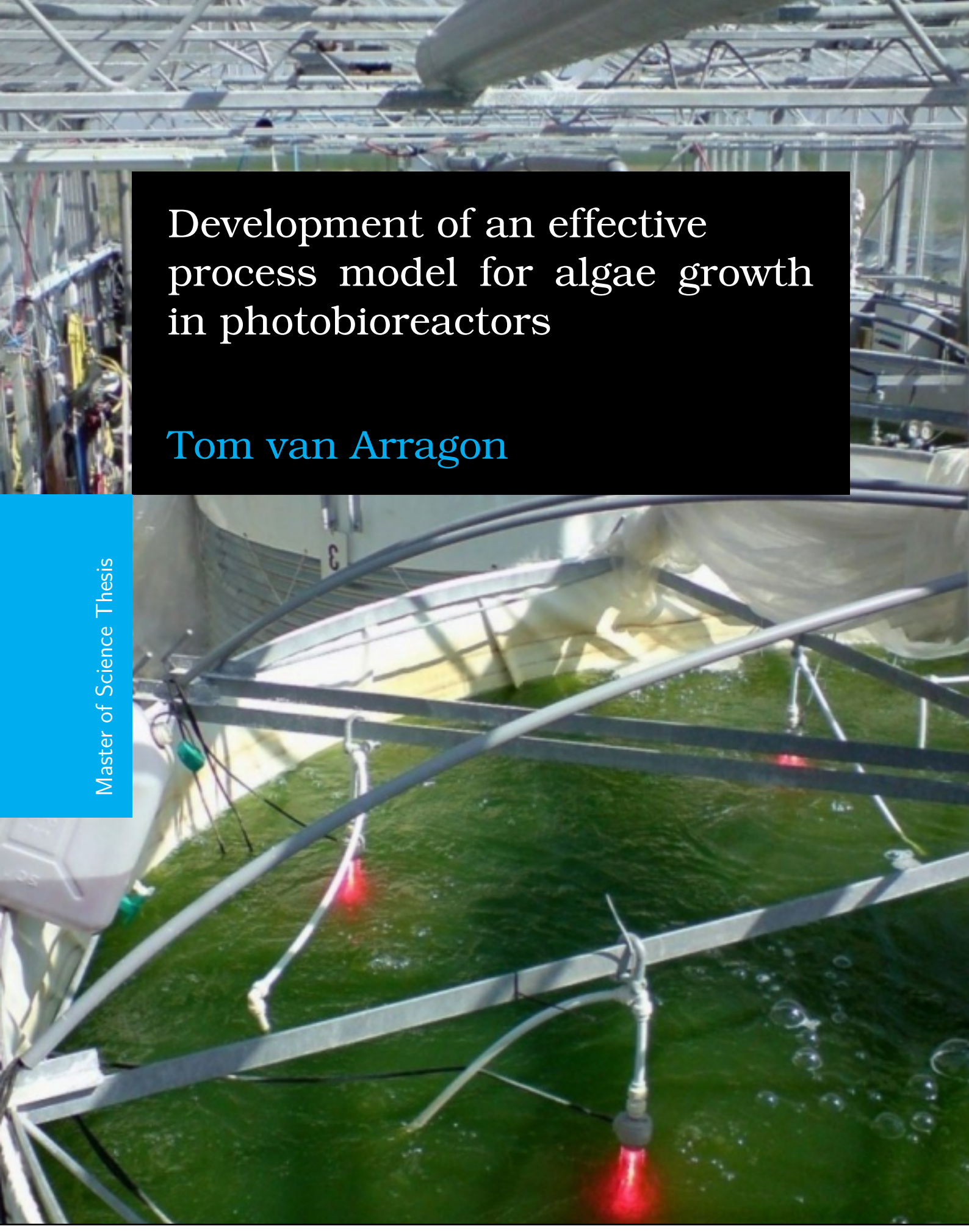

Development of an effective process model for algae growth in photobioreactors

Tom van Arragon

Master of Science Thesis

TU Delft Delft University of Technology

Development of an effective process model for algae growth in photobioreactors

Master of Science Thesis

For the degree of Master of Science in Mechanical Engineering, Track Sustainable Process and Energy Technology at Delft University of Technology

Tom van Arragon

October 2, 2014

Report number 2646

Faculty of Mechanical, Maritime and Materials Engineering (3mE) · Delft University of Technology

Delft University of Technology
Department of
Process and Energy (p&E)

The undersigned hereby certify that they have read and recommend to the Faculty of Mechanical, Maritime and Materials Engineering (3mE) for acceptance a thesis entitled

Development of an effective process model for algae growth in photobioreactors

by

Tom van Arragon

in partial fulfillment of the requirements for the degree of

Master of Science Mechanical Engineering, Track Sustainable Process and Energy Technology

Dated: October 2, 2014

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Abstract

Algae have been a hot topic in recent years due to their potential for several reasons. They have been proposed as an alternative for fossil fuels, a superfood for consumers, a potential CO_2 absorber to reduce green house gas emission, feedstock for nutritional and chemical industry, a waste water treatment technique and more. However, the large scale implementation of algae in industry has not yet been realized.

There is a bridge to be built between the biological work and the scale up to industrial size. In the scientific community there are a lot different approaches and visions for predicting algae growth. No common accepted engineering approach exists. The models found in literature vary from models which only account for illumination to models which account for more then 20 parameters. An effective model is required to close the gap between fundamental research and the scale up to industrial size.

A modelling approach is chosen which divides the photobioreactor into zones of constant light intensity and predicts algae growth by the light intensity in that specific zone. First a basic model with only light as major dependent variable is built to get an understanding about the dynamics in a photobioreactor. This model is extended for nutrient limitations. A submodel is added to simulate the uptake and loss of CO_2 by the algae and the medium. The model is made with Mathworks Matlab. The model has been validated using data from literature for 3 different photobioreactors with different types of algae. These photobioreactors are: a LED illuminated 0.8 m^3 raceway pond using Chlorella sp., a sun illuminated 0.53 m^3 circular pond using Nannochloropsis Salina and a sun illuminated 11.9 m^3 raceway pond using Nannochloropsis Salina.

A 1 litre photobioreactor has been constructed to validate the model with experiments, for this the algae specific parameters of the used algae are required. To determine these parameters a test arrangement is constructed. Experiments with the test arrangement and the photobioreactor have not yet been performed. Performing qualitative and founded tests require time and effort. This is for future work.

Preface

At the university my first encounter with algae was in the course energy from biomass, before the course I only knew them as those annoying green blooms in an aquarium. I was intrigued by the idea to use micro-organisms to address energy issues. My first thoughts when looking for a thesis project went to algae. In cooperation with Algae Food and Fuel (AF&F) and three departments of the Delft University of Technology a process model for algae growth was to be designed and I was the engineer (to be) to do so. The three departments, Process and Energy, Chemical engineering and Biotechnology have a combined partnership in the Delft Process Technology Institute. This project is supervised by by prof. Dr. Roekaerts, Dr. ir. van Ommen and ir. Tamis. Regular meetings where also held with Dr. ir. Kleerebezem and ir. Arnout van Diem of AF&F.

I want to thank my supervisors for giving me the freedom of formulating the problem statement which eventually have lead to the thesis that lies before you. In the eight months of working on this project I, for the first time, experienced working in the field of biotechnology and thanks to the help of Jelmer and Diana I learned a lot in this field. My gratitude goes to the people at AF&F and Tendris Solutions for showing me the algae industry and giving me the opportunity and facilities to build a test arrangement. Interesting discussions about radiation and other related subjects were held with my professor and supervisor Dirk Roekaerts, who always had time for a meeting and from whom I never left empty handed. Thanks to Ruud van Ommen for introducing me in the world of algae and the supervision on this project. I want to thank Jelmer Tamis and Robbert Kleerebezem for bringing me down to earth on several occasions. Finally I would like thank my fellow students for the company, coffee and second thoughts during my stay in the bathtub. Last but not least I want to thank Susanne for her patience with me during the last months.

I would like to conclude with a quote from Bitog et al. (2011) which, despite I did not use CFD for fluid mechanics but for light distribution, I would like to share with you.

"The present practice of photobioreactor design using computational fluid dynamics can be considered both an art and a science because of some numerical simulation issues which are yet to be resolved and the complexity of fluid mechanics inside the PBRs"

Tom van Arragon, Delft, 15 September 2014

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Glossary

List of Terms and abbreviations

Medium The medium is water with all nutrients, trace elements and vitamins added.

Photoadaptation Is the adaptation of photosystem of algae to certain light conditions. See chapter 2-3.

Photoinhibition A negative effect on the growth rate due to over illumination, see appendix A.

Photosynthetic efficiency The photosynthetic efficiency describes the efficiency of converting photons into biomass, see chapter 3-8.

CFD Computational fluid dynamics.

MTFM Modified two flux model is a light distribution model which takes scattering into account, see chapter 2-2.

PSU Photosynthetic Units or Photosynthetic factories, are a modelling approach by Eilers and Peeters (1988) and is discussed in chapter 1-2.

TIC Total Inorganic Carbon, see 2-4.

RTE Radiative Transfer Equation, see 2-2.

List of Symbols

$\bar{C}_{exp}$	Average concentration of experiment
$\dot{V}$	Volume flow, $[m^3/s]$
γ	Growth limiting factor, $[-]$
κ_s	Absorption coefficient , $[1/m]$
λ	Wavelength, $[nm]$
μ	Dynamic viscosity, $[Pa \cdot s]$
μ	Growth rate, $[d^{-1}]$, $[h^{-1}]$, $[s^{-1}]$
μ_{max-a}	Maximum growth rate used for fitting expanded Aiba growth equation , $[h^{-1}]$
μ_{max}	Actual maximum growth rate, $[h^{-1}]$
μ_{min}	Actual negative growth rate, $[h^{-1}]$
ω_s	Scattering albedo , $[-]$
ϕ	Gas hold up, $[-]$
ϕ_{mol}	Mass transfer, $[g/dm^3 s]$
ρ	Density, $[m^2/s]$
σ	Surface tension, $[N/m]$
σ_s	Scattering coefficient, $[1/m]$
A	Cross sectional area, $[m^2]$
a	Interfacial area, $[m^{-1}]$
B	Algae density in the broth, $[kg/m^3]$
$B(0)$	Initial algae density, $[kg/m^3]$
B_P	Biomass production over a given time $[g]$
c	Speed of light, $[m/s]$
c_{CO_2}	Molar concentration of CO_2, $[mol/m^3]$
C_{exp}	Concentration data point of experiment
C_{model}	Concentration data point of model
D	Diffusion coefficient, $[m^2/s]$
D	Reactor diameter, $[m]$
d_b	Bubble diameter, $[m]$
D_L	Diffusion coefficient, $[m^2/s]$
E_λ	Energy per μmol photons, $[J\mu mol^{-1}]$
g	Gravitational constant, $[m/s^2]$
G_η	Incident radiation $[\mu mol/m^2 s]$
h	Planck's constant, [J s]
H_{CO2}	Henry constant for CO_2, $[barm^3/mol]$
I	Light intensity, $[\mu mol/m^2 s]$
$I(0)$	Incident light intensity, $[\mu mol/m^2 s]$
I_b	Local light intensity in backward direction, $[\mu mol/m^2 s]$
I_f	Local light intensity in forward direction, $[\mu mol/m^2 s]$

k	Specific absorption coefficient, $[m^2/kg]$
k_g	Gas mass transfer rate, $[m/s]$
K_i	Photo inhibition light intensity parameter, $[\mu mol/m^2 s]$
k_L	Mass transfer rate, $[m/s]$
k_l	Liquid mass transfer rate, $[m/s]$
$k_L a$	Volumetric mass transfer coefficient, $[s^{-1}]$
K_s	Half saturation light intensity, $[\mu mol/m^2 s]$
K_{CO_2}	Half-saturation constant of carbon dioxide, $[mol/m^3]$
LHV	Lower heating value. $[MJ/kg]$
m	Distribution coefficient between gas and liquid phase [−]
MW	Molecular weight, $[g/mol]$
n	Refractive index, [−]
N_a	Avogadro's number, $[mol^{-1}]$
P	Productivity over a given time $[g/s]$
P_{bs}	Probability of back scattering from particles , [−]
P_{CO2}	Partial pressure of CO_2, $[bar]$
P_{fs}	Probability of back scattering from particles , [−]
R^2	Coefficient of determination, [-]
T	Temperature , $[K]$
U_s	Superficial velocity, $[m/s]$
x	Path length, $[m]$
z	Reactor depth, $[m]$
Bo	Bond number, [−]
Fr	Froude number, [−]
Ga	Galileo number, [−]
Sc	Schmidt number, [−]

Chapter 1

Introduction to Algae and modelling

1-1 What are algae?

In this project a model is developed that predicts the growth of algae in photobioreactors. First an insight is given in what algae actual are and what can be done with them, followed by a discussion about modelling approaches. Algae are defined as small organisms that use photosynthesis to obtain their energy. Most commonly known are eukaryotic algae such as Chlorella species, also prokaryotic cynobacteria such as Spirulina are included in the definition. A eukaryotic organism is a single celled organism with a cell nucleus. A prokaryotic organism is a single celled organism without a cell nucleus. The size of a single celled algae ranges from 1 μm to 150 μm.

How do algae grow?

Algae use their photosynthetic system to harvest light energy and they are able to take up nutrients from the medium. Algae have different photosynthetic pigments to capture photons. A successfully captured photon causes a charge separation which makes energy available to the algae metabolism. Using nutrients and this energy the algae can perform a metabolic task such as, growing, respiring, dividing, etcetera. The growth characteristics of algae are discussed more extensively in appendix A.

Algae are cultivated in different arrangements called photobioreactors. Photobioreactors differ in size from millilitres to many cubic meters. If a sterile or monoculture of algae is required a flat plate or a tubular reactor is used. Large open ponds or circular vessels are used when there are no sterile or monoculture requirements. Costs play a vital role when choosing a type of system, sterile systems are more expensive than non sterile ones. Photobioreactors are discussed more extensively in appendix A.

What are the growth requirements?

Algae require light to activate the photosynthetic pigments. Nutrients, vitamins and trace elements are required as building stones for metabolism and growth. When growing in sus-

pension mixing is required to distribute the nutrients and to keep the light distribution in the suspension optimal. To obtain optimum growth the previously mentioned parameters should be given in adequate amounts, too little as well as too much will affect the growth negatively. For a well operating photobioreactor these parameters should be in optima for the specific algae selected. In this paper a model is developed which can be used to find the optimal design parameters for a photobioreactor.

Why are algae interesting?

Algae are a valuable product or feedstock for various industries. As a consumer product algae are sold as health drinks, superfood and supplements because of the large nutritional value of algae. As a product for industry algae can serve as food for fish and chicken farms. Algae can serve as a feedstock for many different products in industry, nutrient fatty acids in butter and baby food, color pigments or as a base for biofuels. For all applications mentioned different algae are used and different prices apply, figure 1-1 gives an overview of the current prices of algae products and feedstock. It is apparent that algae have a huge potential of becoming a major feedstock in the future, however they should have competitive prices compared to other feed stocks. To get prices down efficiency of production should go up. This thesis will serve as a prediction and analyses model to control and optimize the operation of photobioreactors.

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	36 kg^{-1} 11 mg^{-1}
Chlorella	2000 tonnes dry weight	Taiwan, Germany, Japan	Human nutrition Cosmetics Aquaculture	36 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}

Figure 1-1: Price of various algae products (Brennan and Owende, 2010)

1-2 Model introduction

To classify different types of models we use the definition for model types as used by Bechet et al. (2013). Based on applicability and complexity three different types of models are defined. The first type of model (Type I) defines the rate of photosynthesis of a culture as function of the incident or average light intensity in a culture broth. Type II models calculate the total rate of photosynthesis by summing the rate of photosynthesis of individual layers in the culture broth, with the local rate of photosynthesis based on the local conditions in the culture broth. Type III models account for local conditions as well as second scale light cycles. Type III models are the models with the highest level of detail, which in most cases makes them too complex to apply in the field.

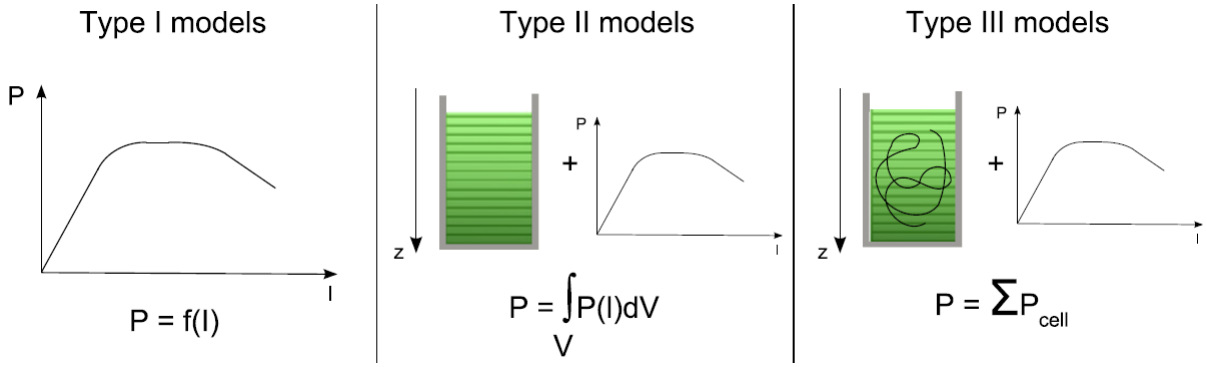


Figure 1-2: Three type of models as defined by Bechet et al. (2013)

Type I models

Type I models predict the rate of photosynthesis as function of the incident or average light intensity. Type I models can be divided into two categories, those working with incident light and those working with an average light intensity.

Incident light intensity Type I models based on incident light intensity predict the rate of photosynthesis based only on incident light. These models are very application specific and thus not universally applicable. Data from these models should only be compared to reactors of identical dimensions and parameters.

Average light intensity Type I models based on average light intensity predict the rate of photosynthesis on the average light intensity within a culture. The idea is that in a well mixed system all algae experience, on average, the same light intensity and thus the same rate of photosynthesis. Here the limitation is that two reactors with different incident light intensities can have the same average light intensity depending on reactor geometry and cell concentration. The corresponding growth rate equations will predict the same growth rate, however in reality the overall growth is dependent on the light limited, saturated and inhibited

cells (see appendix A) which is not accounted for. It is unlikely that this gives a prediction of the actual rate of photosynthesis in the systems (Bechet et al., 2013).

Both variations in Type I models do not account for algae travelling between light and dark zones (short second light cycles), also they do not account for an excess amount of light in the culture. Excess light causes damages to the algae photo system resulting in a reduction in productivity. Type I models are limited to a certain range of incident light intensity, reactor geometry and cell concentration and do not take the effect of different cell states into account. For this project we want to develop a workable, universally applicable, process model that describes the growth of algae. Due to the limitations of the Type I models we shall not further discuss these models.

Type II models

Type II models take the specific light distribution in a photobioreactor into account. The model uses different zones of constant light intensity for which individual growth rate calculations are performed. The different zones take the effect of different light states (limited, saturated and inhibited) of the cells into account. The size of the zones can vary from centimetres to infinitely small (integral). In time the biomass concentration will change and lead to a different light distribution and different productivity of the zones. Type II models can be used to predict the growth using sun light, as well as artificially illuminated reactors.

Input parameters Type II models use different mathematical models to describe growth rate and light distributions. The division of zones can be performed by integrating or summing finite thick layers. Some models are also expanded with a temperature, salinity or pH dependency. Quite some papers which use the sun as an illumination source do not give data about the actual illumination. Those are not included here unless exact illumination profiles are given. An overview of Type II models is given in table 1-1.

As shown in table 1-1 there is a lot of variety in mathematical approaches for the phenomena in a photobioreactor. The lack of consistency in approach makes it difficult to compare different studies with each other. From the wide variety of mathematical descriptions and model types it can be concluded that at the moment there is no generally accepted method using a Type II model to describe the growth of algae.

Type III models

A Type III model tracks an algae throughout the reactor and based on the inputs of its trajectory it calculates a growth rate. By tracking the trajectory it can take photo inhibition, dark zones, nutrient limitations and mixing errors into account. Another advantage is is the applicability of the model to any reactor type. The drawback is the complexity of the calculation. Eilers and Peeters (1988) proposed a model for the growth of algae that is referred to as photosynthetic units or photosynthetic factories (PSU). In 1988 the first model

System	Growth rate expression	Light distribution model	Reference
Cylindrical	$\mu = \mu_m \frac{I}{K_I+I}$	Two flux model	Cornet et al. (1995)
Multiple	$\mu = \rho_M \phi E_a \frac{K_I I}{K_I+I}$	Simplified two flux model	Cornet and Dussap (2009)
Cylindrical	$\mu = \mu_m \frac{I}{K_I+I} - \lambda$	Lambert-Beer Law	Evers (1991)
Annular	$\mu = 2\mu_s \frac{(1-i_c)(i-i_c)}{(1-i_c)^2+(i-i_c)^2}$	Lambert-Beer Law	Muller-Feuga et al. (2003)
Cylindrical	$P = P_m \frac{I}{K_I+I} - \lambda$	Hyperbolic Lambert-Beer	Yun and Park (2003)
Raceway	$\mu = \mu_m \cdot f(I)$	Lambert-Beer Law	Huesemann et al. (2013)
Cylindrical	$\mu = \mu_{max} \frac{I}{K_s+I+\frac{I^2}{K_i}} - \mu_{min}$	Two flux model	van Leeuwen (2012)

Table 1-1: Different modelling approaches for Type II models

was introduced and further expanded by Eilers and Peeters (1998) and Wu and Merchuk (2001).

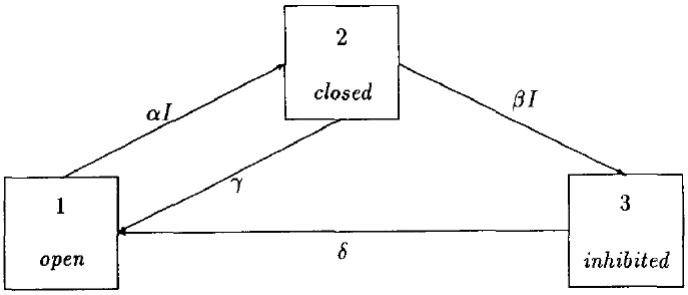


Figure 1-3: PSU model by Eilers and Peeters (1988)

The model knows three different states, (1) an open state, in rest, (2) a closed state, activated and (3) an inhibited state. These states represent the states in which an algae can be. All units start at state (1), the unexcited stage, here the algae is in rest. When the unit is hit by sufficient photons it enters the exited stage, (2), the algae processes the absorbed photons and nutrients. After a certain time step the unit is set back to (1), simultaneously energy is released for maintenance or biomass creation. The interaction between (1) and (2) is the driving force of the growth, every time (2) sets back to (1) useful energy becomes available for growth or metabolism. When too much photons hit the unit the model will go into state (3), which simulates photo inhibition. After a certain time the state is returned to (1) without any energy being produced. The time scale of interaction between (1) and (2) is in order of second while state (3) works in order of hours. When a particle enters state (3) it is put on "pause' and cannot contribute to the cell metabolism.

Equations Consider x_1, x_2 and x_3 as the fraction of the total number of PSU ($x_1 + x_2 + x_3 = 1$). From figure 1-3 we can determine a system of differential equations. as shown in equation 1-1 to 1-3.

$$\frac{dx_1}{dt} = -\alpha I x_1 + \gamma x_2 + \delta x_3 \tag{1-1}$$

$$\frac{dx_2}{dt} = \alpha I x_1 - (\beta I + \gamma) x_2 \tag{1-2}$$

$$\frac{dx_3}{dt} = \beta I x_2 - \delta x_3 \tag{1-3}$$

The model contains four rate constants, αI, βI, γ and δ. Constants γ and δ represent the enzymatic processes and are independent of light intensity. The rate constants αI and βI represent the activation of the photo system and photo inhibition within algae cells. It is difficult to give a physical representation of the parameter used in the equations.
Merchuk et al. (2007) used the model of Eilers and Peeters (1988) and added a maintenance term, this is shown in figure 1-4. This model has a higher level of detail to describe the metabolism of algae than Eilers. More researcher have adopted the basic model of Eilers and modified it to their specific needs.

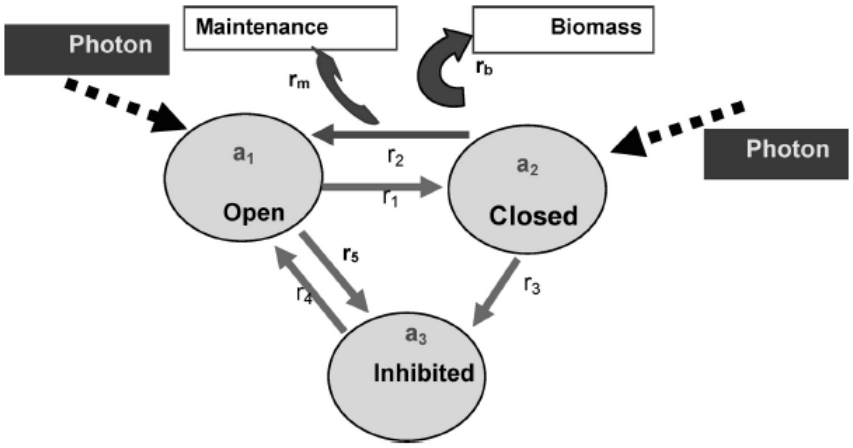


Figure 1-4: Eilers and Peeters (1988) model according to Merchuk et al. (2007)

Though this modelling approach has attracted many researches to use it (Bechet et al., 2013), it has some drawbacks. Tracing an element in a reactor requires Computational Fluid Dynamics (CFD) analysis which is often time consuming and expensive. Coupling the CFD analysis to growth equations results in programming challenges and requires in depth knowledge about the related applied mathematics. Though these problems are solvable, a Type II model is considered a more workable approach to algae modelling.

1-3 Research focus

The goal of this paper is to develop an effective process model for algae growth in photobioreactors. A universal modelling platform for algae growth is pursued. Others should be able to understand the modelling approach and be able to work with the model. This thesis is made from the perspective of a mechanical engineer with a background in process and energy. The focus is to create a bridge between the lab work and the scale up to industrial scale. Literature study has shown that no commonly accepted engineering approach exists to model the growth of algae.

1-4 Research questions and hypotheses

Developing an effective model requires a number of sub research questions and hypotheses. The main areas of investigation are modelling approaches, behaviour of light and the availability of nutrients. A start is made by phrasing the objective of this project:

Create a workable, universally applicable, process model that describes the growth of algae.

The objective is based on the idea that the model should work for different types of algae in different types of photobioreactor. Also the model should be understandable and workable. To pursue this objective a modelling approach needs to be chosen. As discussed in previous sections there are three approaches available. The Type I models are not suitable due to their limitations regarding applicability and universality. Type III models are not used because of their complexity. Type II modelling will be used as a basis to construct the model. The main research hypothesis is that this modelling approach is a good way to predict algae growth. This leads to the following hypothesis:

Algae growth in a photobioreactor can be predicted by determining the productivity of individual layers.

By correctly predicting growth in different sizes and forms of photobioreactors this hypothesis should prove itself.
The next major area of interest is light. Light is one of the major determining parameters in algae growth. Mathematical expressions to describe light distribution exist in simple (Lambert-Beer) and more complex forms (MTFM & RTE). For more information about the models used in this thesis see chapter 2-2. The extra effort required to apply the complex models is larger than that of simple models. To optimize the workability of the model the following sub research question is formulated.

Do the complex light distribution models predict significantly better than the simple models?

If the difference is in significant it would allow for the use of the easy to implement 1D models. However some complex geometries will still require 3D approaches which requires solving the RTE in a CFD program. A sidestep of the previous mentioned sub question is

the scattering behaviour of algae. Hannis (2012) has shown that algae scatter a significant part of the incident photons, however the significance of this effect in a photobioreactor is unknown. The following sub question applies.

Do light distribution models with scattering give a better prediction of algae growth?
This will be tested by performing simulations using a scattering model and a non scattering model. The results should show that the scattering models results in a more accurate description of the algae growth. If the difference in results in insignificant then it could be argued that the scattering effect could be neglected.

The second major factor for algae growth is the dependence on carbon and nitrogen nutrients, in cases where these are readily available their influence on the growth is minimal. However, when nutrients are not available the growth becomes strongly limited. Hence the influence of different relevant parameters such as; volumetric mass transfer rates, half saturation constants and composition of feed gas should be investigated.

What are the sensitive parameters when dealing with nutrient limited growth?

The sensitive parameters can be determined by sensitivity analyses performed on models that have been validated by experiments with nutrient limitations.

1-5 Research methodology

To answer the above mentioned questions and to discuss the hypotheses the following methodology is employed. First a literature study is done on the existing methods to predict algae growth in photobioreactors. After this analysis a choice is made for the modelling and mathematical approaches used for modelling. Now a basic model will be developed and validated using data from literature. Using the basic model a basic understanding can be made about the influence of various parameters. Next functionality will be added to the basic model in the form of nutrient limitations and the handling of complex geometries. This expanded basic model is referred to as the extended model and is also validated by literature. Using the extended model the influence of all relevant parameters can be measured. With the data now available the hypotheses can be discussed and the research questions answered.

Chapter 2

Equations, variables and parameters

2-1 Introduction

Different mathematical approaches for the different phenomena in an algae reactor are found in literature. In this chapter the equations, variables and parameters used in literature will be discussed.

2-2 Light distribution in an algae broth

Different approaches are available to model the behaviour of light in the algae broth, from a simple Lambert-Beer approach to a complicated six flux model. For this work three models are interesting, the Lambert-beer law, the bidirectional scattering model and the full radiative transfer equation.

Lambert Beer model

The Lambert beer law is widely used in literature because of its simplicity and applicability (Huisman et al., 2002), (Weissing and Huisman, 1994), (Merchuk et al., 2007), (Molina Grima, 1994), (Huesemann et al., 2013) and more. However, due to its simplicity it is often considered as a too inaccurate approximation. It is a one dimensional model that describes the absorption of light in a fluid. The Lambert-Beer law is given in equation 2-1.

$$I(x) = I(0) \cdot e^{-kBx} \quad [\mu mol/m^2 s] \tag{2-1}$$

With $I(0)$ being the incident light intensity in $[\mu mol/m^2 s]$, the unit $[\mu mol/m^2 s]$ is explained in appendix C.k being the algae specific extinction coefficient in $[m^2/g]$, B being the algae density in the broth in $[kg/m^3]$ and x is the path length $[m]$ in the broth. The total absorption (kB) is a lumped number for the absorption by the algae particles and water. Values for k come from experimental data, the algae density (B) of a algae culture is measured. As shown

in equation 2-1 the Lamber-Beer law does not account for scattering. Scattering is sometimes added to the Lambert-Beer law by replacing k with $\epsilon = k + \sigma$ with σ being the scattering term. In this case the added σ term increases the lumped parameter which simulates an increase in absorption. This is not the desired effect of a scattering coefficient and should only be used when correlated to experimental data.

Depending on the experiments and data available a scattering or non scattering Lambert beer law can be used. Different expressions for the lumped absorption parameter (kB) are found. (Gharagozloo et al., 2014) uses a specific parameter for the absorption of light by water, the absorption term becomes: $k = (kB + k_{H_2O})$. Yuan et al. (2014) links the absorption coefficient with the pigment (chlorophyll) concentrations The absorption term is $kB = a \cdot Chl + b \cdot B + c$ with a, b and c being constant and Chl proportional to the chlorophyll content.

Bidirectional scattering model

The modified two flux model (M-TFM) or bidirectional scattering model is described by Motegh et al. (2013) and is applied in the thesiswork of van Leeuwen (2012). This model originates from photo catalytic reactors were the behaviour of light in a photo reactor with bubbles is investigated. Since we are only interested in photo catalytic particles (in our case algae) we can neglect the effect of bubbles. The equations from Motegh are reproduced in equation 2-2 and equation 2-3. The local light intensity in forward direction is given by I_f and in backward direction by I_b.

$$\begin{aligned} \frac{dI_f}{dx} &= I_f(n_s a_s \omega_s P_{bs}) + \\ &\quad I_f(n_s a_s(1-\omega_s)) - \\ &\quad I_b(n_s a_s \omega_s P_{bs}) - \\ &= n_s a_s(P_{bs}\omega_s I_b + (-1 + \omega_s - P_{bs}\omega_s) I_f) \end{aligned} \tag{2-2}$$

$$\begin{aligned} \frac{dI_b}{dx} &= I_b(n_s a_s \omega_s P_{bs}) + \\ &\quad I_b(n_s a_s(1-\omega_s)) + \\ &\quad I_f(n_s a_s \omega_s P_{bs}) + \\ &= n_s a_s(I_b(\omega_s P_{bs} + (1-\omega_s)) - (\omega_s P_{bs}) I_f) \end{aligned} \tag{2-3}$$

An overview of the variables used is given in the following table.

Parameter	Physical meaning	Units
n_s	Number concentration of particles	$[\frac{-}{m^3}]$
a_s	Projected surface area of of particles	$[m^2]$
ω_s	Scattering albedo	[-]
P_{bs}	Probability of back scattering from particles	[-]

With

$$\omega_s = \frac{\sigma_s}{\beta_s} = \frac{\sigma_s}{\sigma_s + \kappa_s} \quad [-] \tag{2-4}$$

With σ_s being the scattering coefficient and κ_s being the absorption coefficient.

$$P_{bs} + P_{fs} = 1 \tag{2-5}$$

Motegh assumes that $P_{bs} = P_{fs} = 0.5$ and monochromatic light intensity. The boundary conditions for equation 2-2 and 2-3 are (1) $I_f = 0$ at $x = 0$ and (2) $I_b = 0$ at $x = L$. Substituting equation 2-3 in 2-2 leads to

$$\frac{d^2 I_f}{dx^2} = n_s^2 a_s^2 (1 - \omega_s)(1 + (1 + 2P_{bs})\omega_s) I_f = \beta_s^2 I_f \tag{2-6}$$

The boundary conditions for equation 2-6 are (1) and $\frac{dI_f}{dx} = n_s a_s(-1 + \omega_s - P_{bs}\omega_s) I_f$ which follows from substituting (2) into equation 2-2. The physical representation of β_s is a extinction coefficient of the algae broth. Knowing the boundary conditions, expressions for I_f and I_b are derived.

$$I_f(x) = \frac{e^{-\tau_{x,s}} I_0 + e^{\tau_{x,s}} I_0 \eta}{1 + \eta} \quad [\mu mol/m^2 s] \tag{2-7}$$

$$\begin{aligned} I_b(x) = \frac{1}{P_{bs}(1+\eta)\omega_s} \cdot e^{-\tau_{x,s}} I_0 \Big[\Big(1 + (-1 + P_{bs})\omega_s - a \Big) + \\ e^{2\tau_{x,s}} \cdot \eta \Big(1 + (-1 + P_{bs})\omega_s + a \Big) \Big] \quad [\mu mol/m^2 s] \end{aligned} \tag{2-8}$$

With

$$\eta = \frac{-(1 + (-1 + P_{bs})\omega_s - a)}{e^{2\tau_s}(1 + (-1 + P_{bs})\omega_s + a)} \quad [-] \tag{2-9}$$

$$a = \sqrt{(1 - \omega_s)(1 - \omega_s + 2P_{bs}\omega_s)} \quad [-] \tag{2-10}$$

$$\tau_{x,s} = \beta_s x \quad [-] \tag{2-11}$$

$$\tau_s = \beta_s L \quad [-] \tag{2-12}$$

$$\beta_s = a_s n_s \sqrt{(1 - \omega_s)(1 + (-1 + 2P_{bs})\omega_s)} \quad [m^{-1}] \tag{2-13}$$

Full radiative transfer equation

To describe complex geometries a 1D approximation like the Lambert-Beer law or the M-TFM is sometimes not suitable. A 3D model is required to handle complex geometries, for this the full radiative transfer equation (RTE) is used. The RTE is solved to obtain the light intensity at all positions. The RTE describes the intensity along a ray through a participating medium. The RTE in its general form for a ray along path s is given in equation 2-14

$$\frac{dI_\eta}{ds} = \kappa_\eta I_{B\eta} - \kappa_\eta I_\eta - \sigma_{s\eta} I_\eta + \frac{\sigma_{s\eta}}{4\pi} \int_{4\pi} I_\eta(\hat{\boldsymbol{s}}_{\boldsymbol{i}}) \Phi((\hat{\boldsymbol{s}}_{\boldsymbol{i}}, \hat{\boldsymbol{s}}) d\Omega_i \tag{2-14}$$

The right side of the equation states how the intensity is affected by emission ($\kappa_\eta I_{B\eta}$), absorption ($\kappa_\eta I_\eta$) and scattering ($\sigma_{s\eta} I_\eta$). The final term represents the increase due to in-scattering from other directions. We are interested in the incident radiation at a specific location in the reactor. The incident radiation, G_η, is given by equation 2-15.

$$G_\eta = \int_{4\pi} I_\eta(\hat{\boldsymbol{s}}) d\Omega \tag{2-15}$$

As shown in equation 2-15 the incident radiation is determined by the radiation intensity integrated over all directions, its value represents the radiation intensity given at a given location in the reactor. By combining elements (with a specific volumetric size at that specific location) with the radiation intensity a distribution for the light intensity for all elements can be made. The result will be a distribution of specific light intensities with corresponding volumes sizes. Commercial software packages like ANSYS FLUENT have built in solvers for the RTE. To solve the RTE a geometry needs to be build with certain boundary conditions, this requires a mesh and in-depth knowledge about CFD packages and their operation. A calculation performed by CFD is a time and computer intensive occupation. It is preferred to use an 1D approximation for 3D geometry if the approximation is accurate enough. Some papers also use a CFD package to evaluate the flow within the reactors, others only use the RTE solver to calculate the light distribution.

Absorption and scattering

The surface of the water reflects light, which decreases the amount of light penetrating into the water. Some papers are unclear about where the irradiation is measured, hence it is unknown how much light reaches the algae in the water. The loss by reflection at the water surface is approximated by an factor of 0.9.

As stated, most process models use a Lambert-Beer approach in which scattering is neglected. Hannis (2012) has researched that for a variety of algae species scattering and reflection is present ranging from 10 to 50 % (depending on wavelength and species). A bidirectional model would be a better approximation than a Lambert beer approach, because it accounts for scattering. However, if experimental determination of lumped coefficient was performed the scattering could be party lumped in this coefficient.

Directional light

When considering a pond illuminated by the sun the incident light is unidirectional. The algae antenna pigments only have to focus to in a single location. In photobioreactors the incident light is not coming from a single direction, for example when multiple light sources are used. In fast moving reactors algae are rigorously mixed which do not allow algae to focus their antennas on a single direction. From Hannis (2012) we know that a significant portion of photons is scattered, these scattered photons reach other algae from all directions. We can state that algae are illuminated from all directions, thus we do not take the directionality of light into account. Also because of the complexity of the orientation of an individual algae the directionality of light is not taken into consideration.

Applications of models

The three different light models are implemented to see their differences. First the behaviour in absorption only cases are studied.
Absorption case Setting the scattering coefficient to zero in the MTFM results in the following simplifications in equation 2-7, 2-9 and 2-10.

$$a = \sqrt{(1-0)(1-0+2P_{bs}0)} = 1 \tag{2-16}$$

$$\eta = \frac{-(1+(-1+P_{bs})0-1)}{e^{2\tau_s}(1+(-1+P_{bs})0+1)} = 0 \tag{2-17}$$

$$I_f(x) = \frac{e^{-\tau_{x,s}} I_0 + e^{\tau_{x,s}} I_0 \cdot 0}{1+0} = e^{-\tau_{x,s}} I_0 = I_0 e^{-\beta_s x} \tag{2-18}$$

As shown in equation 2-18 the MTFM is reduced to the Lambert-Beer law. To analyse the absorption of a fluid using different models the MTFM is not explicitly used because it is mathematically the same as the Lambert-Beer law. An analysis of the Lambert-Beer law and a solution of the RTE from ANSYS Fluent is given in figure 2-1. The normalized light intensity is defined as $G(x)/I(0)$. The Lambert-Beer and RTE give the same results for modelling absorption in a fluid without scattering.

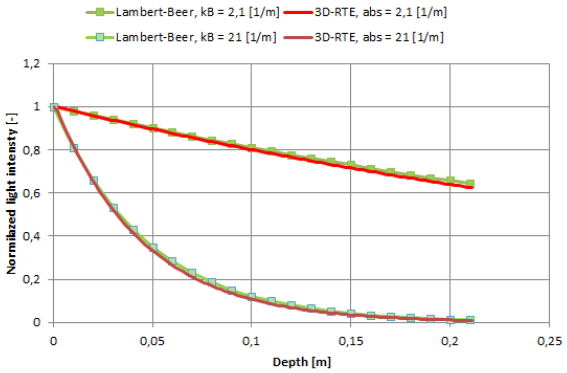


Figure 2-1: Incident light intensity for Lambert-Beer and RTE for kB of 2.1 and 21 $[1/m]$ without scattering

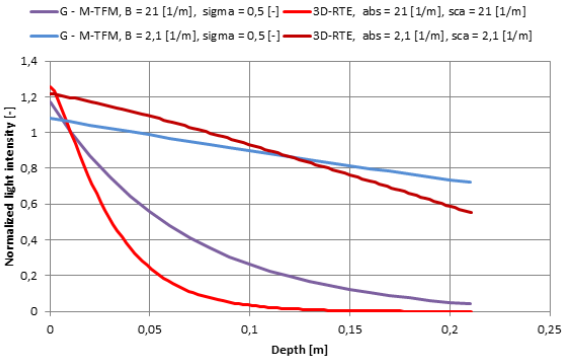


Figure 2-2: Incident light intensity for MTFM and RTE for abs of 2.1 and 21 $[1/m]$ with scattering

Scattering case The incident radiation at a given location for the MTFM is determined similar to equation 2-15, for 1D cases this reduces to equation 2-19.

$$G(x) = I_f(x) + I_b(x) \tag{2-19}$$

The back and forward term are dependent on the given scattering conditions. The MTFM requires a dimensionless scattering albedo while the RTE in FLuent requires a scattering coefficient in $[1/m]$. The scattering albedo can be rewritten to a scattering coefficient by using equation 2-4. In figure 2-2 the difference between the two scattering models is given. The results show that the predictions from the MTFM and Fluent differ significantly. The normalized intensity can become larger than one due to the added backscattering term in equation 2-19. Parameters for the MTFM are $P_{bs} = 0.5$ and $\omega_s = 0.5$. To compare the effect of scattering to the non scattering case a comparison is shown in figure 2-3 and 2-4.

In figure 2-3 and 2-4 the FF term in the MTFM denotes the forward flux. The backward flux is thus G minus FF. The MTFM predicts an overall higher incident radiation than the Lambert-Beer model. The RTE predicts an initially higher incident radiation but predict a faster decay than the MTFM and the Lambert-Beer law. No correlation can be made between the MTFM, the RTE, the Lambert-Beer law and for different absorption and scattering coefficients. To investigate the effects of scattering in photobioreactors, the MTFM will be used.

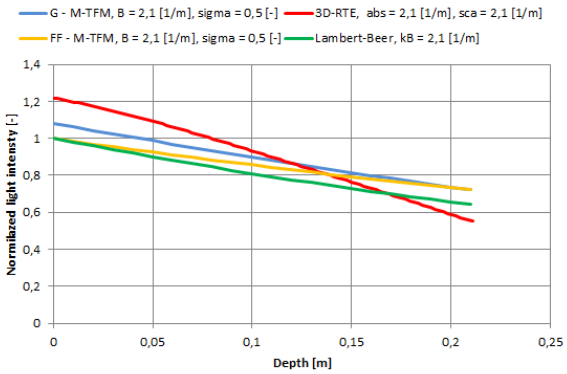


Figure 2-3: Incident light intensity for abs = 2.1 case with scattering

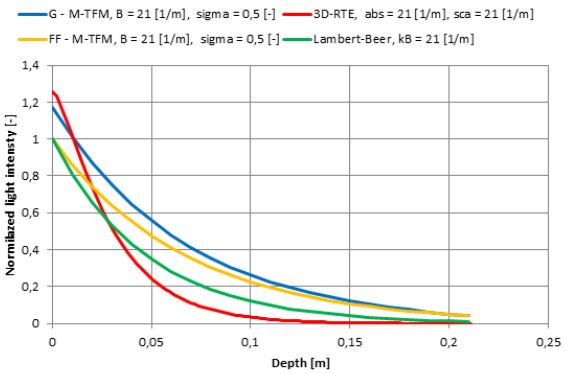


Figure 2-4: Incident light intensity for abs = 21 case with scattering

It has shown slightly different results than the Lambert-Beer law, the RTE has shown very different results from the Lambert-Beer law which creates uncertainty about its application. For the Lambert-Beer law it is known that it has been successfully used many cases. In complex 3D geometries the RTE is a good method to predict incident radiation because it shows the same results as the proven Lambert-Beer law.

The absorption data given in papers is measured by a spectrometer which measures the absorbence of an algae sample in a cuvette. The resulting OD (optical density) is determined as shown in equation 2-20. The total extinction coefficient (β) is back calculated by knowing the optical path length. First a sample with only medium is used to zero the measurement, followed by the actual sample. The measured absorbance is calculated based on the difference in in and outgoing light flux. The extinction coefficient is made up from the biomass density and an algae specific extinction term. The effect of scattering happens in real life and in thus incorporated in the absorbence measurement. It is thus partly lumped in this extinction coefficient and the algae specific absorption, but it cannot be described separately due to the lack of measurements. By using experimental data for the algae specific absorption coefficient scattering is partly taken into account. However, this is only valid when k is determined as discussed here.

$$\ln\left(\frac{I(x)}{I(0)}\right) = -kBx = -\beta x = OD \tag{2-20}$$

2-3 Growth models

A growth model describes the link between the light distribution, growth rate and nutrient conditions. Different growth models are used to take these phenomena into account.

Requirements

Different types of models are available to describe the growth rate (μ) of algae. A specific model is required that takes a selection of effects in account. These effects are: respiration, photo inhibition, photo saturation, nutrient limitation. Also identifiable parameters are preferable for the workability of the model. From literature a number of models are found that meet the requirements, these are displayed in table 2-1.

Equation	Reference
$\mu = \frac{\mu_{max} I}{(K_i^m + I^m)^{m-1}}$	(Bannister, 1979)
$\mu = \frac{\mu_{max} I}{K_s + I + \frac{I^2}{K_i}}$	(Aiba, 1982)
$\mu = \frac{\mu_{max} I_{av}^C}{[I_k(1+(\frac{I_0}{K_i})^a]^C + I_{av}^C} \quad C = b + \frac{c}{I_0}$	(Molina Grima, 1999)
$\mu = \frac{\mu_{max} I}{K_s + I + \frac{I^2}{K_i}} - \mu_{min}$	(van Leeuwen, 2012)

Table 2-1: Growth models

The physical meaning of the growth rate is the amount of algae created in 1 unit of time divided by the total amount of algae (growth rate = number of new algae / number of old algae). The units of growth rate can vary with the experiment or model, growth rates μ are found in units of s^{-1}, h^{-1} and d^{-1}.

The growth model which is chosen to work with in this project is that is based on that of Aiba (1982) and expanded by van Leeuwen (2012). This model takes all the required effects into account and has identifiable parameters, it is shown in equation 2-21.

$$\mu = \frac{\mu_{max-a} I}{K_s + I + \frac{I^2}{K_i}} - \mu_{min} \tag{2-21}$$

With μ_{max-a} being the maximum growth rate $[h^{-1}]$ in equation 4-2. Note that this is not the actual maximum growth rate of an algae species, it is used to fit the growth rate equation as a function of light intensity. The actual maximum growth rate is defined by μ_{max}. μ_{min} is the negative growth rate due to respiration $[h^{-1}]$. I is the light intensity $[\mu molm^{-2}s^{-1}]$ at a given location. K_s is the light intensity $[\mu molm^{-2}s^{-1}]$ where half of the maximum growth rate is reached. K_i is the photo inhibition steering parameter $[\mu molm^{-2}s^{-1}]$.

Nutrient limiting growth

The models described in table 2-1 all consider light as the only growth limiting property. Only the model of van Leeuwen (2012) describes a negative growth as a consequence of an absence of light. The models assume that the growth of algae is not limited by the available nutrients. In real life nutrients are a limitation and additional term for this needs to be added.

If the light growth conditions are met, nitrogen and CO_2 limitation are other growth limiting factors. An appropriate method needs to be found to describe the effect of nitrogen and CO_2 limitation. From other (van Leeuwen, 2012), (Gharagozloo et al., 2014) factors are found to describe the CO_2 and N limitations, these factors are added to be to the growth rate equation.

$$\gamma_{CO_2} = \frac{c_{CO_2}}{K_{CO_2} + c_{CO_2}} \tag{2-22}$$

$$\gamma_N = \frac{c_N}{K_N + c_N} \tag{2-23}$$

With K_{CO_2} being the half-saturation constant of carbon dioxide $[mol/m^3]$ (Leggat et al., 2000) and (Gharagozloo et al., 2014). c_{CO_2} is the molar concentration present $[mol/m^3]$. The addition of different species to obtain the concentrations is discussed in chapter 2-4. Similar to the equations describing nutrient limitation (2-22 and 2-23), the equations from table 2-1 can also be written in a form of a limiting factor. All limiting factors are multiplied to form an expression for the growth rates as shown equation 2-24.

$$\mu = \mu_{max} \cdot \gamma_{Light} \cdot \gamma_N \cdot \gamma_{CO_2} - \mu_{min} \tag{2-24}$$

With γ being the growth limiting factors for light, carbon and nitrogen nutrients. The total growth rate equation as used for our model is given in 2-25.

$$\mu = \mu_{max-a} \cdot \frac{I}{K_s + I + \frac{I^2}{K_i}} \cdot \frac{c_N}{K_N + c_N} \cdot \frac{c_{CO_2}}{K_{CO_2} + c_{CO_2}} - \mu_{min} \tag{2-25}$$

Other growth limiting properties

In the previous sections we mentioned the bases on which the growth rate is determined. There are however a number of other (practical) factors which influence the growth rate of an algae culture which now will be addressed.

Temperature dependence Algae grow optimal at a certain temperature range. This range is highly dependent on the species of algae. For example Chlorella Sorokirina grows between temperatures of 18 $°C$ and a maximum of 40 $°C$ with an optimum of around 30 $°C$ (Kumar et al., 2014).

pH dependence Algae growth is dependent on the pH of the broth. The pH determines the form in which the carbon source is available. The pH can be adjusted by adding an acid or a base, in the field it is common to sparge a reactor with CO_2 to lower the pH. CO_2 dissolves to carbonic acid, bicarbonate and carbonate which releases $[H^+]$ which lowers the pH.

Salinity dependence Some algae species only grow in fresh water while others require salt water. A certain fraction of salt is tolerated by most fresh water algae, but again, this is species dependent. Salinity is not a process variable in our model, it is assumed constant.

Insufficient or excess mixing A reactor needs to be mixed for various reasons, one of those

reasons is to keep the algae in suspension such that the algae are illuminated optimal. If the mixing is insufficient the algae drop out of suspension and will not be illuminated optimally. On the other hand, if mixing is too rigorous the algae can experience stress and grow less optimal. Mixing should thus be present in the reactor, not too soft and not too rigorous.
Grazers In a non sterile photobioreactor (eg. raceway pond) the algae are not the only organisms that live in the algae broth. Bacteria and other organisms are present which consume the algae. In practice a filter is placed with a mesh size slightly larger than the algae to filter out these grazers. The mesh size is in the range of 100 μm. Modelling of grazer plagues is not in the scope of this project.
Photo adaptation Algae use pigments to capture photons they use for photosynthesis, dependent on the light intensity a number of pigments are created. At low light intensity, more pigments are required than at higher intensity. If a cell is transferred from high to low intensity, new pigments are created. Less energy is available for growth and this is thus another growth limiting factor, however the time scale on which this occurs is days. The cells thus adapt optimal to the current light conditions which give them a disadvantage if light conditions change.

One could argue that all these effects should be taken into account, however this would make the model over complex and unworkable. This is why these effected are mentioned, but not taken into account in the model. One should thus be aware of the limitations of the model.

Productivity

The growth rate does not equal productivity. The productivity can be described as a function of the growth rate. We can combine the growth rate μ and the total amount of biomass B to determine the production of biomass.

$$\frac{dB}{dt} = \mu B \quad [g/dm^3 s] \tag{2-26}$$

The solution of this differential equation is given by equation 2-27

$$B(t) = B(0) \cdot e^{\mu t} \tag{2-27}$$

$B(0)$ is the initial biomass concentration in $[kg/m^3]$. The amount of biomass in an algae reactor can be measured by using optical measurement devices, the optical thickness of the algae broth is measured and correlated to dry weight. Equation 2-26 and 2-27 are valid for a batch reactor. The productivity for a continuous reactor is given in 2-28.

$$\frac{dB}{dt} = \mu B - \left(\frac{\dot{V}_{dilution}}{V}\right) B \quad [g/dm^3 s] \tag{2-28}$$

With $\dot{V}_{dilution}$ being the dilution flow rate in $[dm^3/h]$ and V the reactor volume in $[dm^3]$. The solution of this equation is given by equation 2-29.

$$B(t) = B(0) \cdot e^{t \cdot (\mu - \frac{\dot{V}_{dilution}}{V})} \tag{2-29}$$

2-4 Mass Transfer

Algae require nutrients to grow and to support their metabolism. Nutrients are added to a photobioreactor either via gasses or by dissolved solids. On their part when algae grow they produce oxygen which needs to exit the reactor. There are a number of phenomena at play in this process which will be addressed.

Phenomena

There are different phenomena at play when adding and consuming nutrients. How the nutrients are absorbed by the algae on a biological level is not treated. The mass transfer from gas to liquid and vice versa is treated here, kinetic rates are also discussed. The effects that will be taken into account are found in the following list.

- Nutrient transport into the medium
- Nutrient uptake by algae
- Nutrient loss to surroundings
- Mass transfer rates

CO_2 transport into the medium

Nutrients can be supplied to the reactor via either gas or solvable solids and liquids. Adding solids is relatively straightforward, they should be added to the medium in the corrected order and stirred until all are dissolved. Inserting gaseous nutrients into the medium requires more effort. The uptake of nutrient gases depend on many parameters and variables which are often interdependent. The flux from gas to liquid phase (the mass transfer (ϕ_{mol})) is given in equation 2-30. CO_2 is the primary nutrient added.

$$\phi_{CO2} = k_L a \cdot (c_{CO2,max}(aq) - c_{CO2}(aq)) \quad [g/dm^3 s] \tag{2-30}$$

With $k_L a$ being the volumetric mass transfer coefficient in $[s^{-1}]$„ $c_{CO2,max}(aq)$ being the maximum solvable molar concentration of CO_2 in water in [g/m^3] resulting from Henry's law. $c_{CO2}(aq)$ is the current molar concentration of CO_2 in [g/m^3]. Note that the driving force of the reaction is the difference between the maximum solvable and current concentration of CO_2. In most practical cases the $k_L a$ value of a reactor is measured, this option has the preference over making a mathematical approximation, but when an experimental $k_l a$ is not available an mathematical approach is required. The procedure for approximating the $k_L a$ is discussed here. First Henry's law can be used to calculate the maximum concentration of CO_2 in a water mixture $c_{CO2,max}(aq)$ in $[mol/m^3]$. Henry's law is given in equation 2-31.

$$c_{CO2,max}(aq) = \frac{P_{CO2}}{H_{CO2}} \quad [mol/m^3] \tag{2-31}$$

With P_{CO2} being the partial pressure [bar] of the gas and H_{CO2} being the Henry constant for CO_2 in $[barm^3/mol]$. The interfacial area is defined as shown in equation 2-32 (Garcia-Ochoa and Gomez, 2009).

$$a = \frac{6\phi}{d_b} \tag{2-32}$$

ϕ is the gas hold up ($[-]$) and d_b is the bubble diameter ($[m^{-1}]$). A bubble diameter is difficult to predict and model, hence $d_b = 0.006[m]$ is chosen which is widely accepted in literature (Garcia-Ochoa and Gomez, 2009). The corresponding bubble rise velocity V_s is chosen as 0.25 $[m/s]$ which is also widely accepted in literature (Garcia-Ochoa and Gomez, 2009). The gas hold up is defined as the volume fraction of gas in a gas-liquid dispersion. For different types of reactor there are different expressions for the gas hold up with each limited applicability. It is more convenient to find an expression for the volumetric mass transfer coefficient ($k_l a$) term, however there is a wide range of correlations available (Garcia-Ochoa and Gomez, 2009). A correlation is chosen for a Newtonian fluid from Nakanoh and Yoshida (1980) which is displayed in equation 2-33.

$$k_L a = 0.09 \cdot Sc^{0.5} \cdot Bo^{0.75} \cdot Ga^{0.39} \cdot Fr^{1} \cdot \frac{D_L}{D^2} \tag{2-33}$$

With $k_L a$ being the volumetric mass transfer coefficient in $[s^{-1}]$, Sc is the dimensionless Schmidt number which is defined as $\frac{\mu}{D_L \cdot \rho}$. Bo is the dimensionless Bond number which is defined as $\frac{g \cdot \rho \cdot D^2}{\sigma}$. Ga is the dimensionless Galileo number which is defined as $\frac{g \cdot \rho^2 \cdot D^3}{\mu^2}$. Fr is the dimensionless Froude number which is defined as $\frac{U_s}{\sqrt{g \cdot D}}$. The corresponding parameters are defined as; μ is dynamic viscosity in $[Pa \cdot s]$, D_L is the diffusion coefficient in $[m^2/s]$, ρ is the density in $[kg/m^3]$, g is the gravitational constant in $[m/s^2]$, D is the reactor diameter in $[m]$, σ is the surface tension in $[N/m]$. Finally, U_s, the superficial velocity is defined as shown in equation 2-34.

$$U_s = \frac{\dot{V}}{A} \tag{2-34}$$

With $\dot{V}$ being the volume flow of gas in $[m^3/s]$ and A is the cross sectional area in $[m^2]$. As shown in equation 2-30 the the mass transfer is proportional to the $k_l a$ this makes the $k_l a$ one of the crucial parameters in photobioreactor design.

Nutrient uptake and O_2 production

Algae take up nutrients and water and produce oxygen. This phenomena is modelled to model the dynamics of CO_2 and nitrogen limited growth. Simulating the uptake of nitrogen allows the simulation of nitrogen depletion in a photobioreactor. A simplified chemical reaction using a carbon and nitrogen source is given in equation 2-35.

$$aCO_2 + bH_2O + cN \rightarrow C_a H_e O_f N_c + dO_2 \tag{2-35}$$

The exact stoichiometric coefficients vary per species algae, Kumar et al. (2014) has also shown that the ratio is dependent on the nutrient conditions. Table 2-2 shows ratio's for equation 2-35.

Using the general expression for stoichiometry, for each gram of pure C added we get 2 grams of algae. The stoichiometric molar ratio for carbon uptake using CO_2 to algae is 1:1, for nitrogen components 1:0.2 and for oxygen 1:1. The stoichiometric mass ratio for carbon uptake using CO_2 to algae is 1:1.788, for nitrogen components 1:0.15 and 1:1.3 for O_2. The

Species	a	b	c	d	e	f	Reference
General expression	1	0.5	0.2	1	1.8	0.5	(Tamis, 2014)
Chlorella sorokiriana ($5\%CO_2$)	1	1	0.16	1.415	2.01	0.61	(Kumar et al., 2014)
Marine type species	1	0.89	0.04	1.33	1.78	0.23	(Yadala and Cremaschi, 2014)

Table 2-2: Stoichiometric coefficients for different algae species

uptake and production of components is given by equation 2-36 to 2-39 with MW being the molecular weight of the species used as nutrients $[g/mol]$.

$$\phi_{CO_2mol,algae} = \frac{dB}{dt} \cdot \frac{1.788}{MW_{CO_2}} \quad [mol/dm^3 s] \tag{2-36}$$

$$\phi_{CO_2mass,algae} = \frac{dB}{dt} \cdot 1.788 \quad [g/dm^3 s] \tag{2-37}$$

The same can be written for nitrogen component (for example NH_4) uptake.

$$\phi_{NH_4mol,algae} = \frac{dB}{dt} \cdot \frac{0.15}{MW_{NH_4}} \quad [mol/dm^3 s] \tag{2-38}$$

$$\phi_{NH_4mass,algae} = \frac{dB}{dt} \cdot 0.15 \quad [g/dm^3 s] \tag{2-39}$$

The same can be written for oxygen production.

$$\phi_{O_2mol,algae} = \frac{dB}{dt} \cdot \frac{1.3}{MW_{O_2}} \quad [mol/dm^3 s] \tag{2-40}$$

$$\phi_{O_2mass,algae} = \frac{dB}{dt} \cdot 1.3 \quad [g/dm^3 s] \tag{2-41}$$

CO_2 loss to surroundings

In an open pond added CO_2 will be lost to the surroundings. The nutrient gas is rich in CO_2 which allows a higher concentration of dissolved nutrients than an equilibrium with the surrounds would allow. In contact with air the balance is different, hence nutrients will be released from the broth.

$$\phi_{loss} = k_L \cdot a \cdot (c_{CO2,max}(aq) - c_{CO2}(aq)) \quad [mg/dm^3 s] \tag{2-42}$$

With a being the interfacial area ($[m^{-1}]$) between the gas and the liquid. With k_L being the mass transfer rate in [m/s]. Here the CO_2 is diffused out of the water through the water surface, the k_l value can be determined by equation 2-43.

$$k_l = D_L / z_l \tag{2-43}$$

With D_L the diffusion coefficient of CO_2 in water and z_l the thickness of the film. The interfacial area is approximated by equation 2-44.

$$a = \frac{A}{V} \tag{2-44}$$

With V the volume of the reactor and A the surface in contact with the air.

Mass transfer rates

Mass transfer rates have been discussed in the previous section. These rates give the amount of mass transferred from one phase to the other over a certain time span. Mass transfer rates are often measured in reactors, but correlations and approximations such as equation 2-33 are also available.

Dominating terms in mass transfer Mass transfer rates between a gas and a liquid phase can be dominated by the gas or liquid phase. An expression for a total mass transfer rate dependent on both phases is given in equation 2-45.

$$\frac{1}{K_l} = \frac{1}{k_l} + \frac{m}{k_g} \quad [s/m] \tag{2-45}$$

With k_g being the gas mass transfer rate in $[m/s]$ and k_l being the liquid mass transfer rate in $[m/s]$. The coefficient m is the distribution coefficient between gas and liquid phase denoted by $m = \frac{c_g}{c_l}$ with c being the concentration at the interface. The rate of mass transfer for CO_2 differs from that of O_2. A common assumption (Garcia-Ochoa and Gomez, 2009) is to calculate the transfer rates of CO_2 based on that of O_2, this is shown in equation 2-46.

$$\frac{k_l a_{O_2}}{k_l a_{CO_2}} = \frac{D_{O_2}}{D_{CO_2}} \tag{2-46}$$

With D being the diffusion coefficient of a species in water. With $D_{O_2} = 1.92 \cdot 10^{-9}[m^2/s]$ and $D_{CO_2} = 2.1 \cdot 10^{-9}[m^2/s]$ (Cussler, 1997). O_2 is considered to be non reactive to water which makes the liquid phase mass transfer coefficient dominant (Garcia-Ochoa and Gomez, 2009). Then equation 2-45 reduces to equation 2-47.

$$\frac{1}{K_l} = \frac{1}{k_l} \tag{2-47}$$

The parameter k_l can be calculated as shown equation 2-43 or in combination with the interfacial area, a, as shown in equation 2-42.

Chapter 3

Modelling approach

Using the definition of Bechet et al. (2013) a type II model is chosen to serve as a basis as modelling approach. Type I models are not chosen because they do not meet the requirements regarding applicability and universality as discussed in the first chapter. Type III models are not used because of their complexity and limited workability.

3-1 Type II model

In a Type II model the reactor geometry is divided into a number of volume zones, this is the basis for the modelling approach. All relevant parameters for a zone are determined and parameters such as the growth rate and created biomass are calculated for each zone. For the next time step the biomass concentration is averaged over all zones and the calculation is repeated. Unlike the assumption of a Type I model that all algae experience on average the same light intensity, a Type II model assumes that a zone of algae grows with a zone specific growth rate. The zone specific growth rate is function of local light intensity, biomass concentration, nutrients and more.

3-2 Model layout

The goal of this project is to create a workable, universally applicable, process model that describes the growth of algae. To realise this the model has to be set up in a way that is understandable and workable. As discussed in the previous chapters there are a number of important phenomena that need to be modelled. These are defined in the four boxes as shown in figure 3-1. These boxes can be interpreted in two ways, mathematical and physical. On one hand they represent a modelling approach, for example, light can be modelled by a Lambert-Beer law or a six flux model. The same holds for algae, their growth can be modelled by a Aiba equation or by a Monod equation. On the other hand the four boxes represent the physical input of the model. The light box describes the number of lights in a reactor.

The species of algae used is defined by the input parameters for the growth equation. The set of equations of a box can thus vary, as well as the input, what remains fixed is the type of output of the box. This is further explained in the following sections.

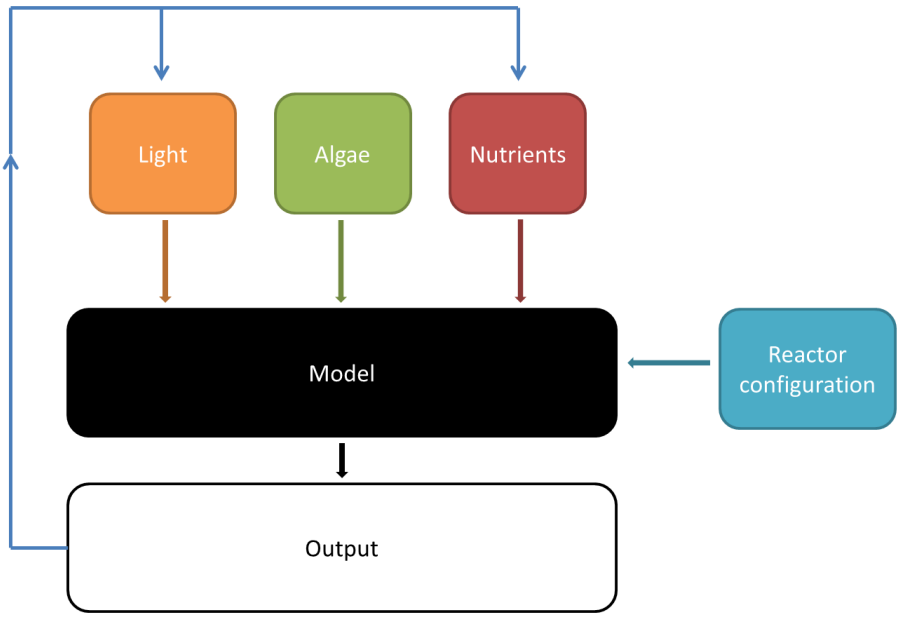


Figure 3-1: Model layout

3-3 Model core and output

The model core (black box in figure 3-1) receives all relevant parameters for the individual zones from the input boxes. The model core calculates the growth rate and new biomass concentration for each zone and the entire reactor. Due to the change in biomass concentration the light distribution and the nutrient balance change. Some output parameters of the model core serve as input for the light and nutrient box. The algae and reactor configuration are not dependent on the output since they are not a function of the changing output parameters. The arrows shown in figure 3-1 show the repetitive transfer of variables in the model over time. At the start of a simulation an initialization is required for external boxes and internal parameters. In the "type" columns all variables marked with an astrix $*$ are parameters which vary during model simulation. The variables scalers are that have the same value in each layer, the variables that are vectors can vary with different layers. The output variables and initialization parameters of the model core are given in table 3-1. After simulation these and other parameters can be used to determine productivity, efficiency and μ, B, η and other output parameters.

Variable	Description	Type	Units
μ_i	Growth rate of specific layers	Vector*	$[h^{-1}]$
B_i	Algae biomass concentration in specific layers	Vector*	$[kg/m^3]$
B	Averaged algae biomass concentration in the reactor	Scalar*	$[kg/m^3]$
ϕ_{CO_2}	Molar uptake of CO_2 by algae	Scalar*	$[mol/dm^3]$
$\phi_{Nutrient}$	Molar uptake of a nutrient by algae	Scalar*	$[mol/dm^3]$
t	Simulation time	Scalar	$[d]$
dt	Time step	Scalar	$[d]$
B_{init}	Initial biomass concentration	Scalar	$[kg/m^3]$

Table 3-1: Output variables and initialization parameters of the model core

3-4 Model box: Light

The modelling approach options for the light box are displayed in figure 3-2a, the different options were discussed in chapter 2-2. The input parameters for the modelling approaches can be different but the output remains identical. The output parameters of the the light boxes are ordered in an array and shown in table 3-2.

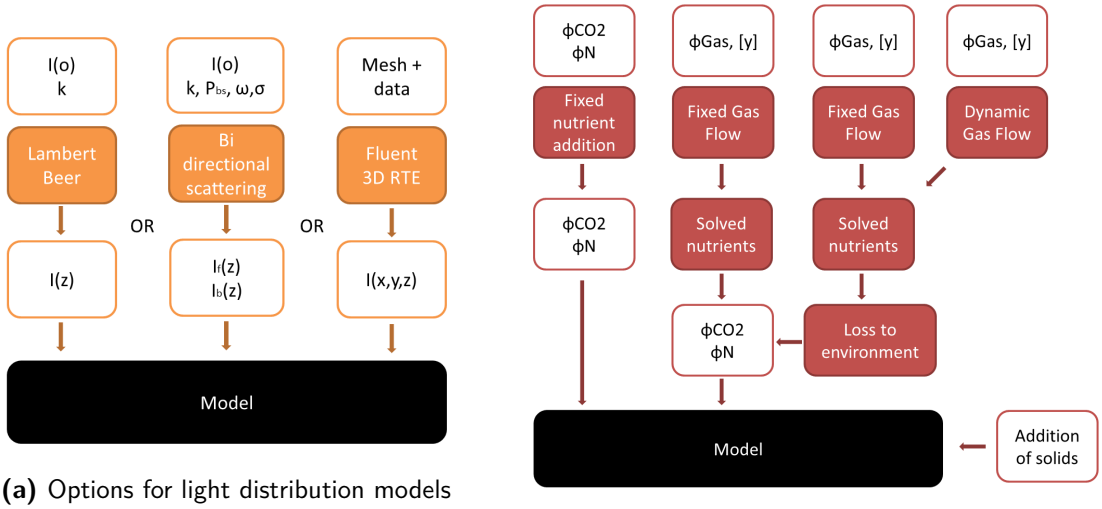
Zone Number, $[-]$	Incident light intensity, $[\mu mol/m^2 s]$*	Zone volume, $[m^3]$*
i_1	I_1	V_1
i_2	I_2	V_2
..	..	..
i_n	I_n	V_n

Table 3-2: Output format of the light box

The number of zones and their corresponding sizes are determined in the light distribution box. In the geometry box preferences can be given for the number of zones. The light box calculates the size and incident light intensity of those specific zones.

3-5 Model box: Algae

The species of algae used is defined by the algae box. The input is a set of algae specific parameters. Prior to the simulation the algae specific growth parameters are to be determined for different light intensities and nutrient conditions. This can be done experimentally or can be found in literature. It is important to stress that the conditions under which the parameters are determined set the limits of the model results. For example, if the parameters are determined with certain light spectra, the simulation outcome will only be valid for that light spectra. The same holds for the used nutrient medium, temperature, salinity and pH. The parameters of the algae box can be found in table 3-3. The equations that use these parameters are equation 2-25 and 2-1.



(a) Options for light distribution models

(b) Options for nutrient handling models

Figure 3-2: Options for different input boxes

Parameter	Description	Type	Units
μ_{max}	Maximum growth rate	Scalar	$[h^{-1}]$
μ_{min}	Negative growth rate	Scalar	$[h^{-1}]$
K_S	Half of maximum growth parameter	Scalar	$[\mu mol/m^2 s]$
K_I	Photo inhibition parameter	Scalar	$[\mu mol/m^2 s]$
κ	Algae specific light absorption coefficient	Scalar	$[m^2/g]$

Table 3-3: Output parameters of the algae box

3-6 Model box: Nutrients

The two major sources of nutrients for algae are nitrogen and inorganic carbon compounds. Nitrogen can be added through ammonia or nitrate. The main source of organic carbon is CO_2 gas. The gas is dissolved in water and reacts to carbonic acid, carbonate and bicarbonate. The output of the nutrient box can be found in table 3-4.

Parameter	Description	Type	Units
c_C	Concentration of organic carbon	Scalar*	$[mol/dm^3]$
c_N	Concentration of nitrogen compounds	Scalar*	$[mol/dm^3]$

Table 3-4: Output parameters of the nutrient box

3-7 Model box: Reactor configuration

The reactor box holds the reactor geometry and is shown in table 3-5.

Parameter	Description	Type	Units
h	Reactor height	Scalar	$[m]$
V	Total reactor volume	Scalar	$[dm^3]$
$Area$	Illuminated Area	Scalar	$[m^2]$

Table 3-5: Output parameters of the reactor configuration box

3-8 Post simulation parameters

After running the model the results can be analysed with some post simulation parameters. These parameters are defined here.

Photosynthetic efficiency The photosynthetic efficiency can be expressed as the chemical energy stored in the algae divided by the light energy inserted. This is shown in equation 3-1

$$\eta_{photo} = \frac{E_{Chem,stored}}{E_{Light,indicent}} = \frac{P_{m^2} * LHV}{\frac{I}{4.6} \cdot t} \quad [-] \tag{3-1}$$

With P_{m^2} being the production per square meter illuminated surface $[kg/m^2]$ over a selected time t. LHV is the lower heating value in $[MJ/kg]$. I is the illumination per square meter $[\mu mol/m^2 s]$. To convert the $\mu mol/s$ units to W a factor 4.6 is applied, this is explained in appendix C, t is time in seconds.

Biomass on energy yield The biomass yield on PAR photon flux is defined by Olivieri et al. (2014) and is given in equation 3-2.

$$Y_{X/E} = \frac{\mu V}{I_0 A k} \quad [gm/J] \tag{3-2}$$

With μ being the specific growth rate (averaged over time) $[s^{-1}]$, V is the volume $[m^3]$, A is the illuminated surface $[m^2]$, I_0 is the incident light intensity $[\mu mol/m^2 s]$ and k is the algae specific absorption coefficient $[m^2/g]$. The $Y_{X/E}$ gives insight about the production of biomass for a given energy input, the higher the number the more biomass produce able from an unit of energy.

Production and productivity The productivity is defined as the net biomass increase in the entire reactor divided by growth time. The production is defined as the net biomass increase in the entire reactor. The equations for production and productivity are given in equation 3-3 to equation 3-6. By using the productivity per litre different operating variables can be compared to each other.

$$B_{P,dm^3} = B(dt) - B(0) \tag{3-3}$$

$$B_{P,reactor} = (B(dt) - B(0)) \cdot V \tag{3-4}$$

With B_P being the biomass production over a given time $[g]$, $B(t)$ being a biomass concentration at a given time t and dt is the time $[s]$.

$$P_{dm^3} = \frac{B(dt) - B(0)}{dt} \tag{3-5}$$

$$P_{reactor} = \frac{B(dt) - B(0)}{dt} \cdot V \tag{3-6}$$

With P being the productivity over a given time.

Model fit on experiments In this thesis model data is compared to experimental data. The coefficient of determination R^2 is number which given information about the fit of the model on actual data. If the model fits the experimental data perfectly then $R^2 = 1$. R^2 is calculated using equation 3-7

$$R^2 = 1 - \frac{\Sigma(C_{exp} - C_{model})^2}{\Sigma(C_{exp} - \bar{C}_{exp})^2} \tag{3-7}$$

With C_{exp} being the concentration data point of the experiment, C_{model} being the concentration data point of the model and $\bar{C}_{exp}$ being the average concentration of experiment.

Chapter 4

Basic model development and validation

4-1 Basic model development

For this thesis two models are created, a basic model and a more extended model. The basic model is a simple approach to algae modelling to lay a foundation for a basic understanding about algae modelling. The extended model will have more advanced features than the basic model. The extended model can be validated and checked to a certain extent by using the basic model. The basic model will be a Type II model as described in chapter 1-2. The model layout for the basic model is shown in figure 4-1. The content and layout of the boxes is globally described in chapter 3 and will be discussed in detail in chapter 4-2.

Assumptions and limitations
To model an algae reactor some assumptions are needed to make the model workable. The assumptions made for the basic model are shown in the following list:

- The reactor is ideally mixed, nutrients and algae are always distributed homogeneous.
- The incident light in the PAR (see appendix A) is considered a lumped number, phenomena at wavelength level are neglected.
- The incident light intensity cannot exceed the maximum range defined by experiments.
- The basic model does not account for multi directional light.
- Addition of nutrients happens instantaneous, there are no mass transfer phenomena.
- The reactor is operated at constant temperature.
- The reactor is operated at constant pH.
- The reactor is operated at constant salinity.

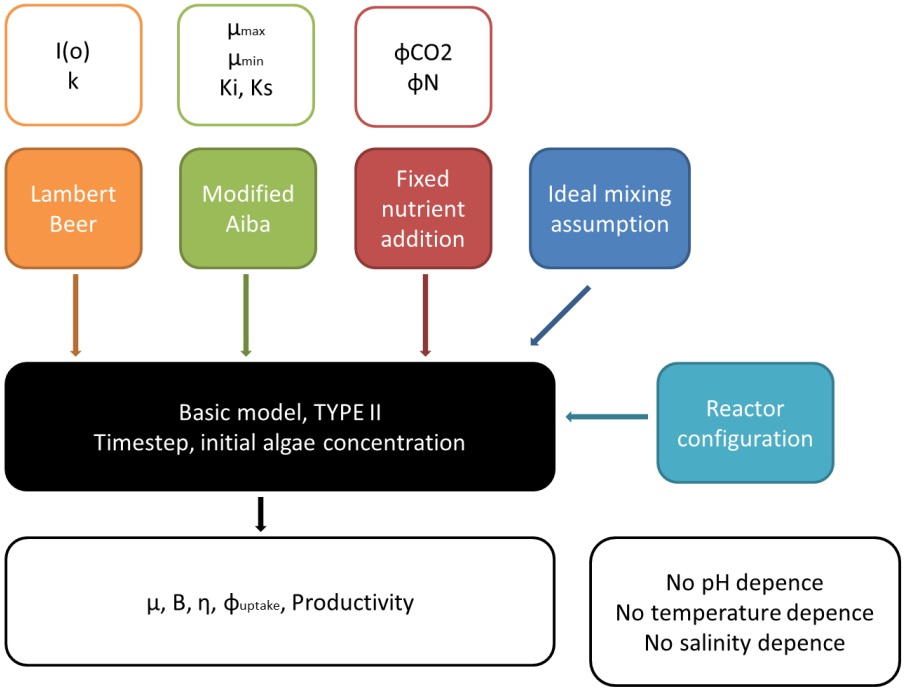


Figure 4-1: Basic model layout

By making the above set of assumptions the model has a number of limitations. The limitations are given the following list:

- Fluid dynamics/airlift/mixing in the actual reactor must satisfy the ideal mixing assumptions.
- The light distribution is calculated by a 1D Lambert-Beer equation, complex 3D reactor geometries cannot be handled.
- The basic model does not handle multi directional light.
- Nutrient mass transfer phenomena are not taken into account.
- The basic model does not account for temperature variation.
- The basic model does not account for pH variation.
- The basic model does not account for salinity variation.
- The basic model does not account for second scale light cycles.

Features
The basic model will have the following features.

- Predict algae growth based in the incident PAR radiation.
- For square geometries, optimal depth can be calculated for different species and light intensities.
- Light intensities can be varied to find an optimal production.

- Photosynthetic efficiency can be calculated for different input parameters.
- Nutrients requirements can be determined.

Model creation
The basic model has been initially created in Microsoft Excel, followed by an implementation in Mathworks Matlab.

4-2 Basic model equations

The equations used in the basic model are described in this section.

Light model

The Lambert-Beer law describes the decay of light intensity in a broth. There is no separate term which describes the absorption of light by water. A separate scattering term is not used because the verification data does not have this data available. The used form of the Lambert-Beer law is given in 4-1.

$$I(z) = I_0 e^{-k\beta z} \tag{4-1}$$

With I_0 being the net incident light intensity (PAR) in $[\mu molm^{-2}s^{-1}]$. k is the algae specific extinction coefficient $[m^2/g]$. β is the population density of the algae culture in $[kg/m^3]$ and z being the local depth $[m]$.

Growth model

The growth model used for the basic model is based on that of Aiba (1982) and expanded by van Leeuwen (2012). It is shown in equation 4-2.

$$\mu = \frac{\mu_{max} I}{K_s + I + \frac{I^2}{K_i}} - \mu_{min} \tag{4-2}$$

With μ_{max} being the maximum growth rate $[h^{-1}]$ in equation 4-2. Note that this is not the maximum growth rate of an algae species, it is used to describe the growth rate as a function of light intensity. μ_{min} is the respiration rate $[h^{-1}]$. I is the light intensity $[\mu molm^{-2}s^{-1}]$ at a given location. K_s is the light intensity $[\mu molm^{-2}s^{-1}]$ where half of the maximum growth rate is reached. K_i is the photo inhibition fitting parameter $[\mu molm^{-2}s^{-1}]$.

Productivity

The basic model simulates a reactor operated in batch mode, the equation that describes the biomass increase is given in equation 4-3 and equation 4-4. The productivity is calculated for each layer (i) separately. After all concentrations are calculated they are volume averaged over the entire reactor (ideal mixing assumption).

$$\frac{dB_i}{dt} = \mu_i B_i \tag{4-3}$$

$$B(t)_i = B(0)_{avg} \cdot e^{\mu_i t} \tag{4-4}$$

With $B(0)$ being the average biomass concentration $[g/dm^3]$, t the time in [h] and μ the layer specific growth rate as shown in equation 4-2. In the basic model all layers have identical volume so equation 4-5 is used.

$$B(t)_{avg} = \frac{\sum_{i=1}^{n} B(t)_i}{n} \tag{4-5}$$

4-3 Basic model validation

The basic model is validated using a paper from Huesemann et al. (2013). In this study a 800 litre raceway pond with a monoculture of Chlorella sp. was grown for 10 days using an LED light source with a spectrum similar to the sun. This data is used to validate the basic model. Huesemann et al. (2013) also developed a model to predict the algae growth in their experiment. Their model predictions will be compared to the predictions of the basic model.

Chlorella sp. Huesemann 2013

Huesemann et al. (2013) first determined the growth properties of algae as function of light intensity. Using Roux bottles and a LED light source the growth rate for different light intensities was determined. The data from Huesemann et al. (2013) is shown in figure 4-2.

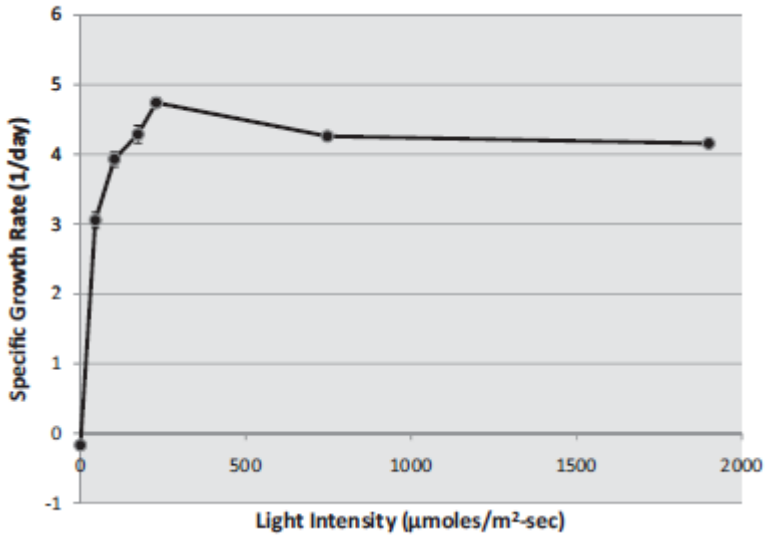


Figure 4-2: Experimental growth rate as function of light intensity (Huesemann et al., 2013)

Using Microsoft Excel equation 4-2 was reproduced and fitted on the growth rate graph of Chlorella SP. The fit was done by optimizing the R^2 value by using the goal seek function. The data point at 250 $[\mu mol/m^2 s]$ was omitted as this was a single measurement and does not follow the trend. The best R^2 value was 0.95 $[-]$ which was found for the fitted parameters as shown in table 4-1.

Another algae specific parameter is the algae specific extinction coefficient (k). Huesemann et al. (2013) performed a number of measurements with different light intensities at constant

Parameter	Value	Unit
μ_{max}	5.1	d^{-1}
μ_{min}	0.17	d^{-1}
K_s	28	$\mu molm^{-2}s^{-1}$
K_i	9510	$\mu molm^{-2}s^{-1}$

Table 4-1: Growth rate parameter for Chlorella SP.

population density. The results have shown that the extinction coefficient is a function of the population density, however, the variation for Chlorella SP is minimal so it is treated as a constant. From Huesemann we find that $k = 0.334\ [m^2/g]$. This data can also be found in appendix D.

Validation using Huesemann

With the growth properties of the Chlorella SP known, the system of Heusemann can be reconstructed. System properties are given in table 4-2. With z being the culture depth and n being the number of slabs in which the reactor is divided. A typical example of a raceway pond is given in figure 4-3.

Figure 4-3: Typical example of a raceway pond

Figure 4-4 shows the modelling results from Huesemann and the basic model. It shows that the results for both models are similar, the data fits well as shown by analyses with $R^2 = 0.97$ but with an over prediction of 7.8 % of OD_{750} at day 9. Huesemann uses a linear correlation between the optical density at 750 nm wavelength and the dry biomass density, the correlation is: $B = 0.194 \cdot OD_{750}$.

Parameter	Value	Unit
V	800	dm^3
z	0.245	m
A	2.75	m^2
n	100	n
B_0	0.0647	$g\ l^{-1}$
dt	0.1	day
I_0	1650	$\mu molm^{-2}s^{-1}$

Table 4-2: System properties of Huesemann et al. (2013)

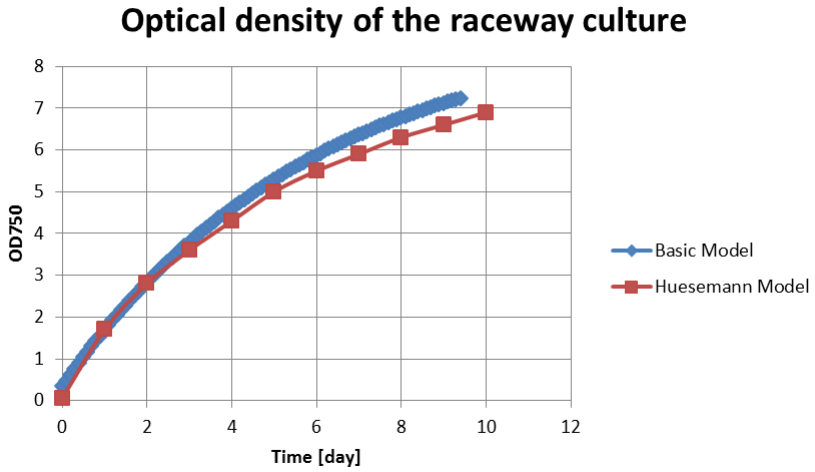


Figure 4-4: Modelled prediction of biomass increase by current basic model and Huesemann et al. (2013) model

Discretization error in Huesemann Model

The time step used for simulation should be chosen small enough to make the influence on the results negligible. A too large time step will lead to inaccurate results and a to small time step will result in longer computational time. Microsoft Excel does not allow for an easy decrease of the time step due to the model structure (several rows per time step). The basic model is also created in Mathworks Matlab which does allow for a variable time step. The results at the same time step for Microsoft Excel and Matlab are identical. The Matlab model was run for different time steps, the results are shown in figure 4-5.

As shown in figure 4-5 the required minimal time step for the model is in the range of 0.01 days (15 min) to reach a non changing result. A time step of 0.1 day thus leads to a discretization error in the mathematical model, our results differs 10 % negatively from Huesemann's model (OD_{750} at day 9). However, the actual experiments do correlate with a simulation using a time step of 0.1 day as shown in figure 4-6. This suggests that there should be other parameters that are not modelled or determined properly. Another reason could be that the modelling approach is not valid, however other papers that use the same modelling approach

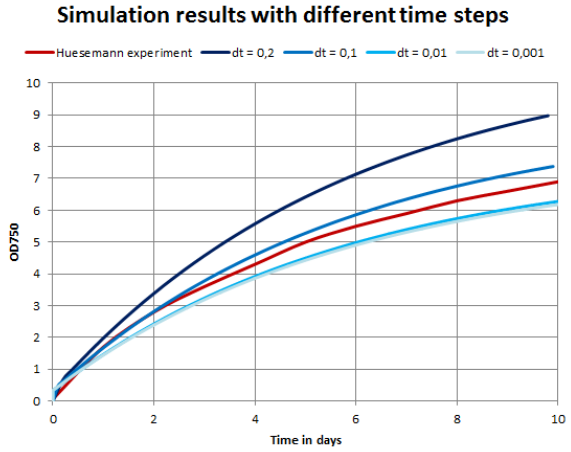


Figure 4-5: Results with different time steps

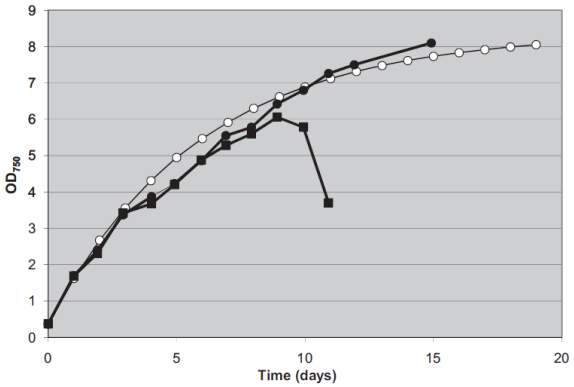


Figure 4-6: Results from Huesemann et al. (2013), white circles are model results, black circles are experiments

do produce valid results (Bechet et al., 2013). The time step size where the results do not significantly change is found to be in the order of 0.01 day. A discussion with the authors of the Huesemann paper was held over email were they acknowledged the time step error in their model, they have already upgraded their model and now use a time step of 5 minutes (0.0035 day).

Still, the paper of Huesemann has some design parameters which are not properly described or measured which could explain the deviation. The algae specific absorption constant, k, was assumed to be constant while other experiments of Huesemann have proven that it is not. While determining the algae specific growth parameter a temperature controlled aquarium with shaker flasks was used. Using shaker flasks always leads to darker zones due to the cap resulting in an inhomogeneous light distribution. These aspect could explain why the model with a correct time step do not represent the results.

4-4 Basic model, parameter variation and nutrient limitation

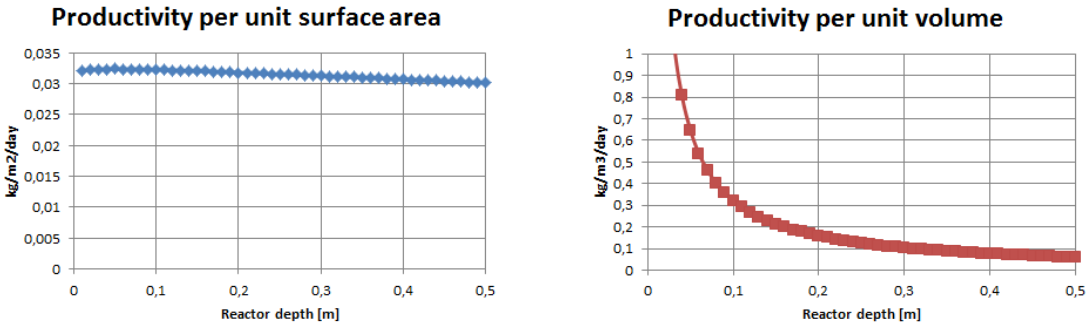
With the simulation result from the basic model known we can modify several parameters to see which are most influential. The main engineering parameters are identified as the incident light intensity and the reactor geometry (depth). These parameters will be varied to determine their influence. The basic model does not account for nutrient limitations, when varying the depth of a reactor, nutrient addition can become an issue due to insufficient height for CO_2 gas to dissolve. Therefore nutrient limitation is also modelled. In the this chapter various design parameters are changed to see their influence, these calculations are done with a time step of 0.1 day.

Depth variation

The reactor depth of the Huesemann experiment is 24.5 [cm]. In this simulation the depth of the reactor is varied from 1 to 50 [cm], by changing the depth the reactor the volume

is also changed. Three key numbers are calculated to compare the performance at different depths, these are; Productivity per unit surface area $[g/m^2/day]$, Productivity per unit volume $[g/m^3/day]$ and total grams produced. The results are found in figure 4-7.

The productivity per unit surface area can be considered a horizontal line. More remarkable



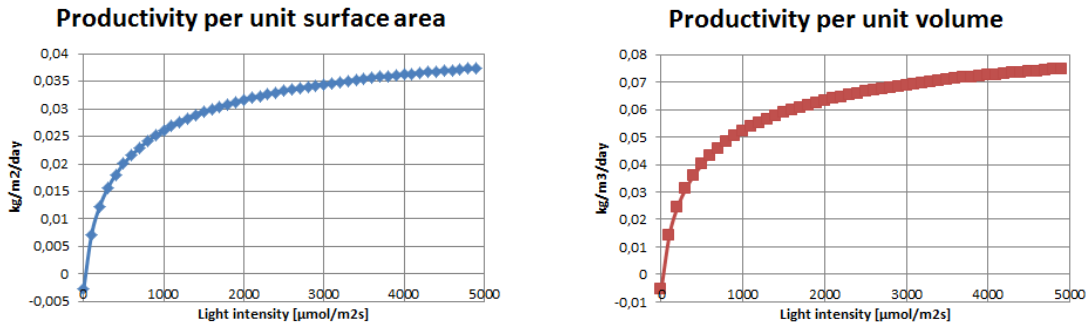
(a) Production per unit area **(b)** Production per unit volume

Figure 4-7: Results for depth variation for basic model

is the production per unit unit volume. Due to the high productivity at low reactor depths the biomass concentration and the optical density grow rapidly. This introduces a number of practical problem such as mixing, adding nutrients and keeping the algae in suspension. These phenomena are not modelled in the basic model which brings some limitations. The productivity should drop if the depth becomes smaller, the exact tipping point is dependent on nutrient feed conditions and reactor depth.

Light intensity variation

The incident light intensity used by Huesemann is 1650 $[\mu mol/m^2s]$. The intensity is varied and again the production per unit surface area and production per unit volume are calculated. This is shown in figure 4-8. Huesemann et al. (2013) measured the growth rate as function



(a) Production per unit area **(b)** Production per unit volume

Figure 4-8: Results for light intensity variation for basic model

of light intensity up to 1850 $[\mu mol/m^2s]$. However, in this analyses light intensities up to 5000 $[\mu mol/m^2s]$ are used. The model shows that after 2 [mm] the light intensities reach

values that lie within the allowed range. Up to 1850 $[\mu mol/m^2 s]$ the graph can be used for as comparison with actual data, above 1850 $[\mu mol/m^2 s]$ it can be used to observe a trend.

Scattering model

To investigate the effect of scattering the modified two flux model has been used to model the Huesemann case. Because no scattering data was available from Huesemann the assumption was made to use $P_{bs} = 0.5$ and to vary the scattering albedo from 0.1 to 0.7. The result for this simulation are shown in figure 4-9.

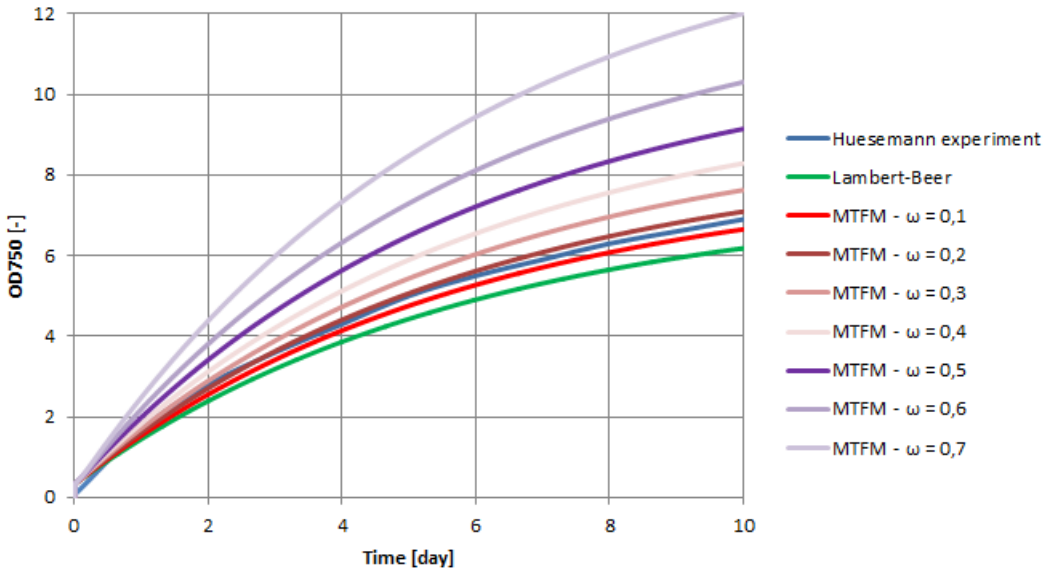


Figure 4-9: Simulation results for different scattering albedo's

As shown in figure 4-9 the scattering albedo has significant effect on the productivity. Hannis (2012) measured the optical properties of different species of algae. The average scattering albedo found was around 0.5-0.7. The simulations using these albedo's over predict the productivity of the model at least 20 %. The determination of the algae specific absorption coefficient by Huesemann was performed by measuring the intensity before and after a cuvette, one with medium and one with algae and calculating the k with Lambert-Beer (see chapter 6-5). By using this method the effects of absorption and scattering are lumped in one k. The k from Huesemann thus does not allow the use of an extra scattering term since it is integrated in it. However, the data in figure 4-9 can be used as a trend to observe the influence of scattering.

Adding nutrient limitations

The basic model has a growth rate equation which does not take nutrient limitations into account. To handle nutrient limitations the basic model is extended with a term for carbon

limitation as shown in equation 4-6.

$$\mu = \frac{\mu_{max} I}{K_s + I + \frac{I^2}{K_i}} \cdot \frac{c_{CO_2}}{K_{CO_2} + c_{CO_2}} - \mu_{min} \tag{4-6}$$

With c_{CO_2} being the dissolved CO_2 concentration in [mmol/dm^3] and K_{CO_2} being the half saturation constant on CO_2 in [mmol/dm^3]. By introducing a concentration factor, more equations need to be stated to handle the consumption and feed phenomena. The equations for the consumption are given in 2-4 by equation 2-36 and 2-37. The time-scale representing the simulation does not allow accurate modelling of feed in of gas, thus for now the feed of nutrients was considered a constant. Figure 4-10 shows the amount of mol CO_2 consumed by the algae in each time step. A time step takes 0.1 day, so 2.4 hours.

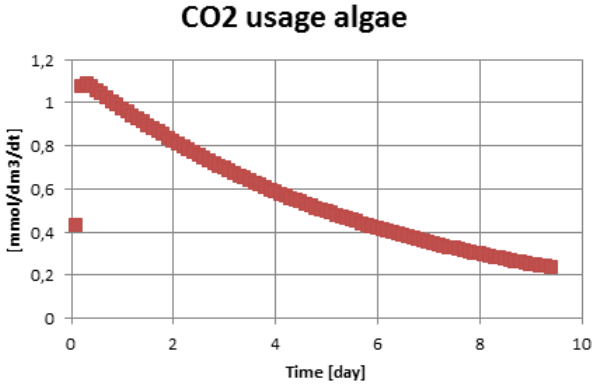
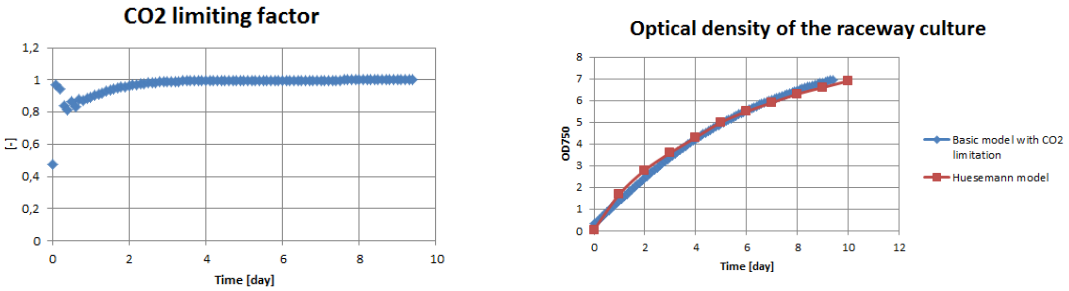


Figure 4-10: CO_2 consumption of one dm^3 of algae

From figure 4-10 it can be concluded that net more than 1 mol of CO_2 per dm^3 per 2.4 hour needs to added to avoid CO_2 limited growth. However, note that CO_2 uptake due to respiration is not accounted for, also the loss of CO_2 to the environment and nutrient gas mass transfer phenomena are not modelled . The actual feed of CO_2 in a reactor will thus be larger than shown in figure 4-10. In appendix B a CO_2 process model is developed which takes these effects into account. The CO_2 feed of the model is set to 0.85 [mmol/dm^3 0.1 day], as shown in figure 4-11a the CO_2 factor is effected as is the growth of the culture, as shown in figure 4-11b.



(a) CO_2 limiting factor

(b) Optical density of the culture

Figure 4-11: Effect of insufficient CO_2 feed

Photosynthetic efficiency

The efficiency of converting energy in photons to biomass is defined by the photosynthetic efficiency, no nutrient limitation are assumed. The energy from the incident light intensity is known, only a conversion factor from $\mu mol/m^2s$ to W/m^2 needs to be applied. The LED's used by Huesemann emit a spectrum which is similar to that of the sun thus a conversion factor of $\frac{1}{4.6}$ can be used, this is explained in appendix C. From the Dutch ECN's (Energieonderzoek Centrum Nederland) biomass database BIODAT values for the net calorific value are found for a Chlorella type algae. The net calorific value for dry algae is 25.09 $[MJ/kg]$. The photosynthetic efficiency of the Huesemann experiment is calculated in equation 4-7.

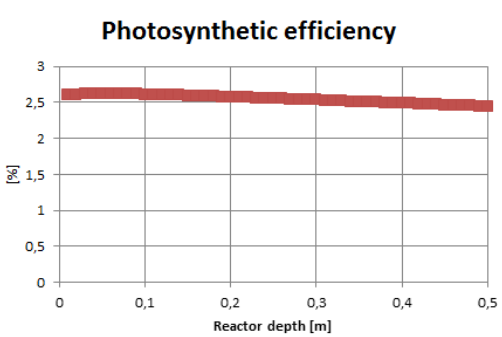
$$\eta_{photo} = \frac{P_{m^2} * LHV}{\frac{I}{4.6} \cdot 9.4 \cdot 24 \cdot 3600} = \frac{0.2966 \cdot 25.09 \cdot 10^6}{\frac{1650}{4.6} \cdot 9.4 \cdot 24 \cdot 3600} = 2.55 \quad [\%] \tag{4-7}$$

The given efficiency is based on dried algae, however the energy required to centrifuge and dry certainly not negligible. Per kg of dry algae about 3 MJ is required for centrifuging and another 20 MJ is required to reduce the water content to 10 %. This depends on the technique used, the same holds for the creation of light. To make a fair comparison we are only interested in the phohtosynthetic efficiency of dried algae.

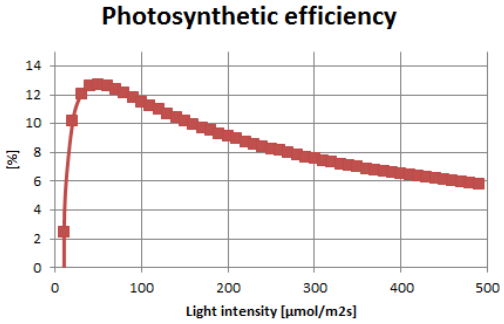
The reactor parameters are varied to find an optimum photosynthetic efficiency, this is shown in figure 4-12. To show the peak in photosynthetic efficiency figure 4-12b does not show the entire range of incident light intensity. The biomass produced at 1650 $[\mu mol/m^2s]$ is 815.7 [g]. The biomass produced at the peak (50 $[\mu mol/m^2s]$) is 122.9 [g]. For this case it can be concluded that lowering the light intensity results in higher efficiencies.

4-5 Basic model, sensitivity analysis

In chapter 4-4 the variation of parameters and their influence was discussed. To obtain a objective comparison a sensitivity analysis is made. Two analysis are considered, one with operational parameters and one with algae specific parameters. The operational parameters analysis can be used to see the influence of operational parameters, operational parameters can be changed physically on a reactor. Algae specific parameter analyses can help to selected a specific algae species. The analysis are displayed in figures 4-13 and 4-14. The analysis is



(a) Photosynthetic efficiency varying with depth



(b) Photosynthetic efficiency varying with light intensity

Figure 4-12: Photosynthetic efficiency with varying parameters

performed by varying the parameters and monitoring the change in production per day. The production per day was averaged over the entire duration of the experiment.

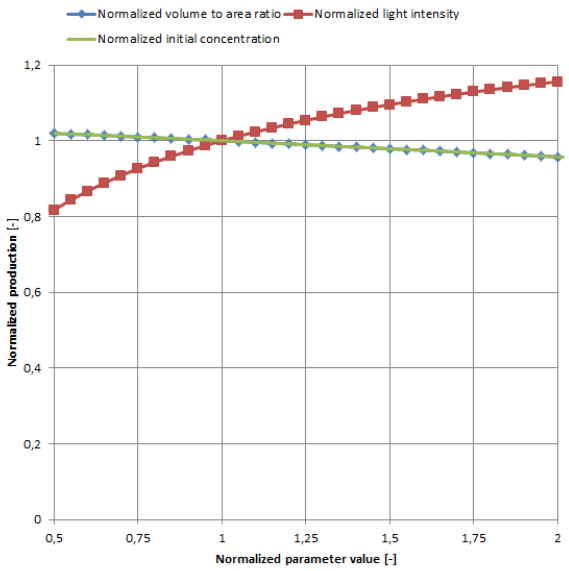


Figure 4-13: Sensitivity analysis of operational parameters

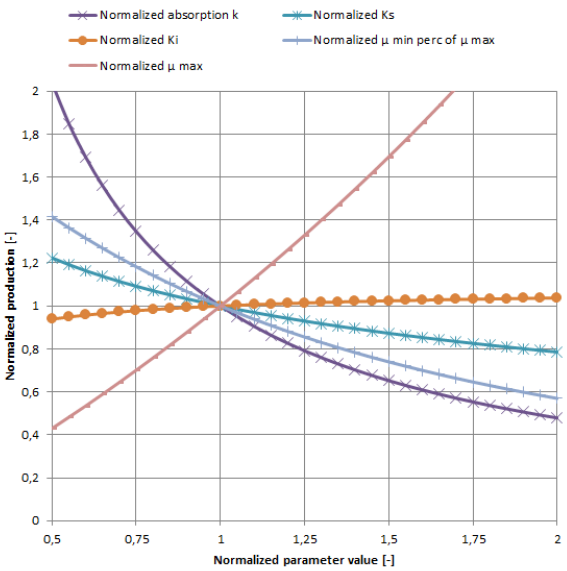


Figure 4-14: Sensitivity analysis of algae specific parameters

Note that there are several limitations to the data presented in the analysis above. These limitations are mentioned in chapter 4-4 and briefly mentioned here. In figure 4-13 the depth (volume to area) cannot be reduced to to small number due the limitations with injecting CO_2. The normalized light intensity is measured in the lab up to a value of 1.15 of the normalized value, without knowing the exact photo inhibition value all values above 1.15 should be considered a trend. The variation of the normalized μ_{min} in figure 4-14 is done as following: $\mu_{min} = N \cdot \mu_{min}$. Note that the algae specific parameters al all measured parameters, based on this analysis a suitable algae species for a given application can be selected.

Analysis show that the most significant operation parameter is the incident light intensity. The most significant algae specific parameters are the maximum growth rate (μ_{max}) and the absorption coefficient (k). Figure 4-14 can be used to select the best algae for a given application, however there a physical limitations to these parameters, for example the maximum growth rate algae can achieve. In this simulation a Chlorella sp. is used which known for its high growth rates, it is unlikely to find a algae species with a growth rate twice that of a Chlorealla sp.

4-6 Conclusions

A basic model has been developed to have a understanding of the influence of different operation and parameter specific parameters. The created model is in good accordance with the model of Huesemann, the $R^2 = 0.97$ but has an over prediction of 7.8% of the final value. Using Matlab the time step of the simulation was changed and a numerical error was found in the model of Huesemann due to a to large time step, decreasing the timestep such that the results are non changing leads to an under estimation of 10% of the final value. Sensitivity analyses on the model show that the incident light intensity is the most sensitive operating parameter. The most sensitive algae specific parameters were the absorption coefficient and the maximal growth rates. Operating parameters are parameters that can be changed in the operation of a photobioreactor. Algae specific properties are properties that belong to a specific type of algae, these cannot be changed, but an algae species can be selected based on these properties.

Chapter 5

Extended model development and validation

5-1 Extended model development

In chapter 4 a basic model was developed with some limitations regarding nutrients and complex geometries. To avoid these limitations the extended model has more features than the basic model. The base of the extended model is similar to that of the basic model, the difference is in the light and nutrient box. The light box can use a full 3D RTE instead of a 1D approximation, also growth limiting factors are added with expressions for the feed in of nutrients. The basic model can be seen as a simplified case of the extended model, all analyses that have been done by the basic model in chapter 4 are also performed by the extended model, the results for both models are identical. Using references from literature the extended model will be calibrated to reality. An overview of the model layout is given in figure 5-1.

The content and layout of the boxes is globally described in chapter 3. The operation of the boxes is described in chapter 5-2. The application of the extended model is done by using data from a paper of Gharagozloo et al. (2014), they use a regular pond and a raceway pond for their experiments. A simple geometry like a raceway pond do not require a complex light distribution approach like the full 3D RTE. In this case a 1D approximation is used to calculate the light distribution, this validation of the extended model does not use the extended model in its full form.

Assumptions and limitations
The extended model has some limitations and assumptions to make the model workable, which are discussed here. The assumptions made for the extended model are shown in the following list;

- The reactor is ideally mixed, nutrients and algae are always distributed homogeneously.

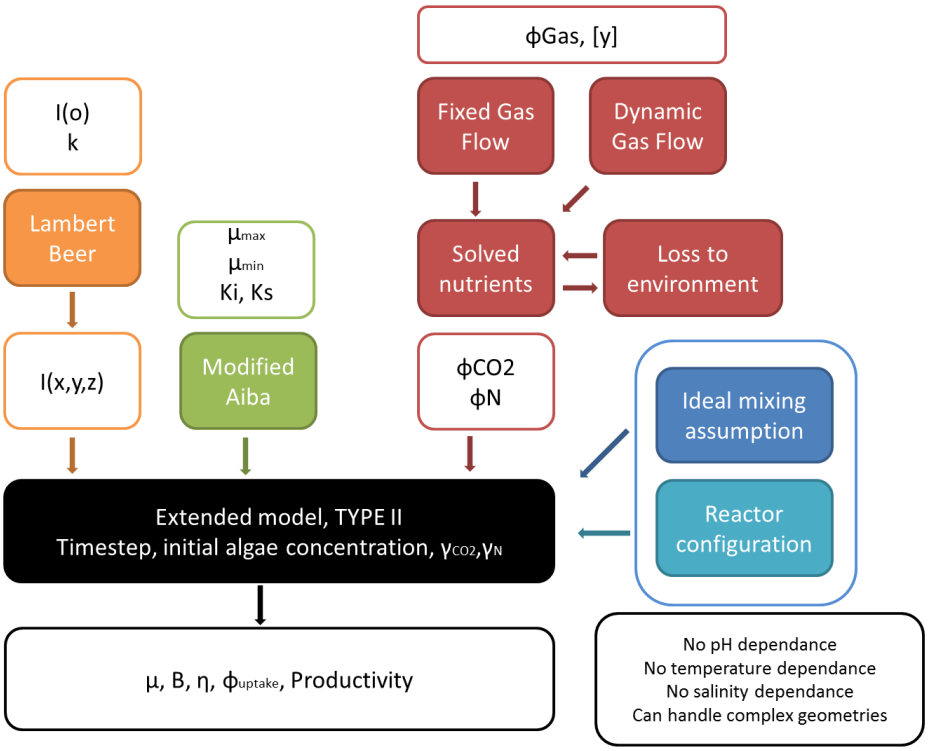


Figure 5-1: Extended model layout

- The incident light in the PAR is considered a lump number, phenomena at wavelength level are neglected.
- The incident light intensity cannot exceed the maximum range defined by experiments.
- The reactor is operated at constant temperature.
- The reactor is operated at constant pH.
- The reactor is operated at constant salinity.

By making the above set of assumptions the model has a number of limitations. The limitations are given in the following list:

- Fluid dynamics/airlift/mixing in the actual reactor should be sufficient to justify the ideal mixing assumptions.
- The extended model does not account for temperature variation.
- The extended model does not account for salinity variation.
- The extended model does not account for second scale light cycles.

Features
The extended model will have the following features.

- Predict algae growth based on the incident PAR radiation, and nutrient availability.

- Light intensities can be varied to find an optimal production.
- Can handle complex geometries.
- Photosynthetic efficiency can be calculated for different input parameters.
- Determine nutrients concentrations as function of fixed or dynamic gas addition.

Model creation
The extended model is created in Mathworks Matlab. To solve the 3D RTE the discrete ordinate method in ANSYS FLUENT is used, grids are made in ICEM CFD.

5-2 Extended model equations

The equations used in the extended model are briefly described in this section.

Light model

For complex reactor geometries the light distribution is calculated by solving the 3D radiative transfer equation using ANSYS FLUENT. Chapter 2-2 describes the equation set used by ANSYS FLUENT to solve this problem. If the reactor geometry is such that the light distribution can be approximated using a 1D approach, that would be preferred option due to the complexity and amount of work required for a full 3D simulation.

Growth model

The growth model used for the extended model is similar to that of the basic model. It has some additions to deal with nitrogen and carbon limitations. It is shown in equation 5-1.

$$\mu = \frac{\mu_{max} I}{K_s + I + \frac{I^2}{K_i}} \cdot \gamma_N \cdot \gamma_C - \mu_{min} \tag{5-1}$$

With μ_{max} being the maximum growth rate $[h^{-1}]$ in equation 4-2. Note that this is not the maximum growth rate of an algae species, it is used to describe the growth rate as a function of light intensity. μ_{min} is the respiration rate $[h^{-1}]$. I is the light intensity $[\mu molm^{-2}s^{-1}]$ at a given location. K_s is the light intensity $[\mu molm^{-2}s^{-1}]$ where half of the maximum growth rate is reached. K_i is the photo inhibition fitting parameter $[\mu molm^{-2}s^{-1}]$.

Productivity

A reactor operated in batch mode is simulated, the equation that describe the productivity is given in equation 5-2. The productivity is calculated for each zone (i) separately. After all concentrations are calculated the concentrations are volume averaged over the entire reactor (ideal mixing assumption).

$$B(t)_i = B(0)_{avg} \cdot e^{\mu_i t} \tag{5-2}$$

With $B(0)$ being the average biomass concentration [g algae/l], t the time in [h] and μ the zone specific growth rate as shown in equation 4-2. The extended model uses zones of different volumes and light intensities in stead of layers with constant volume and prescribed

light intensity. The 3D light distribution calculations result in a array containing zones with specific volumes and light intensities. Zones of similar light intensity can be added up to create a distribution of incident light intensity on a quantity of volume. The growth rate and new biomass density of this volume with constant light intensity is calculated and averaged over the reactor. The expression for the averaged biomass in the reactor is given by equation 5-3.

$$B(t)_{avg} = \frac{\sum_{i=1}^{n} B(t)_i \cdot V_i}{V} \tag{5-3}$$

Nutrients

Equation 5-1 states the limiting factors for nitrogen en carbon sources. They are given by equation 5-4 and 5-5. The equations describing the mass transfer phenomena are discussed in chapter 2-4. The phenomena that are taken into account are: CO_2 adding by bubbling, loss to surroundings, uptake by algae, also dynamic addition can be simulated.

$$\gamma_{CO_2} = \frac{c_{CO_2}}{K_{CO_2} + c_{CO_2}} \tag{5-4}$$

$$\gamma_N = \frac{c_N}{K_N + c_N} \tag{5-5}$$

The carbon component is added as CO_2 in the form of enriched air which is pumped trough the reactor. Depending on the flow, enrichment ratio and contact surface an amount of CO_2 is solved in water and partially converted to bicarbonates. The addition of nitrogen components is usually in the form of Sodium nitrate ($NaNO_3$) or an Ammonium component (NH_4). These components are added at the start of an batch experiment and often supplied in excess. By dissolving the components an instant number for concentration is available which only decreases as the experiment progresses.

5-3 Modelling CO2 limited growth in a pond reactor

Gharagozloo et al. (2014) performed a series of experiments with Nannochloropsis Salina in different photobioreactors. Two of these are of interest, first a circular pond with aeration using a 5% $CO2$-air mixture and air, the second is a raceway pond. Gharagozloo supplied all the input parameters required for the model to operate. Our modelling approach is based on the growth rates of individual zones which requires specific algae input parameters. The algae specific parameters where available from Gharagozloo, however these did not take photoinhibition into account. Huesemann et al. (2013) performed quality tests measuring the algae specific parameters for Nannochloropsis Salina. Using the algae specific parameters from Huesemann and other data from Gharagozloo a simulation is made. The data for the simulation is given in table 5-1. As shown in figure 5-2 the ponds are illuminated by the sun. Gharagozloo has provided data about the illumination time and intensity such that the illumination can be modelled.

The measured growth rate of Nannochloropsis Salina at different light intensities is given in figure 5-3. The corresponding parameters can be found in appendix D-2. The parameters

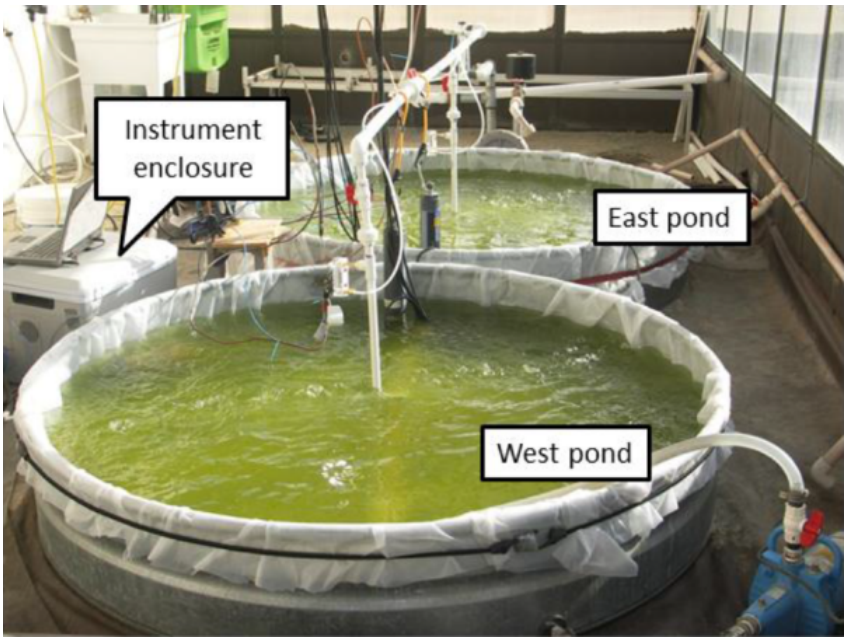


Figure 5-2: Experimental setup of Gharagozloo et al. (2014)

fit the experimental curve with $R^2 = 0.98$. Using the data from Huesemann is justified by the fact that the measurements where performed correctly and match the conditions in the Gharagozloo experiment. Huesemann used; controlled temperature, homogeneous light distribution, similar wavelength and a thin, non self shading, layer of algae culture. Wagenen et al. (2014) performed the same test as Huesemann for Nannochlopris Salina using microplates. The temperature was kept at 20 $^{\circ}C$, their light source is unknown and nutrients are non limiting. Their result is in good accordance with Huesemann's result, the μ_{max} is identical and the curve shapes are similar.

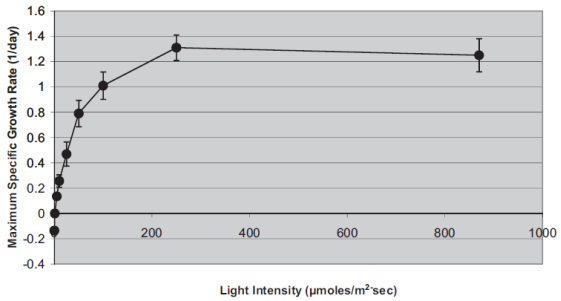


Figure 5-3: P-I curve reproduced from Huesemann et al. (2013)

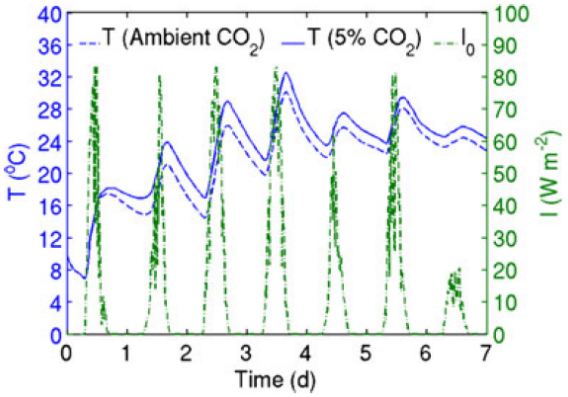


Figure 5-4: Illumenation and temperature profile from Gharagozloo et al. (2014)

Gharagozloo monitored the temperature and the illumination on the the ponds as shown in figure 5-4. The model of Ghargozloo takes temperature dependency into account by a

Parameter	Description	Value	Unit
d	Depth	0.211	$[m^2]$
D	Diameter	1.8	$[m]$
A	Illuminated area	2.505	$[m^2]$
V	Volume	0.528	$[m^3]$
$\dot{V}$	Nutrient gas volume flux	85	$[dm^3/h]$
c_N	Initial nitrogen component concentration	54.7	$[mg/dm^3]$
B_{init}	Initial biomass concentration	0.016	$[g/dm^3]$
t	Simulation time	7	$[d]$
dt	Time Step	0.001	$[d]$

Table 5-1: Operating values for greenhouse pond experiments

limiting function similar to equation 2-24. The extended model did not account for this dependence because the average temperature over time is about 23-24 $°C$ which is similar to the temperature where Huesemann performed his tests. Also, it is undesirable to add another complexity to the model. The extended model allows modelling using a varying source of illumination like shown in 5-4. With all parameters available, simulations are run with a 5%CO_2 enriched airflow and a normal (0.04 %CO_2) airflow. The results are shown in figure 5-5.

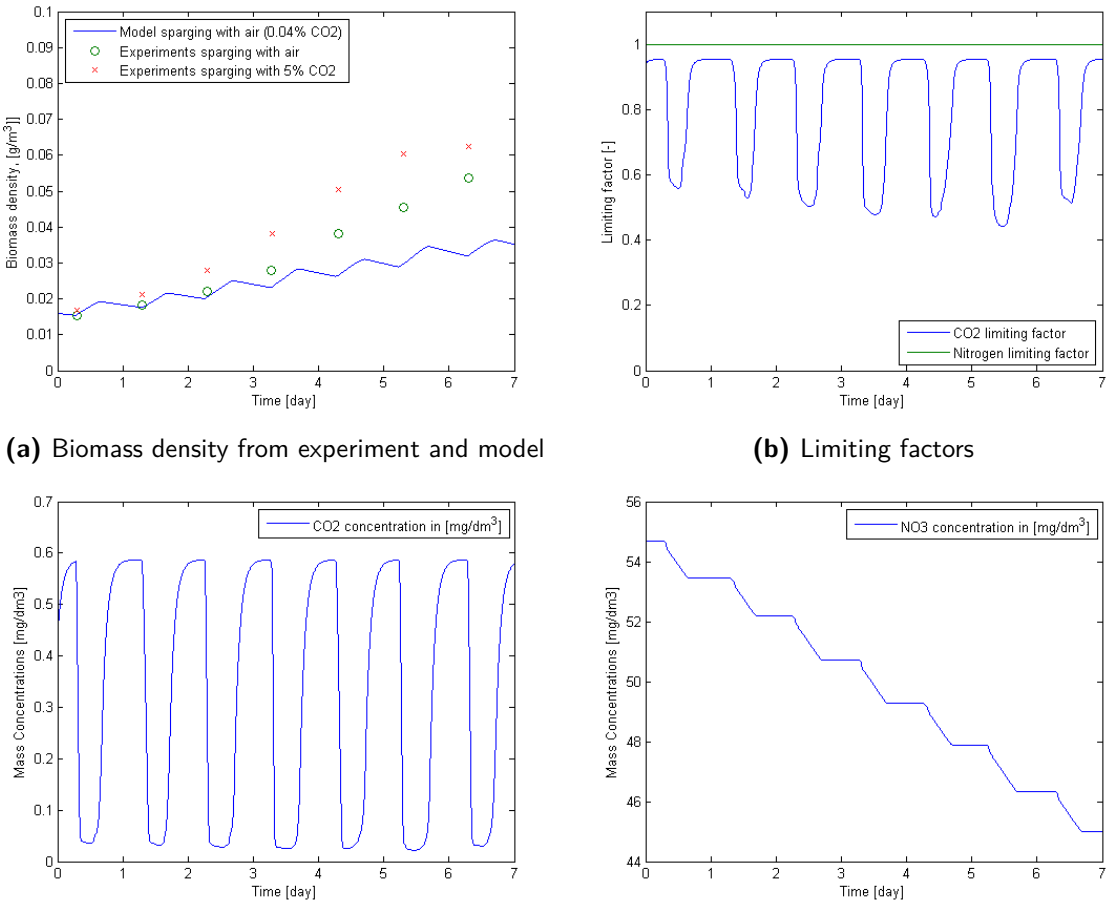
The simulation result for the air fed pond do not show good accordance with the experiments. The R^2 value is 0.34 which means there is a bad fit, which also can be seen from figure 5-5a. From the limiting factors it can be read that CO_2 is the major limiting factor in growth. The assumption was made that the air fed through the reactor has a atmospheric CO_2 content of 0.04 %. However the pond is placed next to a pond which is aerated with 5%CO_2 and they are both placed in a small greenhouse. An small increase over the atmospheric CO_2 level can be expected. In table 5-2 the R^2 for a slight increase in CO_2 levels are given.

CO_2 concentration, [%]	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20
R^2, [−]	0.34	0.57	0.75	0.85	0.92	0.96	0.98	0.97	0.96

Table 5-2: Change of data fit by slight increase in CO_2 concentration

The model predicts the growth rates most accurate for a concentration of 0.16 % (or 1600 PPM) CO_2. It is not unlikely that the CO_2 concentration is higher than 0.04 % since it is located in a greenhouse and 85 $[dm^3/h]$ 5 % CO_2 is bubbled in the pond next to it. Calculations have shown that very few CO_2 is absorbed, most of it leaves the reactor (see appendix B).

The model for the 5 % CO_2 aerated pond proves to be in good accuracy with the experiments. The R^2 for the 5 % CO_2 model is 0.93 and 5 % (day 6) over prediction which is acceptable.



(a) Biomass density from experiment and model

(b) Limiting factors

(c) CO_2 concentration

(d) NO_3 concentration

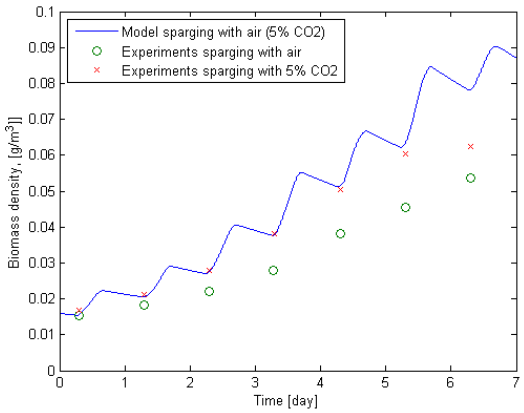
Figure 5-5: Simulation results with 0.04 $\%CO_2$ sparging

The final data point on the 7th day seems to differ from the trend, when this point is removed the R^2 increases to 0.99. Figure 5-6b shows the growth limiting factors, in the 5 % CO_2 case all the factors are constantly 1, hence there are no nutrient limitations in the pond. Notice that the nitrogen component almost runs out at the end of day 7, when this reaches zero, the growth is also haltered. This could explain the halted growth on day 7 if our expression for nitrogen uptake was unsuitable for the type of algae used. [1]

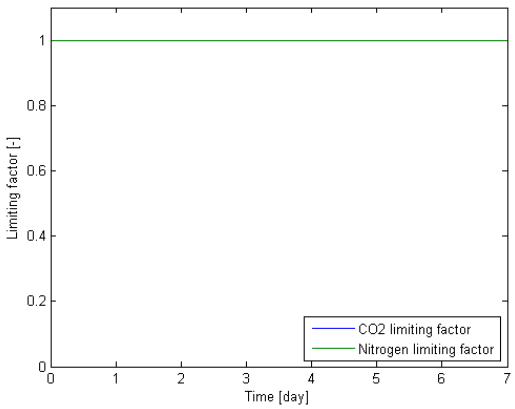
5-4 Modelling a raceway

The second experiment is a large raceway reactor that is outside and illuminated by the sun. Gharalozgloo provided sufficient nitrogen nutrients and there was intermediate bubbling with 1.5-2 % CO_2 gas. Specific aeration conditions where not given but it was stated that there was no CO_2 limitation. The extended model can thus be validated for this specific geometry

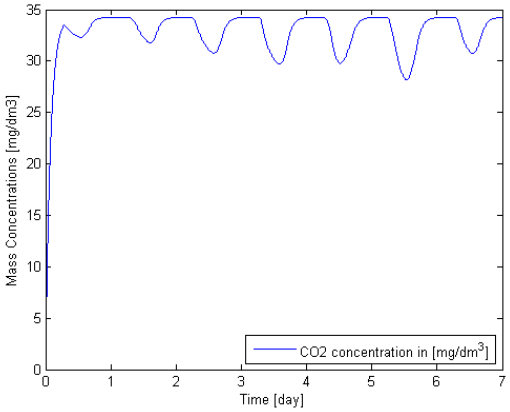
[1] Questions about the exact illumination profile, CO_2 concentrations in the greenhouse and nitrogen limitation on the last day are proposed to Gharalozgloo and waiting for response.



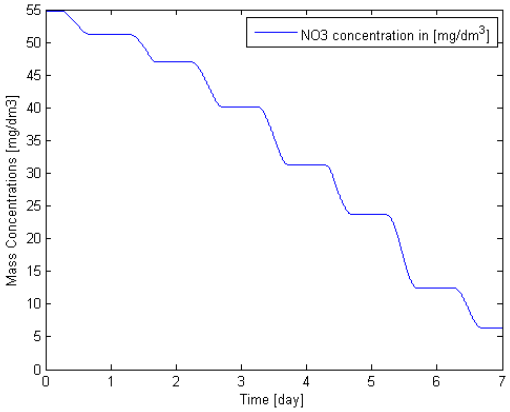
(a) Biomass density from experiment and model



(b) Limiting factors



(c) CO_2 concentration



(d) NO_3 concentration

Figure 5-6: Simulation results with 5 $\%CO_2$ sparging

and illumination conditions. The model input parameters are given in table 5-3.

Again the illumination conditions were obtained from the graphs in the paper, so there is some uncertainty there. The illumination and temperature profile are given in figure 5-7. Figure 5-8 shows the simulation results for the raceway, the R^2 is 0.91 and there is 13 % underestimation (day 6). The simulation under predicts the algae growth, possible causes are: uncertainty in illumination profile or the average high temperature in the culture. As shown in figure 5-7 the average temperature during the experiment was about 28 to 30 $^{\circ}C$, this is at least 6 degrees higher than the temperate at which the growth conditions were determined (23 $^{\circ}C$). Figure 5-8 also shows the model prediction of Gharagozloo's model, it is noteworthy to point out that the negative growth rate due to darkness predicted by Gharagozloo is smaller than what the extended model predicts. This same effected was observed in Gharagozloo 's models of of the greenhouse ponds (not printed). Unfortunately Gharagozloo did not specify values for negative growth rates in their paper so no comparison can be made here. On the 8th day of the model simulation a drop in growth is predicted, this is because there is no illumination data available on the 8th day as shown in figure 5-8.

Parameter	Description	Value	Unit
d	Depth	0.20	$[m^2]$
A	Illuminated area	59.3	$[m^2]$
V	Volume	11.9	$[m^3]$
B_{init}	Initial biomass concentration	0.15	$[g/dm^3]$
t	Simulation time	8	$[d]$
dt	Time Step	0.001	$[d]$

Table 5-3: Operating values for raceway experiment

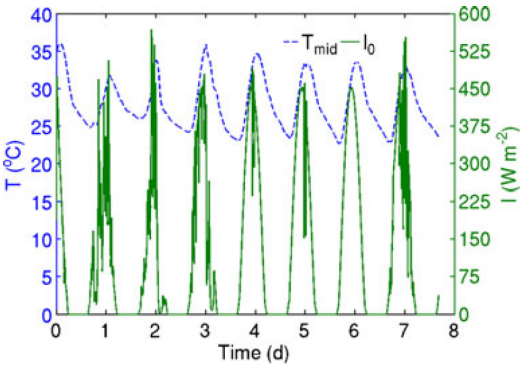


Figure 5-7: Illumination and temperature profile for the raceway

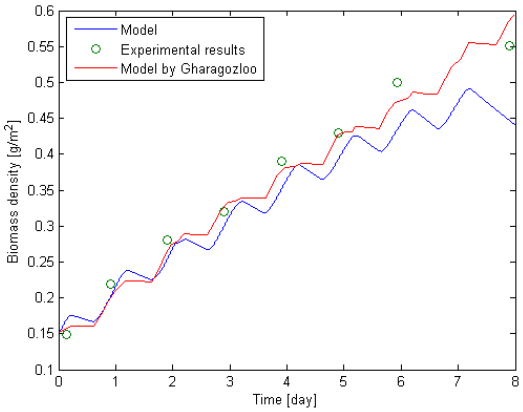


Figure 5-8: Simulation results and experimental data

5-5 Sensitivity analysis

Similar to the sensitivity analysis in chapter 4-5 two analysis are defined. The operating parameters and algae specific parameters. The illumination profile available is from the sun and varies with time and intensity. It therefore can not be used in this sensitivity analysis. Similar to the sensitivity analysis of the Huesemann et al. (2013) two types of analysis are made, one with operational parameter and one with algae specific parameters. The model that was used for the sensitivity analysis is the greenhouse pond. Starting with the operational parameters, the reactor depth and the $k_l a$ are varied. The volumetric feed in of gas ($\dot{V}$) linearly correlated to the $k_l a$ by the Froude number and the superficial velocity in equation 2-33 and 2-34, the effect of changing $\dot{V}$ is the same as changing the $k_l a$.

As expected the relevance of the $k_l a$ is non existent if the molar fraction of CO_2 in the feed in gas is high enough, however when this fraction is low the $k_l a$ becomes an important factor. Different then what was observed in the Huesemann experiment is that by increasing the depth the production is increased. This can be explained by the difference in optical densities

at the end of the experiment. In Huesemann's case this was around 1.35 $[g/dm^3]$ and in greenhouse pond it was about 0.08 $[g/dm^3]$. In the greenhouse pond the light will penetrate deeper and thus a deeper pond will yield higher production.

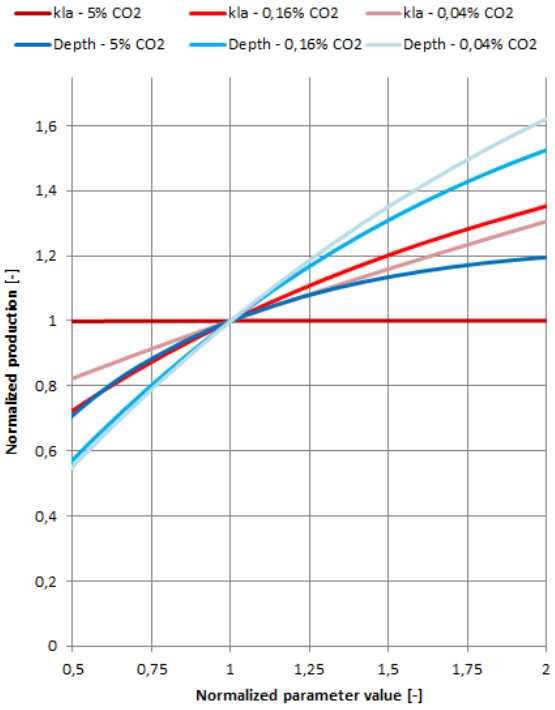


Figure 5-9: Sensitivity analysis of operational parameters at different CO_2 levels

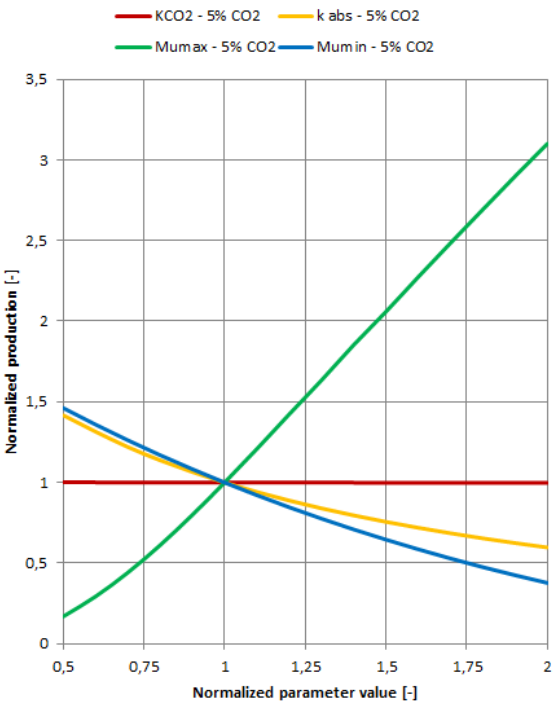


Figure 5-10: Sensitivity analysis of algae specific parameters at 5 $\%CO_2$ levels

Similar to what is found in the analysis of the Huesemann et al. (2013) simulation the maximum growth rate is a very influential parameter for the productivity, this holds for all levels of CO_2. The importance of the half saturation constant for CO_2 (K_{CO_2}) is relatively low as shown by the analysis even at low CO_2 levels. However caution should be taken determining this parameter. The value for K_{CO_2} has been found in literature as 0.015 $[mMol/dm^3]$ (Leggat et al., 2000) and 0.028 $[mg/dm^3]$ (Gharagozloo et al., 2014), converting the value from Leggat results in 0.66 $[mg/dm^3]$ or 0.18 $[mg/dm^3]$ depending if only the C atom is taken into account. This results in a large spread in possible values for K_{CO_2}, it would be best to determine this value for the specific algae before experiments start.

5-6 Conclusions

It has been shown that the extended model can successfully predict the algae growth in a pond with and without carbon limiting conditions. In a CO_2 limited growth case the fit was highly dependent on the percentage CO_2 in the feed stream. By assuming a slight increase in CO_2 level the R^2 increased from 0.31 to 0.98. Non CO_2 limited simulation in the pond yielded $R^2 = 0.99$ and a 5 % overestimation (day 6). The algae growth was predicted in a large raceway pond with $R^2 = 0.91$ and 13 % underestimation (day 6). Sensitivity analysis

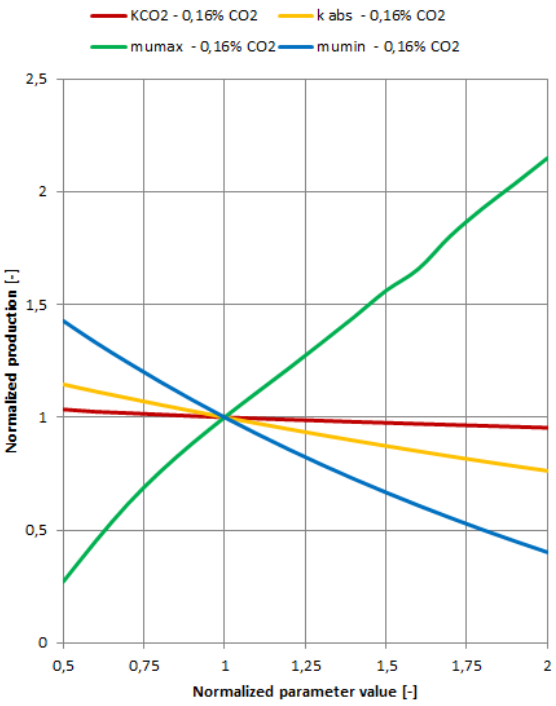


Figure 5-11: Sensitivity analysis of algae specific parameters 0.16 $\%CO_2$ levels

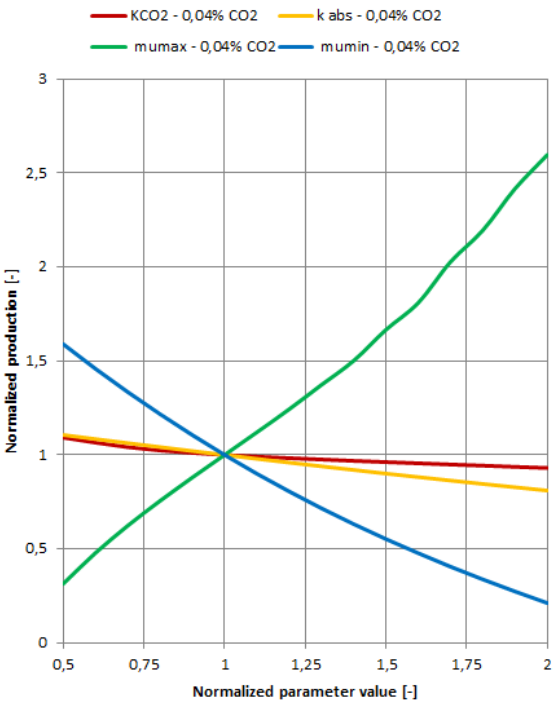


Figure 5-12: Sensitivity analysis of algae specific parameters 0.04$\%CO_2$ levels

has shown that the parameters determining the limiting factors are sensitive in regions where a CO_2 limitation become to play a role. In CO_2 limiting conditions the $k_l a$ shows to be a significant engineering parameter. Small variation in the half saturation constant for CO_2 do not show large significance in productivity, but values from literature vary in order of magnitudes making this an uncertainty in the model.

Chapter 6

Identification of parameters and model validation

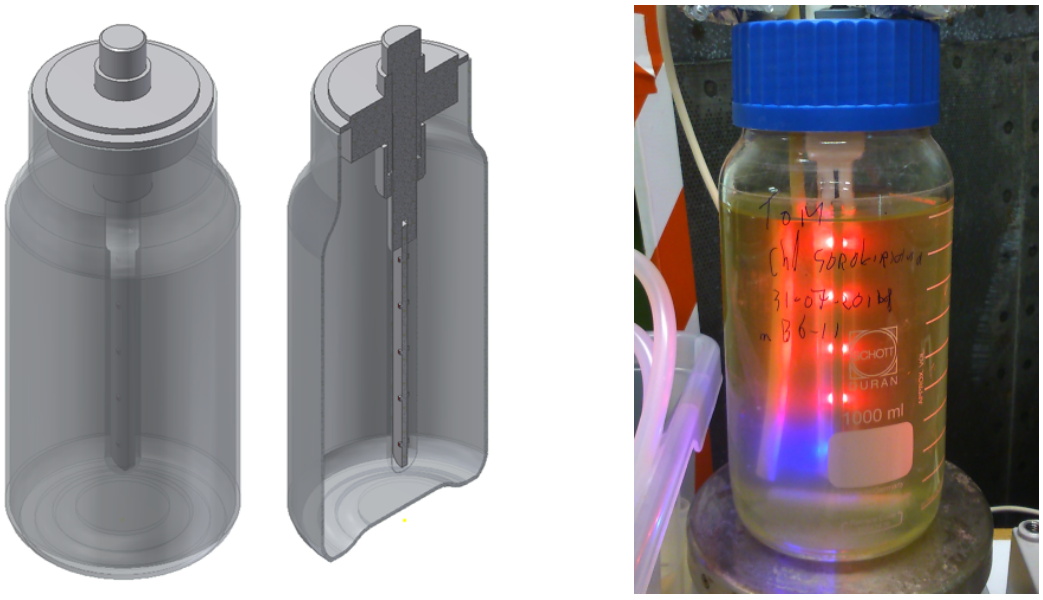
6-1 Validation by experiments

From previous chapters we have seen that the modelling approach gives a good prediction for algae growth with varying light and nutrients conditions. The data used to validate the model came from literature but, while being helpful, the determination of some parameters leaves room for interpretation. To remove this uncertainty two experimental setups are built for parameter determination and model validation. The different boxes as described in chapter 3 and their translation to experiments are discussed in the following sections. The test arrangements has been built but experiments have not yet been performed.

6-2 Light

The light box describes the distribution of light in a reactor. A 1 litre photobioreactor has been made available by Algae Food and Fuel. The reactor consist of a 1 litre glass bottle with a large opening and a purpose build lid. In this lid there are holes for sampling, gas flushing and a central hole for a test tube. Inside the test tube a double sided LED strip is placed with 5x2 LED's on each side. Per side there are 5 blue and 5 red LED's. The LED's are designed to emit in the spectra where the photosynthetic pigments are active. A long needle can be placed through the lid to function as a gas sparger or sampling point. The reactor, shown in figure 6-1, will be used for the validation experiments.

The light distribution in the 1 litre reactor is difficult to obtain with a 1D model because the LED's emit directional light. Figure6-1b shows that there is a high light intensity in a spread form in front of the LED's. To determine the distribution in the reactor the RTE will be solved for a part of the geometry. The axisymmetric geometry of the reactor can only be



(a) 3D model of the 1 litre reactor **(b)** Photo of the 1 litre reactor

Figure 6-1: 1 litre reactor from Algae Food and Fuel

party used, the reactor is split up in 4 equal zones, which means 0 to 90 degree needs to be modelled. Over the reactor height a pattern occurs of repeating LED's, using symmetry only a small part of the reactor needs to be modelled. The modelling of the light distribution in the 1 litre photobioreactor has not yet been performed.

The simulations are run for different absorption coefficient settings. By collecting the histograms of incident light intensities for the fluid zones for different absorption coefficients an interpolation can be made for the light distribution for all absorption coefficients. With this data the incident light intensity on every element of volume is known for different absorption coefficients.

6-3 Nutrients

Carbon nutrients CO_2 can be added to the 1 litre reactor in two ways. The first method is to fill the head space with CO_2 enriched gas which is diffused into culture medium. The reactor volume is 1 litre and the head space volume is 200 millilitre. The k_La of the reactor can be determined with equation 2-43 and 2-44. The second method is to sparge the CO_2 enriched air trough the reactor. The k_La can be calculated using equation 2-33.

Nitrogen nutrients Nitrogen components are added to the medium in which they are in excess. No nitrogen components have to be added after the experiment has started.

6-4 Reactor geometry

The reactor consists of a 1 litre glass flask with an inner diameter of 10 cm and a liquid height of 15 cm. In the center a test tube is placed with a double sided LED strip inside. Two needles stick trough the lid to just above the magnetic stirrer, one for sparging and one for sampling. The reactor is mixed by a magnetic stirrer with a speed of about 100-120 RPM. On the in and output of the sparing tubes filters are placed to prevent contaminations. The complete reactor is suitable for 121 ° autoclaving.

6-5 Test arrangement for algae specific parameters

The algae box describes the growth behaviour of an algae species at different light and nutrient conditions. Depending on a species of algae these parameters vary. As stated in this report and in the recommendations of van Leeuwen (2012) these parameters should be determined before simulating growth in a photobioreactor. To determine the algae specific parameters a test arrangement has been developed. The goal of the test arrangement is to measure the growth rate corresponding to the local light intensity in a layer of algae culture at constant temperature and nutrient conditions.

Huesemann et al. (2013) used shaker flask in a water bath to determine the parameters. By using shaker flask an inhomogeneous light flux is incident on the algae which leads to uncertainties. Gharagozloo et al. (2014) measured the growth properties of algae in a 25 mm test tubes with different growth conditions, they gave only fitting parameters for their own formula sets, not actual test data. The direction of illumination was not specified and a circular geometry (test tube) was used which leads to uncertainties. Wagenen et al. (2014) used a 24 well micro plate to quickly perform a analyses of on multiple samples. The light conditions where well documented, however nutrients conditions were not explicitly mentioned. To overcome these uncertainties a test arrangement is constructed which handles these problems. An overview of the test arrangement is found in figure 6-2.

Light spectrum, distribution and intensity The light sources used are 5x2 LED strips similar to those found in the 1 litre reactor, the emission spectrum is identical. The intensity of the LED's is controlled by a controller box, one led strip can emit up to 300 $[\mu mol/m^2 s]$ at the surface of the flasks. For higher light intensities multiple LED strips are placed. The inside of the test arrangement is constructed from MIRO ® 7 reflective material. The total reflection is 94 % and the diffuse reflection is 84-90 %. This highly reflective material diffuses the directional light from the LED to a more homogeneous light distribution at the bottom of the test arrangement. By measuring the light intensity on 15 points in a grid form on the bottom of the test arrangement the homogeneity of the light distribution was determined. The the maximum deviation from the average light intensity for both the red and blue light was 1.8 %. It can be concluded that on the bottom of the test arrangement the light distribution is homogeneous.

The light intensity reaching the bottom of the test arrangement is not the same as the intensity reaching the culture. First, light scatters from the flask, after this there will be some

loss due to absorption. Reaching the water, again light will be scattered before it reaches the algae suspension. From the manufacturer of the flasks the only optical data available was a transmittance coefficient of 0.93 for red and 0.91 for blue light. They were unable to supply information about the reflective properties of the material. To obtain this data some tests were performed at different light intensities and wavelengths. Similar to the previous measurements the light intensity was measured with a LI-COR LI-190 Quantum PAR sensor. The light intensity was measured under the lid of the flasks, the combined effect of scattering and absorption was measured. The photon flux was reduced by 9% for red and 12% for blue light. Only a factor for the scattering on the water surface needs to determined to find the net incoming photon flux on the algae suspension.

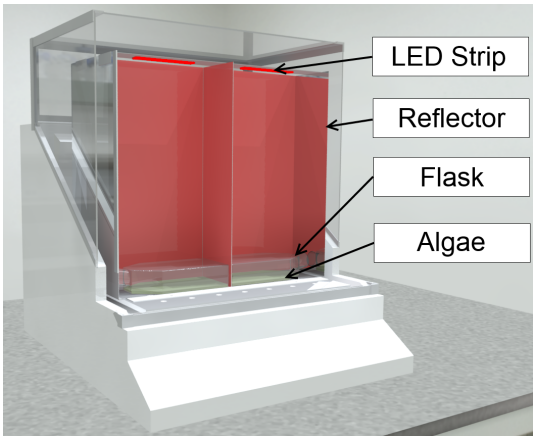


Figure 6-2: Test arrangement for determining algae specific properties

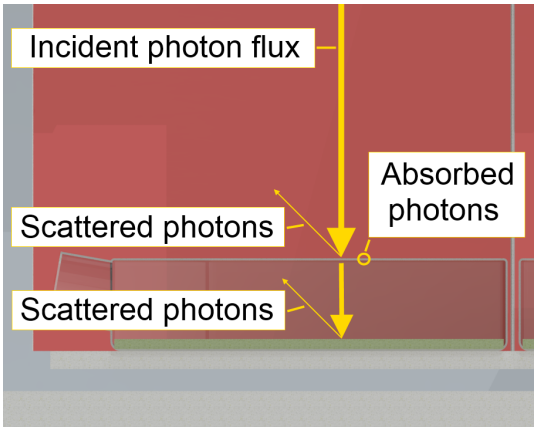


Figure 6-3: Optical behaviour at the flask

Algae An algae culture is cultivated in a flat single use sterile 650 ml culture suspension flask from CELLSTAR ®. A thin, approximately 5 mm, layer of non self shading algae culture is to placed in the bottle (50 ml). The culture should be prepared such that the algae are in their exponential growth phase this is to prevent measuring errors due to algae coming from the lag or stationary phase.

Nutrients Nutrient should be supplied in a amounts such that they do not become a limiting factor. Most mediums have sufficient nitrogen components in them to sustain growth for several day's. Carbon components are not readily mixed into the medium. By flushing the flasks with 5 % CO_2 before a test and sealing them there should be no carbon limitations for the test period. A test period should take a about a day since we do not want to grow the algae beyond the point where they become self shading.

Additional parameters

There are also some algae specific parameters that cannot be measured by this test arrangement. These are: the growth rate due to respiration μ_{min}, the absorption coefficient k, the half saturation constant for CO_2 and NO_3 or NH_4 and the correlation between OD en dry biomass weight. A requirement is that the algae are in their exponential growth phase when

the below mentioned measurement are performed due to a change in optical properties when shifting to a different phase.

Growth rate due to respiration The 'negative' growth rate can be measured by taking a sample and putting it in the dark. It should be stored for the same time as the regular tests and the decrease in OD should be measured over the same time. The sample needs to be at the same temperature and nutrient conditions as the flasks.

Absorption coefficient To model algae growth an algae specific absorption coefficient is required. The model requires a lumped coefficient for both water and the algae, rewriting the Lambert-Beer equation leads to equation 6-1.

$$\ln\left(\frac{I(x)}{I(0)}\right) = -kBx = OD \tag{6-1}$$

A square cuvet with 10 [mm] path length can be used in a photo spectrometer to obtain the OD of a sample at different wavelengths. The machine will ask for a zero test to measure the $\ln\left(\frac{I(x)}{I(0)}\right)$ of the cuvet first, followed by the actual measurement of the sample. The machine will calculate the OD of the sample minus that of the zero test. We are interested in the OD of the sample including the absorption of the medium so in this test the zero test should be performed with an empty cuvette. By knowing the optical density (OD) and biomass density (B) the absorption coefficient k can be determined using equation 6-1.

Half saturation constants The half saturation constants can also be measured with this test arrangement. Light intensity should be kept constant and nutrient concentrations should be varied. This would be possible for the nitrogen component because this is added in solid form. Adding CO_2 in specific concentrations would be more difficult because of the mass transfer between gas and liquid. For now the half saturation constants from literature are used.

Dry biomass concentration By using a link between optical density and biomass concentration a fast estimate can be made about the amount of algae per litre of culture. There are a number of correlations available which link OD and biomass concentration, they vary greatly for different species. Huesemann et al. (2013) uses $B = 0.194 \cdot OD_{750}$ for Chlorella SP and Li et al. (2014) uses $B = 0.5232 \cdot OD_{750} - 0.0248$ for Chlorella Sorokirinana. A series of measurements of OD over the entire spectrum should be made with cultures of different concentrations of biomass. Then the samples need to be centrifuged, dried and weighed. The wavelength at which the OD correlates to the mass measurements the best should be used to create a relation between the wavelength and the the OD. Now a function can be made that links the OD to dry biomass weight.

6-6 Conclusions

Two test arrangement are built to validate the model performance and measure the algae specific parameters. The test arrangement for the algae specific parameters is constructed such

that parameters can be individually measured without interference from other parameters. The test arrangement is designed such that the uncertainties in the tests of Huesemann et al. (2013), Wagenen et al. (2014) and Gharagozloo et al. (2014) are overcome. By correctly measuring the algae specific parameters with the test arrangement the uncertainties are dealt with and they can be compared to values found in literature and be used to serve as input for the model. After determining these parameters experiments can be performed using the 1 litre photobioreactor to validate the model. It is preferred to have little time between the two test due to the risk of contamination and photo adaptation.

Chapter 7

Conclusion

Two models have been developed to predict algae growth in photobioreactors, a basic model without nutrient limitations and an extended model with nutrient limitations. The models have been validated using papers from Huesemann et al. (2013) and Gharagozloo et al. (2014).

The work from Huesemann et al. (2013) was used as input for the basic and extended model. The result from the model was in good agreement (R^2 = 0.97, 7,8 % final value overestimation) with the results from Huesemann. A significant discretization error was found in Huesemann's calculations, leading to an underestimation of 10 % (final value) from the accurate results. Also there where some uncertainties in Huesemann's model formulations which could have effect on the result. These are the precision of the determination of growth rate parameters and assumed constant light absorption coefficient in modelling.

A combination of the work of Gharagozloo et al. (2014) and Huesemann et al. (2013) was used to show that the extended model can successfully predict non CO_2 limited growth in a large raceway pond with $R^2 = 0.91$ and 13 % underestimation at day 6 and in a circular pond with $R^2 = 0.99$ and 5 % overestimation at day 6. CO_2 limited growth was also simulated, but initially had a bad fit. By a slight increase in CO_2 level from 0.04% to 0.16 % the R^2 increased from 0.31 to 0.98. By using the specific growth rate parameters from Huesemann and the operational parameters from Gharagozloo it was shown that careful combination of data from different papers can result in a successful prediction of algae growth.

A test arrangement was built to measure the algae specific growth properties. The test arrangement is designed to measure these properties with minimal uncertainties. A 1 litre reactor has been built to perform verification experiments, in this reactor the algae can be cultivated under controlled conditions.

The main hypothesis, algae growth can be predicted by determining the productivity of individual layers, is confirmed by successfully prediction the algae growth in 3 photobioreators

of different dimensions, algae concentrations and algae species.

The full extended model using light distribution calculations using the 3D RTE has been described but has not been applied yet. The geometries used for validation in Huesemann and Gharagozloo allowed for modelling using a 1D approximation. The research question concerning the significance of a complex light distribution model compared to a simple model has been partly answered. It was shown that in a non scattering case the RTE and the MTFM show identical results to the Lambert-Beer law. A complex 3D geometry can be modelled with the RTE as a non scattering case because the same results are yielded by the proven Lambert-Beer law. It is of importance to use absorption coefficients from experiments due to their lumped extinction coefficients. The same analysis was not performed in a scattering case because there was no algae scattering data available from Huesemann and Gharagozloo.

The research questions regarding the better prediction of scattering models was not tested due to the lack of data for scattering data in the models of Huesemann and Gharagozloo. A simulation did show that an increase in scattering albedo yielded in a increase in production.

In non nutrient limiting cases sensitivity analyses show that the most significant operation parameter is the incident light intensity. The most significant algae specific parameters are the maximum growth rate (μ_{max}) and the absorption coefficient (k). In nutrient limiting cases sensitivity analyses show that the half saturation constant for nutrients K_{CO_2} and the volumetric mass transfer coefficient $k_l a$ have a significant influence on the productivity of a photobioreactor. Also the concentration of CO_2 in the feed gas stream was shown to be a very significant parameter.

Recommendations

The recommendation for future research are;
1) Perform experiments to determine algae specific parameters with the designed test arrangement.
2) Perform light distribution analysis with the 1 litre photobioreactor.
3) Model and validate algae growth in the 1 litre reactor using the measured algae specific parameters from 1) and the light distribution from 2).
4) Repeat step 1 and 3 with different algae species and a mixed culture. Mixed cultures are often used in non sterile systems, this will increase the applicability of the model.
5) Using the light distribution data available for the 1 litre photobioreactor to find simplified 1 or 2D approaches to model the light distribution. This allows for better workability of the model when other geometries are considered.
6) Perform a literature study on the effect of half saturation constants for CO_2 since this parameter is very sensitive in CO_2 limited growth, the short study performed here showed to diverse results.
7) Search for papers where scattering data is available and model these cases in a scattering and non scattering case to revisit the research question about scattering.

Finally a recommendation for researcher involved in the field of algae:
When performing experiments to predict algae growth, be sure to specify all light conditions. This includes, type of lamp used, wavelength spectrum and intensity measured at relevant locations. Mention the wavelength data for the used illumination source, a remark that the source has a spectrum of the sun does not suffice. The exact geometry should also be given as the model is build up from here. Locations of sparging points, nutrient gas concentrations, feeding quantities, feed time and measured $k_l a$ values are important for estimating the nutrient balance. Only in this way a total overview and interpretation about the studied algae and photobioreactor can be made.

Appendix A

Algae for process and energy engineers

In this appendix an introduction is given into the phenomena and characteristics of algae and their growth. For most process and energy engineers algae are not a topic that is dealt with in their curriculum thus a short introduction is given here.

A-1 Light

The the most important parameter in algae growth is light. The behaviour of light can be described by the phenomena in radiative heat transfer, only now at low temperatures.

Photo active region

Photosynthesis in algae is activated by light in the photo active region (PAR), or photo active radiation. The photo active region is located between 0.4 and 0.7 μm wavelength. Only light in this region is available for photosynthesis and thus interesting for growing algae. Light in the PAR is often given different units, depending on the literature, in either $[W/m^2]$, $[\mu Einstein/m^2 s]$ or $[\mu mol/m^2 s]$. The conversion of these units is discussed in chapter C.

When a single number is given to describe to strength of a beam in the PAR it is of importance how this number is established. Dependent on the wavelength spectra of the source the efficiency of photon absorption varies.

Light absorbed by algae

Depending on a species of algae the pigments in the algae and thus the absorptive properties differ. A lot of variation is possible as shown in figure A-3. In general algae cells have two types of pigment which are used for photosynthesis; chlorophyll and carotenoids. The chlorophylls absorb blue and red light and reflect the green light, this explains why plants are seen as green. The Chlorophyll-a is the main photosynthetic pigment, the other two pigments absorb the radiation that is not absorbed by the chlorophyll a.

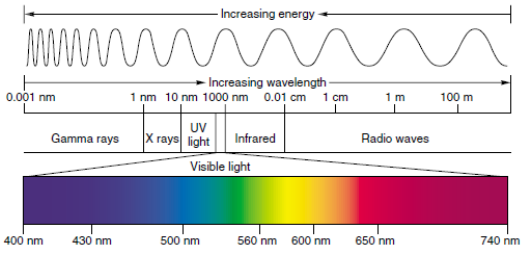


Figure A-1: Spectrum of light from Raven George B. Johnson Kenneth A. Mason (2011)

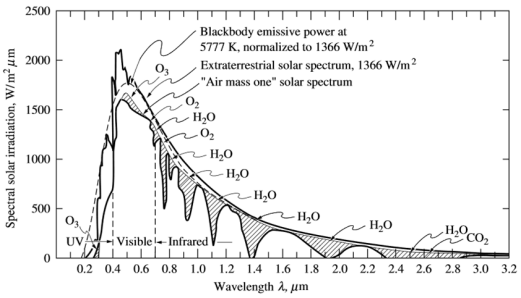


Figure A-2: Incoming spectrum of the sun by Modest (2013)

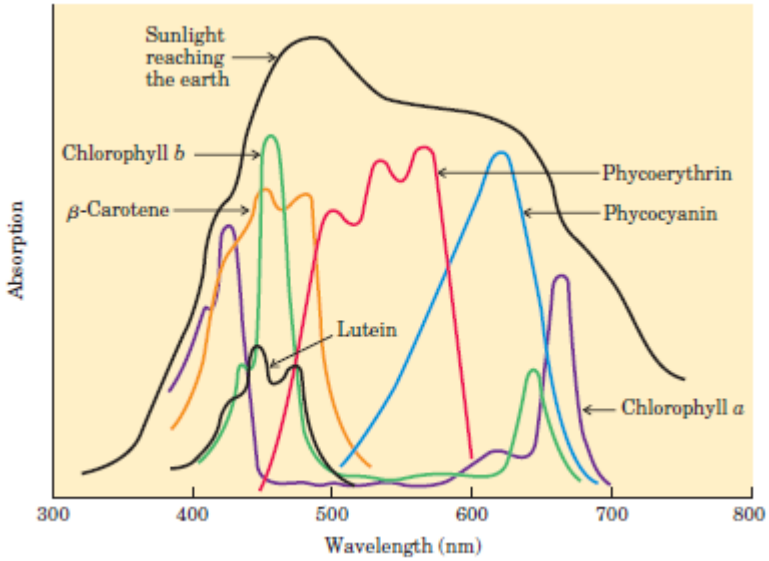


Figure A-3: Absorption spectra of different pigments from Raven George B. Johnson Kenneth A. Mason (2011)

Absorption spectrum and PAR

In literature the incident radiation in the photo active region is given as a whole number. As mentioned earlier, it is important to know how this number is determined. Most literature uses the spectrum of the sun as an reference. The irradiation profile from the sun is given in figure A-2. Figure A-3 clearly shows that a large portion of the incoming light will be reflected instead of absorbed. A crude estimate would be that more than half of the incident light in the PAR is not used for photosynthesis. (45 % (Tredici, 2010)). If growth under sunlight is considered the useful incident radiation is can determined and compared due to same emmision spectrum. However, considering the increase of the usage of LED or other artificial light it is more difficult to make a fair comparison. When comparing experimental results, the spectra used in the experiments should be similar.

Light efficiencies

When it comes to measuring the efficiency of an incident photon a lot of parameters are available. The efficiency of an incident photon cannot be grasped with one number. We will address the different numbers found in literature.

Photosynthetic efficiency, which is abbreviated as PE, is defined as the energy stored as new biomass per unit of light energy incident.

Biomass yield on light energy, which is abbreviated as Y_e (Olivieri et al., 2014), is created with the specific grow rate (μ), the specific absorption constant (k) and the photon flux density. It defines the efficiency of the growth rate dependent on the light and geometry conditions.

Photon absorption efficiency is given by the amount of photons absorbed divided by the number of photons incident.

For now we have mentioned efficiencies that are relevant for when a photon in the PAR is incident. However, for a photon to be useful more is required. From the light that is emitted from the sun only 45 % is in the PAR range (Tredici, 2010). A part of this light is also reflected from either the surface of the water or by the algae particles themselves. Once a photon from the PAR range has successfully hit an algae the algae turn to a exited stage, here another 21 % of energy is lost. This can be considered as a photo reaction efficiency (Exited states/photons absorbed). Then the conversion energy loss from exited stage to chemical energy is another 65 %. Cell respiration accounts for another 20 % energy loss. In general the photonic efficiency is somewhere between 1 and 7 % (Tredici, 2010).

A-2 Growth rate and biomass production

Growth rate

The specific growth rate defines the fraction of increase in biomass over a unit time. There is a wide variety of different models available for the specific growth rate. Figure A-4 gives a realistic profile of the growth rate versus light intensity. Light limited growth occurs from the point just above the x axis to where exponential growth stops, in this region light is the limiting factor for growth. The flat top in the curve is the photosaturated zone, when the curve starts dropping the photoinhibition zone starts.

Figure A-4 shows some important parameters in the P-I curve. At zero illumination the algae respire and use their reserves, in time they will experience negative growth, this is indicated by μ_{min}. The maximum reachable growth rate is defined by μ_{max} and is found at the light saturation point. The growth rate will eventually drop if the light intensity is increased. First, photo saturation occurs, followed by photo inhibition and finally scorching. At the point where the μ_{max} is half the half saturation point of light is defined, this number is used to fit graphs to experimental data.

Biomass production

The biomass production is defined as a function of the specific growth rate, a concentration of biomass and a given time step. A photobioreactor is inoculated with a certain population

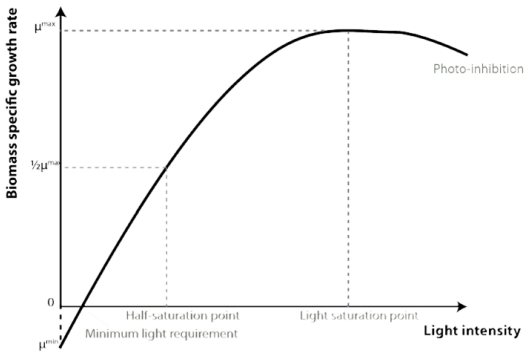


Figure A-4: Typical μ-I curve, reproduced from van Leeuwen (2012)

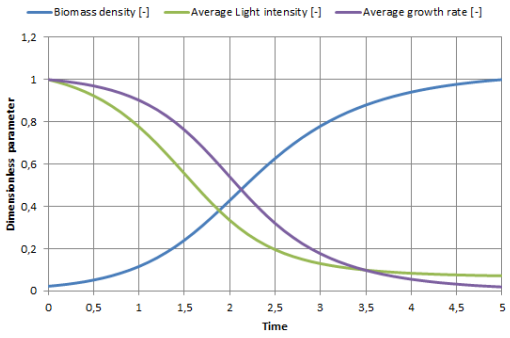


Figure A-5: Typical growth behaviour in a photobioreactor

density B_0. As the biomass concentration increases the optical density is also increased. With an increase in optical density the light penetration decreases and so does the overall growth rate. Three different phases can be defined, the lag, exponential and stationary phase. When all growth conditions are met a certain time span is passed before growth starts, this is defined as the lag phase. When growth has started algae multiply exponentially which happens in the exponential phase. At a certain point optical density is increased to a level where the increase do to growth equals the loss due to respiration an there is no net growth. This is defined as the stationary phase. The dynamics of growth in a photobioreactor are given in figure A-5, lag phase occurs from 0 to 0.5, exponential phase from 0.5 to 3.5 and stationary phase from 3.5 to 5.

A-3 Reactor configuration; mixing, residence time and light flux

One of the most complicated phenomena is the interaction of mixing, the residence time and the light flux. The type and configuration of photobioreactor used determines the interaction between these factors. We shall address these properties and explain their interdependence.

Mixing

Mixing in a photobioreactor is necessary for several reasons. First, nutrients need to be distributed throughout the reactor. Second, algae particles need to be distributed throughout the reactor to utilize the incident light optimally. A practical purpose of mixing is to prevent fouling on the reactor surface. Mixing should not be to rigours, it can cause stress or cell damage to the algae.

By far the most important effect of mixing is to ensure that all algae in a reactor are illuminated. Algae photo systems are designed in such a way that they are allowed a short time span before the photo systems are deactivated. A reactor can thus have unilluminated (dark) zones without a significant loss in production. Mixing in a reactor should ensure that algae that pass from the light zone into the dark zone and re-enter de light zone again within a certain time step.

If a perfect mixing assumption is not used a mixing parameter needs be defined for a reactor. In literature mixing parameters are found as the total volume divided by a pump displacement,

$\frac{Total\ volume[m^3]}{Displacement[m^3/s]} = [s]$, or as the residence time of algae particles [s]. In literature often dimensions and rotational speeds of paddle wheels are given, however this tells us nothing about the actual mixing in a reactor and are thus only suitable when comparing identical reactors. For modelling purposes it is more convenient to assume the ideal mixing assumption and assure that that criteria is met in the validation reactor sufficient.

Residence time

The time an algae particle is illuminated is known as the residence time. The residence time is a function of the local fluid dynamics (mixing), reactor configuration and the population density. As the population density of the algae broth increases the light flux cannot penetrate into the broth thus changing the residence time. We can define different time scales on which residence time can be of importance, this varies from nanoseconds to day's. Are short overview is given below.

Microsecond scale; The metabolism of an algae works on a microsecond scale. If an algae is disturbed these processes do not work optimal.

Millisecond scale; Photons hit the antenna pigments of an algae, when this is photon is successfully absorbed by the algae it turns to a state where it does absorb any other photons for a short time. This process is performed at microsecond scale. Saving energy by flashing at microsecond level is based on this principle (Simionato et al., 2013).

Second scale; Algae particles are mixed in a reactor, going from illuminated zones to dark zones. This process is performed at second scale.

Minute, hour and day scale; Depending on the reactor illumination (LED or sun) the entire reactor is illuminated or not. Algae now respire and use their reserves. When algae are illuminated for long periods of time (day's) they will adjust their photo systems to that specific light setting. For example, algae are illuminated for days with high light intensities need few light capturing antenna's, when illuminated with low intensities the photo system will not be able to capture photons efficient due to a lack of antenna's. This phenomena is known as photoadaptation.

Light flux

Depending on the light source, population density and species of algae used, the light flux at given wavelengths varies in a reactor. A light flux will behave differently in a reactor with red marine algae than with a freshwater green type algae because of the different absorption spectra. With an increase in population density the light flux will not be able to reach into the reactor, thus changing the residence times. Huesemann et al. (2013) has shown that the algae specific absorption coefficient changes with light intensity.

Reactor configuration

Depending on the type of reactor configuration used the previous mentioned factors vary. We shall discuss most common types of reactors.

Flat plate reactor Considering two types of flat plate reactors, thin and thick ones. In a thin flat plate reactor the residence time is infinite, all particles are illuminated at all time.

The optical thickness can not increase beyond a level where self shading leads to dark zones. In thick flat plate reactors the optical thickness can increase to a point where dark zones in a reactor can occur. Residence times will now begin to play a role.

Tubular reactor Tubular reactors are designed in such a way that light penetrate into the tubes, only at high optical densities can dark zones occur.

Open pond In an open pond configuration the residence time is determined by the vertical mixing of the water and the optical thickness of the algae broth.

Circular vessels Circular vessels can be illuminated from within by artificial light of from the outside by the sun or artificial light. With an increase in optical density dark zones start to occur and residence times start to play a role.

Appendix B

CO_2 process model

CO_2 is the most used carbon source in algae growth. Used from pure of mixed gas cylinders or from waste gas streams it is a portable solution which can be applied at virtually everywhere. CO_2 is, like other nutrients, a feedstock which needs to be paid for. In this appendix the efficiency of utilization of CO_2 is investigated.

B-1 Natural balance and loss to the environment

It is common for water to contain a slight portion of dissolved CO_2. This natural balance is determined by the molar fraction of CO_2 present in the air, this is about 0.04 %. Using the Henry constant the equilibrium concentration of CO_2 in water can be determined. The equilibrium concentration is given in equation B-1.

$$c_{CO2,eq} = \frac{P_{CO2}}{H_{CO2}} = \frac{0.0004}{29.411} \cdot 1000 = 0.0136 \quad [mMol/dm^3] \tag{B-1}$$

With P_{CO2} being the partial pressure [bar] of CO_2 of the environmental gas. H_{CO2} is the henry constant for CO_2 in water in $[bardm^3/mol]$. From section 2-4 we know the CO_2 molar flux in and out of the water, which is reproduced in equation B-2

$$\phi_{mol,CO2} = K_L \cdot (c_{CO2,eq}(aq) - c_{CO2}(aq)) \cdot A_{surface} \quad [mol/s] \tag{B-2}$$

With K_L being the rate constant in [m/s], $c_{CO2}(aq)$ is the actual dissolved concentration in [mol/m^3] or [mmol/dm^3]. $A_{surface}$ is reaction surface between the gas and water.

B-2 Uptake by algae

Uptake due to growth

The uptake of CO_2 by algae is explained in section 2-4 and briefly repeated here.

$$\phi_{CO_2mol,algae} = \frac{dB}{dt} \cdot \frac{1.788}{MW_{CO_2}} \quad [mol/\ sdm^3] \tag{B-3}$$

With $\frac{dB}{dt}$ being the increase of biomass over a certain period of time in $[g/dm^3s]$. $\frac{1.788}{MW_{CO_2}}$ is the stoichiometric ratio and molar conversion for the calculation in $[mol/g]$. No uptake due to respiration is defined for this analysis.

B-3 Feed in of $\mathbf{CO_2}$

Feed by gas

The conventional way of adding a carbon source to water is by means of aerating the water with a gas with a certain fraction of CO_2. The molar flow into the water is described by equation B-4 which is almost identical to B-2.

$$\phi_{mol,CO2,feed} = K_L \cdot (c_{CO2,max}(aq) - c_{CO2}(aq)) \cdot t_{residence} \cdot A_{reaction} \quad [mol/s] \tag{B-4}$$

$c_{CO2,max}(aq)$ is the maximum soluble CO_2 concentration corresponding to the partial pressure of CO_2 in the feed gas, the calculation is similar to equation B-1. Other changed terms are the $A_{reaction}$ and $t_{residence}$ term. Per second a certain amount of gas is inserted into a reactor, this is the feed $[dm^3/\text{s}]$. The gas will form bubbles of a certain size, d_b [m], which will rise until they reached the top of the reactor and are lost. The residence time of a bubble can be described by its upward velocity (v_b) and the reactor height (h) as shown in equation B-5

$$t_{residence} = \frac{h}{v_b} \quad [s] \tag{B-5}$$

With v_b being the upward gas velocity [m/s] of a bubble.

$$v_b = \sqrt{\frac{\frac{4}{3} d_b (\rho_l - \rho_g) \cdot g}{C_D \cdot \rho_l}} \quad [m/s] \tag{B-6}$$

With d_b being the bubble diameter [m], ρ_l and ρ_g are the mass densities of the gas and the liquid [kg/m^3], g is the gravitational constant, 9.81 $[m/s^2]$, C_D is the coefficient of drag of the bubble [-]. Coefficient of drag is a function of the Reynolds number, however, for now, we assume it constant. The number of bubbles released and their size determine the reaction surface. A bubble diameter needs to be assumed, this will be in the range of 5-10 [mm]. The number of bubbles released is given by equation B-7.

$$N_b = \frac{feed}{V_b} \quad [1/s] \tag{B-7}$$

The reaction area is the area which comes available per second with a limited residence time and is given by equation B-8.

$$A_{reaction} = 4\pi d_b^2 \cdot N_b \quad [m^2/s] \tag{B-8}$$

Another way to determine the CO_2 transport from the gas to the liquid is to use a correlation for the $k_l a$ value. This is shown in equation 2-33.

B-4 Theoretical case

A theoretical case is considered with a cylindrical reactor with a diameter of 1 meter and a height of 1 meter. The reactor volume is 785.4 dm^3. The equilibrium equation for this vessel is given in equation B-9

$$\phi_{mol,CO2} = K_L \cdot (c_{CO2,eq}(aq) - c_{CO2}(aq)) \cdot A_{surface} \cdot 1000 \quad [mmol/s] \tag{B-9}$$

with $K_L = 0.00096[m/s]$, $c_{CO2}(aq) = 0.0136[mMol/dm^3]$ and $A_{surface} = 0.785[m^2]$. The uptake by algae is given by equation B-10

$$\phi_{CO_2mol,algae} = \frac{dB}{dt} \cdot \frac{1.788}{MW_{CO_2}} \cdot V \cdot 1000 \quad [mmol/s] \tag{B-10}$$

With V = 785.4 dm^3 and $MW_{CO2} = 48[g/mol]$. The $\frac{dB}{dt}$ is given by equation B-11.

$$\frac{dB}{dt} = \mu\gamma_{CO2}B = \mu\frac{c_{CO2}}{K_{CO2} + c_{CO2}}B \tag{B-11}$$

With μ being the growth rate in [1/s] and B the biomass concentration in [g/dm^3]. A CO_2 limiting factor in the growth rate (γ_{CO_2}) is added. The CO_2 feed using gas is given in equations B-4 to B-8. A system of equations can be made for the CO_2 concentration in the cubic reactor.

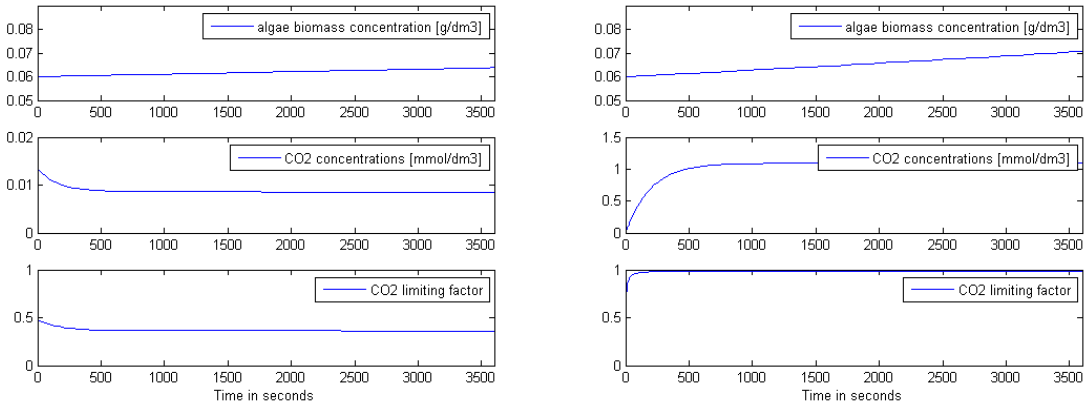
$$\begin{aligned}\frac{dc_{CO2}}{dt} &= \phi_{mol,CO2eq} - \phi_{CO_2mol,algae} + \phi_{mol,CO2,feed} \\ &= K_L \cdot (c_{CO2,eq}(aq) - c_{CO2}(aq)) \cdot A_{surface} \cdot 1000 - \frac{dB}{dt} \cdot \frac{1.788}{MW_{CO_2}} \cdot V \cdot 1000 \\ &+ K_L \cdot (c_{CO2,max}(aq) - c_{CO2}(aq)) \cdot t_{residence} \cdot A_{reaction} \cdot 1000\end{aligned} \tag{B-12}$$

$$\frac{dB}{dt} = \mu B \tag{B-13}$$

Equation B-12 and B-13 and other constitutive equations are implemented in Matlab and simulated.

Results

The simulation is run for a time span of 1 hour with a feed of 0.33 dm^3/s. The molar concentration of CO_2 in the feed gas is set to a value of 0.04 % which represents environmental conditions, a second simulation is run with a CO_2 concentration of 4 % . The bubble size is chosen as 6 mm. The results of the simulation are found in figure B-1. Figure B-1 shows that there is a significant difference between the concentration of CO_2 in the reactor. Both simulations reach a steady state in 1000 seconds. There is an optimum between CO_2 concentration in the feed, the concentration and loss to the environment. A simulation is run for different CO_2 fractions in the feed gas to find an optimum for the highest acceptable CO_2 factor and the lowest possible CO_2 concentration in the feed gas. The results are shown in figure B-2. The simulation time was 1 hour such that steady state was reached. From figure B-2 we can read that in our case the theoretical feed of CO_2 should be in the order of 0.6 % addition of CO_2. For this given case a lower percentage will lead to a decrease in productivity, a higher to an increase in losses.



(a) 0.04% CO_2 concentration **(b)** 4% CO_2 concentration

Figure B-1: CO_2 simulation results

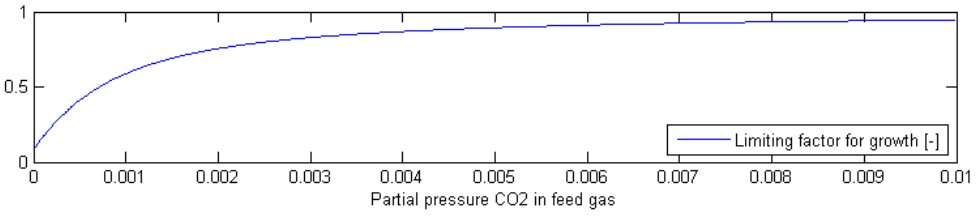


Figure B-2: Simulation run with different partial pressures,

Appendix C

Units of light

C-1 Conversion from different light sources to PAR

In literature different units are found that describe the energy content of an incident light flux. The most commonly used unit is $[\mu mol/m^2 s]$ followed by $[W/m^2]$, $[\mu Einstein/m^2 s]$ is also used but this is the same as $[\mu mol/m^2 s]$. The conversion of $[W/m^2]$ to $[\mu mol/m^2 s]$ and vice versa is discussed in this appendix.

The photo active region is defined as the radiation between 400 nm and 700 nm wavelength. The energy in a photon at a given wavelength is defined as shown in equation C-1.

$$\epsilon_\lambda = hv = h\frac{c}{\lambda} \quad [J] \tag{C-1}$$

With h being Planck's constant of $6.6624 \cdot 10^{-34}$ $[Js]$, c is the speed of light of $2.998 \cdot 10^8 [m/s]$. λ is the wavelength in [nm]. Using equation C-1 it can be calculated that a photon in the blue spectrum (400 nm) has more energy than one in the red spectrum. All photons above 700 nm do not carry sufficient energy to induce charge separation and are their fore unsuitable for photosynthesis. The energy in 1 mol of photons can be calculated with Avogadro's number, N_a, $[mol^{-1}]$. The convention in this field is to measure radiation in PAR in $\mu mol/m^2 s$, hence a factor of 10^{-6} is added.

$$E_\lambda = \frac{N_a \cdot \epsilon}{10^6} \quad [J/\mu mol] \tag{C-2}$$

With E_λ being the energy per μmol photons $[J/\mu mol]$ at a given wavelength λ. Using equation C-2 a conversion factor can be found for photons a specific wavelength, however data for the entire PAR range is required. Considering a source which emits photons with a specific intensity, $I_\lambda [W/m^2]$, per wavelength, the total intensity between 400 and 700 nm can be determined by equation C-3.

$$I_{source} = \int_{400}^{700} I_\lambda d\lambda \quad [W/m^2 sr] \tag{C-3}$$

With I_λ being the intensity coming from a specific source (the sun, fluorescent light, LED's etcetera). The number of photons per second per wavelength is given by $\frac{I_\lambda}{hc/\lambda}$, the number of μmol photons per second per wavelength is given by $\frac{I_\lambda}{hc/\lambda}\frac{10^6}{N_a}$. Expanding this for all wavelengths results in the expression found in equation C-4.

$$I_{\epsilon,photons} = \int_{400}^{700} \frac{I_\lambda}{hc/\lambda}\frac{10^6}{N_a}d\lambda = \frac{10^6}{N_a hc}\int_{400}^{700} I_\lambda \lambda d\lambda \quad [\mu mol/m^2 s\ sr] \tag{C-4}$$

A measurement R by a PAR sensor results in an irradiance number in $[\mu mol/m^2 s]$. The goal is to convert this to $[W/m^2]$, this can be done by a conversion factor based on the energy emitted by the source and the energy in the photons, this is shown in equation C-5.

$$R_{W/m^2} = \frac{I_{source}}{I_{\epsilon,photons}} R_{\mu mol/m^2 s} = \frac{N_a hc}{10^6}\frac{\int_{400}^{700} I_\lambda d\lambda}{\int_{400}^{700} I_\lambda \lambda d\lambda} R_{\mu mol/m^2 s} \tag{C-5}$$

The energy in the photons per wavelength is described by equation C-4. As stated for different sources I_λ changes, the most used source is the sun. From Modest (2013) it is know that the emission from the sun can be approximated by the emission of a black body of 5777 K. Using equation C-7 the intensity at all wavelengths can be determined.

$$I_{b\lambda} = \frac{2\pi hc^2}{n^2\lambda^5[e^{hc/n\lambda kT} - 1]} \tag{C-6}$$

With n being the refractive index [-], T is the temperature in [K]. Combining equation C-6 and C-5 the conversion factor for sunlight can be calculated. For the spectra and emissivity of the sun a conversion factor is found in equation C-7.

$$R_{W/m^2} = 0.2190 \cdot R_{\mu mol/s} \tag{C-7}$$

The conversion factor for irradiation from W/m^2 to $\mu mol/m^2 s$ is $1/0.219 = 4.5661$. The reference value found in literature is often found as 4.6 which closely resembles the calculated value. Some also use 4.56 as a conversion factor, but 4.6 seems the more generally accepted conversion coefficient. An overview of the conversion coefficients are given in table C-1. Other light sources do not have an 'easy' equation which describes the distribution of intensity over the wavelength spectra, for these discrete summations over the measured spectrum are required.

	Light Source					
	Daylight	Metal halide	Sodium	Mercury	White Fluor.	Incand.
To convert	Multiply by					
$[W/m^2]$ (PAR) to $[\mu mol/m^2 s]$(PAR)	4.6	4.6	5.0	4.7	4.6	5.0

Table C-1: Conversion factor for PAR light (Biggs, 2014)

Appendix D

Algae datasheets

The growth rate equation of the extended model (as given in equation 2-25) is reproduced here in equation D-1 for completeness.

$$\mu = \mu_{max-a} \cdot \frac{I}{K_s + I + \frac{I^2}{K_i}} \cdot \frac{c_N}{K_N + c_N} \cdot \frac{c_{CO_2}}{K_{CO_2} + c_{CO_2}} - \mu_{min} \tag{D-1}$$

D-1 Chlorella SP

We find the data for a Chlorella SP type algae from Huesemann et al. (2013).

Growth data

The parameters from table D-1 are only suitable if used in combination with equation D-1. The actual μ_{max} is 4.8 $[d^{-1}]$, the actual μ_{min} is 0.17 $[d^{-1}]$. The R^2 value of the fit with the Huesemann paper is 0.95 $[-]$.

Parameter	Value	Unit
μ_{max-a}	5.1	d^{-1}
μ_{min}	0.17	d^{-1}
K_s	28	$\mu molm^{-2}s^{-1}$
K_i	9000	$\mu molm^{-2}s^{-1}$

Table D-1: Growth rate parameter for Chlorella SP

Loss rate

The loss rate is 3.7 % of the actual μ_{max}, which is in this case is 0.17 $[d^{-1}]$.

Optical thickness

The optical thickness was shown to be constant over a given range. The specific absorption coefficient (k) for a Lambert beer type equation is $k = 0.334$ $[m^2/g]$.

Remarks

Huesemann et al. (2013) did not involve nutrient limitations into his model. The growth parameters where determined at 30-31 °C. The parameters where determined using continuous illumination.

D-2 Nannochloropsis Salina

We find the data for a Nannochloropsis Salina type algae from Huesemann et al. (2013).

Growth data

The parameters from table D-2 are only suitable if used in combination with equation D-1. The actual μ_{max} is 1.3 $[d^{-1}]$, the actual μ_{min} is 0.14 $[d^{-1}]$. The R^2 value of the fit with the Huesemann paper is 0.98 $[-]$.

Parameter	Value	Unit
μ_{max-a}	1.6	d^{-1}
μ_{min}	0.14	d^{-1}
K_s	35	$\mu molm^{-2}s^{-1}$
K_i	6900	$\mu molm^{-2}s^{-1}$

Table D-2: Growth rate parameter for Nannochloropsis Salina

Loss rate

The loss rate is 10.7 % of the actual μ_{max}, which is in this case is 0.14 $[d^{-1}]$.

Optical thickness

The optical thickness was shown to vary over a given range, for now it is averaged. The specific absorption coefficient (k) for a Lambert beer type equation is $k = 0.220$ $[m^2/g]$.

Remarks

Huesemann et al. (2013) did not involve nutrient limitations into his model. The growth parameters where determined at 23 °C. The parameters where determined using continuous illumination. Wagenen et al. (2014) performed similar experiments and found an actual μ_{max} of 1.2 $[d^{-1}]$ and corresponding growth trends.

Appendix E

Matlab model

E-1 Flowchart

The operation of the model is discussed extensively in this report, this appendix discusses the coding and the structure of the model. Figure E-1 displays the flow chart of the model. First some required parameters are initialized, then the algae parameters and geometry are initialized. By using separate scripts that are called the code remains clean and accessible to read. There are separate scripts for each box as discussed in chapter 3, boxes also communicate with each other using global variables and input statements. When the simulation ends all data is available for post processing.

E-2 Matlab Code

In total the model works with a model core and 6 scripts. The extended model using CO_2 limitation for a circular pond is given. The experiments of Gharagozloo et al. (2014) are simulated with this model. The following scripts are used and given in the next subsections.

- Model Core
- Box algae
- Box geometry
- Box light illumination data
- Box light
- Box nutrients
- Box nutrient function

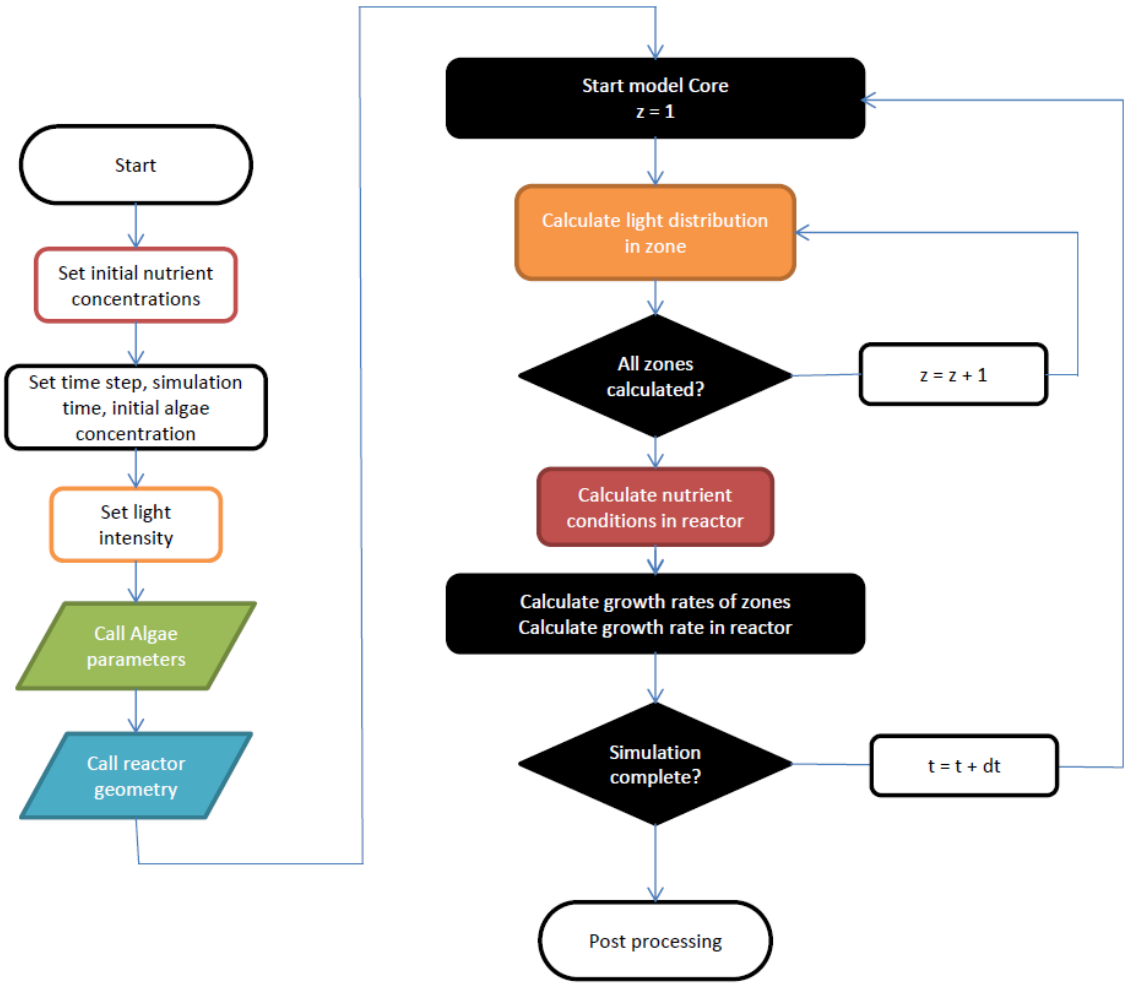


Figure E-1: Flowchart describing the operation of the matlab model

E-2-1 Model core

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Model  Core of Greenhouse pond of Gharagozloo
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

clc
clear all
close all

%Global variables for Light box
global I V Timestep I_in
%Global variables for Algae  box
global mumax mumin Ki Ks
%Global variables for Geometry box
global Slabs Volume
%Global variables for Nutrient box
global c_CO2lmol c_CO2lmass c_Nmol c_Nmass t Timestep_s P_Ts B  ....
    gamma_CO2 gamma_N

%Read the light data from external file
LightArray = xlsread('Light_Greenhouse_Sun.xlsx', 1, 'A1:B84');

%Initializing parameters
p_CO2_bub = 0.05;                   %[bar] partial pressure CO2 gas
p_CO2_air = 0.0004;                 %[bar] partial pressure CO2 in air
c_CO2lmol(1) = 0.01;                %[mMol/dm3]
c_CO2lmass(1) = c_CO2lmol(1)*44;    %[mg/dm3]
c_Nmol(1) =  54.7/(14+16*3);        %[mMol/dm3]
c_Nmass(1) = 54.7;                  %[mg/dm3]
V_dot_gas = 85/(1000*3600);         %[m3/s]

%Operating conditions
B_init = 16/1000;                   %[g/dm3] Initial algae concentration
Total_time_d = 7 ;                  %[day] Total simulation time
Timestep = 0.01;                    %[day] timestep
Timestep_s = Total_time_d*Timestep*24*3600;          %[s] timestep
Total_Timesteps = Total_time_d/Timestep;             %[-] Total Time steps

%Call Aiba equation parameters from Algae box
Box_Algae_Nannochloropsis
%Call reactor geometry from geomerty box
Box_Geometry_Greenhouse

%Model Core starts here
t=1;                                %t is the timestep counter
B(1)=B_init;                        %Set initial biomass concentration
while t < Total_Timesteps
        %Call the specific illumination at a given time
        Box_Light_Time(LightArray)
        %Calculate the light distribution in the reactor
        Box_Light_LambertBeer(I_in(t),B(t))
        %Calculate nutrient conditions in the reactor
        Box_Nutrients(p_CO2_bub, p_CO2_air, V_dot_gas);

        %Calculate Growth rates and Productivity of each layer
```

```
55          j=1;                                    % j is the slab counter
56          while j < (Slabs+1)
57              %Calulate light limiting factor for specific slab
58              gamma_light(j) =  I(j)./(Ks+I(j)+I(j).^2./Ki);
59              %Calulate growth rate for specific slab
60              mu(j) = mumax.*gamma_light(j)*gamma_CO2(t)*gamma_N(t)- mumin;
61              %Calulate new biomass concentration for specific slab [g/dm3]
62              Bs(j) = B(t)*exp(mu(j)*Timestep);
63              %Calculate production of each layer [g]
64              P(j) = Bs(j)*V(j);
65              j=j+1;
66          end
67  Time(t) = t*Timestep;                %Calculate real time
68  Time2(t+1)= t*Timestep;              %Calculate real time with offset
69  B(t+1) = sum(P)/Volume;              %Calculate new biomass concentration [g/dm3]
70  P_Ts(t+1) = B(t+1)-B(t);             %Calculate productivity pertimestep
71  Prod(t)=(B(t)-B(1))*Volume;          %Calculate total prodction
72  t=t+1;                               %Increase timestep and repeat entire process
73  end
74
75  %Load experimental data from Gharagozloo
76  load GreenhouseBiomassAIR.mat;
77  load GreenhouseBiomassCO2.mat;
78
79  %Plot different data results from the model
80  figure
81  plot(Time2, B, GreenhouseBiomassAIR(:,1), GreenhouseBiomassAIR(:,2)/1000, 'o',
        GreenhouseBiomassCO2(:,1), GreenhouseBiomassCO2(:,2)/1000, 'x');
82  xlabel('Time [day]')
83  ylabel('Biomass density, [g/m^3]]')
84  legend('Model sparging with air (0.04% CO2)','Experiments sparging with air','
        Experiments sparging with 5% CO2','Location','NorthWest')
85  axis( [0 7 0 0.1] )
86
87  figure
88  plot(Time,gamma_CO2, Time,gamma_N)
89  legend('CO2 limiting factor','Nitrogen limiting factor','Location','SouthEast')
90  xlabel('Time [day]')
91  ylabel('Limiting factor [-]')
92  axis( [0 7 0 1.1] )
93
94  figure
95  plot(Time2,c_CO2lmass)
96  xlabel('Time [day]')
97  ylabel('Mass Concentrations [mg/dm3]')
98  legend('CO2 concentration in [mg/dm^3]','Location','NorthEast')
99
100 figure
101 plot( Time2, c_Nmass);
102 legend( 'NO3 concentration in [mg/dm^3]')
103 xlabel('Time [day]')
104 ylabel('Mass Concentrations [mg/dm3]')
```

E-2-2 Box algae

```
%Here the algae specific parameters are defined.
function Box_Algae_Nannochloropsis

global mumax mumin Ki Ks k_abs K_CO2 K_N

mumax = 1.6;                        %[d^-1] Huesemann2013
mumin = 0.14;                       %[d^-1] Huesemann2013
Ks = 35;                            %[mu mol/m2s] Huesemann2013
Ki = 6900;                          %[mu mol/m2s]  Huesemann2013
k_abs = 0.157;                      %[m2/g] Gharagozloo2014
K_CO2 = 0.028;                      %[g/m3] [mg/dm3] Gharagozloo2014
K_N = 0.01;                         %[mg/dm3]Gharagozloo2014
end
```

E-2-3 Box reactor geometry

```
%Here the reactor geometry is defined.
function Box_Geometry_Greenhouse

global Volume Slabs Height Area_air D

%Reactor dimensions of greenhouse for Charagozloo2014 pond experiment
Width = 1.67;                               %[m]
Length = 1.5;                               %[m]
Height = 0.211;                             %[m]
Slabs = 100;                                %[m]
D = 1.8;                                    %[m] Reactor diameter
Volume = Width*Height*Length*1000;          %[dm3], calculations in [g/dm3]
Area_air = Width*Length;                    %[m2] Area in contact with air
end
```

E-2-4 Box light time

```
%Here the solar indicent radiation is processed from external .xlsx file.
function Box_Light_Time(LightArray)

global I_in t Timestep

%The light data is repeatedly increasing, decreasing, thus non monotonic,a
%standard interp function yields errors. A small part of the array is used
%to find the incident light intensity for the correct time.

%Split up of data time and illumintation
Day_data = LightArray(:,1);
I_data = LightArray(:,2);
Day_actual = t*Timestep;

% Search for the corresponsing value to the actual day
Lower_boundary = abs(1-Day_data./Day_actual);
[Lowest_Value,G] = min(Lower_boundary);

% Slight modifications to ensure Vect1 and Vect2 are not out of bound
if G >1;
G=G-1;
else
end

if G >80;
    G=80;
else
end

%Create small array with data points.
Vect1 = [Day_data(G) Day_data(G+1) Day_data(G+2)] ;
Vect2 = [I_data(G) I_data(G+1) I_data(G+2)];

%Use Interp to determine the incident light intensity at the given time.
I_in(t) = interp1(Vect1,Vect2,Day_actual);

end
```

E-2-5 Box light distribution

```
%Here the light distribution in the pond is calculated.
function Box_Light_LambertBeer(I_0,B)

global  I V k_abs Slabs Height Volume

%Calculate incident light intensity for each layer, i is layer number.

i = 1;
while i < (Slabs+1)
    V(i) = Volume/Slabs;                              %Volume per slab

    %Path_avg is the distance from the top to the center of the layer
    Path_avg(i) = Height.*((i-0.5)./Slabs);

    %Determine the light intensity at middle of layer, I(i)
    %1000 correction for k_abs conversion to [m2/kg],
    %4.57 is conversion to PAR
    I(i)= I_0*4.57*exp(-k_abs*B*Path_avg(i)*1000);
    i=i+1;

end

end
```

E-2-6 Box nutrients

```
%Here the nutrient data for the reactor is calculated
function Box_Nutrients(p_CO2_bub, p_CO2_air, V_dot_gas)

global c_CO2lmol c_CO2lmass c_Nmol c_Nmass t Timestep_s P_Ts B  Area_air
global dPdt c_CO2lDF_air c_CO2lDF_bub kla_sur kla_bub gamma_CO2 gamma_N CheckB
    K_CO2 K_N D

%Starting conditions
P = 1;                                      %[bar] for use in ideal gas law
T = 300;                                    %[K] for use in ideal gas law
MW_CO2 = 44;                                %[g/mol]
rho_CO2= (MW_CO2*P*100)/(T*8.314*1e-3);     %[g/m3] from ideal gas law
K_henry = 0.8317;                           %[concentration/concentration]
rho_H2O = 1000;                             %[kg/m3]
sigma = 0.07275;                            %[N/m]surface tension
mu = 0.00089;                               %[Pa s]dynamic viscosity H2O
v_l = mu/rho_H2O;                           %[m2/s]kinematic viscosity H2O
D_L = 1.92e-9;                              %[m2/s]CO2 diffusivity in water
D_LO2 = 2.1e-9;                             %[m2/s]O2 diffusivity in water
V_s = V_dot_gas/Area_air;                   %[m/s]superficial velocity

m_CO2_bub = p_CO2_bub*rho_CO2;              %[g/m3] Mass concentration
m_CO2_air = p_CO2_air*rho_CO2;              %[g/m3] Mass concentration
%c_CO2g_bub = m_CO2_bub/MW_CO2;             %[mol/m3][mMol/dm3] Molar cons.
%c_CO2g_air = m_CO2_air/MW_CO2;             %[mol/m3][mMol/dm3] Molar cons.

%Driving force calculations for enviroment (air) and feed gas (bub)
c_CO2lDF_bub = m_CO2_bub*K_henry;           %[mg/dm3]
c_CO2lDF_air = m_CO2_air*K_henry;           %[mg/dm3]

%Parameters for kla determintations
Sc = mu/(D_L*rho_H2O);                      %Smith number
Bo = (9.81*D^2*rho_H2O)/sigma;              %Bond number
Ga = (9.81*D^3*rho_H2O^2)/mu^2;             %Gallileo number
Fr = V_s/sqrt(9.81*D);                      %Froude number

%Volumetric mass transfer coefficient,Measured kla values can replace these
kla_bub = 0.09*Sc^0.5*Bo^0.75*Ga^0.39*Fr^1*(D_L/D^2)*(D_L/D_LO2);
kla_sur = 1.18*10^-5;

%CO2 and N limiting factors [-]
gamma_CO2(t) = c_CO2lmass(t)/(K_CO2+c_CO2lmass(t));
gamma_N(t) = c_Nmass(t)/(K_N+c_Nmass(t));
P_Ts(1) = 0;                                %[g/dm3/dt]Productivity
dPdt(t) = P_Ts(t)./Timestep_s;

% Call function to solve nutrient behaviour during a time step
BC = [B(t) c_CO2lmass(t) c_Nmass(t)];       %Boundary conditions
TR = [0 Timestep_s];                        %Time range
[tfcn,y] = ode23s('Box_Nutrients_fcn',TR,BC);   %Call Script
Algae = y(:,1);                             %Define output vectors
CO2 = y(:,2);
N = y(:,3);

```

```
54 c_CO2lmass(t+1)= CO2(length(CO2));          %Determine CO2 concentration
55 c_CO2lmol(t+1) = c_CO2lmass(t+1)./44;
56 c_Nmass(t+1) = N(length(N));                %Determine N concentration
57 c_Nmol(t+1) = c_Nmass(t+1)/(14+16*3);
58
59 CheckB(t) = Algae(length(Algae));           %Check parameter
60 end
```

E-2-7 Box nutrient function

```
%This is the function that is volved in the nutrient box
function dydt = Box_Nutrients_fcn(tfcn,y);

global dPdt c_CO2lDF_air c_CO2lDF_bub kla_sur kla_bub t gamma_N K_CO2

dydt = zeros(size(y));
%Specify changing concentrations
c_algae   = y(1);
c_CO2lfcn = y(2);
c_Nfcn    = y(3);

%Model simulats creation of nutrients when there is negative growth
%fact is there to prevent this
if dPdt(t)<0;
    fact = 0;
else
    fact = 1;
end

%Constutive equation for during simulation
X = (c_CO2lfcn)/(K_CO2+c_CO2lfcn);

%Evaluate the RHS expression
dydt(1) = dPdt(t)*gamma_N(t)*X;
dydt(2) =  -(dydt(1)*(1.1788*1000*fact)) +(kla_bub*(c_CO2lDF_bub-c_CO2lfcn))+(
    kla_sur*(c_CO2lDF_air-c_CO2lfcn));
dydt(3) = -(dydt(1)*(0.5)*1000*fact);
```

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