	48	21	17
Chlorella pyrenoidosa	57	2	26
Chlorella vulgaris	51–58	14–22	12–17
Dunaliella salina	57	6	32
Spirulina maxima	60–71	6–7	13–16
Spirulina platensis	46–63	4–9	8–14
Scenedesmus obliquus	50–56	12–14	10–17

(8)

Microalgae composition is valuable for several reasons and cultivation of it as a biomass is giving possibility to obtain bio hydrogen (bio H_2O splitting). After extraction of oil it is possible to perform in process of transesteryfication as a biodiesel energy product. Bioethanol is possible to obtain from starch yield via fermentation and biogas can be obtained via anaerobic digestion. Mentioned energy carriers from microalgae are presented on figure 16.

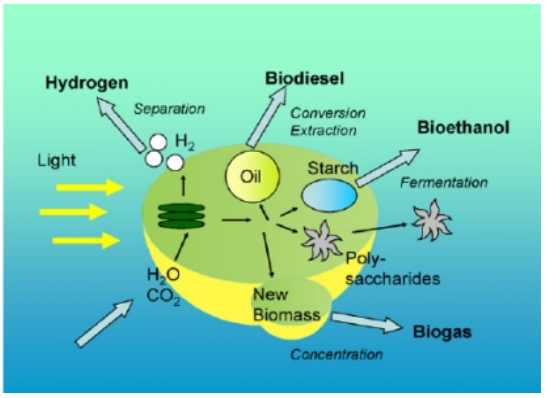


Figure 16 Microalgae cell and possible to obtain product

(24)

Advantages of microalgae as a biomass source were spotted by commercial companies. Microalgae high potential and productivity was appreciated by commercial companies which are using them in many different applications such as listed in table 10.

Table 10 Present state of microalgae production

Microalgae	Annual production	Producer country	Application and product	Price (€)
Spirulina	3000 tonnes dry weight	China, India, USA, Myanmar, Japan	Human nutrition Animal nutrition Cosmetics Phycobiliproteins	35 kg^{-1} 11 mg^{-1}
Chlorella	2000 tonnes dry weight	Taiwan, Germany, Japan	Human nutrition Cosmetics Aquaculture	35 kg^{-1} 50 l^{-1}
Dunaliella salina	1200 tonnes dry weight	Australia, Israel, USA, Japan	Human nutrition Cosmetics B-carotene	 215–2150 kg^{-1}
Aphanizomenon flos-aquae	500 tonnes dry weight	USA	Human nutrition	
Haematococcus pluvialis	300 tonnes dry weight	USA, India, Israel	Aquaculture Astaxanthin	50 l^{-1} 7150 kg^{-1}
Crypthecodinium cohnii	240 tonnes DHA oil	USA	DHA oil	43 g^{-1}
Shizochytrium	10 tonnes DHA oil	USA	DHA oil	43 g^{-1}

(25)

What is most important is that microalgae are very interesting for production of biofuels or energy as oil yields are estimated to be at least 60 times higher than from soybeans, approximately 15 times more productive than jatropha, and approximately 5 times that of oil palm per acre of land on an annual basis (Rodolfi, 2009) **(21).** Productivity and lipid content is presented in table 11.

Table 11 Biomass productivity, lipid content and lipid productivity

Algal group	Microalgae strains	Habitat	Biomass productivity (g/l/day)	Lipid content (% biomass)	Lipid productivity (mg/l/day)
Diatoms	*Chaetoceros muelleri*	Marine	0.07	33.6	21.8
	P. tricornutum	Marine	0.24	18.7	44.8
	Skeletonema costatum	Marine	0.08	21.0	17.4
	Chlorella sp.	Freshwater	0.23	18.7	42.1
	Chlorella sorokiniana	Freshwater	0.23	19.3	44.7
	Chlorella vulgaris	Freshwater	0.17	19.2	32.6
	C. vulgaris	Freshwater	0.20	18.4	36.9
Green algae	*Chlorococcum* sp.	Freshwater	0.28	19.3	53.7
	Scenedesmus quadricauda	Freshwater	0.19	18.4	35.1
	Scenedesmus	Freshwater	0.21	19.6	40.8
	Scenedesmus sp.	Freshwater	0.26	21.1	53.9
	Tetraselmis suecica	Marine	0.32	8.5	27.0
	Monodus subterraneus	Freshwater	0.19	16.1	30.4
	Nannochloropsis sp.	Marine	0.17	29.2	49.7

Microalgae strains cultivated in 250 mL flasks **(26)**

3 PHOTOBIOREACTOR DESIGN – STATE OF ART

Bioreactors based on work mode can be classified as batch, continuous and fed-batch. Additionally they can be classified into systems, such as open where are included raceway ponds, lakes etc. Second type is closed type of system where it is possible to differ tubular, flat plate, conical, pyramidal, fermenter etc. General comparison of closed and open systems is presented in table 12.

Table 12 Comparison of open ponds and closed PBR performance

Factor	Open ponds	Photobioreactors
Space required	High	Low
Water loss	Very high	Low
CO_2-loss	High, depending on pond depth	Low
Oxygen concentration	Low due to continuous spontaneous outgassin	Build-up occurred requires gas exchange device
Temperature	Highly variable	Required cooling
Shear	Low	High
Cleaning	None	Required due to wall growth and dirt
Contamination	High	None
Evaporation	High	No evaporation
Biomass quality	Variable	Reproducible
Harvesting cost	High	Lower
Microbiology safety	None	UV
Automatic cooling system	None	Built in
Automatic heating system	None	Built in
Air pump	Built in	Built in
Energy requirement (W)	4000	1800

(27)

In my master thesis I will concentrate on closed type of PBR.

3.1 Classification of closed PBR

In my thesis I will write only about closed type of PBR as they are more suitable to control in terms of temperature, pH, nutrient concentrations etc. General sketch of closed type of PBR is presented on picture 17.

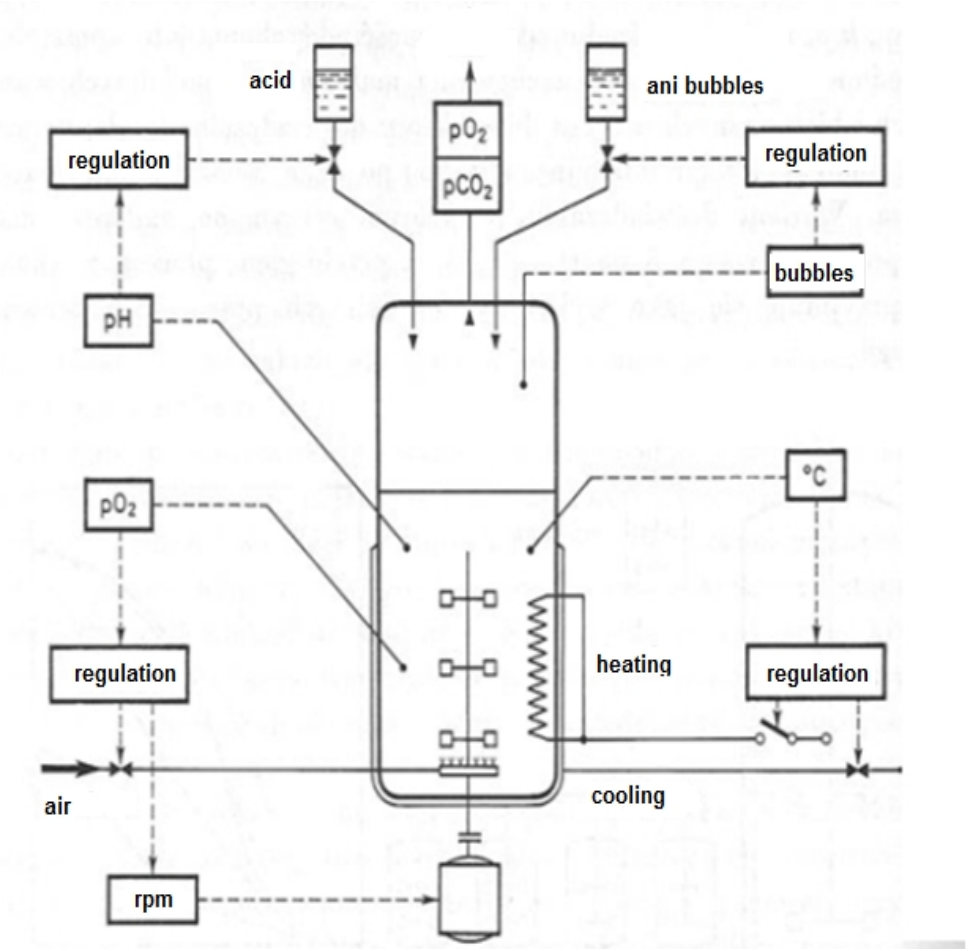


Figure 17 Sketch of classical closed type of PBR

(12)

Amount of biomass which is produced in closed in PBR is ca. three times higher than obtained from open systems.

Usually PBRs are made of materials such as glass, plastics etc. Material got influence on culture of microalgae as in time they can have negative influence. Materials can be toxic, they can start ageing and lose their original color or transparency. In table 13 is characterization of some of materials.

Table 13 PBR materials

Material	Properties	Advantages	Disadvantages
Glass	Density 2.35–2.52 g/cm^3 Transparency 95%	High transparency, chemical stability, durability	Fragile, installation costs are high
Polymethyl methyl acrylate (PMMA)	Mol. Formula $(C_5O_2H_8)_n$ Density 1.19 g/cm^3 Melting point 130–140 °C Tranparency 92%	Good impact strength than PC & PS, high transmittance, excellent environmental stability	Not autoclavable, easily scratched, poor resistance to many solvents
Polycarbonate (PC)	Mol. Formula $(C_{16}H_{14}O_3)_n$ Density 1.22 g/cm^3 Melting point 267 °C Tranparency 92%	Autoclavable, good impact resistance and optical properties, UV absorbing	Diffusible to gases due to low molecular mass, affected by solvents, ammonia, NaOH and concentrated acids
Polyethylene (PE)	Mol. Formula $(C_2H_4)_n$ Density 0.91–0.97 g/cm^3 Melting point 115, 135 °C Tranparency 80–85%	Chemically inert, high resistance to acids, alkalis and solvents	Loss of strength and tear resistance on exposure to light and oxygen
Polypropylene (PP)	Mol. Formula $(C_3H_6)_n$ Density 0.85–0.94 g/cm^3 Melting point 160 °C Tranparency 80%	Autoclavable, good resistance to fatigue, resistance to corrosion and chemical leaching,	Yellowing and loss of transparency on exposure to natural environment
Polyvinyl Chloride (PVC)	Mol. Formula $(C_2H_3Cl)_n$ Density 1.2–1.34 g/cm^3 Melting point 80 °C Tranparency 80%	Excellent resistance to acids and alkalis, low permeability to gases, high tensile strength, UV resistant	Poor resistance to aldehydes, esters, aromatic and halogenated hydrocarbons and ketones, transmittance is low
Polystyrene	Mol. Formula $(C_8H_8)_n$ Density 1.05 g/cm^3 Melting point 240 °C	Thermo plastic,	
Polyethylene terephthalate (PET)	Mol. Formula $(C_{10}H_8O_4)_n$ Density 1.37 g/cm^3 Melting point 260 °C	Strong and impact resistant, low permeability to gases,	Hygroscopic
Polyurethane (transparent)	Mol. Formula $(C_{25}H_{42}N_2O_6)$ Density 1.340 g/cm^3 Melting point 80 °C	High optical transmittance, excellent UV stability (non yellowing)	Cost is high

(28)

3.1.1 Tubular PBR

Can be in form of vertical (bubble, airlift) type where reactors are in shape of simple column (vertical type) with bubbling CO2 (look at picture 18). They can be also represented by shape of horizontal type (horizontal, fence, a – shaped) where its light harvesting and gas exchange units are separated. Another type of tubular PBR is helical type (helical, conical) which can be obtained in preferred, desirable shapes. Last one of tubular PBR is A – shaped type.

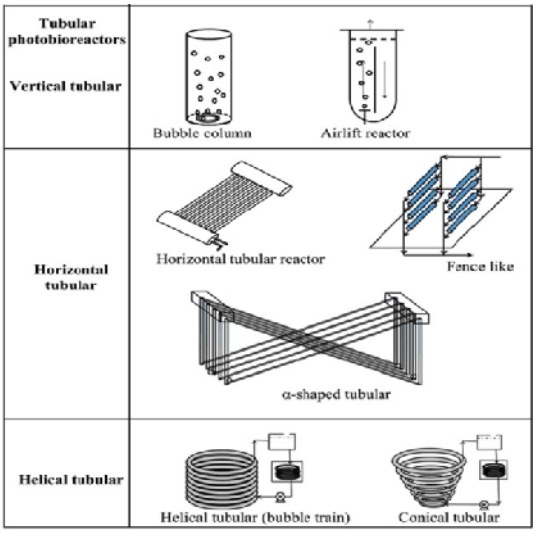


Figure 18 Tubular PBR

(28)

Vertical tubular reactors (VTR) are made of vertical transparent tubes (materials: polyethylene or glass tubes) with bubbling device at the bottom. Airlift bioreactor got good mixing of CO2 and removal of O2 properties. Bubble column got efficient aeration in which there's no need of use of external device **(29).**

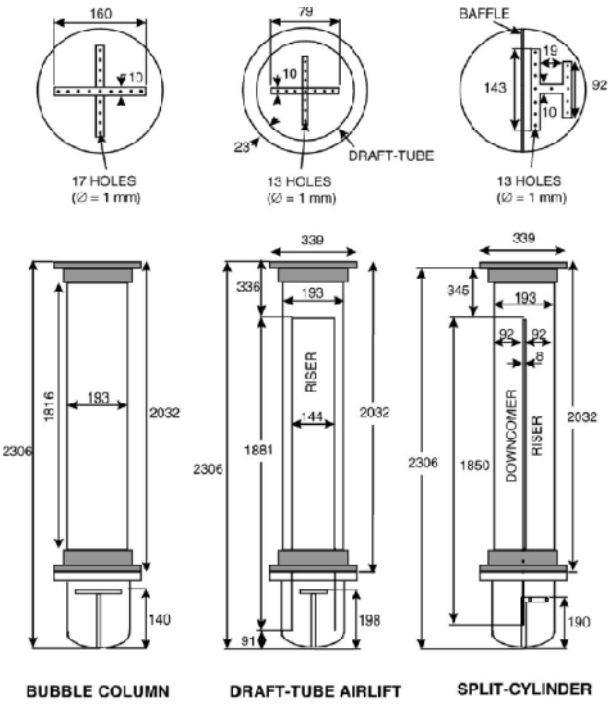


Figure 19 The configurations of photobioreactors and air spares (dimensions in mm).

(30)

The advantages of VTR include low material cost, high transparency, and high area to volume ratio, biomass productivity and low contamination risk. Drawbacks are connected

with scaling up, fragility, and gas transfer at the top regions of the reactors temperature control and gas holdup. Tubular PBR system is presented in figure 20.

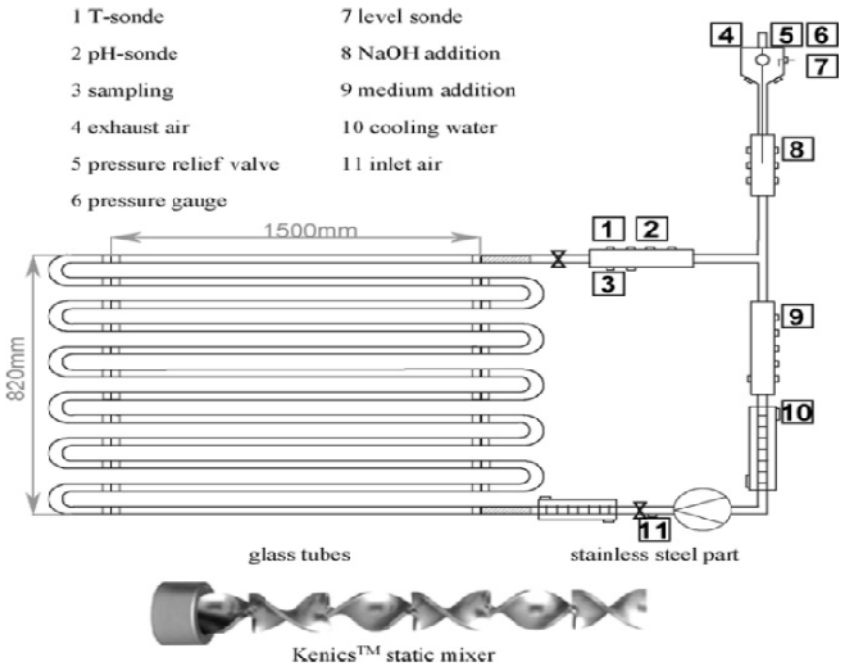


Figure 20 Tubular PBR systems

Possible drawing (30 L pilot scale) tubular photo-bioreactor and illustration of the mixer on the bottom (1) T-sonde; (2) pH-sonde; (3) sampling; (4) exhaust air; (5) pressure relief value; (6) pressure gauge; (7) level sonde; (8) NaOH addition; (9) medium addition; (10) cooling water; (11) inlet air. **(31).**

Fence like horizontal tubular reactors can be presented in picture 21.

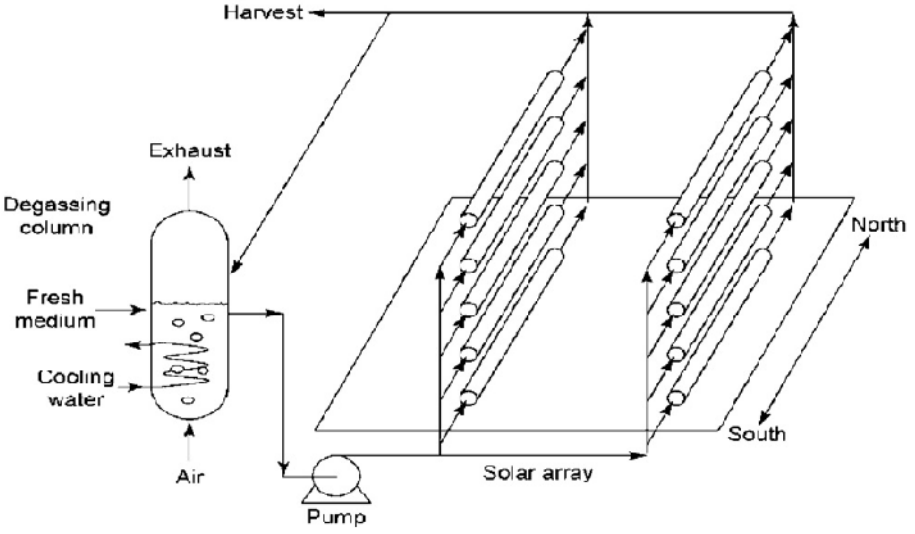


Figure 21 Reactor configurations for microalgae - horizontal tubular reactor

(27)

Horizontal tubular reactors (HTR) are characterized by main advantage, which is their orientation to sunlight and high light conversion efficiency. Gas (CO2) is injected by gas exchange unit. There are few options HTR, such as long tubular with concurrent tubes, looped tubes and near horizontal tubular reactors (NHTR). Last ones are designed by Tredici and are based on parallel tubes (Plexiglas), which are connected by tubular folds. This kind of construction helps in reducing gas holdup and improves oxygen removal. Drawback of HTR is temperature control and photo bleaching (oxygen build-up due to photosynthetic activity and reduced photosynthetic efficiency)

Helical tubular reactors are usually in different shapes to improve light penetration. They are externally coupled with a gas and heat exchanger. Feed is driven by centrifugal pump. Their advantage is high area to volume (A/V) ratio so their photosynthetic efficiency (PE) is relatively high.

3.1.2 Flat plate reactors

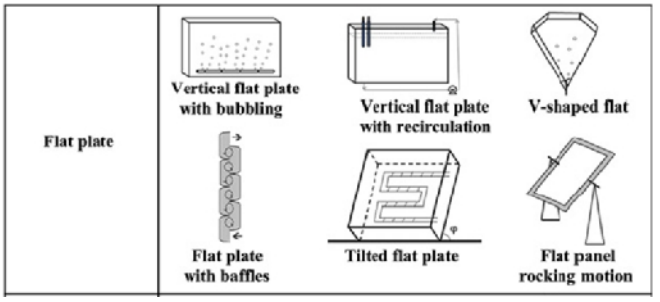


Figure 22 Flat plate

(28)

Flat plates (look picture 22) reactors are characterized by high A/V (area to volume) ratio and minimal thickness. Their orientation can be vertical (transparent sides facing east-west), tilted (north-south) and also horizontal.

Vertical flat plate can be divided into three generations such as first generation which got transparent sheets in a frame. Next one is second generation (alveolar), this kind of bioreactors is made of transparent materials that form rectangular channels – alveoli. Disadvantage is high light saturation and also photo inhibition. Third generation of vertical flat plate consist of two deep-drawing film combined together to perform as static mixers (Subitec GmbH). Mixing is based on bubbling air bottom nozzles or from the sides. These kinds of panels are very good for high density cultures in terms of efficient utilization of light.

V-shaped flat panel is characterized by high mixing rate and relatively low stress on cells of microalgae.

Flat plate reactors with rocking motion which are used to achieve higher turbulence in reactor and overcome sedimentation. Flat plates with rocking motion are obtained by use of motor with eccentric cam motion (e.g. 2 rpm).

3.2 Comparison of PBR

Characterization of all possible PBR which are achievable for various kinds of microalgae is presented on table 14

Table 14 PBR comparison

Reactor type	Mixing	Light utilisation efficiency	Temperature control	Gas transfer	Hydrodynamic stress on algae	Species control	Sterility	Scale-up
Unstirred shallow ponds	Very poor	Poor	None	Poor	Very low	Difficult	None	Very difficult
Tanks	Poor	Very poor	None	Poor	Very low	Difficult	None	Very difficult
Circular stirred ponds	Fair	Fair–good	None	Poor	Low	Difficult	None	Very difficult
Paddle-wheel Raceway Ponds	Fair-good	Fair–good	None	Poor	Low	Difficult	None	Very difficult
Stirred Tank reactor (internal or external lighting)	Largely uniform	Fair–good	Excellent	Low–high	High	Easy	Easily achievable	Difficult
Air-Lift reactor	Generally uniform	Good	Excellent	High	Low	Easy	Easily achievable	Difficult
Bag Culture	Variable	Fair–good	Good (indoors)	Low–high	Low	Easy	Easily achievable	Difficult
Flat-Plate reactor	Uniform	Excellent	Excellent	High	Low–high	Easy	Achievable	Difficult
Tubular reactor (Serpentine type)	Uniform	Excellent	Excellent	Low–high	Low–high	Easy	Achievable	Reasonable
Tubular Reactor (Biocoil type)	Uniform	Excellent	Excellent	Low–high	Low–high	Easy	Achievable	Easy

(32)

What is very important in choice of PBR is selection of strains. Parameters very important for cultivation of microalgae are: biological performance of the alga, cost of labor, used energy, uptake of water, nutrients, climate (if the culture is outdoors) and preferred type of final product. Industrial large-scale close systems need to be choose due to their light utilization efficiency, ability to control temperature, the hydrodynamic stress placed on the algae, the ability to maintain the culture with one algal and or axenic and how easy they are to scale up from laboratory scale to large-scale. **(32).** Well-designed PBRs are able to lower cultivation area by distributing photosynthetic organisms vertically. Vertical tubular photobioreactors are moreover able to increasing carbon dioxide bio fixation by higher carbon dioxide residence time (Ono and Cuello, 2004).

3.3 Type of cultivation in PBR

There is possibility to differed three type of culture growth where there is periodic type, constant type and last one synchronic type.

Periodic type of cultivation is performed in closed type of PBR, where growth of microorganism is active as long as there are substrates of fertilizer or till metabolic side products are not negatively influencing their activity. This type of culture growth biomass and its metabolites are taken from reactor (gaseous products mainly). In this type of reactor its growth can be described as follows on picture 23.

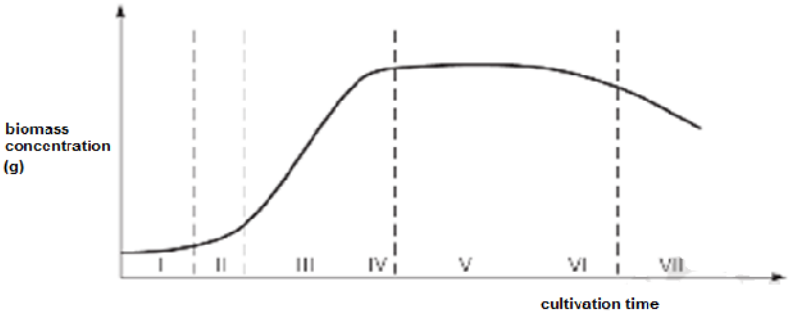


Figure 23 Cultivation of microalgae

Process of periodic cultivation can be differing in steps where (12):

- 1st phase

Adaptation phase or lag phase which is starting from introduction of microorganisms into PBR till their first reproduction. This period varies in terms of many parameters (culture medium, temp, pH, etc.). In this phase growth is raising interpretation in logarithmic way.

- 2nd phase

Acceleration phase which is last stadium of adaptation phase. Microorganisms are strong enough to overcome negative impact of environment. This phase is relatively short period.

- 3rd phase

This is phase of logarithmic growth, acceleration phase in which biomass growth is rising with constant speed – phase of balanced growth. This is determined by environmental conditions and type of culture breeding.

All basic environment characteristic are optimal, microorganism are growing in sequential way:

$$X \rightarrow 2X \rightarrow 2(2X) \rightarrow \ldots \rightarrow 2^n X$$ Equation 18

Where n is number of population or replication. In function of time it can be presented as:

$$X(t) = X_0 \cdot 2^{(t-t_0)/t_d}$$ Equation 19

Where t_d is doubling time and X_o is starting point of biomass.

In logarithmic way it can be presented as:

$$\frac{1}{X(t)} \cdot \frac{dX(t)}{dt} = \frac{1}{t_d} \ln 2 = \mu$$

Equation 20

Where μ is specific growth rate in given function of time.

In this term doubling time of growth is described as

$$t_d = \frac{\ln 2}{\mu}$$

Equation 21

In this phase Monod's equation is applicable.

- 4th phase

It is slower phase of growth, in this one can be observed dead cells due to lack of substrate.

- 5th and 6nd phase

Stationary phase which is characterized by constant level of cells in colony. In this phase cells are using leftovers of substrate. Next phase is based on slow death of cells, overall biomass level is getting lower.

- 7th phase

Phase of logarithmic death, this phase is based on inhibiting influence of substrates which is working in logarithmic way.

Second type of cultivation which is constant culture breeding is one where culture obtain some phase characteristic, there is constant addition of fertilizer and extraction of inhibitors. Volume of biomass is constant all the time, it is in dynamic balance phase between biomass which is growth and biomass which is treated as product of overall process.

In constant culture growth is limited by substrate accessible.

Constant culture can be obtained in chemostat where is kept constant concentration of biomass. It is obtained thanks to dilution speed (D) which is translate as concentration of base flow (F) (dm3/h) and volume of substrate in bioreactor (V)(dm3)

$$D = \frac{F}{V} = \text{const} \quad [\text{h}^{-1}]$$

Equation 22

Synthesis of biomass in chemostat is characterized by limited growth of microorganism by fertilizing substrate (Equation 12)

$$\mu = \mu_{\max} \frac{S}{S + K_S}$$

Maximal – critical dilution of substrate can be characterized by

$$D_{max} = \mu max * \frac{S_o}{S_o + K_s}$$

Equation 23

Type of chemostat are nutristat and pHstat where respectively in first one critical influence is by fertilizing substrate of basis and in second one is based on pH of environment.

Another device in which can be obtained constant culture is turbisat where flow of substrate fertilizer and biomass concentration is kept constant. When concentration is lower than flow is raised and reverse way. Constant culture can be also performing in nutristat and in pH- stat.

3.4 PBR reactor choice

Choice of PBR to operation in system of microalgae cultivation is one of the most important issues to handle. Issues which need to be taken into consideration include mode of operation of PBR. This point should be clearly stated if cultivation would be periodic, constant or synchronous. Another point is reactor type as such as described in previous chapters. There should be also described mass transfer characteristics such as supply/uptake of oxygen, nutrients addition etc. Mixing characteristic is also another point which needs to be concerned in terms of power input and time of performance. Additionally shear should be taken into account as it can provide negative impact on single cell. One of most important point is scalability of PBR and also possibility to provide system which will be reliable and stable (maintenance simplicity, control and monitoring possibility). In choice of PBR is important to pick best performance in terms of operation and measurement of run. Such issues as maintenance of pH, supply of oxygen, temperature level, mixing speed and nutrient supplementation need to be taken into account. In terms of PBR choice need to be also included substrates requirements and supply issues. In terms of PBR choice need to be taken into account possibility of application of substrates and possibility to kept optimal concentrations (stoichiometry, microalgae metabolism and its mass transfer). PBR requirements also include possibility to kept with upstream constraints such as sterilization requirements and none or low inhibiting concentrations. PBR should be also able to keep downstream processing in terms of by-product disposal and fluids moving. What is also very important apart from technological issues is also cost of PBR in terms of grass root, operation and maintenance.

3.5 Scale up of PBR

Scale-up process is to increase scale of process from concept phase to commercial use. Scaling include stages such as lab scale, than pilot scale and final one industrial scale. Most difficult step is between lab scale and pilot scale phase. Process of modeling of PBR can be presented as follows on picture 24 (12, Liden 2003).

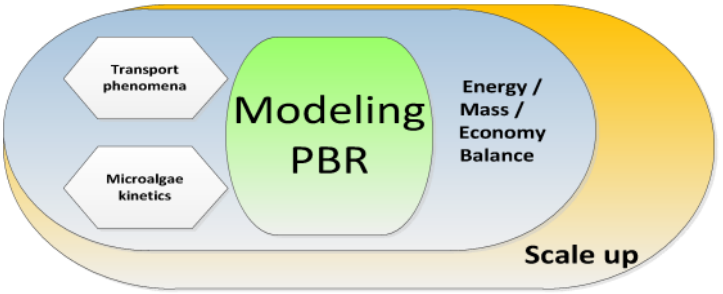


Figure 24 Process of modeling of PBR

Most important is identification of biological system, as during scaling from laboratory to pilot/industrial phase it can be assumed that in same conditions, behavior of microalgae is already mastered. Key issue is to provide same conditions as in terms of lab phase to perform in same background. Exemplary scale up approach in biological means was described by S. J. Wanga, 2007. Bioreactor modeling design can be presented as schema on picture 25.

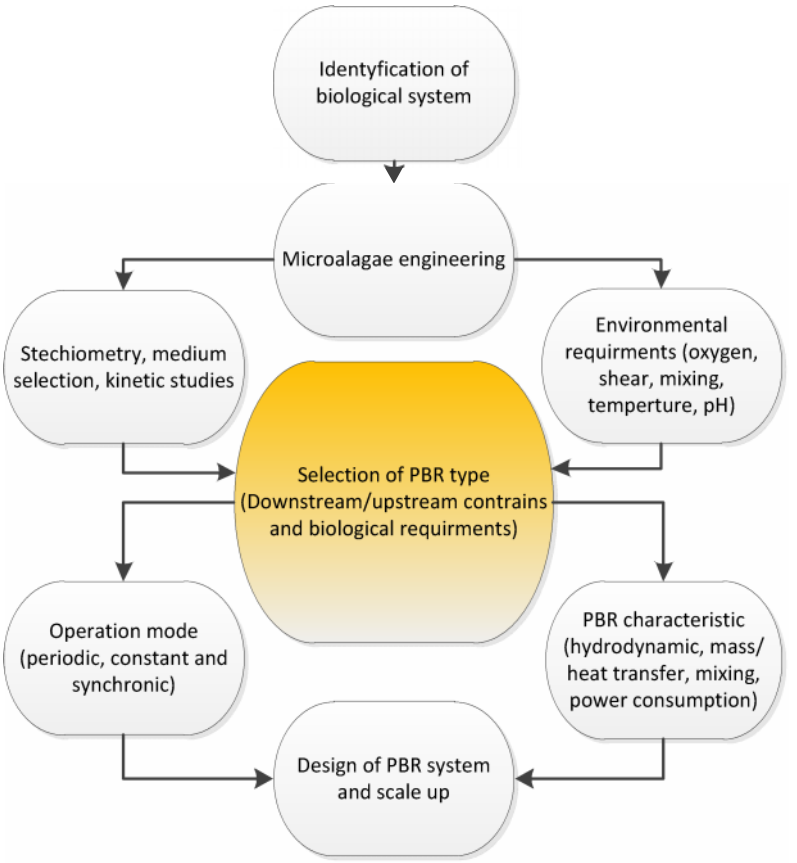


Figure 25 Bioreactor modeling design

(Merchuk, 1995)

Bioreactor modeling is described by many parameters which are described in complex mathematical approach which can be performed by specialist modeling tools. This part of PBR of description is not included in work.

Biological system is one of major part in scaling up of PBR as presented in figure above. In this aspects growth and metabolism is most important to determine. Issues which need to be taken into account are:

- biosystem identification (e.g. metabolic pathways)
- optimum growth conditions (pH, temperature, salinity etc.)
- catabolic activity (function of process parameters)
- specific growth rate and doubling time
- product/substrate yields and also uptake rates (product synthesis, substrate consumption, byproduct formation)
- shear resistance for stress
- stress-causing factors (inhibition and toxicity);
- stability of culture (over period of time, contamination risk).

In master thesis will be analyzed biotechnological side of selected PBR approach. In this chapter will be only listed factors essential for biological side – closed PBR. Crucial factors for PBR in my master thesis are high level, carbon dioxide supply and also nutrients supply. These factors are listed due to character of a system and main aim of performance. Additionally other requirements for closed PBR are: water mixing, O2 removal, constant preferable temperature and pH. In estimation of optimal requirements it is essential to include some of features such as presented below in the picture 26.

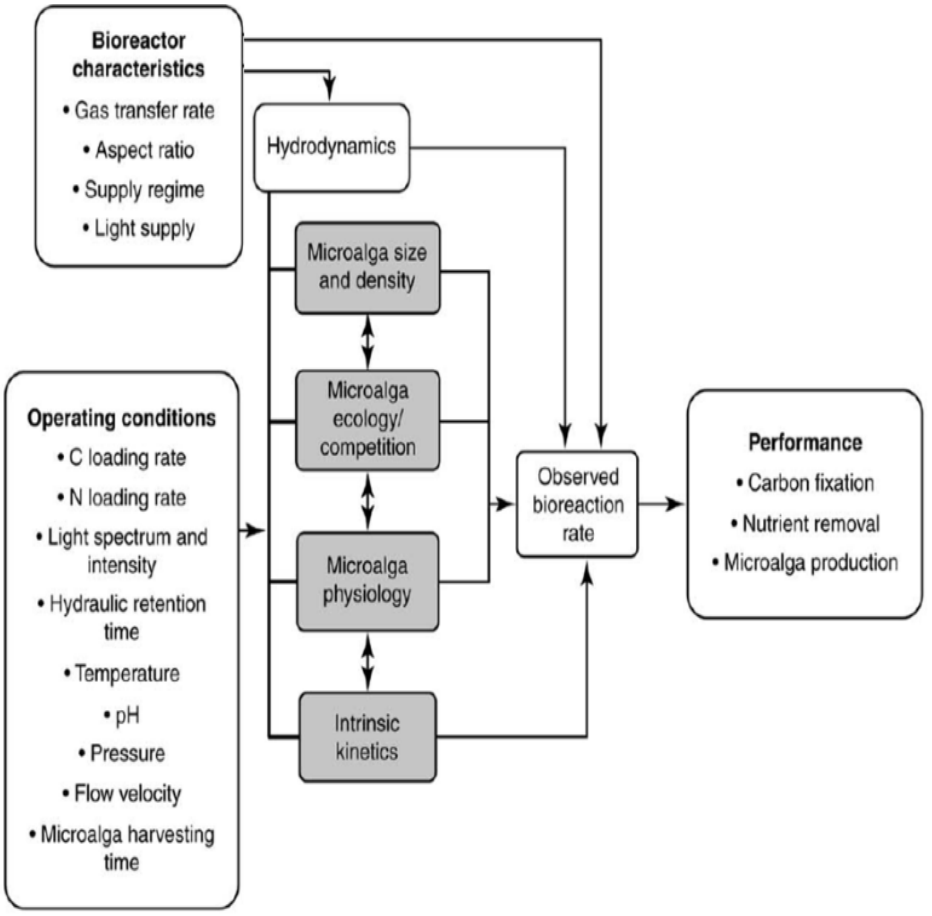


Figure 26 Requirements for closed PBR cultivation

(33)

3.6 Bioreactor design

Bioprocess engineering is dealing with issues based on field of microbiology, chemistry and engineering in one system combining biological, chemical, physical and mechanical considerations in one subject. Issues which need to be concerned in PBR design can be presented on picture 27.

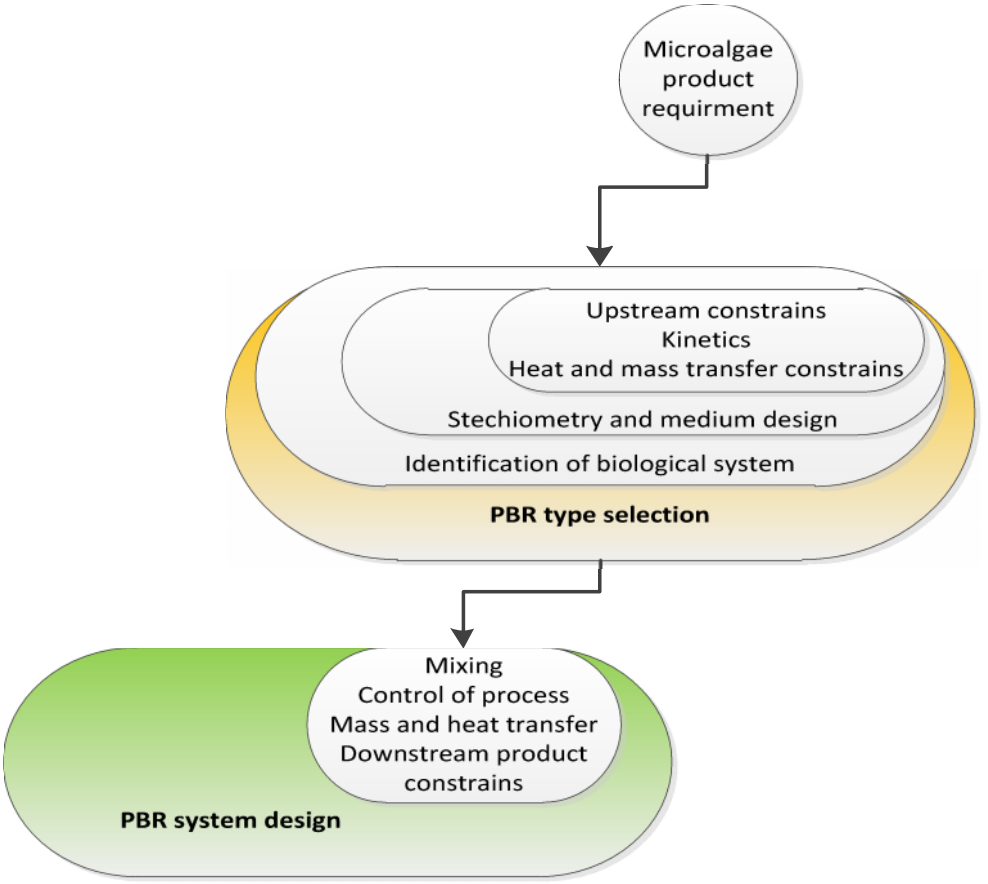


Figure 27 PBR design issues

Where upstream part of a bioprocess refers to the first step in which biomolecules are grown, usually by bacterial or mammalian cell lines (see Cell culture) in bioreactors. When they reach the desired density (for batch and fed batch cultures) they are harvested and moved to the downstream section of the bioprocess. Downstream part of a bioprocess refers to the part where the cell mass from the upstream are processed to meet purity and quality requirements. Downstream processing is usually divided into three main sections, a capture section, a purification section and a polishing section **(17).**

PBR is a core biological reaction point where chemical and biological processes got major influence on performance of culture biomass production PBR is a core in pant design performance. There are several factors that got influence on design criteria in this chapter I will describe most commonly distinguish ones. Productivity of PBR can be estimated based on several factors charities for PBR closed type. Among the most important it is essential to mention Vr (L) which is described as total working volume of reactor (liquid and gas phase). Ground area is Ag (m3) for description of area which is actively collecting light energy for PBR, it is area requirement (also between two reactors). High facilities got small footprint but large tailed area. All required area OAP (m3) for PBR installation, is a difference between footprint and area requirement. Total surface area Ar (m^2 or ha) is area of transparent part, determined light that can enter the reactor. Volumetric productivity Pr (g/Ld) is a product formation during period of time. Areal productivity Pg (g/m^2d) areal characterizes large PBR, and it is depending on irradiation during measurement period. This value is giving idea of energy efficiency between incident light as main energy source and biomass product formation on areal basis. Another important factor is irradiance on surface in photon flux density PFD Io (micro Einstein/ (m^2sec) where E is mol photons.

Photon flux density described as PPFD (W/m2) is light that can be used effectively by plants on wave length of 400nm-700nm. It can be presented in W/m^2, this factor is describing power density for studies of bio-energy production. Photo conversion efficiency PCE (%) is fraction of solar energy that converts solar energy to chemical energy. In this case max theoretical value is 9% for full sunlight. Photosynthesis efficiency is PE (%) is describing plant performance on light uptake (more about PE please look in table 3).

All mentioned parameters are visualized on picture 28.

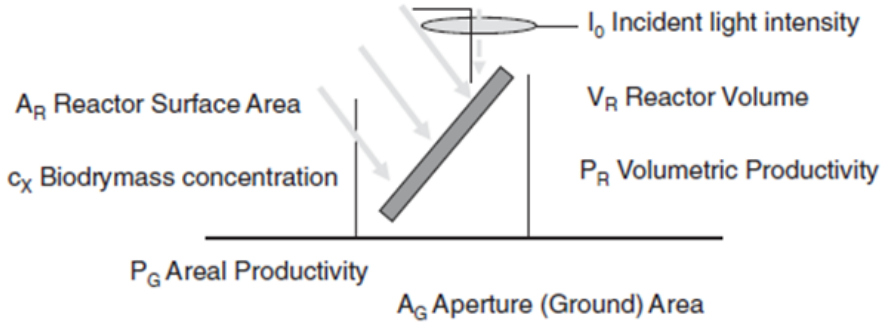


Figure 28 PBR design parameters

(34)

Yield production (g/L) is describing mass of produced microalgae per unit volume. Productivity (L-1 · hour-1 or g · L-1 · day-1) is a yield of produced biomass per unit time and is often expressed in terms of growth. The growth conditions that produce maximal yield are rarely the same conditions that produce maximal productivity. **(35).**

Good parameters for PBR should be optimized in terms of light intensity/ penetration, wavelength of light and time and period of microalgae exposure to light. Light intensity and penetration can be characterized by such factors as: cell density, type of PBR, supply of CO2 bubbles into the PBR, used type of light (natural type day and seasonal changes). Photosynthesis radiance is estimated to be 43–45% in the wavelength range of 400–700 nm. **(36).** Only 5% of full sun irradiance is converted by microalgae to chemical energy so in terms of energy balance this number is highly inefficient. In relation mechanical energy input has to be restricted to obtain a reasonable energy balance for overall system. Light irradiance is spread all over PBR and is characterized by considerable losses so surface to ground area ratio AR/AG should be characterized by range of 10 or higher (optimum depends on strain, region in terms of outdoor PBR). PBRs are usually oriented outdoor in position north/south **(34).** Light source for PBR is based on natural light or most commonly used light emitting diodes (LED). In terms of natural light use in PBR its penetration can be presented as fallows on picture 29.

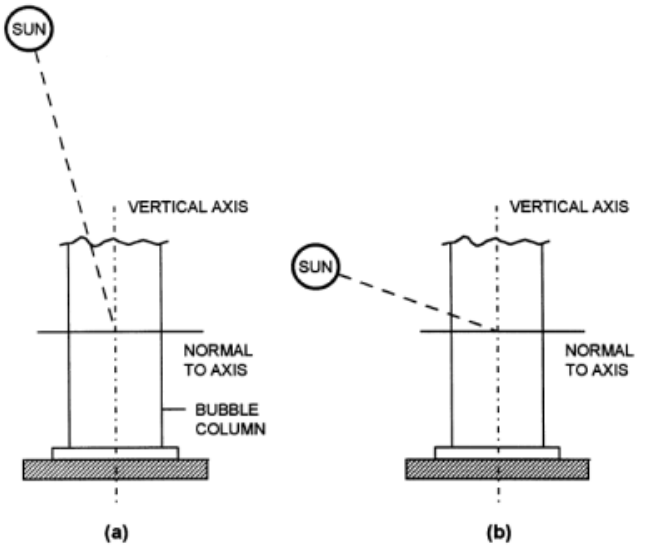


Figure 29 Light penetrations in PBR

Schematic presentation of light penetration with respect to the axes of the bubble column in the northern hemisphere: (a) at solar noon; and (b) in afternoon or early morning **(37).** Too high light level of light intensity is harmful for microalgae, but it can be easily minimalized by use of greater surface area of PBR by which light will be diffused. Greater surface area is also minimalizing negative impact of shading of high density cell concentration. Critical cell concentration is describing maximum level of cell density which got no negative influence of shading in culture. Bubbles of carbon dioxide are also influencing light penetration into PBR. In the picture 30 is presented influence of bubbles shading in tubular column PBR (picture 30).

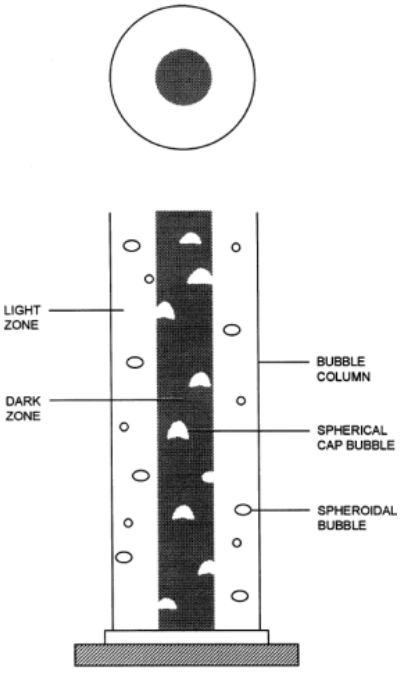


Figure 30 Bubbles in PBR

Bubbles are influencing light penetration in PBR which is presented as central, dark core. In the picture/experiment bubbles were ellipsoidal (diameter ca. 0.006 m) **(37).**

In the picture 31 is presented ideological influence of gas bubble which is creating shade. Dependent on light from overhead or sideway it is giving different size of shade on microalgae.

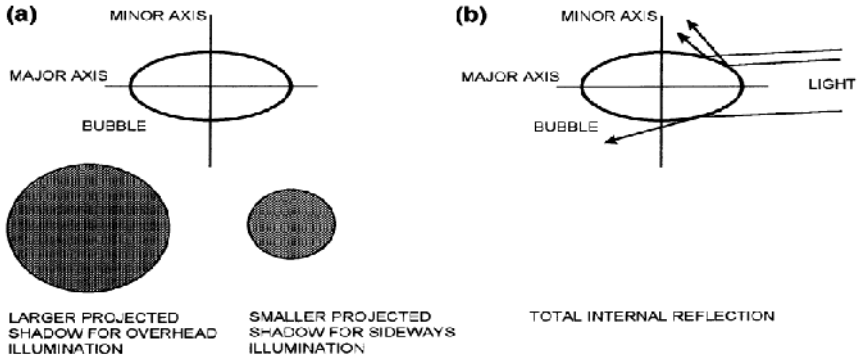


Figure 31 Irradiation and bubbles influence

Shadows of bubbles illuminated from top or side (a). Shadow is larger for overhead illumination (b) Total internal reflection at bubble **(37).** Short light path is very favorable for achieving high light efficiency. However, light sources should not be in close contact with culture, because they can generate some amount of heat. In table 15 are presented major features and electricity consumption for different artificial light sources **(38).**

Table 15 Light influence

Light source	Feature	Operation stability	Electricity consumption of the light source[a] (kw-h)
Conventional artificial light sources	Higher biomass productivity, higher stability, large illumination area, low constructing cost	High	40.32
LED	Lower energy consumption, lower heat generation, longer life-expectancy, tolerate higher frequency of on-off switching, higher stability, low constructing cost	High	20.16
Optical fiber excited by metal-halide lamp (OF-MH)	Higher energy consumption, lower area of land required, good light path, uniform light distribution, lower space requirement, low contamination risk	Moderate	36.0
Optical fiber excited by solar energy (OF-solar)	Low electricity consumption, good light path, uniform light distribution, lower space requirement, low contamination risk, lower cost	Low	1.0
LED/OF-solar combined with wind power/solar panel	No electricity consumption, good light path, uniform light distribution, lower space requirement, low contamination risk	High	0

a) The electricity consumption of light sources was based on a 40 L photobioreactors.

Considerable problem in terms of indoor, artificial illumination systems is very high cost of its installing and operating. Additionally, light intensity is decreasing exponentially from reactor wall due to rising concentrations of cell and nutrients

$$\frac{I_L}{I_o} = \exp(-\Upsilon L) \qquad \text{Equation 24}$$

I_L is light intensity at given depth L, and Io is original incident intensity where Υ is the turbidity.

Light intensity also decrease because of formation of thin layer of biofilm on the surface of bioreactor. **(38).** Characteristic of light emission is presented in the picture below. Light (photon) is entering reactor on the edge of light emitting ring. Light is entering ring at a given point in which it is defined by statistical angle. In the picture 32 is presented elevation angle.

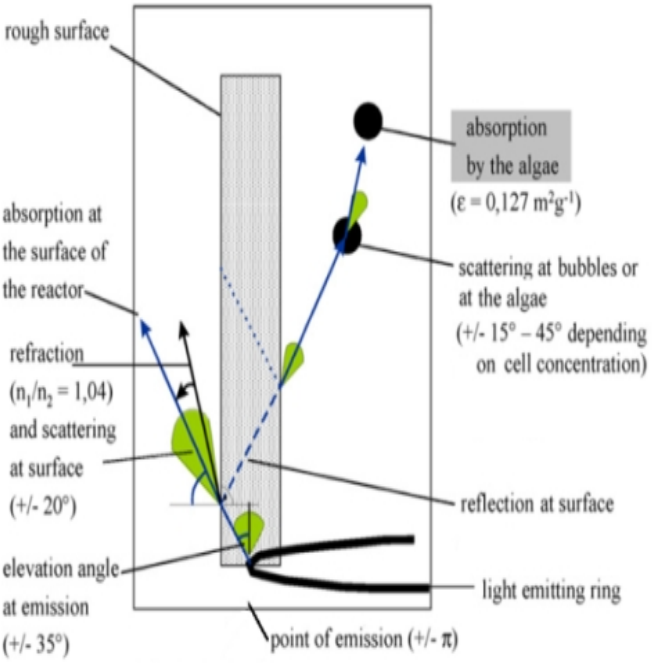


Figure 32 Influence of light on elevation edge

The values in the presented picture were determined experimentally and they are changed in simulations **(31).** Surface of the photobioreactor should be designed to minimize reflection and refraction; those made with tightly curved surfaces like tubes will have less light available than those made with flat surfaces **(35).**

3.6.1 Mixing

Mixing is believed to be one of the most important factors that influence growth of microalgae (if environmental conditions do not limit growth rates). It is influencing growth in two ways. Firstly it improves productivity, thanks to mixing cells are simultaneously exposure to light and dark parts in reactor, so it is beneficial for photosynthesis efficiency. Secondly it is increasing mass transfer, it is upgrading level of performance between the nutrients and cells in even way. Gas entrance velocity and volume of formed bubble got influence on either cell damage or its death.

Optimal waste water treatment is possible with support of mixing by right supply. Oxygen providing and mixing device should be:

- Provide fast dilution of provided waste water (oxygen) in overall volume of reactor.
- Keep in constant motion all biomass and provide easier contact with substrates
- Support homogenous conditions in PBR

Supported oxygen is used in processes of respiration and obtained energy is used in life metabolism processes and growth. This can be presented by equation of Pirt and Herbert that shows relation between use of oxygen (ro) and biomass productivity **(12)**

$$r_{O_2} = Y_{OX}\mu X + m_{O_2} X$$

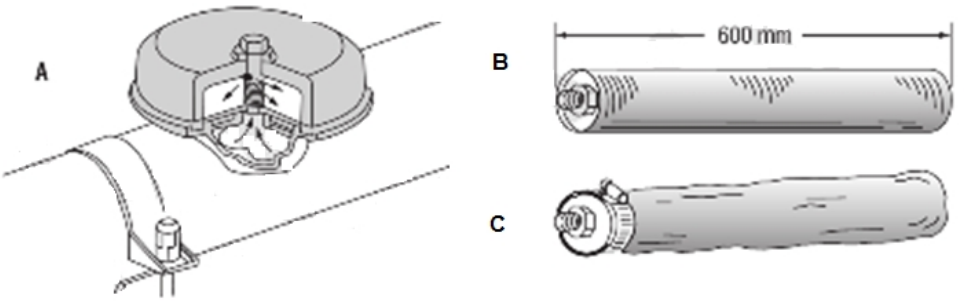
Equation 25

In presented equation Y_{ox} is factor of unit use of oxygen for biomass productivity and also m_o stands for oxygen use for metabolism performance. Usually in terms of waste water treatment microorganisms are in concentration of 0,5g/m3 but in reality it is as high as 2-3 g/dm3.

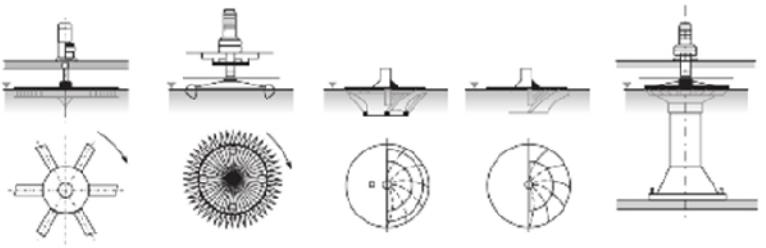
Oxygen supporting device in waste water treatment bioreactors are usually based on:

- mechanic type of oxygen support: mechanical aerator with horizontal or vertical axis
- diffuser system: compressed oxygen is supplied from bottom of PBR
- stream system: use of pump

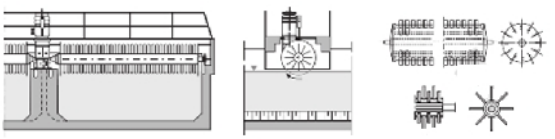
In practice first two are the most common devices in commercial use in picture 33.



Most commonly used diffusors for oxygen supply: A – plat type, B – pipe type, C – elastic tube diffusor



Mechanical aerators with vertical axis.



Mechanical aerators with horizontal axis.

Figure 33 Mixing device

(39)

Process of support of oxygen is based on diffusion which is mixing of medium in PBR with supplied particles. Mass which is supported to PBR in period of time is in relation to gradient of concentration of substrate. Transport of mass of oxygen can be described by Flick law **(39)**

$$\frac{dm}{dt} = (-d_F A)\frac{\Delta c}{\Delta x}$$

Equation 26

On presented equation D is factor of diffusion and A stands for area of section in relation of gradient concentration.

Process of penetration of oxygen can be described by two layers law of Whittman. It is describing oxygen penetration based on area of diffusion between medium with limited thickness. Thickness of water is L and speed of penetration of oxygen is dc/dt, so **(39).**

$$\frac{dc}{dt} = d_F A\frac{S_{O_2,i} - S_{O_2,L}}{L} = K_L A(S_{O_2,i} - S_{O_2,L})$$

Equation 27

Where S_{o2i} stands for concentration of oxygen on boundary of layers and S_{osl} is concentration of oxygen in water. In given equation L is thickness of liquid – water and Kl is factor of oxygen penetration.

To apply mentioned equation (applicable for pure water) there should be taken into account resistance of oxygen and microorganisms. Ability and efficiency of oxygen diffusion is most important characteristic of productivity and economic characteristic of oxygen diffusion device. Ability to oxidizing is expressed as Oxidation Capability and can be described as mass of oxygen which is dissolved in volume of PBR in time of one hour (liquid is pure water) thanks to use of oxygen supplying device when starting concentration is 0gO2/m3, with temperature 20C and atmospheric pressure 1013hPa. Mixing is also increased frequency of the light/dark cycles of microalgae cell which contributes to higher specific growth rate. However mixing should be optimal as it can lead to damaged cells or lead to stressed by high local intensities of mechanical energy **(34).**

3.6.2 Water Consumption

Close PBR do not require fresh water in their cultivation. Microalgae can grow in many different type of water. In my thesis in closed system of is used wastewater, which can be additionally treated in terms of addition of nitrogen and phosphorus.

3.6.3 CO2 Consumption

In order to provide easier algal Co2 cells up take there should be partial pressure of 0.1–0.2 kPa in the fluid phase is necessary (avoid carbon limitation **(34).**

Carbon dioxide can be supplied to microalgae in form of atmosphere air (0.03–0.06% CO_2) or flue gases (e.g., flue gas and flaring gas). Typical coal-fired power plants contain up to 13% or 15% **(40)** CO2, presence of NOx and CO did not inhibit the growth of microalgae **(41).** Carbon dioxide can be supplied by soluble carbonates such as Na_2CO_3 and $NaHCO_3$.

Supply of 1% to 5% CO_2 concentration by volume often lead to maximum growth of microalgae. However, experiments are working on 5-15% CO_2, or even pure CO_2. Carbon

dioxide can be supplied by use of diffusion through a gas permeable membrane, thanks to this it is providing equal level of CO_2 to PBR and prevents CO_2 inhibition. **(41).**

3.6.4 Oxygen removal

High level of oxygen with sunlight is promoting photo oxidative damage of cells. Horizontal tubular PBR are very hard to scale up in terms of tube length which has to be limited due to concentration of dissolved oxygen.

3.6.5 Nutrient Supply

Major nutrients that are essential to right performance of grow and lipid content of microalgae are nitrogen and phosphorus. Phosphorus need to in excess as it react with metal ions. Shortage of mentioned two is creating stress and can increase lipid percentages but also limit grown rate with nutrient supply – shortage or surplus is influencing yield of lipid as shown in picture 34.

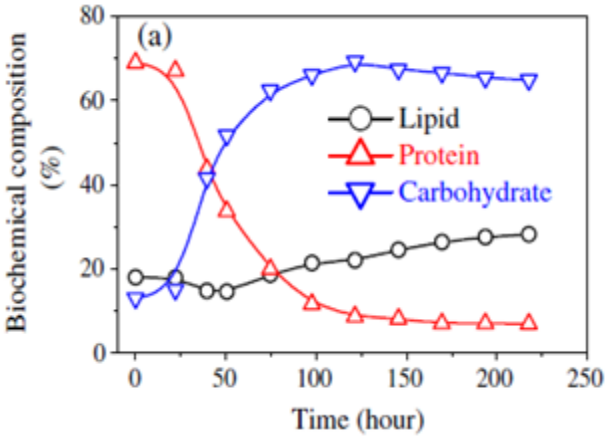


Figure 34 Biochemical composition microalgae

(42)

Additional nutrients, which are important, are carbon, hydrogen, oxygen, sulphure, calcium, magnesium, sodium, potassium, and chlorine. Vestigial nutrients include iron, boron, manganese, copper, molybdenum, vanadium, cobalt, nickel, silicon, and selenium. Heavy metals can be work as inhibitors for microalgae photosynthesis because they replace or block the prosthetic metal atoms in the active site of some enzymes or cause morphological changes. **(33).** Some compounds can be toxic for microalgae such as heavy metals and different gases e.g. CO_2, NOx, SOx, O_2 and NH_3. Optimal concentrations for each species vary greatly **(33).**

3.6.6 Temperature

In terms of outdoor PBR ambient temperature is influencing performance and depends on geographic region. Microalgae are able to grow at various temperatures, but their optimal growth is characterized by specific value to each strain. It is essential to control temperature in closed PBR by use of such solution as evaporate cooling or shading.

3.6.7 pH

Same as with temperature each strain got its optimal performance in specific pH. Lowering of pH of medium is connected with rising concentration of dissolved DIC from injected CO2. pH is affecting liquid chemistry of polar compounds in medium and availability of iron, organic acids, and even CO2. Most microalgae species are favored by neutral pH, whereas some species are tolerant to higher pH (e.g. Spirulina platensis at pH 9) or lower pH (e.g. Chlorococcum littorale at pH 4) **(33).** CO2 acidifies the culture medium however nitrate addition causes an alkalization of the culture **(35).**

3.6.8 Cell density

Considerably high cell densities (410 g/L) are characterized by higher electrical energy efficiency of mixing and during downstream processing. High cell densities can be obtained by lowest thickness of reactor. Additionally they can be obtained short dark/light cycles **(29).**

3.6.9 SVR

Installation of many plates very close to each other is providing high surface to volume ratio and also areal water coverage (AWC is total fluid volume per ground area). On the other hand, there could be taken into account possibility of light saturation and damage of cells **(29).**

3.7 Other Considerations

Very important factor for choice of best PBR is possibility of integration of reactor design with process of thermochemical conversion of biomass (figure 35) **(43).**

Reactor design can be presented as element in bigger picture of separation and recycle system. Separation of microalgae with recycle of nutrient is clue concern in design of PBR. Additional more important is ability to treat the effluent from system and also ability to perform on dispose of by-products. Last issues which need to be taken into consideration are cooperation with cooling and heating system. All of elements need to be greatly cooperating to perform as one coherent system. In general, process of SunChem is built on PBR reactor (open/closed). Any added element into plant need to be considered in relation to previous elements all need to be taken into account and should not be changed

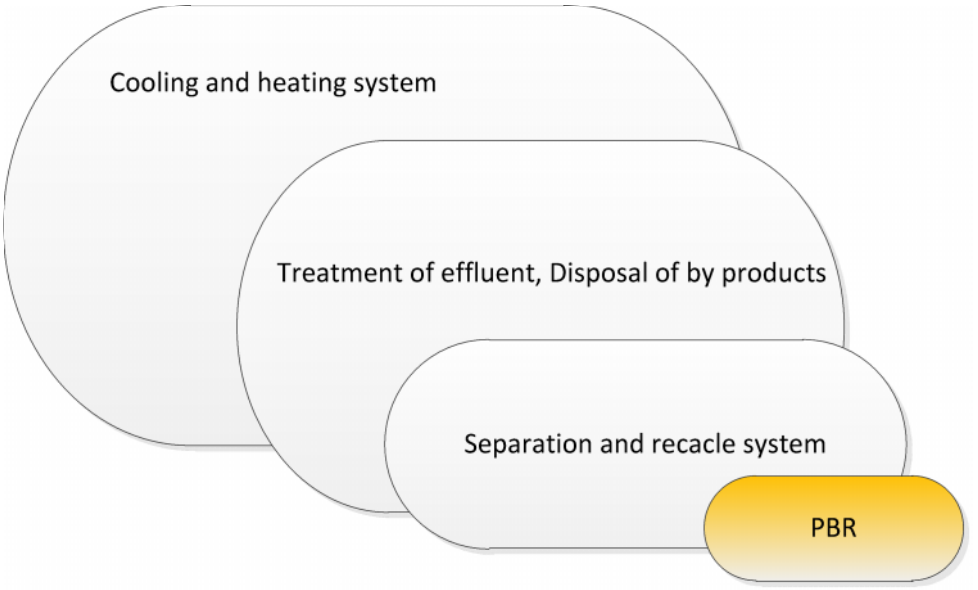


Figure 35 PBR in system

(Smith, 2005)

4 PARAMETERS MICROALGA GROWTH

Biological reactions which occur in PBR can be described by various equations. In my work i will present and analyze equations which suit best one inhibitor/catalyst in PBR. There is no description of overall inhibiting performance. Algae specific growth and its maximum productivity is very important factor, as in the end is energy obtained product yield methane should be highest.

4.1 Biochemical reaction

Biochemical reaction varies in its speed in terms of quality of substrates, presence of acceptors, electrons and other environmental issues such as: pH, temperature, oxygen arability and fertilizers.

Algal strain should be characterized by requirements which were listed in previous chapter about strain characteristic. Additionally chemical composition of algae as a feedstock got major influence on composition of SNG gas and possible yield of methane. In terms of open ponds right selection of microalgae is crucial. In terms of closed PBR there is possibility to cultivate strain which would developed desired characteristic - accommodate to environment naturally. Microalgae should not be genetically modified or raised only in terms of technological energy purposes. Modified/engineered species can lead to impact which can be hard to estimate on other species or in terms of use of nutrients – on human.

Described reactions depends on type of performed culture (continues, unlimited etc.) and influencing factors. Description of culture type got major influence on performed factors parameters.

4.2 Biotechnology basic kinetics

Description of microorganism growth and related inhibiting/catalyzing factors were described in previous chapters. However, in this chapter will be performed short description of factors to present most influencing and important ones.

Microorganism growth is based on growth of population. Growth of population can be described as growth of biomass (g/dm3). Growth of biomass can be calculated as difference between starting and ending point of biomass growth.

$$\Delta X = X - X_o \qquad \text{(Equation 1)}$$

Main attribute in microalgae culture that should be described is specific growth rate which is describing growth of biomass in relation to overall growth of biomass s in related time (look at equation 21) **(39)**.

$$\mu = \frac{1}{X} * \frac{dX}{dt} \qquad \text{(Equation 2)}$$

Very important is also efficiency of biomass factor based on substrate accesible which can be described as:

$$\frac{Yx}{S} = \frac{\Delta X}{\Delta S} \qquad \text{(Equation 4)}$$

Where ΔX is biomass growth and ΔS stands for substrate addition.

Other type of factor is biomass growth factor based on starting point of substrate addition.

$$YS_o = \frac{\Delta X}{S_o} \qquad \text{(Equation 5)}$$

Volumetric productivity can be described as

$$\mathrm{P} = \frac{dX}{dt} \qquad \text{Equation 28}$$

It is amount of biomass which is produced during specific period of time. Doubling time is essential to report on growth rate estimate. Doubling time can be presented in equation as (Equation 21).

$$t_d = \frac{\ln 2}{\mu}$$

μ is specific growth rate **(8).**

4.3 Inhibition or catalyst kinetics

As mentioned before in bioreactors are taking place biological reactions which due to their complexity can be described based on known data and relationships. On culture growth got influence major factors such as biotic and abiotic. In master thesis biotic will not be taken into consideration as there is no interference with other culture of microorganism. Below

are described some of abiotic factors which are working in some culture conditions as catalysts or inhibitors.

4.3.1 Temperature influence

Temperature influence on cultivation can be described as equation in unlimited growth (characteristics were described in previous chapter). Most suitable temperature influence can be described as **(12):**

$$\mu maxT = \mu max * \exp\left(-2{,}3 * \frac{(T - Topt)}{(Tsup - Topt)}\right)^2$$ Equation 29

For T > Topt

$$\mu maxT - \mu max * \exp\left(-2{,}3 * \frac{(T - Topt)}{(Tinf - Topt)}\right)^2$$ *Equation 30*

For Topt >T

In presented equations (equations 29 and 30) µmax is described as maximum specific growth for given degree of temperature. In this equations are taken into account values of optimal temperature Topt, in which is expected highest maximum growth rate of microorganisms. In equation 30 there is mentioned maximum cultivation temperature Tinf in which microalgae can grow. In equation 29 Tsup stands for minimum possible cultivation temperature, in which microalgae can grow. In given equations all cultivation conditions are taken into account and thanks to this there can be tracked growth rate of culture from marginal conditions to optimal ones.

In calculation was chosen factor - 2,3 because it was suiting curve of culture specific growth of real experimental data performance from article *Kinetic model for growth of Phaeodactylum tricornutum in intensive culture photobioreactor, Campus Rio San Pedro, 2008*. As was previously mentioned, so far there is no available data concerning PBR cultivation regarding SunChem project system.

I calculated specific growth rate of microalgae strains based on given equations and suited to curve presented in figure 36.

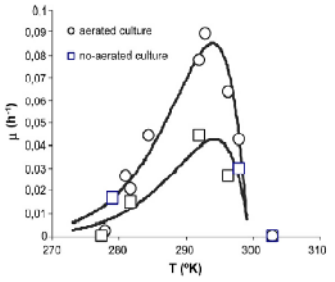


Figure 36 Specific growth rates at different temperatures

Influence of temperature on specific growth rate is calculated for type of unlimited cultivation. Presented basis are concentrated only on temperature influence and all other environmental conditions are neglected.

4.3.2 pH influence

In terms of pH influence it is possible to differ equation which is based on simple Monod's equation for limited type of culture cultivation. Equation which is suitable to apply is in form of **(44)**

$$\mu = \frac{\mu_{max}}{1 + ([H^+]/K_1) + (K_2/[H^+])}$$

Equation 31

H+ stand for 10^{-pH} and it is expressed as protons concentration (mol/liter). In presented equation factors such as K_1 and K_2 are corresponding kinetic constant (mol/liter).

Equation was based on approach from *Kinetic model for growth of Phaeodactylum tricornutum in intensive culture photobioreactor, Campus Rio San Pedro, 2008*. In the presented approach is not taken into account marginal pH conditions.

In equation factors such as K_1 and K_2 were calculated based on referential curve, which is presented in figure 37.

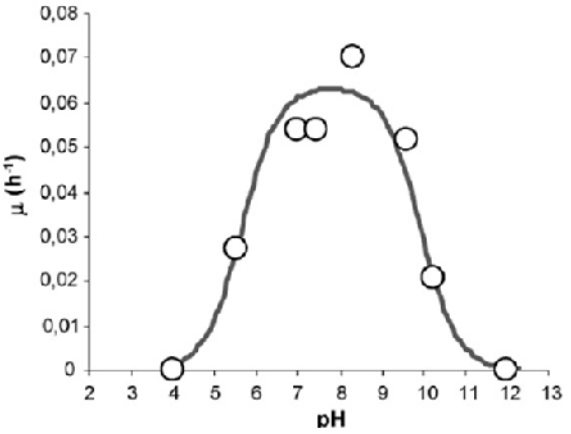


Figure 37 Specific growth rates at different pH values

Calculated specific constants (K_1 and K_2) are presented in table 20.

Microorganisms which are neutrophils (pH 6,5 -7 optimum) are able to uptake HCO_3 and H_2CO_3 in accordance to equations presented in chapter 2.2. Presence of pH not higher than 8 is promoting HCO_3. In this form it is possible to perform high biofixation level of carbon.

4.3.3 Carbon dioxide influence

Carbon dioxide influence on culture specific growth rate was described based on experimental data performance from article CO_2 biofixation and fatty acid composition of Scenedesmus obliguus and Chlorella pyrenoidosa in response to different CO2 levels, Shanghai Jiao Tong University, 2010. Following experimental data presented on picture 38 was calculated behavior of microalgae strain specific growth rate yield.

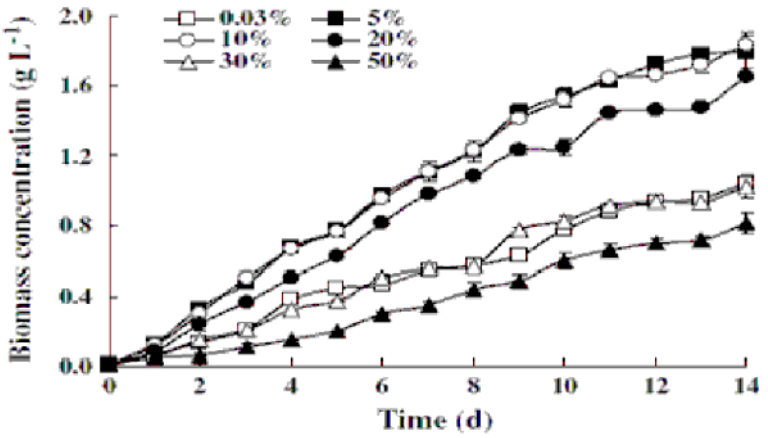


Figure 38 Concentration of microalgae biomass at different CO2 yield in flue gases

Following given experimental data presented on picture 38 was calculated specific growth rate in period of time for 14 days. According to presented experimental data results it is possible to obtain specific growth rate performance. Specific growth rate is calculated based on simple relationship where specific growth rate (1/d) is equal to multiplied concentration of biomass (g/L) in last day of cultivation and volume of PBR (L), divided by multiplied time of cultivation (d) and initial concentration of biomass (g). Data presented in figure 39 is based on given time in culture which is estimated as 14 days, initial concentration on 0,05g/L and volume of PBR assumed on 1 L level. Thanks to described relationship and assumed date it is possible to obtain values of specific growth rates for reference microalgae.

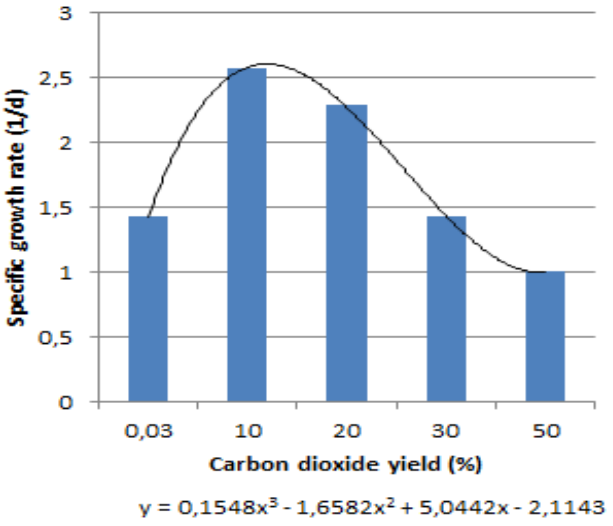


Figure 39 Specific growth rates at different carbon dioxide levels

Thanks to obtained results it is possible to spot relationship between specific growth rate (1/d) and carbon dioxide yield in flue gas (%). There is calculated relationship describing carbon dioxide influence on microalgae specific growth rate:

$$y = 0{,}1548x^3 - 1{,}6582x^2 + 5{,}0442x - 2{,}1143 \qquad \text{Equation 32}$$

Where y stands for specific growth yield (1/d) and x is described as carbon dioxide yield (%) in flue gases.

According to equation 33 it is possible to calculate supply of carbon dioxide in mg in each supplied m3 of air/flue gases, it can be described as **(17):**

$$\mathrm{mg/m^3} = \frac{\mathrm{ppm} \times M_\mathrm{r}}{24.45}$$

Equation 33

Mr stands for molecular weight of carbon dioxide (44g/mol) and where 22,45 (L/mol) is molar volume of ideal gas at 25 °C and 1 atmosphere.

Described streams of carbon dioxide in flue gas in rate of 0,03 to 50% of CO2 can be easily calculated as follows in table 16.

Table 16 Stream of carbon dioxide calculations

Ppm	**%**	**(g/m ^{3})**
385	0,038	0,69
100000	10	179,9
200000	20	359,9
300000	30	539,8
500000	50	899,7

Source: Own calculations

Biomass for each cultured kilogram can average uptake stechometrical ca. 1,9 kg of carbon dioxide from supplied stream. Carbon is fixed on 0,52 kg per 1 kg of microalgae and oxygen is used in process of photosynthesis. Following the equation such as:

$$L = \left(\frac{MBiomass}{Mcarbon\ dioxide}\right)$$

Equation 34

L stands for stechiometry biofixation rate of CO_2 in biomass, where B is molecular weight of biomass (g/mol) and CO_2 is molecular weight of carbon dioxide (g/mol). Additionally it is possible to use carbon utilization efficiency (CUE) by strain, it can be calculated as **(44)**

$$\mathrm{CUE} = \frac{0.45 M_\mathrm{DW}}{\sum_{i=0}^{n} C_\mathrm{fi}}$$

Equation 35

M_{Dw} stands for produced dry biomass weight (g) and C_{fi} is carbon fraction, supplied by carbon dioxide addition to given point of time - day n. Number 45 is related to % level of carbon content in dry weight biomass.

4.3.4 Irradiation

Photosynthetically active radiation (PAR) is associated with spectral range (wave band) of solar radiation 400 to 700 nanometers that photosynthetic organisms are able to use in the process of photosynthesis. Irradiance which is fixed number of photosynthetically active photons is representing a produced quantity of oxygen (about nine photosynthetically active Einstein's per mole of oxygen formed).

Equation for relation between specific growth rate and irradiation origin from approach from *Kinetic model for growth of Phaeodactylum tricornutum in intensive culture photobioreactor, Campus Rio San Pedro, 2008*. Catalytic influence of irradiance on growth of microorganisms can be presented by use of simple Monod equation in form of **(44):**

$$\mu = \frac{\mu_{\max} I}{I + K_i}$$

Equation 36

Specific growth rate is calculated based on I irradiance inside culture (µEinstein/m^2sec), K_1 is described as associated parameter (µEinstein/m^2sec) and µmax is maximum growth rate of strain (1/h).

K_1 parameter was calculated separately for all analyzed culture strains and reference data table presented in figure 40.

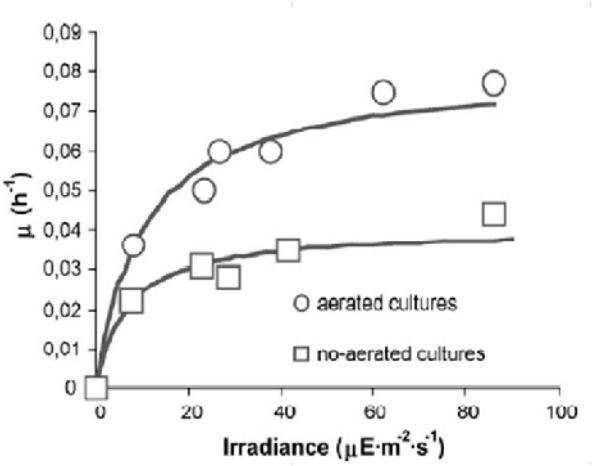


Figure 40 Specific growth rates at different irradiance level

Data concerning irradiance inside culture was collected from various articles.

4.3.5 Nutrients shortage

In case when there are several inhibiting substances which are nutrients, they can be described as resultant of them based on each of inhibiting factors. Substrates can be described as ones which are essential (source of carbon, oxygen, and nitrogen) and ones promoting growth (mineral particles).

This can be presented by Tsao-Hansen equation:

$$\mu = \left(1 + \sum_j \frac{k_j \cdot S_{\text{E},j}}{K_{\text{E},j} + S_{\text{E},j}}\right) \prod_i \frac{\mu_{\text{m},i} \cdot S_{\text{S},i}}{K_{\text{S},i} + S_{\text{S},i}}$$

Equation 37

S_{si} stands for concentration of substrate which is essential to growth and S_{fo} is concentration of substrate which is promoting growth.

However, this relationship is not included in master thesis due to lack of data.

4.4 Summary

Described simplified equation is set up to describe cultivation relationship on PBR. Simplified approach is due to clear presentation of catalyst/inhibiting complex issues. Analyst of one after another influence factor is used to analyze step by step major factors. There is strong need to analyze general complex approach of all factors. However, in this master thesis it is neglected due to lack of ability of reliable data and restricted filed of performance. Recommending is to analyze additionally metal and nutrition influence on culture.

5 CASE STUDY – SELECTED STRAINS AND MICROALGAE

In this chapter will be describe influence on microalgae growth in PBR according to equations of state from chapter 5. Purpose of this part is to develop a model which will contribute on microalgae specific growth rates in first step of PBR modeling design. Model is serving as quantitative description of dependence on design parameters. Growth rate is highly important in terms of obtain culture productivity. Amount of produced microalgae biomass is supplied to HTG process and converted into valuable grid quality methane. In my work I concentrate on several species of microalgae which are commercially available and widely described in literature.

During my research I found problems with available microalgae characteristic description as process is still commercially sensitive.

5.1 Microalgae biomass characteristic

Microalgae biomass characteristic can be described in terms of proximate and ultimate analysis. Ash content is (general proximate analysis) is set up as characteristic of microalgae Spirulina Platensis (Phyllis database 2011) and is assumed on 7,7% dw (dry) biomass. Moisture content in used microalgae biomass is estimated on ca. 87%.

Ultimate analysis is based on data description of several authors and final characteristic is described as average percentage value from all presented. In the table 17 is stated literature review.

Table 17 Biomass characteristic

Source	Composition						Composition (%)				
	C	**H**	**O**	**N**	**S**	**g/mol**	**C**	**H**	**O**	**N**	**S**
A	1	1,71	0,48	0,19	0	24,2	49,6	31,74	31,74	11	0,62
B	1	1,57	0,33	0,12	0,01	20,78	57,76	25,29	25,29	8,1	1,3
C	1	1,54	0,65	0,01	0	24,39	49,24	42,4	42,4	0,8	1,3
D	1	1,49	0,68	0	0	24.32	49,34	44,43	44,43	0,08	0,02
E	1	1,64	0,41	0,13	0	22,16	54,15	29,7	29,7	8,23	0,5
F	1	1,88	0,59	0,13	0	25,21	47,6	37,41	37,41	7,09	0,47
G	1	1,62	0,33	0,16	0,01	21,37	56,15	24,81	24,81	10,71	0,76

A) M Gassner Materials, B) Haiduc SunChem 2009, C) Shear stress tolerance and biochemical characterization of Phaeodactylum tricornutum in quasi steady-state continuous culture in outdoor photobioreactors, 2003, university of Almeria, D) C. Gattiker, 2009, E) ECN – microalgae Phyllis database, F) ECN - microalgae Spirulina Phyllis database, G) Microalgae cultivation in a wastewater dominated by carpet mill effluents for biofuel applications, the university of Georgia, 2010

Average biomass microalgae molecular formula was calculated based on available data in terms of percentage and molecular formula type. Calculated data is presented in table 18.

Table 18 Average biomass characteristic

	Composition						**HHV (MJ/kg_{dry})**	**LHV (MJ/kg_{dry})**	**Mol mass (g/mol)**
	C	H	O	N	S	P*			
Chemical formula	1	1,62	0,46	0,11	0,01	0,02	23,7	22,1	22,8
Percentage yield (%)	52,7	7,13	32,6	6,76	0,87	No data			

*Phyllis database Spirlulina Platensis

Presented biomass characteristic are describing types of feedstock on which will be performed process of HTG.

5.2 Selection of algae strain

There is restricted literature source on subject on microalgae specific growth rate. Obtained characteristic of strain are helpful in quantitative description of optimal environment conditions. Microalgae strains were select based on available source. Most commonly described strains are listed in table 19.

Table 19 Most common commercially available strains of microalgae

Microalgae	μmax (1/d)	pH min	pH opt	pH max	Tinf (C)	Topt (C)	Tsup (C)
Scenedesmus obliguus	0,5 (8)	4 (1)	7 (1)	9,3 (1)	10 (1)	31 (1)	36 (1)
Chlorella vulgaris	0,29 (7)		7 (2)		25 (2)	37 (1)	43 (1)
Dunaliella salina	0,3 (6)	5,5 (1)	9 (2)	10 (1)	30 (2)	35 (1)	40 (2)
Spirulina platensis	0,528 (5)	4**	9 (2)	10 (2)	18 (1)	36 (1)	40 (1)
Phaedactylum tricornutum	0,8 (9)	4**	8 (2)	12**	18 (2)	22 (2)	24 (2)
Haematococcus pluvialis	0,64 (3)	4**	7 (2)	10**	18 (2)	20 (2)	22 (2)
Aphanothece Nageli	0,303 (4)	4**	8 (4)	10**	14**	25 (4)	30*

Source: various authors (listed below)

*based on average temperature of outdoor culture in Brazil (http://www.climatetemp.info/brazil/), **based on culture performance, average pH above level of 11 is not able to uptake dissolved CO2; pH opt as average

1) Microalgae biotechnology, 1989, Anders, 2) Algae culturing techniques, 2005, 3) Modeling of growth and accumulation of carotenoids in hematoccocus pluvalis as a function of irradiance and nutrients supply, university of Almeria, 2005, 4) Biotransformation's of carbon dioxide in photobioreactors, Federal University of Pelotas, 2010, 5) Influence of light quality and intensity in the cultivation of Spirulina Platensis from Toliara (Madagascar) in a closed system, Ecole Centrale Paris, 2008, 6). Pilot culture of three strains of Dunaliella Salina for B-carotene production ponds in the central region of Iran, University of Isfahan, 2006, 7). potential carbon dioxide fixation by industry important microalgae, Federal university of Parana, 2010, 8) Carbon dioxide biofixatrion and fatty acid composition of Scenedesmus Obliguus and chlorella pyrenoidosa in response to different co2 levels, Shanghai Fiao Tong University, 2010, 9) Particulate and dissolved lipid classes in cultures of Phaeodactylum tricornutum grown in cage culture turbidostats with a range of nitrogen supply rates, Dalhousie university, 1987

As presented in table there is various requirments on growth performance in terms of microalgae cultivation. However, this is not a withdrawn as selection of only one strain and suiting of environmental conditions for one type can perform in very high productivity.

In selection was no take into account ability to overcome harsh environmental conditions. Nor were analyzed nutrient supply needs for each of strain and many more issues. Mentioned issues are crucial in terms of in commercial type of cultivation. In next section will be performed quantitative analysis of modeled data.

Strains of microalgae were selected according to their specific characteristics such as

- High productivity - Aphanotnacea nageli, Hematoccocus pluvalis
- High lipid content – Phanadacteum tricornitum
- Wide commercial appliance possibility – chlorella vulgaris, Scenedesmus obliguus, Spirulina platensis etc.

5.3 Modeling of microalgae growth rate

Growth parameters influence on culture is described in chapter 3.5 and also in in chapter 2.3. Additionally equations which were used in modeling were previously described in chapter 4.

In evaluated data the presented and select microalgae strains were marked as:

- A - Scenedesmus obliguus
- B - Chlorella vulgaris
- C - Dunaliella salina
- D - Spirulina platensis
- E - Phaedactylum tricornutum
- F - Haematococcus pluvialis
- G - Aphanothece Nageli

5.3.1 Temperature influence on specific growth rate

In terms of selected strain of microalgae there is performed modeling based on equation 29 and 30 from chapter 4. 3.1. Where Tmin is described as lowest part and Tsup as highest part were growth is inhibit. Topt is an optimal temperature in which can be expected best performance of growth and highest productivity. Quantitate results of modeling are present in picture 41.

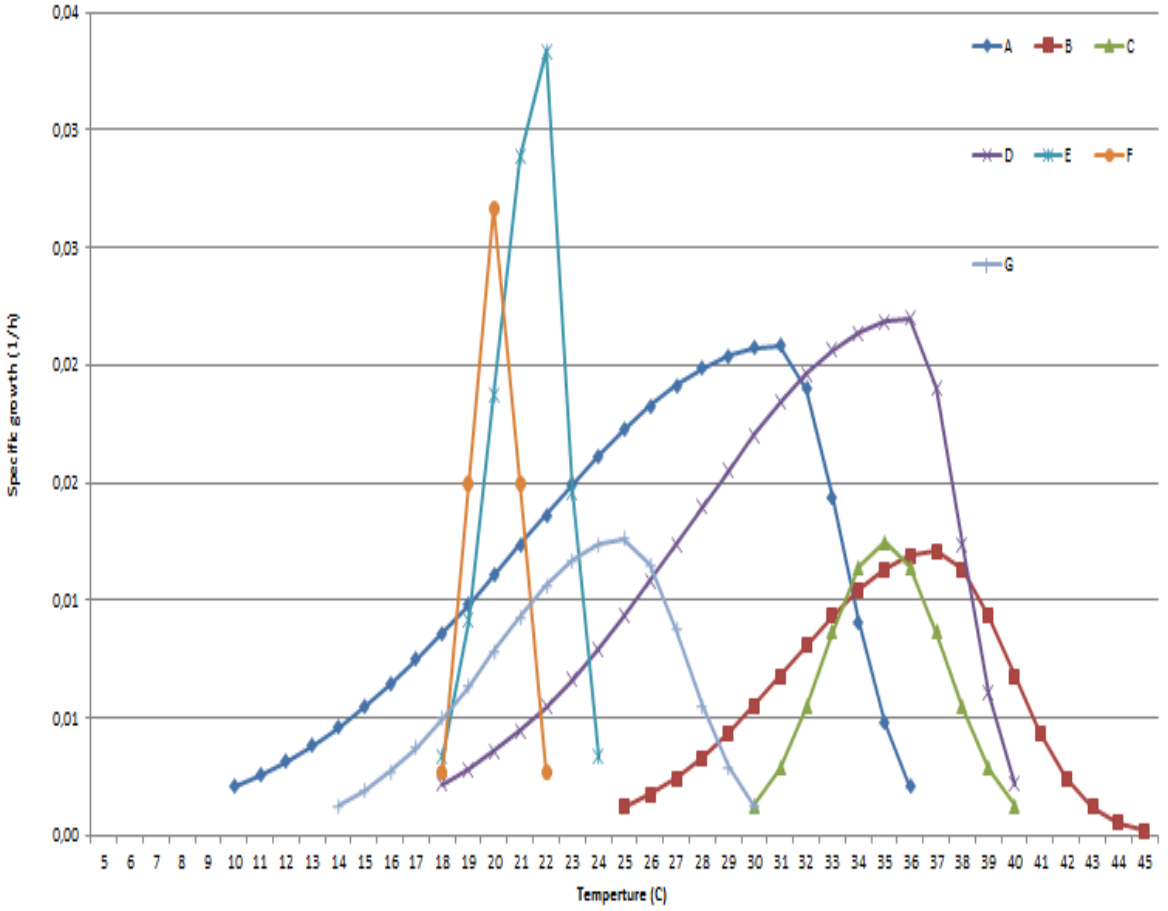


Figure 41 Temperature influence on growth rate

Chlorella vulgaris, Spirulina platensis and Duanlliella salina can be cultivated in nearly same temperature range. Second group which can be cultivated in same yield is Phanadctylum tricornutum and Hematococcus pluvalis. Rest two strains are not associated in any of temperature range.

5.3.2 pH influence on specific growth rate

pH influence on growth rate of microalgae is based on equation 31 from chapter 4.3.2. Calculated specific constants (K_1 and K_2) for each of selected microalgae are presented in table 20.

Table 20 Calculated specific constants for each microalgae strain

Number	Microalgae	K1 (10^{-6}) (mol/liter)	K2 (10^{-10}) (mol/liter)
1	Scenedesmus obliguus	9,5	9
2	Chlorella vulgaris	9	9,5
3	Dunaliella salina	6,5	0,0015
4	Spirulina platensis	7	0,002
5	Phaedactylum tricornutum	3	1,1
6	Haematococcus pluvialis	9,8	6
7	Aphanothece Nageli	9,7	0,11

pH values above minimal or maximal range are completely inhibiting growth of microalgae and presented in picture 42.

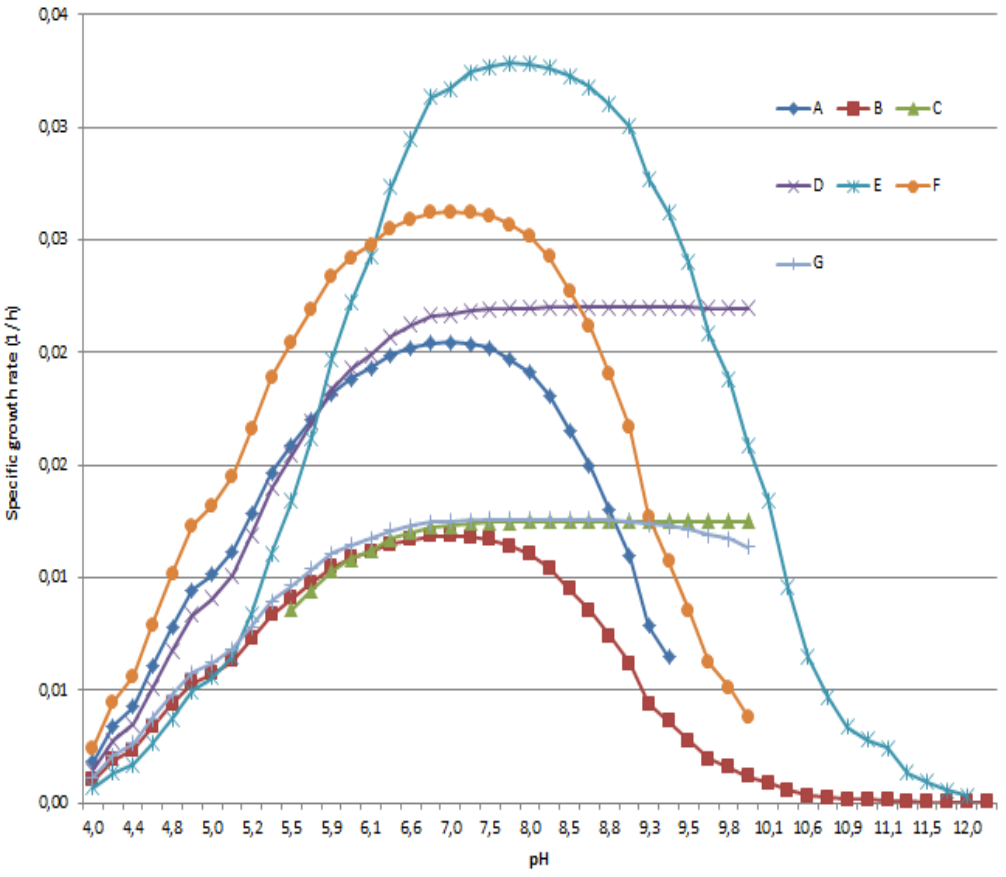


Figure 42 Influence of pH on growth rate

Most of analyzed microalgae are in range of 7 and 8 that means – Scenedesmus obligus, Chlorella vulgaris, Hamatecus pluvalis, Phatanecum tricornutum and Aphanocothece nageli. Rest of them – Dunatella salina and Spirulina platensis reach max growth at 9 pH.

5.3.3 Carbon dioxide influence on specific growth rate

Microorganisms which are neutrophils (pH 6,5 -7 optimal) are able to uptake HCO_3 and H_2CO_3 as dissolved CO_2. According to data for analyzed microalgae inhibiting influence can be presented in picture 43. **(45).**

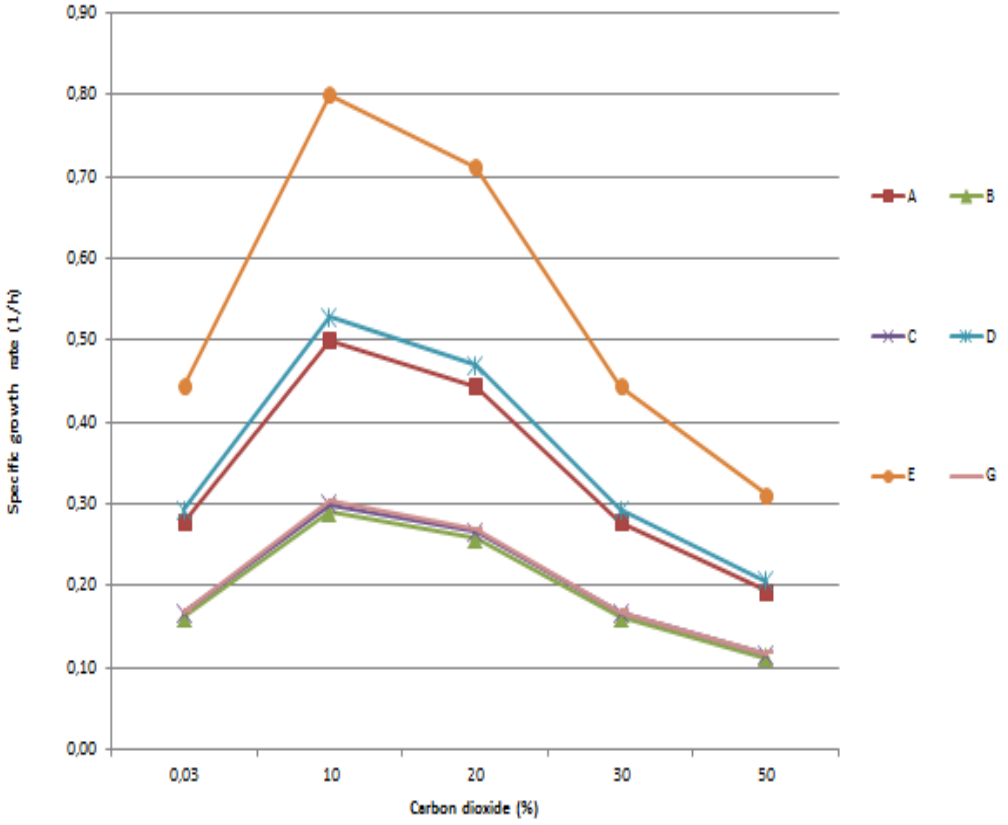


Figure 43 Influence of carbon dioxide on growth rate

In detail overall relationship can be presented as fallows on picture 43. Best performance is noticed for 10% of CO2 in supplied gas stream and worst can be observed with rising percentage of carbon dioxide in supplied flue gases. It is due to higher concentration of carbon dioxide in PBR and associated low level of pH. Low level of pH is not required in culture in PBR.

5.3.4 Irradiance influence on specific growth rate

Light intensity requirements can be described for each microalgae strain as follows in table 21.

Table 21 Light intensity requirements for max specific growth rate

Number	Microalgae	μmax (1/h)	Maximum saturation level for strain (μEinstein/m^2sec)	K1 Average irradiance inside culture (μEinstein/m^2sec)
1	Scenedesmus obliguus	0,021	100 (A)	5,5
2	Chlorella vulgaris	0,012	60 (B)	5
3	Dunaliella salina	0,013	150 (C)	25
4	Spirulina platensis	0,022	100 (D)	17
5	Phaedactylum tricornutum	0,033	56 (E)	2
6	Haematococcus pluvialis	0,027	60 (F)	3
7	Aphanothece Nageli	0,013	86 (G)	1,5

Where source are: A) A comparative approach towards thylakoid membrane proteome analysis of unicellar green alga Scenedesmus Obliguus, university of Crete, 2007 B) Enhanced lipid production of Chlorella vulgaris by adjustment of cultivation conditions, Zhejiang university, 2010 C) impact of environmental conditions on photosynthesis, growth and carbon allocation strategies of hyper saline species of Dunaliella, Politechnic of Milano, 2009 D) Response of Spirulina platensis C1 to high temperature and high light intensity, King Mongkut university of Technology, Thonburi, 2005 E) Effect of cell density and irradiance on growth, proximate composition and eicosapentaenoic acid production of Phaeodactylum tricornutum grown in a tubular photobioreactors, School of biological and Environmental Science, 1994 F) Modeling and accumulation of ceratoid in Haemotococcus pluvalis as a function of irradiance and nutrients supply, university of Almeria, 2005 G) based on other microalgae performance, average data.

Presented relationship of light requirement can be presented as follows on picture 44.

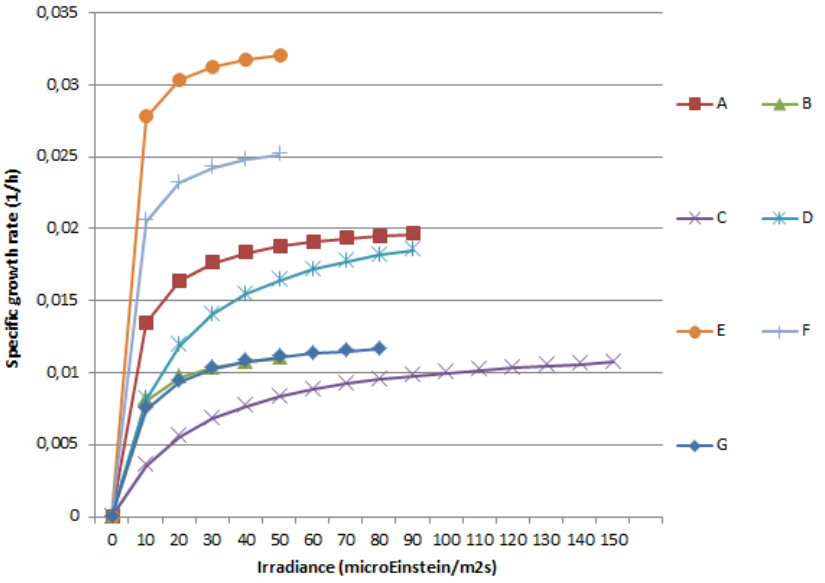


Figure 44 Irradiation influence on growth rate

Thanks to presented data it is possible to notice that Phanactylum tricornutum, Chlorella vulgaris and Hematoccoucus pluvalis is characterized as most efficient by lowest need of light irradiance. Duanaliella Salina needs the highest level of PAR irradiance (picture 45).

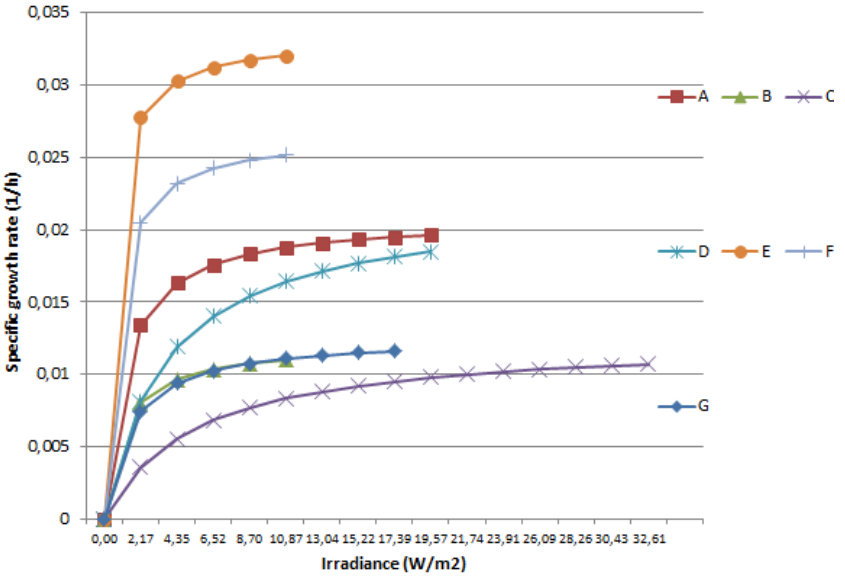


Figure 45 Irradiation influence on growth rate

5.3.5 Nutrition supply

Nutrient which are essential for growth of microalgae is phosphor and nitrogen. According to equation there is a need to supply given amount of salts. Nutrients which are essential for microalgae growth can be calculated.

Liquid algal slurry can be in general characterized by overall formula according to $CH_{1,62}O_{0,46}\ N_{0,11}P\ _{0,02}$ overall characteristic of microalgae (characteristic from average biomass and Phyllis data base, 2010).

Mass balance of nutrients can be calculated as on equation 38

$$2CO_2 + 0{,}04PO_4^{3-} + 0{,}22NO_3^{-} + 0{,}72H_20 + 1{,}8H^{+} \rightarrow 2CH_{1,62}O_{0,46}\,N_{0,11}P\ _{0,02} + 2{,}31O_2$$

Equation 38

Content of sulphure is neglected due to not essential value in nutrient context for growth. Based on stoichiometric calculation where biomass is characterized by $CH_{1,6}2O_{0,46}N_{0,11}P_{0,02}$ and can be stechiometry, need of nutrients is based on molecular weight of nutrient divided by biomass molecular weight (same as equation 34) . According to mentioned, there is a need to supply 1,21 of N_2 per 1 kg of microalgae. There is also need to supply 1,34 kg of phosphor per kg of microalgae and 1,39 kg of sulphore per kg of microalgae.

5.4 Selected strain - summary

In PBR microalgae can be cultivated as single strain and its growth than can be optimized in relation to best conditions. In case of one strain selection there are several factors that need to be taken into account.

Summary of selected strain performance with concern of all mentioned issues from chapter 5.3 is analyzed in table 22.

Table 22 Comparison of microalgae strain performance

Microalgae	**μmax (1/d)**	**Irradiation (μEinstein/m^{2}sec)**	**Temperature (C)**	**pH**	**Carbon dioxide or nutrient uptake (g/gbiomass)**
Scenedesmus obliguus	0,5		31		Highest carbon uptake
Chlorella vulgaris		60	37		Lowest nutrient need
Dunaliella salina			35	9	Lowest nutrient need
Spirulina platensis	0,528		36	9	Highest carbon uptake
Phaedactylum tricornutum	0,8	56		8	Highest carbon uptake
Haematococcus pluvialis	0,64	60			
Aphanothece Nageli					Lowest nutrient need

Growth rate is most important factor as it got influence on level of produced biomass, carbon dioxide uptake and nutrients requirement. Most interesting strains were differed in table 21. However, this is not only factor there are few several which need to be considered in terms of overall system performance. In regard to temperature there is preferred to choose as high as possible, not to use energy required for cooling of looped effluent. In this case strains differed in table are considered as most interesting for process performance. However, with rise of temperature there is also lowered uptake of carbon dioxide (look at figure 11, chapter 2.2). Best performance in chosen yield of temperature is for Dunalliela Salina and worst is for Chlorella Vulgaris. However, difference in temperature is ca. 1C so these are considerably small relations in amounts of dissolved carbon dioxide. Low pH can negatively influence culture breeding and also is not preferable as in acid pH carbon dioxide is in form of H_2CO_3. Best would be strain characterized by optimal pH (look at picture 12). It is due to obtained carbon dioxide form in solution as in range 6,5 to 10,5

carbon dioxide is in form of HCO_3 and also small amount of H_2CO_3 and CO_3. Last two forms can be not easy to uptake by microalgae. In the table were chosen most interesting strain for process. Lowest irradiation for optimal growth is giving lowest requirement for used energy, in these strain such as such as Phanadyclum tircornutum was selected. Secondary issue which is tackled in SunChem project is CO2 uptake yield. Based on high growth rate there is assumed that there is higher need of CO2. Same assumptions is based on nutrient requirement. However it is preferable to choose lowest nutrient uptake due to environmental and economic reasons.

Most interesting for process performance as one strain in PBRs is strain – Spirulina platensis or Phanadcylum tricornitum. Spirulina platensis in terms is characterized by not high oil yield in contribution to Phanadactylum ticornutum (high oil got positive influence on economic aspects of investment). Additionally Spirulina platensis is considered as valuable, very high source of proteins estimated as high as 63% (look table 9.).

For simultaneous cultivation most interesting are strains characterized by nearly similar requirements - Chlorella vulgaris and Spirulina platensis. Simultaneous cultivation can be performed in order to perform production although targeted on high SNG (electricity) or combined oil and SNG (electricity). Biomass after oil extraction (residue) is a process feedstock characterized by considerably lower heating value.

Based on presented data for further analysis is chosen Spirulina Platensis. Spirulina is a strain of blue-green alga with size of 2 to 8 microns (source – Warsaw University of Technology lectures) which can be cultivated both in salt or fresh type of water. Spirulina (look at picture 46) is characterized by high amount of protein ca. 55% to 77% by dry weight.

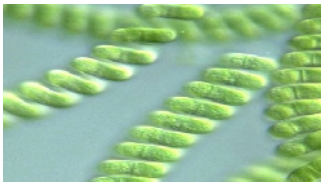


Figure 46 Spirulina platensis

Source: **(46)**

5.5 Selection of PBR

Some of the feature of PBRs – open and closed were analyzed in previous chapters. Open ponds and their comparison to closed ones were also widely discussed in chapter 3.3 and 3.6. Comparisons of selected PBRs were discussed already in table 14.

In thesis are compared two types of reactors which are tubular PBR and flat plate airlift PBR. Selected PBR are mostly selected due to their performance of work and validated in terms of commercial applicability. Most of important feature are presented in table 23.

Table 23 Advantages and limitations of open ponds and photobioreactors- comparison

Production system	Advantages	Limitations
Raceway pond	Relatively cheap Easy to clean Utilises non-agricultural land Low energy inputs Easy maintenance	Poor biomass productivity Large area of land required Limited to a few strains of algae Poor mixing, light and CO_2 utilisation Cultures are easily contaminated
Tubular photobioreactor	Large illumination surface area Suitable for outdoor cultures Relatively cheap Good biomass productivities	Some degree of wall growth Fouling Requires large land space Gradients of pH, dissolved oxygen and CO_2 along the tubes
Flat plate photobioreactor	High biomass productivities Easy to sterilise Low oxygen build-up Readily tempered Good light path Large illumination surface area Suitable for outdoor cultures	Difficult scale-up Difficult temperature control Small degree of hydrodynamic stress Some degree of wall growth
Column photobioreactor	Compact High mass transfer Low energy consumption Good mixing with low shear stress Easy to sterilise Reduced photoinhibition and photo-oxidation	Small illumination area Expensive compared to open ponds Shear stress Sophisticated construction

(25)

It is worth to analyze bags types of PBR (look picture 47) which are very interesting in terms of technological, environmental and economic reasons but they are newel and so there is limited literature data possible to collect. Actually RWE Power in Germany is interested in commercial use of bags type of PBR. Research is performed in RWE Algae Project.

Figure 47 Bags type of PBR RWE Algae project (RWE)

Based on **Producing synthetic natural gas from microalgae via supercritical water gasification: A techno economic sensitivity analysis** by Martin Brandenberger there was performed quantitative analysis of PBR in terms of CO2 uptake and production of microalgae biomass of Spirulina Platensis.

Analyzed PBR (picture 48, source 48) were based on open pond type, tubular PBR and flat plate airlift PBR. There was Spirulina Platensis analyzed, which was characterized by growth rate of 0,528 1/d.

Figure 48 Example of analyzed PBR types for cultivation of microalgae Spirulina Platensis

5.5.1 Cultivation scenarios

In first scenario was assumed for PBR reactor volume needed for utilization of carbon dioxide from flue gases. Values of produced carbon dioxide from flue gases were assumed as 3435 kg/h for 20 MW HTG systems.

Based on given quantity of CO2 there was calculated needed volume of PBR (m3) which is calculated based on supplied CO2 (kg/h) from flue gas multiplied by required removal efficiency (%) and divided by carbon dioxide uptake rate (g/gbiomass /h/L) times biomass concentration (g/L).

In accordance to this were used values for biomass concentration taken from paper reference number **47** (M. Brandenberger) – 0,5; 3,8 and 8 g/L. Required utilization of carbon dioxide was on 95% level and uptake rate was assumed as 0,4g/hL). Mass flow of carbon dioxide was given by M. Gassner on 3434,18 kg/h level. In case of required CO2 utilization level and uptake rate of biomass numbers were assumed due to lack of data for Spirulina Platensis. High carbon dioxide utilization level is giving best possibility to biofix carbon from flue gas. All mentioned parameters are presented in table 24.

Table 24 Data presented on PBR volume

Description	**Unit**	**Open pond**	**Tubular PBR**	**Flat PBR**
Biomass concentration	(gdw/L)	0,5	3,8	8
Mass flow of carbon dioxide	(kg/h)		3434,183	
Carbon dioxide uptake rate	(g/Lh)		0,4	
Required removal level	(%)		95	
Volume of reactor	(m^3)	16312,4	2146,4	1019,5

According to given values there was calculated PBR which will be able to uptake all carbon dioxide flue gas from process of 20MW plant. Obtained data analysis is presented in table 25.

Table 25 General characteristic of closed PBRs required utilizing on level of 95% carbon dioxide form 20MW HTG plant

Description	Unit	Open pond	Tubular PBR	Flat PBR
Growth rate	(1/d)		0,528	
Volume	(m^3)	16312,4	2146,4	1019,5
Surface volume ratio*	(m^2/m^3)	5	80	52,5
Surface required	(ha)	8,2	17,2	5,4
Occupied land area / volume ratio*	(m^2L/m^3)	5	63,5	35,4
Surface occupied	(haL)	8,2	13,6	3,6
Initial concentration	(kg)	369,9	745	647
Harvesting concentration*	(g/L)	0,5	3,8	8
Harvesting ratio*	(%)	4,6	14,9	4,2
Harvested biomass per one run	(kg)	375,2	9236,1	5481
First day of harvesting	(day cultivation)	42	21	24
Number of harvest in a year time	(n/a)	177,7	155,1	170,7
Harvested biomass in a year time	(tdw/unit/a)	66,66	1432,43	935,58
Areal surface productivity	(t/ha/a)	8,17	83,42	174,79
Volumetric productivity	(g/Ld)	0,01	1,9	2,5
Flow of biomass into system	(kgdw/sec)	0,0021	0,05	0,03
Biomass injected into catalytic reactor	(kgdw/sec)	0,0019	0,04	0,03
Phosphor requirement for growth	(tP/tbios/a)	89,3	1919,5	1253,7
Sulfur requirement for growth	(tS/tbios/a)	92,7	1991,1	1300,5
Nitrogen requirement for growth	(tN2/tbios/a)	80,7	1733,2	1132,1

* assumed values based on article reference to 47

Surface to volume ratio (SVR) was assumed same for 47 M. Brandenberger paper from SunChem for open pond, tubular and flat plate it was assumed 5; 80 and 52,5 respectively. Occupied area to volume ratio (m2l/m3) is giving relation of real working area of PBR to its volume. Working area is calculated apart from tails and other devices which are considered as auxiliary devices. There was assumed that occupied area to volume ratio is characterized for open pond, tubular and flat plate as 5; 63,5 and 35,4 respectively. SVR and occupied area to volume ratio differs. Harvesting ratio is assumed as percentage of biomass which is removed when culture is in required concentration. Harvesting concentration is describing concentration on which need to be taken biomass from culture. Concentration of biomass was assumed as 0,5 g/l for open pond and 3,8g/l and 8 g/l for closed ones. Biomass concentration for open ponds is usually assumed as 0,1 to 0,5 g/l as maximum values. For closed PBR concentration is assumed on levels between 0,5 to 8 g/liter **(49).** Harvested biomass is based on concentration on which biomass is harvest biomass for given volume of PBR obtained from each run of harvesting. Biomass which is harvested in one run is calculated as volume of PBR multiplied by harvested biomass (table 24). Harvesting ratio was chosen from research paper 47 and in both cases was based on assumption that growth, starting phase of cultivation is taking 6 - 8 weeks for open pond case. In terms of closed PBR cultivation is taking time during 2 to 4 weeks **(49).** Number of harvest per one month is calculated as harvest number in first month. Afterwards it is sufficient to calculate harvesting runs for all year. In first month of operation number of harvest and obtained biomass is much lower than performance during rest of the year. This is due to accommodation phase, which is assumed as very important for culture growth **(50).** Volumetric productivity (kg/ld) is showing how much biomass is produced in relation to given period of time in described volume of PBR. Energy (W/m2 or kW/ha)) which is essential for cultivation was calculated based on average irradiance for surface of PBR. Carbon dioxide supply, nitrogen, phosphate, sulfur demand was calculated stechiometry and assumed that for each kilogram of microalgae biomass $2CH_{1,62}O_{0,46}N_{0,11}P_{0,02}$ is need of:

- 1,9 kg of carbon dioxide,
- 1,34 of phosphate,
- 1,39 of sulfur,
- 1,21 of nitrogen.

Presented values are estimated for specific strain of microalgae only in term of technological advantage. Photosynthesis efficiency is best in case of flat plate due to minimal solar irradiance losses. Even though tubular PBR got highest surface to volume ratio (80 m^2r/m^3) it is still not sufficient in terms of photosynthesis efficiency (3,58 % for flat plate reactor) and surface of illuminated area (highest for pond raceway). Same high factor can be observed in terms of volumetric productivity due to overall optimal technological conditions, especially in terms of high photosynthesis level. Performed analysis give highest value of cultivated biomass for tubular type of reactor on level of 1432 tons in a year time. Flat plate PBR, was able to produce ca. 935 tons of biomass. Lowest values were obtained for open type of pond – only 66 tones. Initial concentration was estimated for open pond, tubular and flat plate as 364, 745 and 647 kg respectively. Harvesting ratio was chosen same as in paper of M. Branderburger **(47).** Starting phase was assumed as longest for open pond type of cultivation ca. 42 days. For closed type of PBR starting phase was assumed as 21 and 24 days. From first harvesting run it was

possible to obtain even 9236 kg of microalgae biomass. Volumetric productivity was calculated based on difference from obtained biomass minus initial biomass intake. Volumetric productivity was calculated for each PBR with respect to its volume. Highest volumetric productivity was assumed as high as 2,5 g/Ld for tubular PBR. Analyzed system was set up to perform analysis of utilization of PBR closed system as carbon dioxide sink. Performed calculation showed however that biomass which is produced in such system is not enough as biomass provision for 20 MW systems. Presented data is sufficient for ca. 1MW HTG biomass production. In order to obtain system which will be able to provide required 20MW biomass bulk amount there is analyzed biomass production system (table 26).

Table 26 General characteristic of biomass source 20MW PBRs closed loop

Description	**Unit**	**Open pond**	**Tubular PBR**	**Flat PBR**
Growth rate	(1/d)		0,528	
Number of units	(No.)	433,65	20,18	30,9
Volume	(m^3)	7073927,6	43313,6	31499,9
Surface required	(ha)	3537	346,5	165,4
Surface occupied	(haL)	3537	275	111,5
Initial biomass concentration	(t)	160,4	15	20
Harvested biomass in a year time	(1000tdw/ unit/a)		28,906	
Flow of biomass into system	(kgdw/sec)		0,929	
Areal surface productivity	(t/ha/a)	8,2	83,4	174,8
SNG produced from microalga biomass injected to grid	(kg/sec)		0,2381	
Carbon dioxide mass flow in flue gases	(kg/h)		3435	
Phosphor requirement for growth	(1000tP/tbios /a)		38,7	
Sulfur requirement for growth	(1000tS/tbios /a)		40,2	
Nitrogen requirement for growth	(1000tN2/tbi os/a)		35	

System which provide required biomass – ca. 29000 tons of microalgae on dry basis is calculated as 434 units of PBR or 20 units of tubular reactors or 31 flat plate reactors. Mentioned amount of biomass is providing to system continuous flow of biomass on 0,929 kgdw/sec into HTG process. Mentioned reactors are requiting in overall 3537 ha of open pond cultivation PBR. Lower surface is required in terms of tubular 346ha and flat plate reactors – 165 ha. In system real working surface of PBR should be estimated as 275ha for tubular and 111ha for flat plate reactors. Initial biomass for system performance is estimated as 15 for tubular plate and 20 for flat plate reactors. Biomass which is harvested in tubular reactor got highest bulk production potential of microalgae.

Presented quantities are showing that in terms of microalgae production as biomass feed for 20MW there is possibility to utilize carbon dioxide from flue gases from additional 19 or 29 installed capacity 20MW HTG plant. This is very promising in terms of carbon dioxide biofixation CCS process. However, in terms of single source of biomass production, presented quantities are not promising and need to be analyzed in terms of other than Spirulina Platensis microalgae. Additionally there should be calculated PBR production performance on side of CO2 uptake rate and required utilization level. Moreover, what is worth to add is that open ponds in each scenario present worst cultivation performance than closed types.

5.5.2 Discussion of results

There will be only discussed values obtained from cultivation for biomass production performance. Cultivation for carbon dioxide mitigation in obeys as it is not main assumption in SunChem project.

Open pond surface which is required to produce biomass on level of 29000 Mg to supply HTG plant 20MW is estimated as 3537 ha in my work. Mentioned number is considered as lower in terms of produced biomass and higher in terms of required surface area cultivation as in terms of MSc thesis of C. Gatticel **(6)** mentioned numbers for produced biomass and required surface cultivation area in best case scenario were 51 870 Mg and 2020 ha respectively. Proposed pond performance with surface requirements in my case is inefficient. Additionally it is worth to mentioned that in C. Gatticel Msc was used lower initial algae concentration for harvesting – 67 mg/L and other harvesting ratio performance. However, obtained value is probably based on selected highly productive microalgae strain and it is maximum specific growth rate as it is characterized by very good productivity performance with lower demand on surface area.

In relation to work presented in 47 which is characterized by same value on basic cultivation assumption - harvesting ratio, harvesting concentration and also PBR parameters it is possible to notice that my obtained produced biomass is also lower with higher surface requirement. It is estimated as need of 2246,1 ha of surface required with 97 030 tones produced in a year time. In conclusion in my work should be selected microalgae which are characterized by higher max growth rate. Mentioned numbers are presented in table 27.

Table 27 Comparison of results cultivation open type of PBR

Open pond	Unit	C. Gatticel *	M. Brandenberger**	My work
Produced biomass	(tdw/year)	51870	97030	28906
Required surface area	(ha)	2020	2246,1	3537
Areal surface productivity	(tdw/yr/haL)	23,6	38,5	8,17
Harvesting concentration	(g/L)	0,067	0,5	0,5

Source: * 6, ** 47

In my Msc I based my assumptions on article 47 and I will discuss my obtained values with relation to his work. However, based on analysis above I can notice that obtained by analysis values in terms of biomass produced per year will be much lower.

In case of tubular PBR in my case there is lower production of biomass but also lower estimation of required land area for cultivation (275 haL for surface requirement cultivation). Areal surface productivity thanks to this is much higher. Comparison is provided in table 28.

Table 28 Comparison of results closed PBR tubular type

Tubular PBR	Unit	M. Brandenberger**	My work
Produced biomass	(tdw/year)	88767	28906
Required surface area	(ha)	1151,3	346,5
Areal surface productivity	(tdw/yr/haL)	75,1	83,4
Harvesting concentration	(g/L)	3,8	3,8

Source: ** 47

In case of flat plate PBR is same case as in tubular PBR, in my case there is lower production of biomass and also lower estimation of required land area for cultivation (112 haL for surface requirement cultivation). Areal surface productivity thanks to this is much higher (174 t/ha/year). In table 29 is provided comparison between flat plates PBR.

Table 29 Comparison of results closed PBR flat airlift type

Flat plate PBR	Unit	M. Brandenberger**	My work
Produced biomass	(tdw/year)	89007	28906
Required surface area	(ha)	1094	165,4
Areal surface productivity	(tdw/yr/haL)	79	174,8
Harvesting concentration	(g/L)	8	8

Source: ** 47

In case of closed loop PBR I can assume that there was a selected microalga which is characterized by better specific growth conditions which got tremendous impact on performed cultivation. Calculation provided by me is giving much better parameters in terms of production of biomass for 20MW plant feedstock requirement. .

5.6 Oil extraction process biomass

First step after cultivation in PBR is dewatering and optional extraction of lipids. Algal slurry is dewatered with use of filter belt to obtain dry matter content ca. 20 wt.% (process is supposed to consume energy consumption of 0.080 kWh/m3) (Gatticel, 2009).

Lipid content in algae varies in between strains but also between populations in strain. Nutrient supply – shortage or surplus, irradiation and also other influencing abiotic factors got impact on lipid as shown on picture 49 (figure 34).

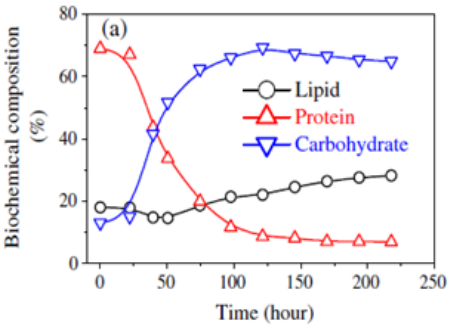


Figure 49 Biochemical composition

(51)

Not all lipids which are recognized in microalgae can be fully used. There are some types of oils which are recognized and widely used in commercial way. Basically recognized lipids are ca. 60% of overall lipid yield (dry weight). Oil yield in microalgae is based on several types of oils which are listed in table 30.

Table 30 Lipid which is recognized in microalgae

Lipids	Yield (%)	Normalized 100%
Palmitic	20,62	30,77
Palmitoleic	6,47	9,65
Oleic	10,58	15,79
Linoleic	26,01	38,81
Myristic	1,91	2,85
Stearic	1,43	2,13
Summary	67,02	100

Source: **(52)**

Most commonly recognized lipids are presented in table. Presented values in table are calculated by carbon molecule and are representing normalized numbers (to 100% of overall lipids). Data provided in table 31.

Table 31 Lipid characteristic

Lipids	C	H	O	Mol. mass (g/mol)
Palmitic	1	2	0,12	16
Palmitoleic	1	1,87	0,12	15,87
Oleic	1	1,88	0,11	15,66
Linoleic	1	1,77	0,11	15,55
Myristic	1	2	0,14	16,28
Stearic	1	2	0,11	15,77

Source: own calculation

Overall lipid formula for presented lipids is

$$CH_{1,88}O_{0,22}$$ Equation 39

(own calculation)

Calculated lipid was firstly normalized to carbon molecular and then calculated based on sum of % of each lipid content multiplied by moles of hydrogen and then estimated in same way for mole of oxygen.

Extraction of biomass and then calculation of residue for HTG process can be resented in form of:

Biomass → lipids + residue

In this equation residue is used in further HTG process performance.

Lipid extraction is calculated based on equation 40 in form of

$$CH_{\tilde{r}_{bm,H}}O_{\tilde{r}_{bm,O}} \rightarrow (1-\tilde{c}_{\mathbf{lipid}})\,CH_{\tilde{r}_{\mathbf{reś},H}}O_{\tilde{r}_{\mathbf{reś},O}} + \tilde{c}_{\mathbf{lipid}}\,CH_{\tilde{r}_{\mathbf{lip},H}}O_{\tilde{r}_{\mathbf{lip},O}}$$ Equation 40

In given equation C_{lipid} is representing lipid fraction in biomass (chosen microalage ca. 9%). $\tilde{c}_{\mathbf{lipid}}$ is representing molar fraction in biomass where is known share of lipid yield (equation 43).

All presented data can be calculated based on equations.

$$\tilde{r}_{\mathbf{reś},H} = \frac{\tilde{r}_{bm,H} - \tilde{r}_{\mathbf{lip},H}}{1-\tilde{c}_{\mathbf{lipid}}} + \tilde{r}_{\mathbf{lip},H}$$ Equation 41

In this equation r_{lipidH} stands for division between fraction of hydrogen and carbon from obtained lipid formula (similar way for calculation in terms of biomass $r_{biomassH}$).

$$\tilde{r}_{\mathbf{reś},O} = \frac{\tilde{r}_{bm,O} - \tilde{r}_{\mathbf{lip},O}}{1-\tilde{c}_{\mathbf{lipid}}} + \tilde{r}_{\mathbf{lip},O}$$ Equation 42

In this equation r_{lipido} stands for division between fraction of oxygen and carbon from obtained lipid formula (similar way for calculation in terms of biomass $r_{biomassO}$).

$$\tilde{c}_{\mathbf{lipid}} = \frac{\tilde{m}_{biomass}}{\tilde{m}_{\mathbf{lipid}}}\,c_{\mathbf{lipid}}$$ Equation 43

In equations $\tilde{r}$, represents molar ratios and $c_{\mathbf{lipid}}$ and $\tilde{c}_{\mathbf{lipid}}$ the mass and molar fraction of lipid in the feedstock, respectively.

According to presented biomass chemical composition and calculated values by equations it is possible to differ residue which can be used in HTG as direct biomass feed (table 32).

Table 32 Residue composition after lipid extraction

Micro algae type	Composition						Composition (%)				
	C	H	O	N	S	g/mol	C	H	O	N	S
A	0,96	1,63	0,47	0,19	0	23,5	49,01	6,92	32	11,32	0,64
B	0,96	1,49	0,32	0,12	0,01	20,08	57,37	7,44	25,46	8,38	1,34
C	0,96	1,46	0,64	0,01	0,01	23,69	48,62	6,17	43	0,82	1,34
D	0,96	1,42	0,67	0	0	23,62	48,77	5,99	45,14	0,08	0,02
E	0,96	1,57	0,4	0,13	0	21,46	53,67	7,31	30	8,5	0,52
F	0,96	1,8	0,58	0,13	0	24,51	46,99	7,34	37,8	7,29	0,48
G	0,96	1,54	0,32	0,16	0,01	20,67	55,72	7,46	24,96	11,07	0,79

A M Gassner Materials, B Haiduc SunChem 2009, C Shear stress tolerance and biochemical characterization of Phaeodactylum tricornutum in quasi steady-state continuous culture in outdoor photobioreactors, 2003, university of Almeria, D C. Gattiker, 2009, E ECN – microalgae Phyllis database, F ECN - microalgae Spirulina Phyllis database, G Microalgae cultivation in a wastewater dominated by carpet mill effluents for biofuel applications, the university of Georgia, 2010

Available literature is showing that lipid yield in microalgae varies considerably. Data concerning percentage of lipids in dry matter of particular microalgae strain is presented in table 33.

Table 33 Lipid yield in microalgae

Microalgae	Recognized oil yield (%)		Source
	Low	High	
Scenedesmus obliguus	11,76	12,66	A
Chlorella vulgaris	11,04	11,52	B
Dunaliella salina	9,6	26,4	C
Spirulina platensis	8,52	9,78	D
Phaedactylum tricornutum	11,22	26,88	E
Haematococcus pluvialis	6	18	F
Aphanothece Nageli	4,26	4,5	G

A) Microalgae as a sustainable energy source for biodiesel production: A review, University Sains Malaysia, 2010 B) Microalgae as a sustainable energy source for biodiesel production: A review, University Sains Malaysia, 2010 C) Lipid production by dualiella Salina in batch culture: effects of nitrogen limitation and light intensity, M. Huesemann, C. Share.D) influence of inoculum age and concentration in Spirulina platensis cultivation, university of Sao Paulo, 2002 E) Microalgae as a sustainable energy source for biodiesel production: A review, University Saints Malaysia, 2010 F) Accumulation of oleic in Haematococcus pluvlais (chlorophyceae) under nitrogen starvation or high light is correlated with that of astaxanthin esters, Ben Gurion university of the Negev, 2002 / Extraction of

Highest yield of recognized oil is observed in Chlorella vulgaris, Scendesmus obligus, Dunaliella salina and also in Phanaceaum tricornitum. Extracted oil can be used by external companies and sell in market for cosmetic or pharmacies purposes (as mentioned 215 - 2150 Euro per kg of used microalgae Dunaliella Salina). Residue is directed into thermochemical processes and purifies to obtain methane grid quality. Extraction of lipids and left residue which can be described as stated in table 34.

Table 34 Calculated residue composition after lipid extraction

Microalgae type	Composition high						Composition low					
	C	H	O	N	S	g/mol	C	H	O	N	S	g/mol
Scenedesmus obliguus	0,88	1,41	0,27	0,11	0,01	18,03	0,87	1,4	0,47	0,11	0,01	21
Chlorella vulgaris	0,89	1,43	0,29	0,11	0,01	18,34	0,88	1,42	0,47	0,11	0,01	21,2
Dunaliella salina	0,9	1,45	0,31	0,11	0,01	18,98	0,74	1,14	0,44	0,11	0,01	18,6
Spirulina platensis	0,96	1,57	0,43	0,11	0,01	21,62	0,95	1,54	0,48	0,11	0,01	22,37
Phaedactylum tricornutum	0,89	1,42	0,28	0,11	0,01	18,26	0,73	1,13	0,43	0,11	0,01	18,52
Haematococcus pluvialis	0,94	1,52	0,38	0,11	0,01	20,56	0,82	1,3	0,45	0,11	0,01	20,07
Aphanothece NagelI	0,96	1,55	0,41	0,11	0,01	21,33	0,96	1,55	0,48	0,11	0,01	22,42

After lipid extraction from Spirulina Platensiss which is considerably low in relation to other strains there is residue which can be used in process of HTG. In case of Spirulina Platensis there was assumed that average yield of lipid for residue calculation was ca. 9,15% according to equation 44.

$$CH_{1,63}O_{0,49} \rightarrow 0,9CH_{1,6}O_{0,53} + 0,1CH_{1,88}O_{0,22}$$ Equation 44

6 SUNCHEM PROCESS

SunChem process is a process of catalytic supercritical water gasification of biomass. Properties of water (above critical point which is at 374 ^{o}C and 22.1 MPa) which act as reactant are characterized by different structure and reduced hydrogen bonds. Dialectic

constant is changed and it is similar to apolar organic solvent (THF tetrahydrofuran, diethylether or hexane). In described process biomass is firstly decomposed by gasification process and then catalytic synthesized (gas – H_2/CO) into CH_4 and CO_2. In general assumptions, hydrogasification can be expressed as equation 45 in where carbon atom is used as reference value:

$$CH_{1,63}O_{0,46} + 0,19H_2O \rightarrow 0,5CH_4 + 0,5CO_2 \qquad \text{Equation 45}$$

Considered characteristic of Spirulina Platensis as biomass characteristic is presented in table 18 in chapter 5.

Process of HTG of microalgae and its thermochemical analysis was performed by Martin Gassner based on data base from EPFL. Biomass gasification part was calculated according to a detailed process model which refers to the *paper Process design of SNG production by hydrothermal gasification of waste biomass: Thermo-economic process modeling and integration, by E. Marechal and M. Gassner, 2010* **(53).** Process was calculated with use of Belsim – Vali program for modeling the conversion processes (non-linear, intensive part) and MILP programming (in-house EPFL code) for the mass and energy integration (linear, extensive part). Mixed Integer Linear Programming (MILP) can be performed by proposed several numbers of approaches such as: cutting place algorithm, implicit enumeration algorithms or branch and bound algorithm. However, in my work is not analyzed modeling part of SunChem thermochemical HTG, more detailed information can be found in PhD thesis of M. Gassner from 2010. General approach for process design methodology can be presented as follows on picture 50.

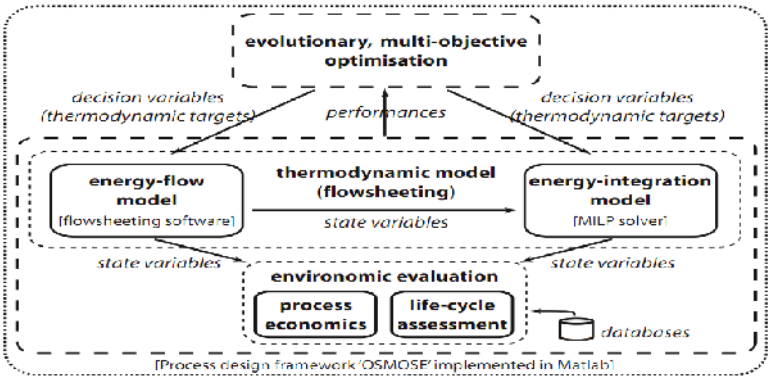


Figure 50 Process design methodology

(54)

Energy integration program in this case has been optimized with respect to maximum combined yield of SNG and electricity. In thesis (same as in relevant paper – 53 and 54) main performance indicators can be presented as overall efficiency of products. Additionally there is taken into account overall energy efficiency, exergy efficiency and chemical efficiency. Mentioned performance can be described as efficiencies of obtained products **(53):**

$$\varepsilon_{SNG} = \frac{\Delta h^0_{SNG} \dot{m}^-_{SNG}}{\Delta h^0_{biomass} \dot{m}^+_{biomass,daf}} \qquad \text{Equation 46}$$

In presented equation ε_{SNG} is conversion efficiency of SNG production.

$$\varepsilon_{el} = \frac{\dot{E}^{-}}{\Delta h^{0}_{biomass} \dot{m}^{+}_{biomass,daf}}$$

Equation 47

Ɛel represent electrical efficiency of products.

In two mentioned equations (equation 46 and 47) Δh represents dry lower heating value and $\dot{m}_i$ is a mass flow of biomass microalgae and $\dot{E}$ represents electrical power.

Additional another mentioned efficiency are expressed by efficiencies of product conversion to SNG and also electricity and can be described as **(53)**

$$\varepsilon = \frac{\Delta h^{0}_{SNG} \dot{m}^{-}_{SNG} + \dot{E}^{-}}{\Delta h^{0}_{biomass} \dot{m}^{+}_{biomass,daf} + \dot{E}^{+}}$$

Equation 48

$$\eta = \frac{\Delta k^{0}_{SNG} \dot{m}^{-}_{SNG} + \dot{E}^{-}}{\Delta k^{0}_{biomass} \dot{m}^{+}_{biomass,daf} + \dot{E}^{+}}$$

Equation 49

$$\varepsilon_{chem} = \frac{\Delta h^{0}_{SNG} \dot{m}^{-}_{SNG} + \frac{1}{\eta_{NGCC}} \frac{\Delta h^{v}_{SNG}}{\Delta k^{0}_{SNG}} \dot{E}^{-}}{\Delta h^{0}_{biomass} \dot{m}^{+}_{biomass,daf}}$$

Equation 50

In given equation Δk stands for exergy value and Ɛ is overall energy efficiency. In given equations η stands for exergy efficiency and $Ɛ_{chem}$ is standing for chemical efficiency. In equations subscripts + refer to indicate produced, and – consumed services.

In given equation *NGCC* (Natural Gas Combined Cycle) efficiency is considered on level of 55%.

The overall gross thermal energy efficiency **(47)** of the process $\eta_{process}$ can be described as

$$\eta_{process} = \frac{E_{SNG} - E_{required}}{E_{algae}} \times 100\ \%$$

Equation 51

Where $E_{required}$, the external electric energy input required producing the SNG in kWh. In terms of standalone and self-based there can be used different assumptions. In self-sufficient process, where electricity required for the PBR microalgae cultivation and for example for auxiliary devices (e.g. pumps) can be obtained from conversion of the SNG into electrical energy in a combined cycle gas turbine (NGCC - CCGT). The energy efficiency for the stand alone system is $\eta_{autarkic}$ can be described as:

$$\eta_{autarkic} = \frac{E_{SNG} - \frac{E_{required}}{\eta_{el}}}{E_{algae}} \times 100\ \%$$

Equation 52

Energy efficiency which includes sunlight conversion η_{SUN} into SNG in a self-sufficient process can be present by equation **(47)**

$$\eta_{SUN} = \frac{E_{SNG} - \frac{E_{required}}{\eta_{el}}}{E_{SUN}} \times 100\ \%$$

Equation 53

Where E_{SUN} (kWh) is the energy received by solar irradiance on the occupied land area (PBR). More information about mentioned equations and given assumptions are presented in paper of M. Brandenberger **(47)** from 2010 and also in paper of M. Gassner and F. Marechal **(53).**

6.1 Overview of the SunChem process

Hydrogasification in SunChem process can be divided into steps which are based on biochemical and thermochemical processes. Basic parameters of process on which was based modeled system presented in table 35.Assumptions are widely described in paper **53**.

Table 35 Basic parameters of process

Section	Operating conditions		Unit	Default
Feedstock	Type		-	wood
	Ash content		$\%wt_{dry}$	0.6
	Composition (C, H, O, N)		$\%wt_{daf}$	51.1, 5.8, 42.9, 0.2
Pretreatment	Total solids content of diluted feed		%wt	20
	Process pressure	p_{tot}	bar	300
Salt separation	Inlet temperature	$T_{ss,in}$	°C	350
	Maximum temperature	$T_{ss,max}$	°C	480
	Internal heat decrease	$\Delta T_{ss,int.}$	°C	20
	Outlet temperature	$\Delta T_{ss,out}$	°C	460
	ΔT at bottom	$\Delta T_{ss,bottom}$	°C	20
	ΔT at top	$\Delta T_{ss,top}$	°C	20
	Organic loss in salt brine		%	10
Gasification	Inlet temperature	$T_{g,in}$	°C	413
	Outlet temperature	$T_{g,out}$	°C	400
Water scrubber column	Bottom temperature		°C	30
	Pressure	$p_{hp,sep}$	bar	300
	Equilibrium stages	$N_{s,H2O}$	-	5
	CH_4 purity[a]	$\tilde{c}_{CH4,hp,out}$	%mol	94
Selexol column	CH_4 recovery	$r_{CH4,sel}$	%	98
	Absorption factor	A_{sel}	-	1.4
	CH_4 purity[a]	$\tilde{c}_{CH4,sel,out}$	%mol	94
SNG membrane	Material[a]	$y_{memb.}$	integer	2
Power recovery	Vapour phase	y^{v}_{prec}	integer	1
	Liquid phase	y^{l}_{prec}	integer	1
	Reheat temperature of vapour	$T_{g,s}$	°C	var
Turbomachinery	Efficiency (isentropic)		%	80
Rankine cycle	Steam production pressure	$p_{s,p}$	bar	40/20[b]
	Steam superheat temperature	$T_{s,s}$	°C	350/270[b]
	Intermediate utilisation level	$T_{s,u}$	°C	200/120[b]
	Condensation level[c]		°C	19
	Efficiency, backpressure stages		%	80
	Efficiency, condensation stage		%	70
POX gas turbine	Pressure	p_{POX}	bar	14
	Fuel choice[d]	y_{fuel}	integer	1
	Additional steam per fuel *i*	$r_{fi,H2O}$	kg kg^{-1}	0.5
Energy integration	Fuel preheat temperature		°C	400
	Minimum approach temperatures (vapour & supercritical, liquid, phase-changing, reactive streams)	$\Delta T_{min}/2$	°C	8, 4, 2, 25
NG grid specifications	CH_4 purity	$\tilde{c}_{CH4,grid}$	%	96
	Grid pressure	p_{grid}	bar	70

a) For final SNG upgrading with a polymeric membrane. Material choice (properties as in Gassner and Marechal) 1. Cellulose acetate, 2. Polysulfide b) with/without VL separation at high pressure c) corresponds to the low temperature utilization level d) candidate fuels 1. Crude SNG, 2 recovered depleted stream from flash 3) membrane permeable, combinations 4) 1&2, 5). 1&3, 6). 2&3, 7 all

(53)

SunChem process is in general way presented in form of diagram in the picture 47. There were neglected issues such as Heat Exchanger Network and Heat Recovery Steam Generator system (HRSG) as this subject is to brad for considerations in this thesis work (figure 51).

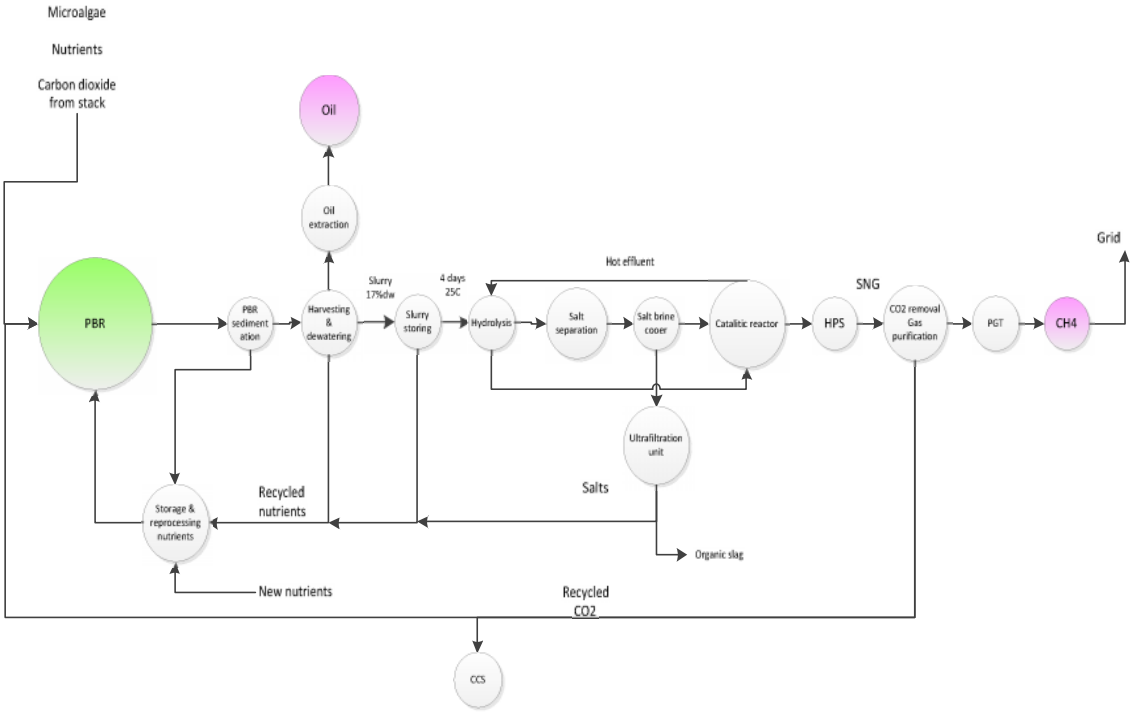


Figure 51 SunChem process design

Process of SunChem main approach is to directly produce SNG but also electricity. Electricity can be used by system itself but also, in case of surplus production, can be sold to external companies on free market. In the system is also integrated system of heat exchangers and Heat Recovery Steam Generator which is using cycle with boiler **(55).** Steam is expanding in steam turbine and obtained mechanical power is converted by generator to electrical energy. Than steam is condensed, remaining heat is extracted and used for SunChem process (figure 52). Steam turbine is based on high, intermediate and low pressure stages. More on subject in previously mentioned papers.

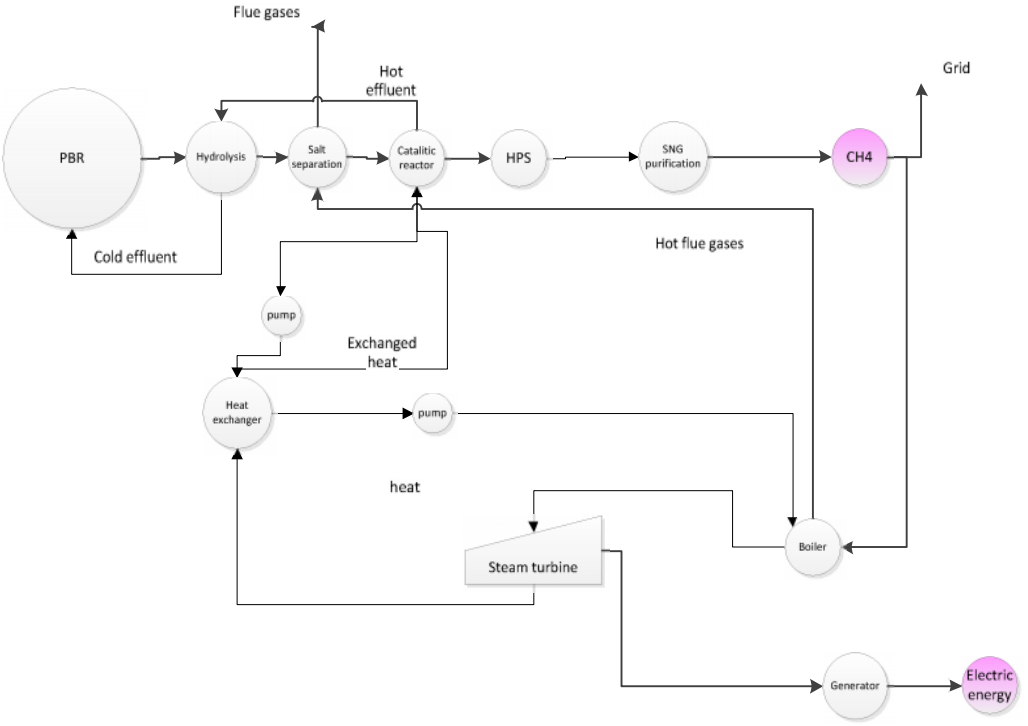


Figure 52 Integrated SunChem process design

Detailed description of SunChem process is discussed below.

1. Supply of carbon dioxide

Carbon dioxide origin from external industrial source (combustion source - coal power plant, cement plant, biogas plant etc.) or from process of SunChem itself, that means lopped from end stage of process.

In process other fumes such as oxides of nitrogen and sulphure (NOx, SOx) and of volatile metals, particles PM are not taken into account. It is assumed that gas from stack is directly cleaned by relevant devices. Carbon fractions are supplied to PBR by mentioned flue gas and nutrients are supplied by external devices. Flue gas is composed of 15% of CO_2 and 85% of N_2 (based on source 47 and 53).

Composition of gas is fixed in SunChem paper proposal and it is mentioned in related to project scientific literature. In case of requirement of microalgae, CO2 which is essential for growth and that can be bio fixed is calculated stechiometrical based on specific biomass composition.

2. PBR

Most important issue in this step is selection of best algae strain and also PBRs type. In my thesis I am decided to use algae strain Spirulina platensis, my choice was justified in previous chapter. In my work I am analyzing only closed type of PBR. Into consideration was firstly taken biomass productivity such as annual aerial surface biomass productivity

(t/haL/a) and also volumetric biomass productivity (g/l/d). Mentioned parameters with assumption of percentage of up taken carbon dioxide were influencing estimation of size of microalgae cultivation system PBR. In this step unit of calculated PBR were multiplied by required number of units to obtain biomass bulk that will satisfy process of 20MW HTG plant. Several numbers of units of PBR is providing continuous harvesting and supplying process. Heating of Spirilina Platensis in PBR to optimal temperature of 36C is obtained thanks to re-looped, hot fume gases and form compensator from last stages of process. Additionally irradiance is also supporting optimal temperature level approach. Quantitative number of required heat is obtained by use of U tube HX- heat exchanger and medium is CO2 which afterwards is injected into PBR.

$$Qt=U*A*F*(T_1-T_0) \qquad \text{Equation 54}$$

Where:

Qt –heat load from CO2 (kJ/sec)

U – heat transfer coefficient

A –area of heat exchanger (m2)

F – correction factor (kJ/s)

(T_1-T_0) – temperature difference (C)

Selected strain is picked up due to its temperature requirement, which is influencing economical part of process. Thanks to considerable temperature level (ca. 36 C) it is not requiring much cooling device. However, there is still need of application of control panel and this is associated with higher capital and operation costs.

As was mentioned Spirulina platensis got high productivity estimated as 28906 Mg/year. Microalgae biomass is characterized by high hydrogen content and low ash content (ca. 7%) and it is providing higher overall energy efficiency process performance than conventional biomass (wood). Thanks to low ash content there is less energy used for process performance.

3. Additional reactor

Microalgae are kept in additional reactor where biomass can be sediment, treated to separate and then mechanically dewatered (or alternatively grind) to 20% of dry mass.

4. Harvesting of microalgae

Major commercially developed techniques in harvesting of microalgae are centrifugation, flocculation, filtration and screening, gravity, sedimentation, flotation and electrophoresis techniques. Harvesting technique depends on properties of microalgae its density, size, value of the desired products. Microalgae harvesting can be divided into a two major step such as bulk harvesting and then thickening. Bulk harvesting is a process of separation of microalgae biomass from slurry, in this process total solid mater is ca. 2–7% using flocculation (dispersed particles are aggregated), flotation, or gravity sedimentation. Thickening is based on concentration of slurry and also filtration and centrifugation (high gravitational and shear forces which are damaging cell structure)

More on subject of harvesting is presented in article **Cultivation, photobioreactors design and harvesting of microalgae for biodiesel production: A critical review, National Cheng Kung University, 2011.**

Separated water with nutrients are recycled to PBR and then reused for algal cultivation.

5. Dewatering and oil extraction

Dewatering of microalgae need to be dewatered in mechanical way so that biomass still is characterized by same biomass composition parameters. Proposed dewatering is based on belt on which is provided biomass. Next, after mechanical press microalgae are collected in the reactors. Dewatered biomass is desired to obtain dry matter on level of 15-30% of dw. In order to obtain average value there will be used dewatering on 20% level. In account are taken energy provision and also overall efficiency of the process.

More specific information on subject in **PhD thesis Biomass drying and dewatering, Carolyn J. Roos, Ph.D, 2008.**

Additionally in the process can be applied extraction of bio-oils which are highly desired by pharmaceutical/nutrition/cosmetic etc. companies. This point will be beneficial in terms of economic benefits. Possible to obtained lipid can be estimated in microalgae on 50% level. However, in case of my master thesis Spirulina Platensis lipid yield is estimated as ca. 9% of dry matter. Dewatered microalgae slurry is pictured in figure 53.

Figure 53 Dewatered microalgae slurry with 20%dw

(56)

6. Reactor tanks

In this step slurry is kept in reactors to fully lose surplus water. Dewatered microalgae slurry is stored in tanks for maximum of 4 days at operating temperature of 25^{o}C. Time is limited due to avoidance of start of anaerobic digestion process.

7. Pumping

After separated reaction tanks microalgae slurry is pumped by high pressure pump to pressure of ca. 30 MPa.

8. Hydrolysis

During this step biomass is hydrolyzed/decomposed at subcritical conditions (350-380C, 300 bars) into very small. Biomass is required to be in very small size due to easier access to catalyst site in gasyfier. Microalgae biomass is in form of simple organic compounds.

Lignocellulose biomass, in this case CH1, 62O0, 48 is breakdown into cellulose, hemicellulose and lignin. In the process hemi cellulose is degraded into (with adding of 5-hydroxymethyl furfural) into glucose, carboxylic acid, aldehydes and alcohols. Lignin is converted into phenolic, aromatic compounds and then to same products as cellulose and hemicellulose.

To obtain required heat (desired temperature of 350-380o C) there is recycle effluent from catalytic reactor from gasification. Thanks to pressurized conditions (above the critical pressure of water - 22.1 MPa) evaporation of water is avoided **(53).**

Heat demand required to keep temperature conditions just below critical point (a temp. 300–350 C) and pressure above critical pressure of water (22.1 MPa), that means around 30 MPa can be calculated based on equation 55. In this step required thermal energy from gasification effluent is calculated according to equation **(47):**

$$\dot{Q}_{pre-heater} = \dot{m}_{HT} \cdot (h_{H_2O}(T_{HT}) - h_{H_2O,20^\circ C}) \cdot \eta_{pre-heater}$$

Equation 55

where:

$Q_{pre\ heater-}$ is the heat flow transferred from the hot reactor effluent to the cold feed stream in the pre-heater in (kJ·s-1),

$\dot{m}_{HT}$ the mass flow rate of the catalytic reactor effluent in (kg·s-1),

$Th_{H2O\ HT}$ is the enthalpy of water in the hot reactor effluent (HT) in (kJ kg-1),

$h_{2,20\ H\ O\ C\ o}$ is the enthalpy of water at 20 degr. C in (kJ· kg-1), which is the assumed inlet temperature of the algal biomass slurry.

Where $\eta_{pre-heater} = 0.72$ is the pre-heater efficiency calculated based on work M. Branderburg from SunChem materials.

In presented equation for calculation purposes all enthalpies are assumed for pressure of 30 MPa. Enthalpies of the obtained product gases are neglected. In this phase large molecules of biomass are broken down (hydrolyzed) to smaller particles which are easily accessible to catalytic reactor. Obtained residual organic content in effluent is very low (ca. >99%).

9. Superheating salt separation

Hydrolyzed material - subcritical slurry - is injected through dip tube into heated vessel. Conditions are characterized by above pseudo critical conditions. In this conditions fluid density decrease and solubility of water is lower. In this process water acts as reactant and behaves as non-polar solvent. Organic fraction which is still present in solvent promotes salts formation. Precipitated salts got negative impact on further processes if they are not separated. Salts can promote corrosion of reactor vessel walls. Second negative influence is deactivation/plugging the catalyst which is influencing very negatively overall process efficiency. In conclusion organic particles and salt brine need to be removed before entering catalyst in fixed bed reactor gasifier **(53).** Process which is taken place in salt separation is described below.

Best performance is observed, when biomass characterized by low salts level is proceed.

In the beginning of slurry is injected through a dip tube into heated vessel to obtain supercritical conditions, and then salts are separated by gravitation in cyclone equipment. Precipitated salt brine is kept on the bottom of cyclone vessel. Temperature of injected fluid increase and flow of microalga slurry is moving in reverse way to the top of cyclone. Than heated slurry is able to leave the vessel at the top.

Described process is obtained by heat exchanger, where are observed different flow patterns and also heat transfer characteristics. Vessel is divided by zones such as dip tube, flow reversal and salt brine zone. Dip tube zone is characterized by performance where heat is exchanged between entering cold fluid and exiting stream, and also between outer wall between exit stream and external heating medium. In flow reversal zone heat flow is directed from external heating medium to mixture. In salt brine layer zone only precipitated salt slurry is affected at the bottom of the vessel. Salt separator acts as reverse flow gravity separator.

During this supercritical temperature phase, microalgae residue is superheated to required state. Heat required by the super-heater can be calculated based on **(47)**

$$\dot{Q}_{super-heater} = \frac{\dot{m}_{HT,H_2O} \cdot (h_{H_2O}(T_{SP}) - h_{H_2O,20^\circ C}) + \dot{m}_{BM,PBR} \cdot (h_{wood}(T_{SP}) - h_{wood,20^\circ C}) - \dot{Q}_{pre-heater}}{\eta_{super-heater}}$$

Equation 56

$Q_{\text{sup er heater}-}$ is given in (kg·s-1),

$m_{,2HTHO}$ the total water mass flow rate inside the hydrothermal system in (kg·s-1),

$m_{,BMPBR}$ the biomass mass flow rate entering the salt separator in (kg·s-1),

$h\,T_{H2OSP}$ the enthalpy of water at salt separator temperature in (kJ kg-1),

$h_{2,20HOC\,o}$ the enthalpy of water at 20 oC in (kJ kg-1),

$Q_{pre\ heater-}$ the heat flow transferred in the pre-heater (kJ·s-1),

$h_{,20\ wood\ C\,o}$ and $(\,)\,T\,h_{\ wood\ SP}$ are the enthalpies of wood at 20 degrees C and at salt separator temperature, respectively at 0.1 MPa. Here can be used enthalpies of wood, due to lack of reliable value of enthalpy of algal biomass. Heat transfer efficiency for super pre heater was given by MB on level of 0.893 $_{\text{sup}} = \eta_{\ er-heater}$ is the super$_{pre}$ heater heat transfer efficiency.

In this process heat flow is supplied by hot flue gases from the external process burner (look at figure 51 and 52) to the fluid which is inside the salt separator.

Possibility of heat transfer in salt separation vessel can be presented as fallows on picture 54 (based on material from reference 53)

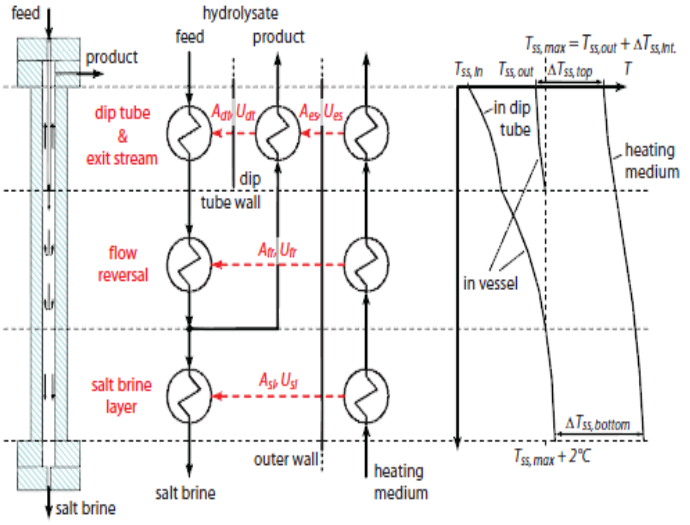


Figure 54 Schematic of the salt separator and its heat transfer model representation

(53)

In calculated model it is assumed that all nutrients which are mostly nitrogen and phosphate are removed, just before gasification part. Compounds of NH3 and P are removed as phosphate in the salt separator ($\dot{m}_{inorganic}$). Elemental composition of the biomass changes in the salt separator according to equation **(self-calculation)**

$2CH_{1,63}O_{0,46}N_{0,11}P_{0,02}$ -> $2CH_{1,24}O_{0,46}$ + 0,22NH_3+ 0,04H_3PO_4 +0,000089H_2O Equation 57

It is assumed that during this process ca. 10% of original biomass input is lost by separation of biomass salts. Microalgae slurry is treated in ultrafiltration unit and salt brine is directed for cooling.

10. Salt brine cooler

In this phase salt brine and additional organic material is cooled down due to possibility to been relooped via ultrafiltration unit to PBR as nutrient medium **(53).**

11. Ultrafiltration unit

In terms of SunChem process, after ultrafiltration unit, 90% of originally fed microalga to the system is directed on catalytic reactor. In this step biomass is separated. Organic material – microalgae biomass is directed to hydrothermal gasification process. Left salt brine with additional small particles of organic material (10% of injected biomass) can be recycled to PBR. Nearly degraded biomass should not be injected to PBR, as it negatively influence algae metabolism **(53).**

12. Catalytic reactor - catalytic fixed bed reactor

Phase occurs in supercritical conditions. Process of gasification is performed in temperature of 350-450 degrees C which is favoring mainly methane formation due to use of catalyst on fixed bed. Gasification performed as low temperatures is designed to favor methane fractions. Hydrogasification process is endodermal process where 99,9% of

organic macromolecules are broken down to methane, carbon dioxide and traces of hydrogen and carbon oxide. This got influence on higher volumetric calorific value of gas. Obtained flue gas composition is mostly in 80% based on water (look at reference table 35 and 37). There is no formation of tars and ashes **(53).**

For overall process - there is no need of biomass dewatering/thermal drying on the beginning of process which is favoring lower use of energy. Also methanation is not performed which is favoring energy savings. in methanantion large energy dedicated to formulation of hydrogen and carbon oxide components. Hot gases from gasification are cooled to 150C before entering filter.

For reactor materials should be used corrosion resistance compositions. It is due to possibility to corrode and accumulate in effluent, which after recycling than can negatively influence microalgae growth.

Reactor performance is in process of temperature between 350-450oC with pressure at 300bar. In reactor biomass passed through fixed bed with nickel or rheum catalyst on coconut carbon. Rutheum catalyst is characterized by better performance with many different substrates (e.g. Ethanol, phenol etc). More than 99,9% of fed organic matter is converted into mentioned gases. The mass flow rate $\dot{m}_{HT}$ (kg·s-1) which is entering the catalytic reactor can described by equation **(47)**

$$\dot{m}_{HT} = \dot{m}_{HT,organic} + \dot{m}_{HT,H_2O,SP} = (\dot{m}_{BM,PBR} + \dot{m}_{HT,H_2O}) \cdot (1 - c_{Loss}) - \dot{m}_{Inorganic}$$ Equation 58

where

$\dot{m}_{HT\,organic}$ being the mass flow of organic material after the salt separator in (kg·s-1),

$\dot{m}_{2\,HT\,H\,O\,SP}$, the water mass rate flow after the salt separator in (kg·s-1),

$m_{2\,HT\,H\,O}$ the total water mass flow entering the salt separator (kg·s-1),

$\dot{m}_{BM\,PBR}$ the biomass mass flow rate entering the salt separator in (kg·s-1),

c_{Loss} is fraction of water and biomass which leaves the HT plant through the salt separator and

$\dot{m}_{inorganic}$ the mass flow of inorganic material (here N and P) that leaves the HT plant through the salt separator (kg·s-1). Hydrothermal conversion of microalgae biomass can be described as **(47)** (based on materials of reference source 53):

$$CH_{1.25}O_{0.41(s)} + \alpha H_2O_{(l)} \rightarrow \beta CH_{4(g)} + \chi CO_{2(g)} + \delta H_{2(g)} + \varepsilon CO_{(g)} + \phi C_2H_{6(g)}$$

$$\alpha, \beta, \chi, \delta, \varepsilon, \phi = f(T, p, c)$$ Equation 59

Or in terms of my thesis

$$1{,}5CH_{1{,}243}O_{0{,}46} + 0{,}12H_2O \rightarrow 0{,}525CH_4 + 0{,}4CO_2 + 0{,}000009H_2 + 0{,}01CO + 0{,}2825C_2H_6$$

Presented equation is giving composition of the final product gas after the hydrothermal catalytic reactor. It is a function of temperature “T”, pressure “p” and biomass concentration “c” in the feed.

Presented above equation is showing that carbon absorbed by microalgae is converted in HTG process into 52% of CH4 and remaining fraction is converted to CO2 on level of 40%.

The gas composition of SNG leaving the catalytic reactor is calculated by Martin Gassner in model Matlab based framework. Composition of output bioSNG as is based on the elemental composition of the algal biomass.

In case of left organic residue some of organics and salts are forming strong catalyst poison such as H_2S, HS^- and S_2^- (with relevant pH). Other not removed nutrients such as NH_3, H_2S are forming ammonium and sulphuric salts. Compounds which are poisoning catalyst are lowering gasified yield of biomass. There should be used surplus amount of catalyst which can be calculated based on total sulphure in algae and number of active surface sites on catalyst.

Catalysis poisoning of the gasifier by residual sculptures occur when the salt concentration at outlet is estimated with the solubility correlation for Na_2SO_4 in supercritical water **(53):**

$$\ln\left(\frac{\tilde{c}_{Na2SO4}}{\tilde{m}}\right) = \frac{-31.337}{\tilde{R}T_{ss}} - \frac{0.16661}{\tilde{R}} + 7.132\ln\left(\frac{\rho_{ss}}{\tilde{m}}\right) \qquad \text{Equation 60}$$

Where

˜ *cNa*2*SO*4 is the molar fraction of diluted salt,

˜*R* the ideal gas constant,

T ss, the temperature,

g*ss* density

m˜ and molar weight of the saturated fluid at the separation temperature.

It is assumed that after cooling effluent from catalytic reactor process it can be recycle to PBR. However, traces of catalyst such as nickel or rutheum can be strongly inhibiting medium for microalgae growth. Samuel Stucki (Stucki, 2009) report that nickel in concentration of 10ppm is considerably inhibiting microalgae growth.

Hydrothermal gasification process is considerably attractive as it is able to perform on complete conversion of SNG into methane.

13. High pressure separator

Cooling of effluent from catalytic reactor is giving possibility to condense water, which is in considerable amount in obtained SNG (ca. 80%).

14. Carbon dioxide removal

Carbon dioxide removal is process performed based on Selexol process or with use of pressure swing absorption. PSA is based on absorption under pressure with regeneration of solvent at sub atmospheric pressure. Purity of gas is based on duration of absorption,

recycling and purging period. Pressurized water scrubbing is giving ability to separate CO2 the methane in a concentrated form (enrichment factor of 800-1000 compared to the inlet CO2 concentration) **(53).** Separated CO2 can be recycle to PBR or treated as CCS option. Carbon dioxide from separation unit can heat the PBR with cultivated microalgae.

Methane which is obtain from the process of HTG can be used in gas burner, which is heating up the salt separation **(47)**

$$\dot{V}_{CH_4} = \frac{\dot{Q}_{super-heater} - (\dot{V}_{H_2} \cdot H_{u,H_2} + \dot{V}_{CO} \cdot H_{u,CO} + \dot{V}_{C2H6} \cdot H_{u,C2H6})}{H_{u,CH_4}}$$

Equation 61

$\dot{V}_{CH_4}$ is the volumetric methane flow rate for the super-heater in (Nm3·s-1),

$\dot{V}_{H_2,CO,C2H6}$ the volumetric hydrogen, carbon monoxide and ethane flow rate for the super-heater in (Nm3·s-1),

$\dot{Q}_{super\ heater}$ the required heat flow to be provided to the super-heater to reach the desired temperature in the salt separator is given in (kJ·s-1),

H_{u,H_2}, $H_{u\ CO}$, $H_{u,C2H6}$, are the lower heating values of hydrogen, carbon monoxide and ethane (MJ·m-3)

H_{u,CH_4} the lower heating value of methane in (MJ·m-3).

15. Gas purification

Gas cleaning is for removal of traces of external compositions such as chlorines, metals and possible traces of tars which are obtained as product of hydrogasification.

Cold gas cleaning include baghouse, gas filters for tars or scrubber for ammonia, metals, residual tars removal or guard beds for oxidation of hydrogen sulphuric.

Injected to grid produced methane should be characterized by 96% mol purity in the natural gas grid with pressure of 50 bar. I should be firstly cleaned from water, carbon dioxide and hydrogen **(53).**

In program was calculated energy performance by M. Gassner with use of Balsim Vali and OSMOSE, computed results origin from program Energy Integrator. Calculated values were presented for microalgae biomass and for microalgae residue obtained after oil extraction.

Given calculations are provided by Martin Gassner concern biomass in Appendix I for microalgae biomass and Appendix II for residue after lipid extraction process.

16. Summary

Overall process efficiency of SunChem is estimated as ca. 61,6% on dry base. Efficiency is defined as based on lower heating value of the net methane produced to the lower heating value of the biomass dry matter fed to the hydrothermal gasifier.

System energy heating performance can be presented on Grand composite Curve diagram in the picture 55 and 56.

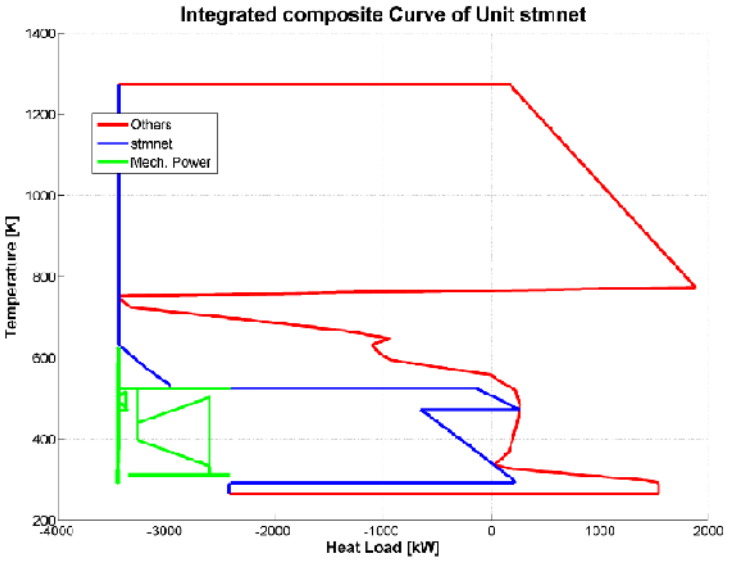


Figure 55 GCC thermochemical HTG process microalgae biomass

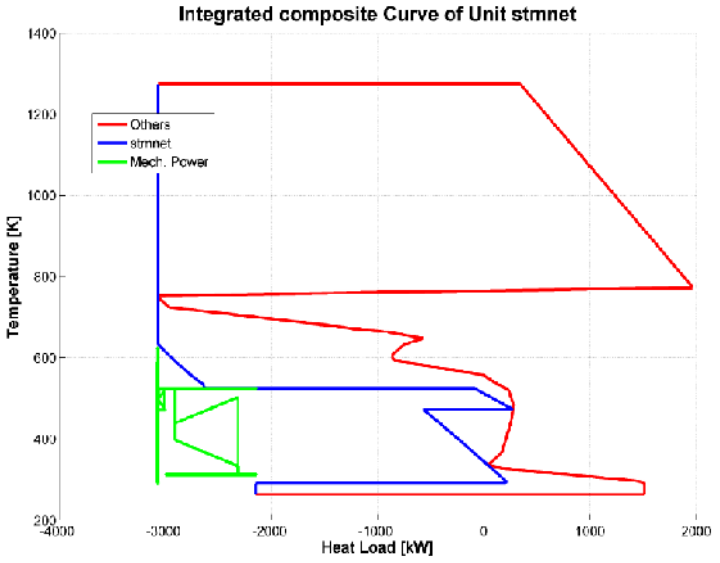


Figure 56 GCC thermochemical HTG process microalgae residue after lipid extraction

Presented streams are assigned a minimum temperature difference (Δ Tmin/2) that is required to be able to transfer the heat in a heat exchanger. In this case cold stream that needs to be heated up and hot stream that needs to be cooled down are not completely differed. There are more than 20 streams in the process, so the composite curves in the modeling paper show only the major contributions. In presented the drawing stmnet is the steam cycle (for power recovery), 'others' stands for other streams (process, combustion, cooling). Green turbines on provided drawing are showing extracted produced steam. They represent the load before and after the steam extraction at the utilization level. In the picture are presented pinch points. The pinch point is the temperature that limits the heat transfer in the process. Above this temperature, additional heat must be supplied by external streams. This heat is supplied by boiler.

Below, heat must be withdrawn and is recovered in a steam cycle (network) and partly converted to electrical power. In the diagram, the pinch is at roughly 480°C. Pinch point is determined by the salt separator. The pinch point is created by the requirement of the salt separator.

The reference for the heat load is chosen by program and it's arbitrary: enthalpy values are just relative and the 0 is arbitrarily placed by used software.

All mentioned aspects and detailed performance of system was previously detailed explained in work of F. Marechal and F. Vogel in *Process design of SNG production by hydrothermal gasification of waste biomass: Thermo-economic process modeling and integration from 2010* **(53).**

7 ECONOMICS OF THE PROCESS SUNCHEM

In the economic analysis of process of closed loop system of production of SNG both microalgae cultivation and thermochemical system were taken into account. However, actual system of biomass cultivation was analyzed separately, same as thermochemical process. It is due to possibility to differ part which is concentrate on cultivation and second one based on production of energy carrier or green electricity.

In my work I perform economic analysis on basis of paper of MB 2010 which concentrates on three types of PBRs. There was analyzed open pond and closed type such as flat plate and tubular.

Part which analyzed economical part of HTG was performed by M. Gassner based on research paper (**53)** from 2010. Analyzed system of SNG production in HTG process was based on integrated performance of steam turbine (expressed there as a steam network), main HTG process devices and boiler.

Based on process model of M. Gassner cost of one megawatt-hour of SNG (CHF/MWhSNG), is calculated as 120 Euro/MWh for SNG, assuming 33 Euro price per MWh of biomass feedstock for and accounting for revenue from selling the coproduced electricity at 180Euro/MWh. Presented numbers are considerably profitable for investor due to developed financial support instruments. In Switzerland support is from CRF and it is Cost-covering remuneration for feed in to the electricity grid dedicated to green electricity. In the process of HTG due to lack of data biomass concerning microalgae, there was used reference price of wood. In Switzerland cost of mentioned feedstock is on level of 33Euro/MWh characterised by 50% humidity.

In paper reference 47 was mentioned that price of dry algal biomass produced in raceway pond are estimated as high as 3, 3 - 10 Euro/kg (2 to 6, 67 Euro/kg). Additionally cultivation of microalgae itself is estimated as 1666, 67 Euro per ton of algal biomass cultivated in China. In paper of MB 2010 cultivation costs for algal biomass in closed type of PBRs such as tubular or FPA are much higher than microalgae cultivated in open types of ponds. It is estimated as 2-4 times higher in relation to closed type of cultivation. Where 5, 28 Euro/kg dry algal biomass is estimated cost of tubular PBR and 3,048 Euro/kg for the FPA-PBR. According to **(47)** production part in process of SunChem is weak point in technology as it is assumed that nearly 95% of investment share is dedicated to cultivation part.

All points of interest and devices which were evaluated are presented in related tables. Presented evaluation on subject is performed below.

According to paper (**47)** have calculated general cost for microalgae cultivation in closed PBR. Based on given percentage share presented in table 36. I was able to recalculate cost for required size of investment.

For future development is recommended to calculate operating cost in time scale (Euro/year) or per produced biomass (Euro/MWh of biomass).

Table 36 Economic assumptions- references

Delivered equipment costs (PBR, air blowers, paddle wheels and pumps)			
Raceway ponds [16] €/ha$_L$ 20'000	Tubular PBR [11] €/ha$_L$ 460'000		FPA-PBR [11] €/ha$_L$ 460'000
Construction expenses: Ratio factors (% from delivered equipment costs)	[54]		[53]
Installation cost	*40%*		*39%*
Instrumentation and control	*15%*		*13%*
Piping	*40%*		*31%*
Electrical	*10%*		*10%*
Buildings	*20%*		*39%*
Yard improvements	*10%*		-
Service facilities	*20%*		*55%*
Engineering and Supervision	*30%*		*32%*
Land (for PBR)	*0%*		*6%*
Maintenance (% from construction expenses)	4%		-
Contractor's fee	*5%*		*10%*
Contingency	*6%*		*15%*
Depreciation [Years]	*15*		
Insurance	*0.50%*		
Debt service, 100% equity	*6.00%*		
Tax (Property, Purchase)	*20%*		
Labor			
Workers	7	Persons/100 ha$_L$ [59]	
Salary	20	€/h	
Operational hours	8400	h/a	
Supervision	20%		
Payroll charges	25%		
General plant overheads (% from maintenance and Labor costs)	55%		
Raw Materials			
Culture Medium Phosphorus [t/a]	1000.0	€/t	
Culture Medium Nitrogen [t/a]	800.0	€/t	
Water [m³/a]	1.00	€/m³	
Utilities			
Power	0.11	€/kWh	

(47)

Reference numbers were calculated based on given data and obtained calculations are presented in table 37. More information about obtained values and data is presented in Appendix III.

Table 37 Economic assumptions – reference/nominal values

Description	Unit	Tubular PBR	Flat PBR
Reference value	(Euro/haL)	460000	460000
Surface	(haL)	1151,3	1094
Factor used	(Euro/haL)	529597747	503261905,2
Construction expenses	(Million Euro)	1808,58	1761,42
Labor cost	(Million Euro)	238,5	0,2
General plant overheads	(million Euro)	1125,9	968,9
Raw materials	(Million Euros)	398,5	520,56
Utilities	(Million Euro)	Marginal	Marginal
Summary	(Million Euro)	3571,6	3251,1

As it is observed there are considerably high cultivation costs connected with labor and construction expenses ca. 57% for tubular reactor and 54% for Flat plate reactor. To obtain data about cost of my case studies I firstly obtained numbers from papers of MB and then used them as reference, nominal values in relation to required size (ha) of analyzed pond. Cost of each component mentioned in table was firstly calculated according to equation 62. Where required cost of new premises (Euro) is calculated based on size (ha) of new plant in relation to reference value of previous plant, multiplied by reference cost and powered by given factor.

$$C = \left(\frac{A}{Aref}\right) C_{ref}^{\ exp}$$

Equation 62

Where exp is estimated as 0, 7 (average for system performance). Calculations were based on actual occupied surface area of PBR (occupied land area). My scenario based on uptake of CO2 origin from plant which is producing CO2 amount from 20MW plant. Calculated economic assumptions for system concentrated on utilization of carbon dioxide is presented in table 38. More information about calculated values and obtained data is presented in Appendix IV.

Table 38 Calculated economic assumptions for system concentrated on utilization of carbon dioxide

Description	Unit	Tubular PBR	Flat PBR
Surface	(haL)	13,6	3,6
Factor used	(Euro/haL)	23727300,8	9218259,2
Construction expenses	(Million Euro)	81	32,26
Labor cost	(Million Euro)	10,86	0,18
General plant overheads	(million Euro)	50,54	17,85
Raw materials	(Million Euros)	3,39	2,12
Utilities	(Million Euro)	marginal	marginal
Summary	(Million Euro)	145,8	52,4

In both cases labor and construction is on ca. 60% level of overall cost of cultivation.

In second scenario it is assumed that ponds are able to be single source of biomass for 20MW HTG plant. Calculations were based on same equations are previously stated. Cultivation costs for tubular and flat plate reactors for 20MW are presented in table 39. More information about calculated values and obtained data is presented in Appendix V.

Table 39 Calculated economic assumptions for system concentrated biomass cultivation

Description	Unit	Tubular PBR	Flat PBR
Surface	(haL)	275	111,5
Factor used	(Euro/haL)	194398607,4	101762440,3
Construction expenses	(Million Euro)	663,9	356,16
Labor cost	(Million Euro)	87,66	0,18
General plant overheads	(million Euro)	413,34	195,99
Raw materials	(Million Euros)	66,76	66,75
Utilities	(Million Euro)	marginal	marginal
Summary	(Million Euro)	1231,6	619,1

In this case labor and maintenance is giving nearly 60% of total cost of investment.

Presented investment costs are scaled on reference investment cost of PBRs. Investment cost is described as power function of required area for actual surface of PBR. Thanks to the graph it is possible to estimate relation between analyzed data. According to the power function where area and investment cost are calculated, trend in investment cost for new area PBR will be (picture 57):

$$y = 149,94x^{2,9293} \quad \text{Equation 63}$$

Where:

y- Investment cost of new PBR [Euro/year]

x- new required actual surface area for PBR [ha]

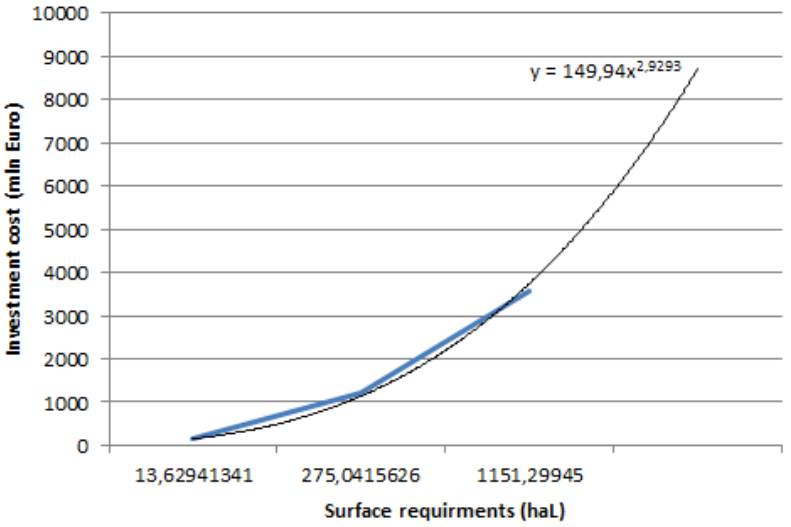


Figure 57 Trend investment costs

Economic analysis of process HTG was performed by M. Gassner based on information obtained from data base EPFL.

In the process was used equipment which was recalculated in order to meet size requirement. Recalculation was based on nominal, reference capacity of equipment from process. In the paper (**53)** is provided information what was taken into account regarding economic analysis of SunChem. Investment cost and relevant economical equations were presented and calculated by M. Gassner on the basis of the paper (**53).** Cost of production is calculated based on evaluation where:

Total cost in project=total fixed cost (TFC) + total variable costs (tvc) Equation 64

In case of this project it can be settled in equation based on cost of feedstock CRM, catalyst Ccat, operating labor COL, maintenance CM and also factor that stands for substituting profit from the by-produced electricity, CBP. All mentioned costs are calculated based on following equations **(53):**

$$C_{OP} = C_{RM} + C_{cat} + C_{OL} + C_M - C_{BP} \quad \text{Equation 65}$$

$$C_{RM} = \frac{\Delta h^0_{biomass} \dot{m}^+_{biomass,daf}}{\Delta h^0_{SNG} \dot{m}^-_{SNG}} \cdot C_{biomass}$$ Equation 66

$$C_{OL} = \frac{C_{salaries}}{t_a \cdot \Delta h^0_{SNG} \dot{m}^-_{SNG}}$$ Equation 67

$$C_M = 0.05 \cdot \frac{C_{GR}}{t_a \cdot \Delta h^0_{SNG} \dot{m}^-_{SNG}}$$ Equation 68

$$C_{BP} = \frac{\dot{E}^-}{\Delta h^0_{SNG} \dot{m}^-_{SNG}} \cdot C_{el}$$ Equation 69

In given equations Cbiomass and Cel correspond to the prices of biomass and electricity. Csalaries are related to employees' total yearly salaries and ta is yearly operating time of plant. CGR is representing the investment (grass roots) cost.

Maintenance cost maintenance cost is supposed to be rated to 5% share of investment divided by annual production **(53)**

$$MC_{sng} = \frac{0.05 * \mathrm{TIC}_{sng}}{YP_{sng}}$$ Equation 70

were:

MC_{sng}- maintenance cost [€/MWh]

TIC_{sng}- total investment cost [€]

Catalyst cost Ccat is determined from its replacement rate m˙ cat (flow rate of catalyst) with respect to the sulphure loading.

Total production cost CPSNG [e MWh/SNG] for one unit of fuel is obtained thanks to discounting the annualized investment at an interest rate i r over the economic lifetime n of the plant. Lifetime of plant is predicted for 15 years of operation. Mentioned total production cost can be expressed as **(53)**

$$C_{P,SNG} = C_{OP} + \frac{(1+i_r)^n - 1}{i_r(1+i_r)^n} \cdot \frac{C_{GR}}{t_a \cdot \Delta h^0_{SNG} \dot{m}^-_{SNG}}$$ Equation 71

CPSNG is an indicator which includes profit from selling electricity but not from SNG. Due to mentioned this indicator can be misleading (suggest to enhance the production of the by-product). To avoid mentioned, there is introduced economic performance which is expressed as maximum acceptable biomass cost for the plant to break even, Cbiomass, be [e MWh−1 biomass] **(53)**

$$C_{biomass,be} = (C_{SNG} - C_{P,SNG}) \cdot \frac{\Delta h^0_{SNG} \dot{m}^-_{SNG}}{\Delta h^0_{biomass} \dot{m}^+_{biomass,daf}} + C_{biomass}$$ (27) Equation 72

In the equation first term represents the net profit obtained from the conversion of 1 MWh of biomass.

In my thesis is used wood as there is little reliable data for performance. Wood is assumed with 50% of dry weight and its cost can be written as **(53):**

$$C_{biomass} = \left(\frac{LHV_{biomass} * m_{biomass}}{LHV_{sng} * m_{sng}} \right) * P_{biomass} \qquad \textit{Equation 73}$$

where:

$C_{biomass}$ cost of biomass [€/MWh of SNG]

$LHV_{biomass}$, LHV_{sng}- lower heating value of biomass and syngas [kJ/kg]

$m_{biomass}$, m_{sng}- mass flow rate of biomass and syngas [kg/s]

$P_{biomass}$- price of biomass [€/MWh]

In table 40 are presented economic assumptions (M Gassner, based paper of **53**) for microalgae biomass and residue (after oil extraction).

Table 40 Economic assumptions for microalgae biomass and residue HTG process

Parameter		Unit	Value
Wood price (Φ_{wood}=50%)	$C_{biomass}$	€ MWh^{-1}	33
Electricity price (green)	C_{el}	€ MWh^{-1}	180
SNG price	C_{SNG}	€ MWh^{-1}	120
Catalyst price		€ kg^{-1}	200
Operators		per shift[a]	4[b]
Operator salary		€ $year^{-1}$	60'000
Maintenance cost		% of C_{GR} $year^{-1}$	5
Interest rate	i_r	%	6
Discount period	n	years	15
Yearly operating time	t_a	7690 h	
Marshall & Swift index		-	1302[c]
Currency exchange rates		US$ $€^{-1}$	1
		CHF $€^{-1}$	1.5

(53) Where a) full time operation requires three shifts per day with working time of five days per week and 48 weeks per year, one operator per shift corresponds to 4,56 employers. b) for a plant size of 20MWth biomass, for other production scales, an exponent of 0, 7 with respect to plant capacity are used. c) average of year 2006.

Main assumptions about process of HTG of microalgae biomass is presented in table 41 and was performed by M. Gassner. Evaluation of economical part of HTG of microalgae biomass in presented in Appendix VI.

Table 41 Evaluation paper – economic part microalgae biomass

Description	Unit	Microalgae biomass scenario
Lifetime of investment	(years)	15
Total grass root cost	(kEuro)	25488
Total operating cost	(Euro/MWh)	90,5
Biomass cost yield in operating cost	(%)	48
Catalyst cost yield in operating cost	(%)	17
Production cost	(Euro/MWh)	120,56

Where production of SNG and electricity from microalgae is computed as stated in table 42.

Table 42 Production of SNG and electric energy from microalgae biomass

Description	Unit	Energy	Exergy
SNG	kW	11357	11748
Electricity	kW	966,39	966,39

Main assumptions about process of HTG of residue of microalgae biomass is presented in table 43 and was performed by M. Gassner. Evaluation of economical part of HTG of microalgae biomass in presented in Appendix VII.

Table 43 Main assumptions about process of HTG of residue of microalgae biomass

Description	Unit	Microalgae biomass scenario
Lifetime of investment	(years)	15
Total grass root cost	(kEuro)	25435
Total operating cost	(Euro/MWh)	90,78
Biomass cost yield in operating cost	(%)	48
Catalyst cost yield in operating cost	(%)	17
Production cost	(Euro/MWh)	120,77

Where production of SNG and electricity from microalgae residue is computed and presented in table 44.

Table 44 Production of SNG and electric energy residue after lipid extraction

Description	Unit	Energy	Exergy
SNG	kW	11357	11748
Electricity	kW	945,82	945,82

Both production cost of microalgae and residue biomass are on same level of ca. 120 Euro/MWh SNG. Price that is paid by consumer for SNG is estimated as in best scenario (external governmental financial support) as 120 Euro/MWh for product SNG. It can be easily spotted that side of producer is not gaining profits. Higher profit can be obtained in terms of selling electricity to external market. Maximization of profits is thanks to governmental support and it is estimated as high as ca. 60Euro per MWh.

What is worth to add is that presented value is not integrated with cultivation/production costs of PBR side of SunChem. As was mentioned production/cultivation cost of microalgae in PBR were very high. Even though, process of HTG is based on widely available woody feedstock it is still considered as investment which is not maximizing its profits. Solution that can be applied here is additional use of waste biomass. Mix of biomass from cultivated PBR and obtained from eutrophic pond/lake microalgae biomass would lower production cost. Biomass cost is estimated as ca. 48% yield from overall production cost. Use of natural blossom of undesirable microalgae in summer time, is high concern in eutrophic/highly organic lakes. Thanks to on-going cultivation in PBR, there still would be controlled process of carbon dioxide uptake (carbon) from process itself or

from external CO2 source. In terms of only microalgae use as a single biomass source mentioned idea for HTG part can be a great solution. Mentioned harvesting can fulfilled biomass requirement on possibly high level. However, this issue need to be checked with available possibilities and quantity presented.

In terms of obtained product – electricity, producer got profit from investment. However, investment relies on actual governmental support. Mentioned support need to be reliable and planned for whole time of plant operation (minimum 15 years) to continue on same or higher financial support level as estimated in calculations. Another issue which is ca. 17% of production cost is concerned as catalyst use. Repetition process of replacement of catalyst need to be lowered. As mentioned this issue is not only bottleneck in terms of technological (CH4 production efficiency) but also economical means. Catalyst deactivation can be obey if would be applied higher temperatures in salt separation device. This part relays on effective reception of salts. Maximization of profits can be obtained from microalgae oil extraction. Analysis was performed for Spirulina platensis which is characterized by 9% dw. oil yield (8, 52 – 9, 78%, table 31). Oil extraction is not included in model but in terms of residue analysis there should be added on benefits side income. This can be assumed as 125 – 1250 Euro per used kg of microalgae. In terms of my thesis oil extraction yield is estimated as 9% of dry weigh yield. Net profit from microalgae oil extraction is estimated as follows in table 45.

Table 45 Economic benefits from extracted oil from microalgae and residue after lipid extraction

Energy carrier	**Unit**	**Carbon dioxide utilization**			**20MW biomass bulk production**		
		Open pond	**Tubular plate**	**Flat plate**	**Open pond**	**Tubular plate**	**Flat plate**
Microalgae biomass	(Mg)	58,7	1468,1	917,6		28906,4	
Extracted oil	(Mg)	5,28	132,13	82,58		2601,57	
Extracted oil income	(millions €/year)	11,93	298	186		5873,1	

Where it was assumed that investor can gain profit out 2257,5 Euro per kg of microalgae.

Although need to be included withdrawn cost, still presented assumptions are giving beneficial way to upgrade economical side of investment.

In terms of simulations cultivation for Phanadectum Tricornutum can be expect much higher yield of obtained oil – on level of 19, 05% (11, 22 – 26, 88%).

In paper **47** cost of one kilowatt-hour of produced SNG in integrated system of cultivation and thermochemical process was estimated as 0.0067 €/MWhSNG for the raceway pond, 0,00173 €/MWhSNG for the tubular PBR and 0,00096 €/MWhSNG for the FPA PBR configuration. Natural gas in Switzerland cost ca. 0,000057 €/MWhNG. In relation to conventional energy carrier economical part of integrated system of PBR and HTG is not

beneficial according to **47.** As mentioned before natural gas in Switzerland cost ca. 0.057 €/kWhNG (MB 2010) with comparison to obtained price of SNG from process of SunChem, which is 120 €/MWh and electricity 180 €/MWh it can be easily concluded that process is not competing with conventional energy carriers on economic grounds. Benefits are thanks to support mechanism that financially upgrades benefits of production. There are other means on which conventional natural gas and 'green' gas are competing. In general there is strong need to develop renewable sources as conventional ones are getting lower. Additionally conventional ones are characterized by high pollution emission which got negative impact on human health and also environment. Carbon dioxide which is one of greenhouse gasses is contributing to global warming. It is estimated that 1kWh of natural gas is performing in emission of 0, 2 kg of carbon dioxide. In terms of produced SNG from microalgae biomass and residue after lipid extraction there is avoided 2271, 4 kgCO2 per kWh. It is recommended that there should be performed total capital investment calculation for overall process of SunChem. In this part it is necessary to calculate

- cultivation of microalgae
- process of oil extraction, dewatering and storing of slurry
- integrated production of SNG
- heat exchanger network design
- as overall process performance

for the future development it is recommended to calculate both expenses for biological (PBR) and thermochemical part (HTG).

8 POLAND CASE

Total primary energy supply in Poland during last 40 years was mostly based on coal, oil and gas supply (picture 58). It can be noticed that after 1988 (Communism bias very strong till 1989) energy efficiency increase and thus energy supply start decreasing (mainly coal and peat).

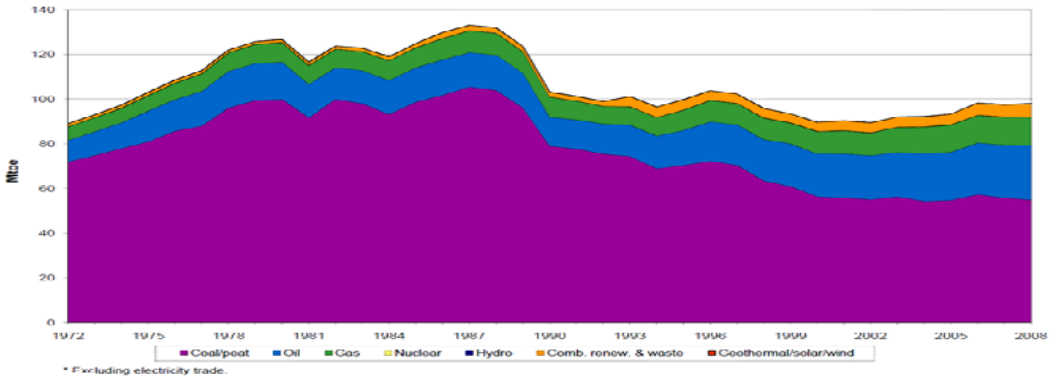


Figure 58 Primary energy requirements in Poland

(57)

In 2006 Polish energy reserve was based on conventional energy carriers (bituminous coal and lignite) but also on imported ones (petroleum and gas) (picture 59). Requirement of primary energy are fulfilled mainly by bituminous coal and lignite and gas (ca. 82%).

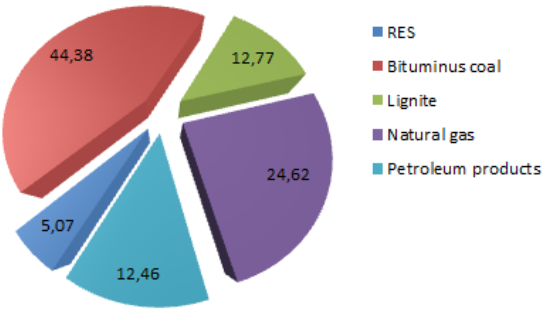


Figure 59 Requirement of primary energy in Poland 2006

It was estimated that Polish reserves are ca. 13587, 7 mln. Mg of lignite and ca. 43088 mln. ton bituminous coal which is estimated as ca. 60% of type of primary energy **(58) and (59).** Coal based energy is guarantee of constant supply of energy but it is one most inefficient energy carrier source. In 2006 efficiency of production of final energy from primary energy was estimated as 67%.

Coal is not only inefficient carrier but also highly polluting one. Emission origin from 1kWh of used energy carrier is presented din table 46.

Table 46 Carbon dioxide emissions from various energy carriers (kg CO2 per kWh of carrier

Energy carrier	Lignite	Bituminous coal	Mazut	Light fuel oil	Natural gas	Mix electrical energy Poland	Heat from coal based plant	Biomass
Carbon dioxide	0,4	0,33	0,28	0,26	0,2	1,1	0,07	0

(60)

In Poland main electrical energy plants are emitting ca. 55% of national emission of SO2, 30% emission of NOx, 10% emission of solid particles (PM10, PM5) and 45% emission of CO2 **(61).**

Mentioned emission of carbon dioxide and additional pollutants can be avoided by use of microalgae in conventional plants. Utilization of carbon dioxide on level of 26,6 1000 Mg per year can be easily utilized by microalgae operating surface for 14ha of tubular reactor and ca. 4ha for flat plate type of PBR.

Analyzed system of a closed loop system in Poland is dedicated to indoor cultivation. Polish average temperature lies between 5 and 9 C and sun operation is estimated for average 3,5 to 4,5 h per day (figure 60). Mentioned characteristic are far too low for requirements for microalgae continuous cultivation in ponds. It is recommended to cultivate microalgae in indoors with relation to Polish climate.

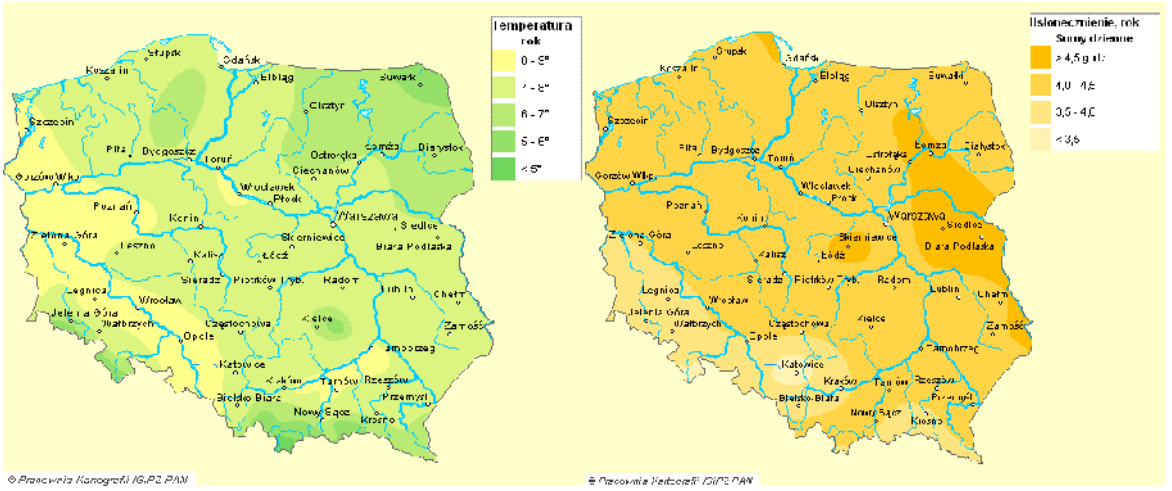


Figure 60 Yearly average temperature and irradiation time in Poland

(62)

In Polish conditions SunChem project is considerable solution for emission mitigation. However it is not providing basis for plant based on only microalgae biomass a sit require huge land surface. Project can suit for small scale energy production (auxiliary devices on site of energy plant production (picture 61). There is great market potential for microalgae cultivation indoor for CO2 mitigation mainly in part of south of Poland.

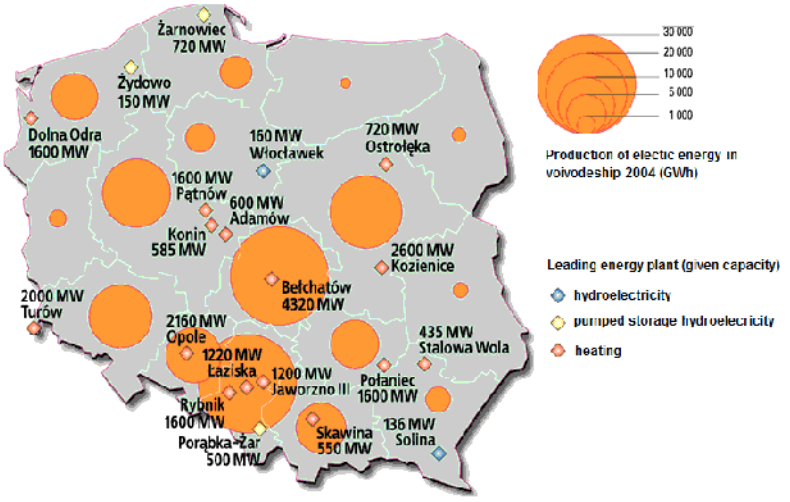


Figure 61 Main energy plants with given capacity production of electric energy in Poland in 2004

(63)

In terms of application of SunChem process and cultivation of microalgae as only biomass source for energy plant it is not recommended to perform. In Poland there is no supporting climate for outdoor cultivation and indoor cultivation present considerable requirement of energy and labor which is pricy.

However, still microalgae are very promising biomass source. Research in subject of energy performance of microalgae (anaerobic digestion) is developed by University of Warmia & Mazury in Olsztyn. Project is supported till 2013 by European Union in frame

of Program Innovative Economy with 40 mln. PLN (10 mln. Euro if 1Euro is 4 PLN). Project is not dealing with cultivation of biomass but with use of surplus amount of algae to energy performance in summertime from Gdansk Bay, Vistula Lagoon and from one of lakes in Kortowo.

Commercial advantage of use of microalgae was spotted by private companies such as Swedish company Vattenfall and German RWE which are on phase of research and development in the subject of carbon utilization and high biomass yield production. Vattenfall runs on 21st of July 2010 pilot project in Lausitz Germany, which is using algae to absorb greenhouse gas emissions from a coal-fired power plant (continue until October 2011), Half the funding origin from project MiSSiON (Microalgae Supported CO2 Sequestration in Organic Chemicals and New Energy) Vattenfall and rest is supported by European Union **(64).** Prospective future is open for microalgae use in coal based plants as CO2 mitigation tool.

9 CONCLUSIONS AND FURTHER DEVELOPMENT

Bottleneck of SunChem system is cultivation of bulk biomass of microalgae for energy related purpose (presented in chapter 5.5). As presented in chapter 5 there is strong necessity to cultivate biomass in close type of PBR. This kind of cultivation is requiring much lower surface for cultivation and it is characterized by higher biomass production. Obtained specific growth rate relations are a valuable contribution for process of PBR scale up in terms of laboratory and pilot scale approach. Selected microalgae strains, chosen PBR and performed scenarios are performing as a strong basis for laboratory scale cultivation.

Microalgae cultivation is one of ways to perform carbon neutral process in terms of energy production but also carbon dioxide bio fixation. Biomass such as microalgae is considered as relatively young (relation to conventional type of fuels, thousands of years' time) and thus potential source of energy which is not adding carbon dioxide to overall cycle of carbon dioxide in the world. Microalgae's are characterized by very intensive production processes which require not only nutrient but also carbon. They are able to uptake ca. twice carbon dioxide that they weight and including 0,52 of pure carbon. Assimilated oxygen is used in photosynthesis process. Microalgae are giving great possibility to perform carbon mitigation for industry which is emitting considerable amount of this compound. However, microalgae are attractive to cultivate not only of carbon dioxide uptake but also due to their high productivity performance. Several commercial companies noticed possibility and invest in research and development phase of this subject.

Process of SunChem is performed on biomass which is not attractive for major part of energy conversion patches. Wet biomass is relatively cheap but not easy to handle. Obtained product – methane is on same level of quality as natural gas and it is concerned as carbon neutral energy carrier (European Directive 2009/28/EC). Presented process of integrated cultivation of microalgae and HTG, after overcoming mentioned obstacle is able to develop in commercial sector. It is due to its very high efficiency of performance, cheap medium feedstock and high quality obtained product.

SunChem process is estimated as project for next 2 years (till 2013) during which need to be fulfilled points such as (Source: SunChem project proposal) listed in chapter 1.1.

Recommendations for the future development are to work on productivity of microalgae in consulate inhibiting and catalytic conditions on PBR side. Different conditions in terms of biotic and abiotic should be influencing performance in PBR. Additionally modeled equations should be handled in different types of PBR as listed in chapter 3 - that is bags type, helical type and other. Moreover mentioned issues should be quantity analyzed in possibility of combining them with HTG production and system integration analysis. Afterwards there is required performance of optimization of system.

In the past in report of NREL from 1998 was assumed that production of alternative fuel is not efficient on base of economic reasons as there is too much requirement of labor, nutrients, water and total costs which in the end are not economically beneficial. In 2008 in article of Christi was stated that microalgae biomass production will still not be competitive, even if were used decline by 9 in relation to conventional fuels. As an example was used barrel of oil which in that time cost around 100$ (according to latest news barrel of oil is now estimated on 100, 25$ on 31/01/2011). However, in April 2008 started operation biodiesel production plant (Cornell, 2008) which is in operation till today. This example is proving that technological development and time plays a major role in new and innovative technologies introduction. Well planned process and project development with downstream suited requiring for obtained product in the future will perform in commercial success. However, right now SNG obtained from system SunChem is not economically competitive with conventional natural gas carrier.

Introduction of SunChem project on Polish grounds is giving great possibility to lead exemplary role in field of innovation and development on international arena. Additionally, what is worth to add Poland as a member of European Union is obligated to fulfill requirement of European Directives. Participation or introduction of ideas from SunChem is providing great possibility to perform.

LIST OF FIGURES

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LIST OF EQUATIONS

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APPENDIX I

Evaluation report microalgae biomass

Raw material input

Composition (dry, ash-free):	C	51.71	% wt
	H	7.04	% wt
	O	34.11	%wt
	N	6.44	%wt
	S	0.7	%wt
Lignin content (dry, ash-free):		28	%wt
Ash content (dry):		7.15	%wt
Humidity (as received):		87	%wt
LHV (dry, ash-free):		21518	kJ/kg dry
LHV (wet, ash-free):		5182.1	kJ/kg dry

Process Conditions

Scale:	Input capacity:	20	MW biomass
	Dry mass flow:	0.92945	kg/s biomass

	Total slurry mass flow:	4.6473	kg/s
Feed preparation:	Pressure:	300	bar
	Total solids content of slurry:	20	%wt
	Processing:	dewatering	
Salt separation:	Inlet temperature:	623.15	K
	Maximum temperature:	753.15	K
	Hydrolysate outlet temperature:	733.15	K
	Salt slurry outlet temperature:	755.15	K
	temperature difference (top):	20	K
	temperature difference (bottom):	20	K
	Relative hydrolysate loss:	10	% of inlet
Gasification:	Inlet temperature:	672.92	K
	Outlet temperature:	673.15	K (adiabatic reactor)
High pressure separation:	Flash drum		
	- temperature:	303.15	K
	- pressure:	300	bar
	- equilibrium stages:	1	-
	- recovery bottom flash stage:	N/A	
	- additional washing water:	N/A	kg/kg crude product
Product expansion:	Vapour: turbine expansion		
	- reheat temperature	673.15	K
	Liquid, high pressure: liquid expander		
	- superheat temperature	N/A	K
	Liquid, intermediate pressure: liquid expander		
	- intermediate pressure level	70	Bar
	- superheat temperature	N/A	K
Upgrade at grid pressure:	Selexol wash		

Energy integration

Feed preparation:	Pressure:	300	bar
Steam Network:	Production Pressure:	40	bar

Production Temperature:	524.64	K
Superheat Temperature:	623.15	K
Utilisation level:	473.15	K

Stream composition

		Gasification		High pressure separation		Grid
		Wet	Dry	Wet	Dry	Dry
CH4	%vol	9.8335	55.863	59.296	59.296	96
H2	%vol	0.4302	2.4439	2.2694	2.2694	2.1535
CO	%vol	0.66000E-02	0.37494E-01	0.24000E-02	0.24000E-02	0.40000E-02
CO2	%vol	7.3327	41.656	38.419	38.419	1.8425
H2O	%vol	82.397	-	0.14000E-01	-	-

Gas Quality

CH4 purity:	96	%vol
Wobbe Index:	14.059	kWh/Nm3
LHV:	47.707	MJ/kg

Electricity

Gross Consumption:	Feed pump:	168.36	kW
	Absorption pump:	0	kW
	SNG upgrade (grid pressure):	202.3	kW
	total:	370.66	kW
Gross Production:	Power recovery, vapour:	202.43	kW
	Power recovery, liquid:	79.738	kW
	Power recovery, fuel:	128.45	kW
	Partial oxidation turbines:	0	kW
	Steam cycle:	926.43	Kw

total:	1337.1	kW	
Net production:	966.39	kW	

Energy Conversion

		Energy		Exergy	
Consumption:	Biomass:	20000	kW	22294	kW
	Electricity:	0	kW	0	kW
Production:	SNG:	11357	kW	11748	kW
	Electricity:	966.39	kW	966.39	kW
Efficiency:	dry basis:	61.615	%	57.032	%
	wet basis:	255.85	%	57.032	%
- SNG only:	dry basis:	56.783	%	52.697	%
	wet basis:	235.79	%	52.697	%
- Electricity only:	dry basis:	4.832	%	4.3348	%
	wet basis:	20.064	%	4.3348	%
- SNG-equivalent:	dry basis:	65.276	%		
	wet basis:	271.05	%		

APPENDIX II

Evaluation report residue biomass after oil extraction

Raw material

Composition (dry, ash-free):	C	51.88	%wt
	H	6.99	%wt
	O	33.5	%wt
	N	6.84	%wt
	S	0.79	%wt

Lignin content (dry, ash-free):	28	%wt
Ash content (dry):	7.47	%wt
Humidity (as received):	87	%wt
LHV (dry, ash-free):	21632	kJ/kg dry
LHV (wet, ash-free):	5295.9	kJ/kg dry

Process Conditions

Scale:	Input capacity:	20	MW biomass
	Dry mass flow:	0.92456	kg/s biomass
	Total slurry mass flow:	4.6228	kg/s
Feed preparation:	Pressure:	300	Bar
	Total solids content of slurry:	20	%wt
	Processing:	Dewatering	
Salt separation:	Inlet temperature:	623.15	K
	Maximum temperature:	753.15	K
	Hydrolysate outlet temperature:	733.15	K
	Salt slurry outlet temperature:	755.15	K
	temperature difference (top):	20	K
	temperature difference (bottom):	20	K
	Relative hydrolysate loss:	10	% of inlet
Gasification:	Inlet temperature:	672.75	K
	Outlet temperature:	673.15	K (adiabatic reactor)
High pressure separation:	Flash drum		
	- temperature:	303.15	K
	- pressure:	300	Bar
	- equilibrium stages:	1	-
	- recovery bottom flash stage:	N/A	
	- additional washing water:	N/A	kg/kg crude product
Product expansion:	Vapour: turbine expansion		
	- reheat temperature	673.15	K
	Liquid, high pressure: liquid expander		

	- superheat temperature	N/A	K
	Liquid, intermediate pressure: liquid expander		
	- intermediate pressure level	70	bar
	- superheat temperature	N/A	K
Upgrade at grid pressure:	Selexol wash		

Energy integration

Feed preparation:	Pressure:	300	bar
Steam Network:	Production Pressure:	40	bar
	Production Temperature:	524.64	K
	Superheat Temperature:	623.15	K
	Utilisation level:	473.15	K

Stream composition

		Gasification		High pressure separation		Grid
		Wet	Dry	Wet	dry	Dry
CH4	%vol	9.8874	55.919	59.332	59.332	96
H2	%vol	0.4309	2.437	2.2641	2.2641	2.1456
CO	%vol	0.66000E-02	0.37327E-01	0.24000E-02	0.24000E-02	0.40000E-02
CO2	%vol	7.3569	41.607	38.387	38.387	1.8504
H2O	%vol	82.318	-	0.14000E-01	-	-

Gas Quality

CH4 purity:	96	%vol
Wobbe Index:	14.057	kWh/Nm3
LHV:	47.696	MJ/kg

Electricity

Gross Consumption:	Feed pump:	167.41	kW
	Absorption pump:	0	kW
	SNG upgrade (grid pressure):	202.35	kW
	total:	369.76	kW
Gross Production:	Power recovery, vapour:	202.12	kW
	Power recovery, liquid:	79.144	kW
	Power recovery, fuel:	127.93	kW
	Partial oxidation turbines:	0	kW
	Steam cycle:	906.39	kW
	total:	1315.6	kW
Net production:		945.82	kW

Energy Conversion

		Energy		Exergy	
Consumption:	Biomass:	20000	kW	22277	kW
	Electricity:	0	kW	0	kW
Production:	SNG:	11357	kW	11748	kW
	Electricity:	945.82	kW	945.82	kW
Efficiency:	dry basis:	61.513	%	56.982	%
	wet basis:	251.26	%	56.982	%
- SNG only:	dry basis:	56.784	%	52.736	%
	wet basis:	231.94	%	52.736	%

- Electricity only:	dry basis:	4.7291	%	4.2457	%
	wet basis:	19.317	%	4.2457	%
- SNG-equivalent:	dry basis:	65.096	%		
	wet basis:	265.89	%		

APPENDIX III

reference	Open	Tubular	Flat
System - normalized by most productive tubular PBR			
Cost (Euro/haL)	20000	460000	460000
Units in system (n)			
Volume (m3)	4492131	181307	309053
occupied land area ratio (ml2/m3)	5	63,5	35,4
surface (mL2)	22460655	11512994,5	10940476,2
Surface (haL)	2246,1	1151,3	1094,0
CONSTRUCTION EXPENSES Euro			
Factor	44921310	529597747	503261905,2
Instalation cost		211839098,8	196272143
instrumentation and control		79439662,05	65424047,68
piping		211839098,8	156011190,6
eleectrical		52959774,7	50326190,52
buildings		105919549,4	196272143
yard improvements		52959774,7	0
service facilities		105919549,4	276794047,9
engineering and supervision		158879324,1	161043809,7
land			30195714,31
maintanance		21183909,88	
contractors fee		26479887,35	50326190,52
contingency		31775864,82	75489285,78
depreciation		79439662,05	
insurance		2647988,735	
debt service		31775864,82	
tax (property, purchase)		105919549,4	
Summary Euros		1808576306	1761416668
Summary euros mln		1808,58	1761,42
LABOR Euro			
workers		80,6	76,6
salary (20E/h) - 8736 h		174720	174720
operational hours 8400h (year)		8400	8400
supervision		105919549,4	
payroll charges		132399436,8	
Summary Euros		238502186,7	183196,5833
summary euros (mlnE)		238,5	0,2
Labour and Construction expenses Euros summary		2047078493	1761599865
Labour and Construction expenses Euros summary		2047,08	1761,60
General plant overheads -process		1125893171	968879925,6
General plant overheads -process Euros mln		1125,9	968,9
RAW MATERIALS			
culture medium phosphotus (t/a)	130020,2397	118948,9956	119269,7338
culture medium nitrogen (t/a)	117406,3358	107409,1677	107698,7894
water (m3/a)	4267524,45	172241,65	293600,35
culture medium phosphotus (Et/a)	130020239,7	118948995,6	119269733,8
culture medium nitrogen (Et/a)	117406335,8	107409167,7	107698789,4
water (E/m3/a)	4267524450	172241650	293600350
Summary Euros	4514951025	398599813,4	520568873,2
Summary Euros mln	4514,951025	398,5998134	520,5688732
UTLITIES			
belt	0,8	0,8	0,8
centifruge (kwh/m3)	1	1	1
Power (kWh)	8085835,8	326352,6	556295,4
Price (Euro for electicity)	889441,938	35898,786	61192,494
SUMMARY euros		3571607376	3251109856
SUMMARY mln EUROS		3571,607376	3251,109856

APPENDIX IV

1	Open	Tubular	Flat
produced tonnes pr year (t/a)		3132,9	3132,9
Cost (Euro/ha)	20000	460000	460000
Units in system (n)	1	1	1
Volume (m3)	16312,37	2146,36	1019,52
occupied land area ratio (ml2/m3)	5	63,5	35,4
surface (mL2)	81561,84	136294,13	36091,12
Surface (ha)	8,2	13,6	3,6
CONSTRUCTION EXPENSES Euro			
Factor	880030,3	23727300,8	9218259,2
Instalation cost		9490920,3	3595121,1
instrumentation and control		3559095,1	1198373,7
piping		9490920,3	2857660,4
eleectrical		2372730,1	921825,9
buildings		4745460,2	3595121,1
yard improvements		2372730,1	0,0
service facilities		4745460,2	5070042,6
engineering and supervision		7118190,2	2949843,0
land		0,0	553095,6
maintanance		949092,0	0,0
contractors fee		1186365,0	921825,9
contingency		1423638,0	1382738,9
depreciation		3559095,1	0,0
insurance		118636,5	0,0
debt service		1423638,0	0,0
tax (property, purchase)		4745460,2	0,0
Summary Euros		**81028732,3**	**32263907,3**
Summary euros mln		**81,0**	**32,264**
LABOR Euro			
workers		0,95	0,25
salary (20E/h) - 8736 h		175200,00	175200,00
operational hours (year)		8400,00	8400,00
supervision		4745460,16	
payroll charges		5931825,20	
Summary Euros		**10860886,32**	**183600,25**
summary euros (mlnE)		**10,86**	**0,183600**
Labour and Construction expenses Euros summary		**91889618,58**	**32447507,58**
Labour and Construction expenses Euros summary		**91,89**	**32,45**
General plant overheads		**50539290,22**	**17846129,17**
General plant overheads -process Euros mln		**50,54**	**17,85**
RAW MATERIALS			
culture medium phosphotus (t/a)	78,69	1967,27	1229,54
culture medium nitrogen (t/a)	71,06	1776,42	1110,26
water (m3/a)	15496,75	2039,05	968,55
culture medium phosphotus (Et/a)	78690,87	1967271,68	1229544,80
culture medium nitrogen (Et/a)	56845,34	1421133,57	888208,48
water (E/m3/a)	15496,75	2039,05	968,55
Summary Euros	151032,96	3390444,29	2118721,83
Summary Euros mln	0,15	3,39	2,12
UTLITIES			
belt			
centifruge (kwh/m3)			
Power (kWh)	29362,26384	3863,455769	1835,14149
Price (E for electicity)	3229,8	425,0	201,9
SUMMARY euros		145819778,1	52412560,44
SUMMARY mln EUROS		145,8	52,4

APPENDIX V

2	Open	Tubular	Flat
produced tonnes pr year (t/a)			
Cost (Euro/ha)	20000	460000	460000
Units in system (n)	1	1	1
Volume (m3)	7073927,59	43313,63	31499,91
occupied land area ratio (ml2/m3)	5	63,5	35,4
surface (mL2)	35369637,95	2750415,63	1115096,86
Surface (ha)	3537,0	275,0	111,5
CONSTRUCTION EXPENSES Euro			
Factor	61730266,3	194398607,4	101762440,3
Instalation cost		77759443,0	39687351,7
instrumentation and control		29159791,1	13229117,2
piping		77759443,0	31546356,5
eleectrical		19439860,7	10176244,0
buildings		38879721,5	39687351,7
yard improvements		19439860,7	
service facilities		38879721,5	55969342,2
engineering and supervision		58319582,2	32563980,9
land			6105746,4
maintanance		7775944,3	
contractors fee		9719930,4	10176244,0
contingency		11663916,4	15264366,0
depreciation		29159791,1	
insurance		971993,0	
debt service		11663916,4	
tax (property, purchase)		38879721,5	
Summary Euros		**663871244,3**	**356168541,1**
Summary euros mln		**663,9**	**356,169**
LABOR Euro			
workers		19,25	7,81
salary (20E/h) - 8736 h		175200,00	175200,00
operational hours (year)		8400,00	8400,00
supervision		38879721,48	
payroll charges		48599651,85	
Summary Euros		**87662992,59**	**183607,81**
summary euros (mlnE)		**87,66**	**0,183608**
Labour and Construction expenses Euros summary		**751534236,9**	**356352148,9**
Labour and Construction expenses Euros summ		**751,53**	**356,35**
General plant overheads		**413343830,28**	**195993681,91**
General plant overheads -process Euros mln		**413,34**	**195,99**
RAW MATERIALS			
culture medium phosphotus (t/a)	38734,61	38734,61	38734,61
culture medium nitrogen (t/a)	34976,78	34976,78	34976,78
water (m3/a)	6720231,21	41147,95	29924,92
culture medium phosphotus (Et/a)	38734610,99	38734610,99	38734610,99
culture medium nitrogen (Et/a)	27981420,47	27981420,47	27981420,47
water (E/m3/a)	6720231,21	41147,95	29924,92
Summary Euros	73436262,67	66757179,41	66745956,38
Summary Euros mln	73,44	66,76	66,75
UTLITIES			
belt			
centifruge (kwh/m3)			
Power (kWh)	12733069,66	77964,53742	56699,84009
Price (E/kWh)	1400637,7	8576,1	6237,0
SUMMARY euros		1231643823	619098024,2
SUMMARY mln EUROS		1231,6	619,1

APPENDIX VI

Capital Costs:	Feed preparation:	735.35 kEUR
	Salt separation:	3076.6 kEUR
	Gasification:	2949.9 kEUR
	High pressure separation:	527.4 kEUR
	Product expansion:	761.76 kEUR
	SNG upgrade:	2739.4 kEUR
	Combustion (incl. cat.):	2336.5 kEUR
	Heat exchanger network:	11635 kEUR
	Steam turbine:	726.14 kEUR
	POX gas turbine:	0 kEUR
	Total grass roots cost:	25488 kEUR
Operating Costs:	Biomass:	58.702 EUR/MWh SNG
	Electricity:	-15.317 EUR/MWh SNG
	Labour:	12.681 EUR/MWh SNG
	Maintenance:	14.593 EUR/MWh SNG
	Catalyst:	19.847 EUR/MWh SNG
	Total operating costs:	90.506 EUR/MWh SNG
	Depreciation costs:	30.051 EUR/MWh SNG
Production costs:		120.56 EUR/MWh SNG

APPENDIX VII

Capital Costs:	Feed preparation:	733.98 kEUR
	Salt separation:	3068.2 kEUR
	Gasification:	2933.2 kEUR
	High pressure separation:	526.7 kEUR
	Product expansion:	759.7 kEUR

	SNG upgrade:	2736.4	kEUR
	Combustion (incl. cat.):	2330	kEUR
	Heat exchanger network:	11628	kEUR
	Steam turbine:	718.72	kEUR
	POX gas turbine:	0	kEUR
	Total grass roots cost:	25435	kEUR
Operating Costs:	Biomass:	58.702	EUR/MWh SNG
	Electricity:	-14.991	EUR/MWh SNG
	Labour:	12.681	EUR/MWh SNG
	Maintenance:	14.563	EUR/MWh SNG
	Catalyst:	19.825	EUR/MWh SNG
	Total operating costs:	90.78	EUR/MWh SNG
	Depreciation costs:	29.988	EUR/MWh SNG
Production costs:		120.77	EUR/MWh SNG