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**Integration of a microalgae-utilizing biorefinery
into a pulp and paper mill**

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Abstract

Traditional pulp and paper industry in Western countries is in transition phase due to increased costs and competition, decreased prices and changes in consumption habits. Biorefineries — factories that process biomass into variety of products — are seen as one way to extend the product portfolio and to open up new business opportunities.

The main objective of this study is to present and evaluate a microalgae-utilizing biorefinery that is integrated into a traditional pulp and paper mill in order to produce high-value algal products, fertilizer and biogas. Microalgae has been considered because their biomass productivity is very high, valuable products can potentially be extracted out of the algae, they utilize carbon dioxide from the mill in their growth and they can utilize process waters as their growth medium.

Initial data from a Scandinavian pulp and paper mill is used as a basis for calculations. Flows and product yields are estimated using mass balances and a program is written to do the computations. Calculation results indicate that the proposed process is technically viable, but verification of starting values is necessary in order to draw definite conclusions. Solubility of nitrogen after waste activated sludge digestion seems to be restricting algae production and thus feasibility of the proposed process: given values allow 0.53 kg/d ω -3 fatty acid, 2.8 t/d methane and 88 t/d fertilizer production from 30 t/d waste activated sludge and 87 t/d ash input, while more relaxed assumptions that are considered to reflect real situation better enable 190 kg/d ω -3 fatty acid, 4.0 t/d methane and 90 t/d fertilizer production.

Further research is needed on the digestion process and algae growth properties. Also, sensitivity analysis, evaluation of different process options and economic assessment are required in order to find out an optimal configuration and estimate the economic feasibility.

Keywords biogas, biorefinery, fertilizer, microalgae, ω -3 fatty acids

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Tiivistelmä

Perinteinen länsimainen sellu- ja paperiteollisuus on muutostilassa suuremman kilpailun, lisääntyneiden kustannusten, madaltuneiden hintojen ja muuttuneiden kulutustottumusten vuoksi. Eräänä ratkaisuna ongelmaan tunnistetaan biojalostamot: tehtaot, jotka muokkaavat biomassaa moniksi tuotteiksi. Nämä voisivat osaltaan laajentaa tuotteiden kirjoa tehtaalla ja luoda uusia mahdollisuuksia yritystoiminnalle.

Tämän tutkimuksen päätavoite on esitellä sellu- ja paperitehtaaseen integroitava mikroleviä hyödyntävä biojalostamo sekä arvioida tuotteiden saantoja prosessissa. Esitelty biojalostamo tuottaa korkean jalostusarvon levävalmisteita, lannoitetta ja biokaasua. Prosessissa käytetään mikroleviä, koska niiden biomassan tuotanto on suuri ja arvokkaita tuotteita voidaan erottaa massasta; lisäksi levät hyödyntävät tehtaalta saatavaa hiilidioksidia ja prosessivesiä kasvussaan.

Suoritettut laskutoimitukset perustuvat lähtötietoihin pohjoismaiselta sellu- ja paperitehtaalta. Massavirtoja ja tuotteiden saantoja arvioidaan massataseilla, joiden ratkaisemista varten on kirjoitettu tietokoneohjelma. Tulokset osoittavat, että esitetty prosessi on teknisesti toteutettavissa, mutta tarkempien johtopäätösten tekeminen edellyttää lähtötietojen varmistamista. Typen liukoisuus biolietteen mädätyksen jälkeen vaikuttaa rajoittavan leväntuotantoa ja samalla prosessin kannattavuutta: lähtötietojen perusteella prosessi voi tuottaa 0.53 kg/d ω -3 -rasvahappoja, 2.8 t/d metaania ja 88 t/d lannoitetta 30 t/d:sta biolietettä ja 90 t/d:sta tuhkaa, kun todenmukaisempana pidetyillä lähtöarvoilla saavutetaan 190 kg/d ω -3 -rasvahappojen, 4.0 t/d metaanin and 90 t/d lannoitteen tuotanto.

Lisää tutkimusta tarvitaan mädätysprosessiin ja levien kasvuominaisuuksiin liittyen. Näiden lisäksi on tarkasteltava tulosten herkkyyttä, arvioitava eri prosessivaihtoehtoja ja tarkasteltava prosessia taloudelliselta kannalta, jotta voitaisiin löytää ihanteellinen prosessivaihtoehto ja laskea tämän taloudellinen kannattavuus.

Avainsanat biojalostamo, biokaasu, lannoite, mikrolevät, ω -3 -rasvahapot

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Nomenclature

Glossary

anaerobic digestion A biological conversion process in which organic matter is transformed into methane and carbon dioxide in the absence of oxygen.

biorefinery A plant for processing biomass into multiple products, for example chemicals, fuels, materials, heat and power.

chemical oxygen demand Amount of oxygen that would be needed to fully oxidize all organic compounds in a stream to carbon dioxide and water. Chemical oxygen demand is often used to indicate the amount of organic compounds in wastewaters and is thus used as a measure of water quality.

integrate A number of factories on the same physical site that share for instance infrastructure, logistics, utility systems or raw materials, or produce intermediate products for one another.

mesophile An organism that grows best in moderate temperatures (20 °C to 50 °C)

process integration An approach to process design in which systems are analysed as a whole rather than separate processes. The method allows global planning, analysis and optimization of the whole system.

thermophile An organism that grows best in high temperatures (50 °C to 90 °C)

volatile solids Solids that are lost when a material sample is heated to dryness at 550 °C (U.S. EPA 2001). The amount of volatile solids in a substance is normally close to the amount of solid organic matter.

waste activated sludge Excess microbial matter that is removed from an activated sludge wastewater treatment process.

Acronyms

COD chemical oxygen demand

DHA docosahexaenoic acid

EPA eicosapentaenoic acid

PBR photobioreactor

SRT solids retention time

VS volatile solids

WAS waste activated sludge

List of symbols

Symbol	Description	Value	Unit
A	area		m^2
d	diameter		m
l	length		m
M	molar mass		kg/mol
m	mass		kg
N	number		
n	amount		mol
p	pressure		Pa
q	specific heat consumption		J/kg
R	universal gas constant	8.314	J/molK
Re	Reynolds number		
T	temperature		K
t	time		s
V	volume		m^3
v	speed		m/s
x	proportion	0 ... 1	
y	solids content	0 ... 1	
γ	mass concentration		kg/m^3
μ	volumetric growth rate		$\text{kg/m}^3 \text{ s}$
ν	kinematic viscosity		m^2/s
Φ	power		W
ρ	density		kg/m^3
τ	residence time		s

1 Introduction

1.1 Motivation and background

According to Intergovernmental Panel on Climate Change (IPCC), energy service related greenhouse gas emissions have had a significant contribution to the historic increase in atmospheric greenhouse gas concentrations (Arvizu et al. 2011). The observed anthropogenic increase of these emissions has in turn caused most of observed increase in global average temperatures since the mid-20th century with more than 90 % probability, carbon dioxide (CO₂) being the most important of the greenhouse gases (Solomon et al. 2007).

In order to avoid the detrimental effects of global warming, many global actors such as the European Union are conducting programmes to reduce greenhouse gas emissions, especially those of CO₂. It is acknowledged that there are multiple options for lowering greenhouse gas emissions while still satisfying the global demand for energy services (Arvizu et al. 2011) — among the options are increasing energy efficiency of industrial processes, reducing fossil fuel consumption and capturing or recycling carbon dioxide.

Combining separate industrial processes into one integrate allows one to use such side streams of a process as an input for another process that would otherwise be disposed of due to lack of economic feasibility or no possibilities of further usage. An example of such could be for instance low-temperature level process waters. Even such material streams that would be classified as waste in other processes can be upgraded to valuable products with careful design and thus be converted to source of income instead of being a cost, while also reducing the environmental burden.

Furthermore, as the competitive position in pulp and paper industry is changing rapidly and the South American companies have gained advantage due to cost-effective eucalyptus pulp, many traditional pulp and paper companies are forced to search for new value-creating business opportunities (Pätäri, Kyläheiko and Sandström 2011). Innovation and focusing is hence needed if traditional pulp and paper companies want to stay operational. Biorefineries are one strategic option that could allow production of multiple high-value products and regaining sustainable competitive advantage.

This thesis is a part of a project that aims at providing a way to integrate a microalgae-utilizing biorefinery into a traditional pulp and paper mill. In the biorefinery, microalgae is grown in order to produce valuable fatty acid products and to absorb the CO₂ emissions that originate from other parts of the integrate. The algae will use wastewaters and industrial effluents as their main source of nutrients. Furthermore, biogas and organic fertilizer are intended to be produced, whose use facilitate the reduction of fossil methane and conventional fertilizer usage, which have non-renewable inputs. In addition to this, energy efficiency is going to be enhanced by increased level of process integration.

Pulp and paper mills provide a good basis for forest-based biorefining industry: infrastructure, procurement and logistics are already present and there is broad experience in the usage of wood as a raw material. Current forest integrates can actually be seen as one kind of biorefineries, albeit the variety of products is comparatively low. In addition, there is already extensive knowledge about the usage of residual biomass in combined heat and power production. The utilization of algae in the biorefinery process allows substantial production of biomass per area utilized and digestion enables methane production and nutrient recycling in algae growing.

Many aspects of the proposed biorefinery process have already been studied separately: research on for instance production of soil conditioners and fertilizers from pulp and paper mill fly ash and wastewater treatment sludge¹, pulp and paper mill sludge digestion², algae growing in anaerobic digestion effluent and anaerobic digestion of algae³ have been published previously. In distinction to prior research, this thesis utilizes existing knowledge about subprocesses and presents a biorefinery configuration that combines all elements into one.

1.2 Objectives and problem formulation

The main objective of this study is to present and to evaluate a microalgae-utilizing biorefinery that is integrated into a traditional pulp and paper mill in order to produce high-value algal products, fertilizer and biogas.

Information about subprocess details will be acquired through a literature study; further calculations and modelling will be done based on this information and process data from project partners. At this stage no effort is made to evaluate

¹See e.g. Hackett, Easton and Duff 1999; Lindh, Isännäinen and Mursunen 2001.

²See e.g. Bayr and Rintala 2012; Jokela et al. 1997; Karlsson et al. 2011; Puhakka, Alavakeri and Shieh 1992.

³See e.g. Wahal 2010; Prieto 2011; Alcántara, García-Encina and Muñoz 2013; S. Park and Li 2012; Sialve, Bernet and Bernard 2009.

different designs or to find out the best process configuration — only one process is presented and analysed in the study. A process configuration will be selected based on process prerequisites and conducted calculations whilst taking into account technical feasibility and performance of the whole integrate.

Initial values from a Scandinavian pulp and paper mill will be used as a basis for calculations. Mass flows and product yields are calculated with mass balances. A simulation model will be made to assist in calculations and in evaluation of different biorefinery configurations during latter stages of the research project. The scope does not include analysis of how biorefinery implementation would affect existing processes nor calculations of energy flows that are needed to keep the process running — it is assumed that the amount of excess heat at the site is sufficient for the biorefinery. Economic evaluation of the process outcome is not presented.

2 Description of existing pulp and paper integrate

The analysed forest industry integrate consists of a pulp and paper mill, a chemical pulp mill, a combined heat and power plant, an air separation plant and a wastewater treatment plant. In the current chapter, operations that are relevant to this thesis are briefly introduced.

2.1 Pulp and paper mill

Figure 2.1 shows a generalized diagram of fibre flows in a paper mill. Raw material comes to the mill as logs, chips, pulp or recycled fibre, which are processed separately. Wood is converted to pulp by chemical or mechanical means and all raw materials are mixed together, diluted and additives and fillers are added to the mix. In paper production, the stock suspension is distributed to a thin web to form the paper and to drain off water. Pressing and thermal drying are applied to remove more water and the paper is then processed according to the intended usage, for example coated or calendered.

The pulp and paper mill consists of following units:

- debarking
- mechanical pulp manufacturing
- coating kitchen
- paper machines
- fluff pulp plant.

The paper contains approximately 50 % mechanical pulp, which is manufactured on-site and the rest chemical pulp that is bought from co-located chemical pulp mill or other producers. Propane is used at paper machines to dry the coating colour: about 15 000 t of propane is used yearly.

Most of the mill's wastewater load originates from mechanical pulp manufacturing. The pulp is bleached according to the requirements of currently produced paper

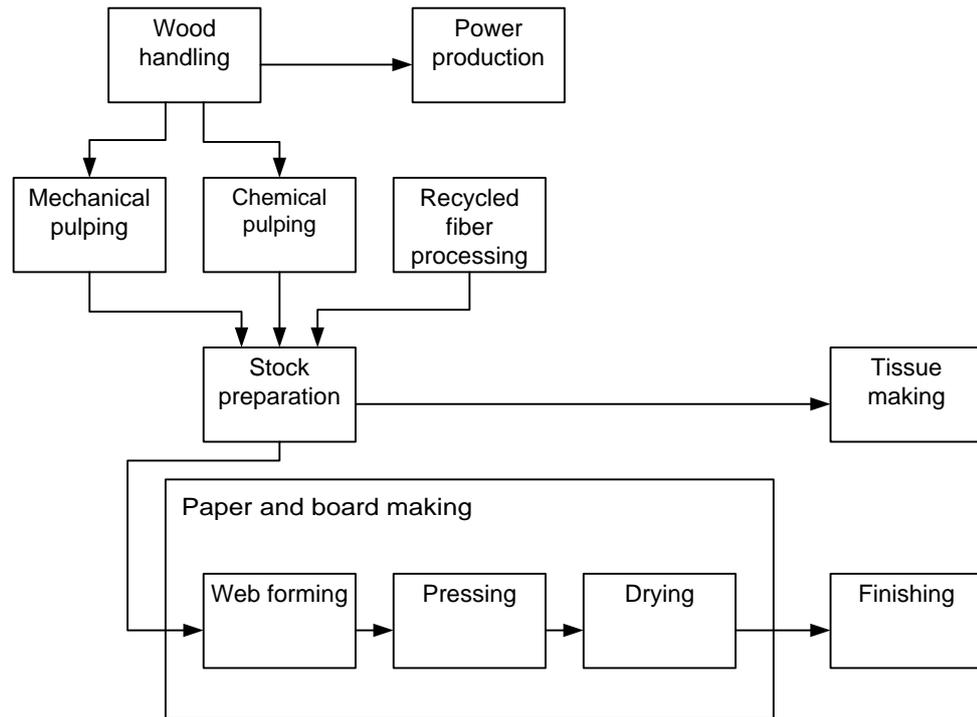


Figure 2.1: Fibre flows in a generic paper mill. The pulping processes may or may not be present on site; imported pulp may as well be used.

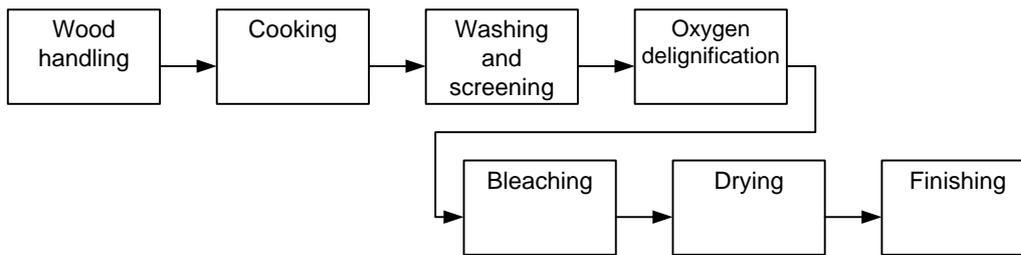


Figure 2.2: Fibre line of a generic chemical pulp mill

quality; a small increase in brightness can be reached with dithionite and larger increase requires peroxide bleaching. Majority of paper machine process waters are recycled, but still $1 \text{ m}^3/\text{s}$ flow of raw water is handled in a water supply plant to provide new process water to the integrate.

2.2 Chemical pulp mill

The fibre flow in a generic chemical pulp mill is depicted in Figure 2.2. Wood that arrives at the mill is processed into chips that are led to cooking, where chemicals and heat are used to separate lignin from the fibres. Most of lignin is dissolved and continues with the cooking chemicals to chemical recovery, while fibres continue to washing, oxygen delignification and bleaching, where remaining cooking chemicals and lignin are removed and coloured substances are removed or brightened. The pulp is then screened, dried, cut and baled or it can be transferred directly to paper production in pipelines.

The chemical pulp mill on the site produces elemental chlorine free (ECF) pulp, mainly from softwood and with varying amount of hardwood. The fibre line consists of wood handling, pulping, turpentine and soap separation, pulp washing, screening, oxygen delignification, bleaching and drying. The majority of wastewaters have their origin in wood handling and pulp bleaching.

2.3 Wastewater treatment plant

The wastewater treatment plant handles all wastewater from the integrate, as well as majority of municipal wastewaters from the nearby city. A schematic representation of the plant is presented in Figure 2.3: wastewaters from the integrate are led to primary clarification, where primary sludge is removed as a sediment. The flow is then directed to neutralization and cooling, after which it goes to aeration stage, where biological treatment takes place. The municipal wastewaters are directed

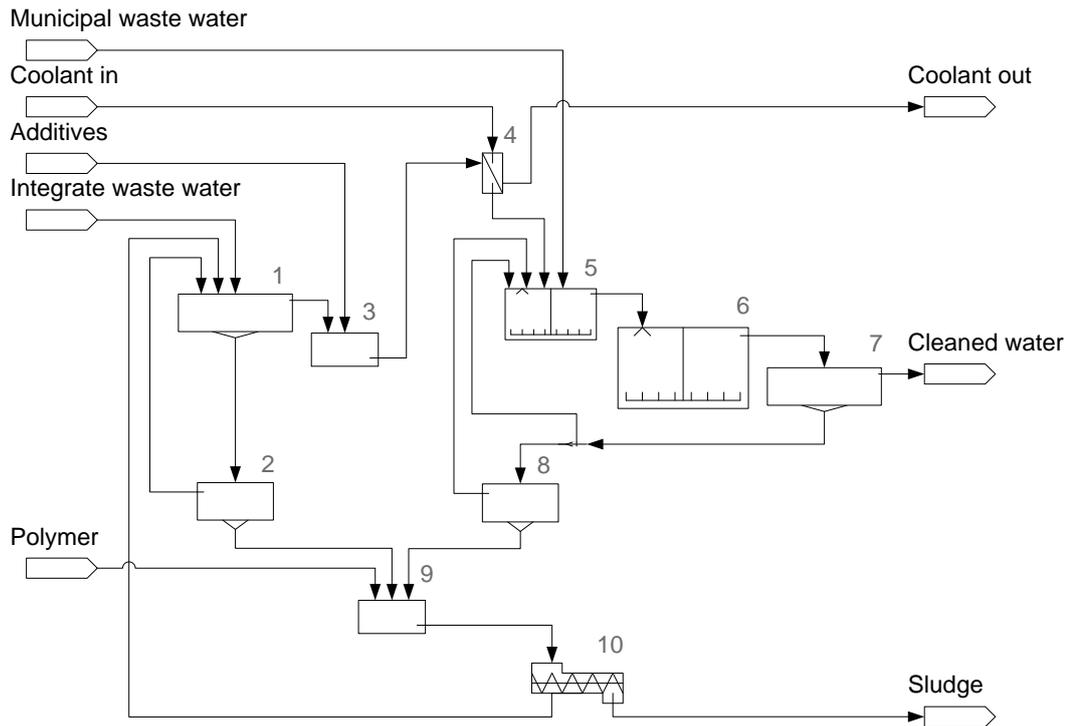


Figure 2.3: Schematic process diagram of the integrate wastewater treatment plant. 1: primary clarification, 2: primary thickening, 3: neutralization, 4: cooling, 5: aeration, 6: aeration, 7: secondary clarification, 8: secondary thickening, 9: combining, 10: dewatering.

straight to the aeration stage. After aeration the wastewater flow is directed to secondary clarification, where cleaned water is released to the environment and waste activated sludge (WAS) is removed at the bottom of the secondary clarifier. Primary and secondary sludges are thickened separately and then mixed and dewatered in screw presses with additional polymer. The dewatered sludge is burned in the integrate power plant.

Sulphuric acid and lime are used in pH control. Since the wastewaters do not contain enough nutrients to maintain an efficient biologic treatment process, additional phosphoric acid and urea are added to provide phosphorus and nitrogen to the organisms.

2.4 Combined heat and power plant

The combined heat and power plant of the integrate produces process steam and electricity to the pulp and paper mill and district heating and electricity to the

municipal power company. Steam can also be provided to the chemical pulp mill, when needed. The power plant consists of two fluidized bed boilers and two oil-fired standby and peak boilers. The fluidized bed boilers use primarily bark and logging residue and to a lesser extent recycled fuel, waste sludges, wood waste, coal, peat, heavy fuel oil, waste oils and paper. Ashes from the power plant will be utilized at no cost in a land filling application until 2020.

2.5 Air separation plant

In the integrate there is also a cryogenic air separation plant, which produces 35 000 t/a gaseous oxygen per year. This is used in the chemical pulp bleaching process, in addition to which a small amount of the separated nitrogen is led to the tall oil distillery on site.

3 Literature and theory

3.1 Process integration

Process integration is an approach to process design, operation and retrofitting in which industrial systems are analysed as a whole rather than separate processes. The method allows global planning, analysis and optimization of the whole system and it helps to determine attainable performance targets and to make decisions that would lead to realization of these targets. Typical applications are mass and energy integration, in the first of which generation and routing of matter and in the latter heat recovery and energy utility systems are optimized throughout the process. (El-Halwagi 1998) Integration studies can be used for instance to reduce material and energy-related costs as well as environmental impacts.

Process integration methodology contains following activities: task identification, targeting, synthesis, analysis of alternatives and optimization. The first step is to express the desired goal as an actionable task, after which performance targets are set, ahead of detailed design. Next, process units and streams are connected as a logical whole in synthesis stage. Here, alternative combinations are generated and one or several of those are selected, typically based on some performance metrics. The selected alternative and its detailed characteristics are then analysed more deeply. Once a synthesis and analysis are conducted, it is possible to determine whether the performance targets are met. If not, synthesis and analysis stages are iterated until an optimal solution is found. (El-Halwagi 2006, Chapter 1) Pinch analysis techniques are central tools that are used both in energy and mass integration studies (El-Halwagi 1998).

Many recent studies in forest industry use process integration methodology. A good potential for heat integration possibilities has been detected in various circumstances¹ and also reductions in water and material use and pollution have been pointed out². Nevertheless, economic assessment may point out even investments which would gain seemingly large material savings to be unprofitable³.

¹See for example Isaksson et al. 2012; Fornell and Berntsson 2012; Chew et al. 2013; Mesfun and Toffolo 2013.

²See e.g. Chew et al. 2013; Anderson and Toffolo 2013; Shukla et al. 2013.

³See e.g. Anderson and Toffolo 2013.

3.2 Biorefineries

Biorefining is defined by IEA Bioenergy (2009) as ‘the sustainable processing of biomass into a spectrum of marketable products and energy’. A biorefinery might use any kind of biomass, including wood and agricultural crops, organic residues and aquatic biomass to produce intermediates or final products, such as food, feed, materials, chemicals, fuels, power or heat. The definition is broad and many traditional biomass processing plants might well be classified as biorefineries, including pulp and paper mills as well as sugar and starch refineries. (IEA Bioenergy 2009) A diagram of identified biorefinery pathways is presented in Figure 3.1.

Biorefineries allow similar products to be obtained as from traditional oil refineries, but with renewable inputs (de Jong et al. 2012); in addition the feedstocks are widely available and of relatively low cost. (IEA Bioenergy 2009) The wide range of input materials increases security of supply in comparison to oil-based refineries (de Jong et al. 2012), but it also forces operators to evaluate potential refining processes according to individual circumstances, such as feedstocks properties and availability, possible products and their markets.

As in all industrial production, return on employed capital plays a major part in biorefinery investments. Therefore, development of biorefinery systems that allow highly efficient and cost-effective production is a key factor in the realization of a bio-based economy (de Jong et al. 2012). Increasing oil prices, consumer demand for more environmentally friendly products, limited amount of non-renewable resources and population growth are opening possibilities for biorefineries, but the main driver as of today is the transport sector. Political decisions have caused an artificial increase in transportation biofuel demand, even though they can hardly be produced profitably at current crude oil prices. Producing multiple value-added products in a biorefinery is considered to bring down production costs in a competitive way. (de Jong et al. 2012)

Pulp and paper mills are considered as a good basis for a biorefinery: infrastructure, networks for suppliers and services, procurement and skilled labour force are readily available (Moshkelani et al. 2013). Moreover, they might be able to utilize by-products of technologies implemented on site, provide utilities and treat effluents. Altogether, these integration opportunities can make intended biorefineries economically viable earlier or in smaller scale than in the case of stand-alone biorefineries. (Towers et al. 2007) Furthermore, as there is a trend of decreasing pulp and paper prices, increasing wood costs, increased competition from low-cost producers (Berntsson et al. 2008), declining newsprint usage and increased energy costs, the industry requires revitalizing and biorefineries are considered as one way forward (Towers et al. 2007). There are multiple options for implementing a biorefinery into

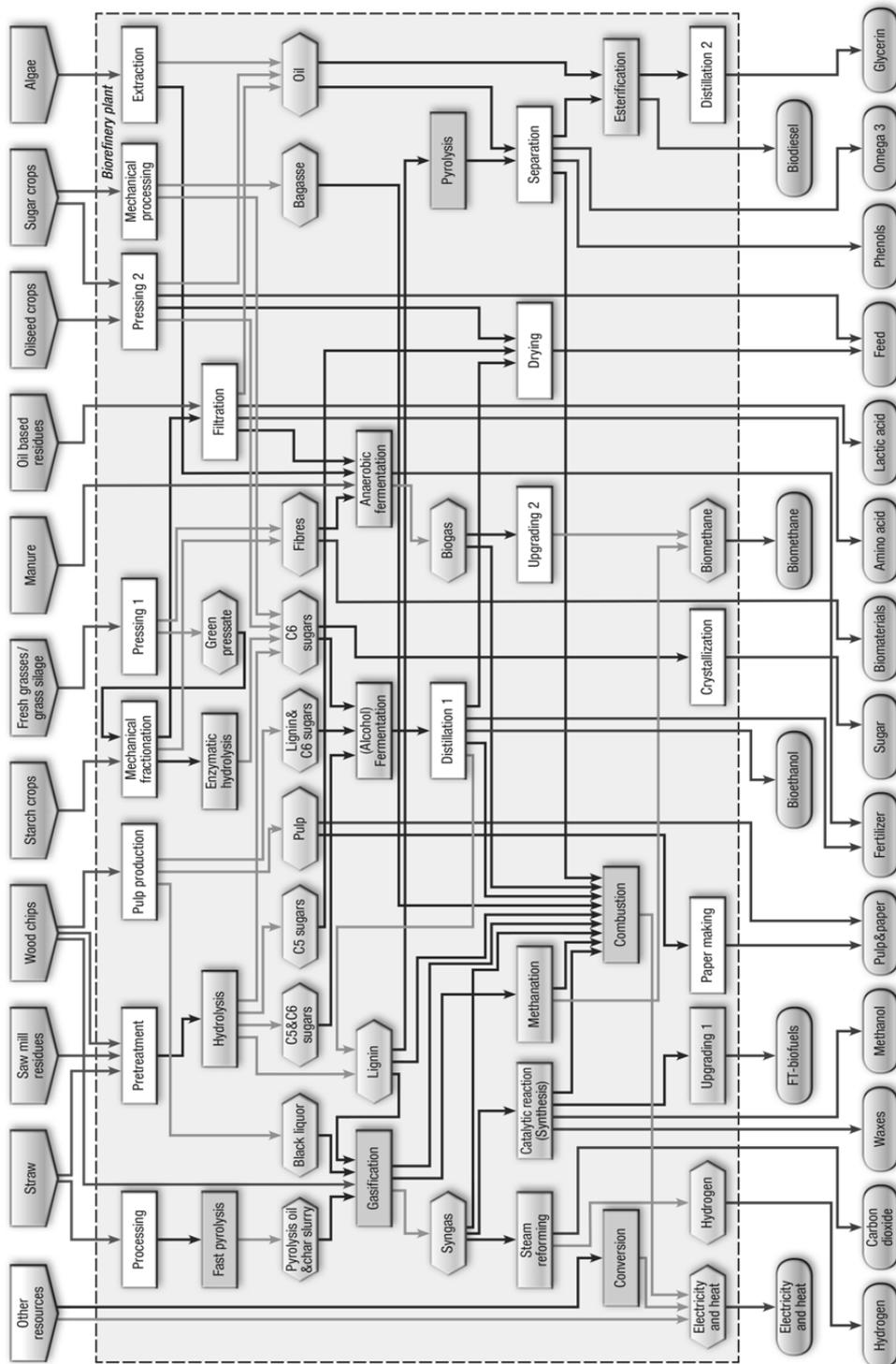


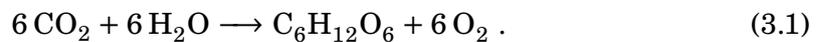
Figure 3.1: Biorefinery classification based on raw materials, intermediate platforms, processes and end products (van Ree and de Jong 2013)

a pulp and paper mill: among others lignin, hemicellulose and extractives might be converted to various chemicals, bark and logging residues might be fermented to ethanol, black liquor might be gasified to produce chemicals and energy might be produced in a variety of ways (Berntsson et al. 2008). Ultimately the feedstocks and product markets will determine most feasible configuration in each case (Towers et al. 2007). The process scheme that is investigated in this thesis is presented in Section 4.1.

3.3 Microalgae

3.3.1 Microalgal biology

Microalgae are unicellular photosynthetic organisms that are present in all ecosystems on earth (Mata, Martins and Caetano 2010). There are numerous opportunities of using microalgae in for example energy and biomaterials production and the pathways have been studied a lot during recent years. There are many benefits in microalgal biomass production: for instance, they are easy to cultivate, have very high growth rates in comparison to conventional forestry or agricultural crops, require little land area and can use water that is unsuitable for human consumption (Mata, Martins and Caetano 2010). Examples of growth rates are shown in Table 3.1. Microalgae can absorb carbon dioxide from the atmosphere with photosynthesis, which may be simplified with reaction equation



Thus microalgae cultivation acts as a carbon sink. As a drawback, costs of microalgal biomass production are high, particularly in harvesting and dewatering steps, and for instance utilization of microalgae-based biofuels has been impeded by these processing costs (Uduman et al. 2010).

In order to grow, microalgae need carbon, nutrients and vitamins. The carbon can be metabolized from inorganic or organic carbon sources, while the energy for growth can be obtained from light via photosynthesis or organic carbon compounds. (Mata, Martins and Caetano 2010). The required nutrients include large amounts of nitrogen, phosphorus, sulphur, potassium and magnesium (so called *macronutrients*), small amounts of iron and manganese and trace amounts of cobalt, zinc, boron, copper and molybdenum (*micronutrients*) (Carvalho et al. 2006). Naturally available nutrient-rich streams — such as effluent from anaerobic digestion — can be used as a growth medium for microalgae, but their growth may often be restricted by the availability of light (Wahal 2010). Optimal growth temperature for microalgae is

Table 3.1: Annual areal growth rates for algae, Finnish forest and some agricultural crops

Biomass	Growth rate	Source
Microalgae	350 . . . 480 t/ha	Chisti (2007)
Forest	3.8 . . . 4.6 m ³ /ha	Metla (2012)
Reed canary grass ¹	6 . . . 8 t/ha	Pahkala et al. (2002)
Reed canary grass ²	2.93 t/ha	Tike (2013)
Sugar beet	37.6 t/ha	Tike (2013)
Rape	1.65 t/ha	Tike (2013)

¹ Achievable dry matter growth rate

² Actualized growth rate in 2012

generally around 20 °C to 25 °C, but even such strains exist that are able to grow in 4 °C to 32 °C⁴.

There are many components in microalgae that could be utilized as raw materials for high-value products: carbohydrates, lipids, pigments and proteins all have their applications. Accumulation of different components however requires different cultivation conditions and operation modes. (Yen et al. 2013) Furthermore, the chemical composition of microalgae is not constant, but it varies depending on the algal strain and environmental factors, such as temperature, illumination and nutrient supply (Becker 1994, Chapter 12).

The share of carbohydrates could reach over 50 % of dry mass in microalgae. Carbohydrates could be used in ethanol and hydrogen production and the included polysaccharides fraction have utilization opportunities in food, cosmetics, textiles, stabilizers, emulsifiers, lubricants, thickening agents and clinical drugs. Lipids account normally for 30 % to 50 % of dry weight and they can be divided into two groups according to the number of carbon atoms: fatty acids with 14 to 20 carbon atoms serve best in biofuel production and polyunsaturated fatty acids (PUFAs) with more than 20 carbon atoms as health food supplements. Of the latter group, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are ω -3 fatty acids that are of particular interest due to their bioactivity. Microalgae contain large quantities of high-quality EPA and DHA: 10 % to 30 % or 30 % to 50 % of total fatty acids and 1 % to 4 % or 10 % to 30 % of dry biomass for some species are EPA and DHA, respectively. Chlorophyll, carotenoids and phycobiliproteins are yet another group of products from microalgae that have high value: for example carotenoid astaxanthin that can reach up to 4 % of dry algal weight is sold for over 5300 euros

⁴See for example Ahn et al. 2012.

per kilogram and phycobiliproteins for 2 €/mg to 20 €/mg⁵. (Yen et al. 2013) After separation of components, the remaining algal matter can be utilized for example as food or animal feed (Becker 2007) or in energy production via anaerobic digestion⁶.

3.3.2 Microalgae cultivation and harvesting

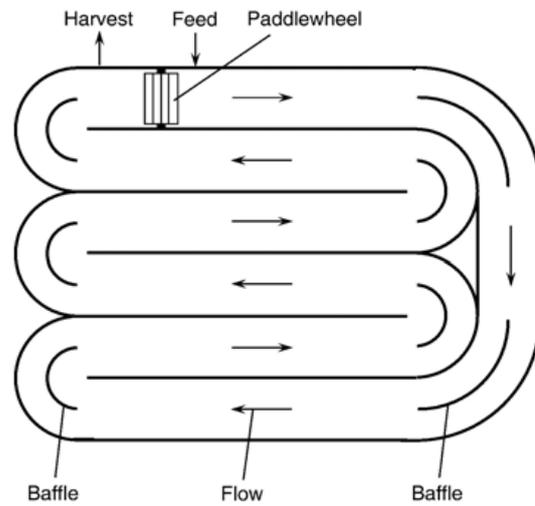
Open and closed-culture systems may be used in suspended microalgae cultivation. Most common open-culture systems are raceway ponds, which are shallow ponds constructed as an endless loop, circular ponds which are agitated by a rotating arm and inclined systems, in which mixing happens via gravity-assisted flow and pumping. Closed-culture systems or photobioreactors (PBRs) include most notably flat or tubular photobioreactors, of which the latter may be arranged in horizontal, inclined, vertical or spiral as well as manifold or serpentine configurations. (Mata, Martins and Caetano 2010) Raceway ponds and tubular photobioreactors are considered the only practical cultivation systems in industrial scale (Chisti 2007), while most of the current large-scale installations are open systems (Wang, Lan and Horsman 2012). Schematic visualizations of these two major types are presented in Figure 3.2.

Open-culture systems are typically less expensive to build and operate in comparison to photobioreactors. However, they offer low control on temperature, evaporation and lighting and are affected by contamination with other algae and microorganisms that feed on algae. (Chisti 2007; Mata, Martins and Caetano 2010) Photobioreactors offer higher controllability, achieve higher biomass concentrations and consume less land area, but they have their inherent limitations — overheating, fouling and oxygen accumulation among others. Biomass production cost may be even one order of magnitude higher in photobioreactors than in ponds. (Mata, Martins and Caetano 2010) According to Chisti (2007), photobioreactors can have a volumetric productivity of approximately 1.5 kg/m³ d algae, whereas raceway ponds attain 0.1 kg/m³ d yield. Areal productivities for these two are on same scale: 0.05 kg/m² d for photobioreactor systems and 0.04 kg/m² d for raceway ponds (Chisti 2007).

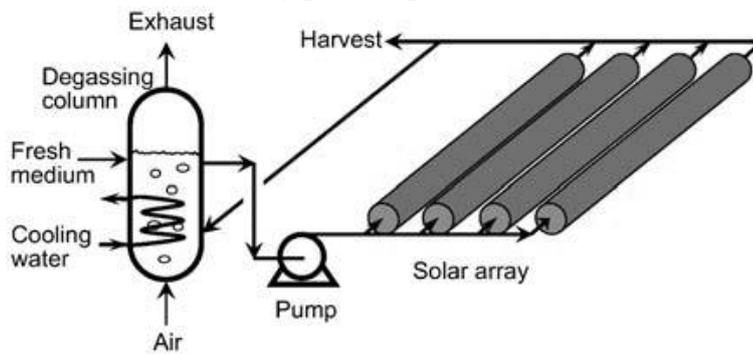
Tubular photobioreactor is depicted in Figure 3.2b: it consists of an array of straight transparent tubes, where the microalgae capture light and grow. These tubes are connected to a degassing unit, where oxygen that is generated during the cycle is removed and carbon dioxide is added to the growth medium, usually by bubbling. Fresh medium is added to the degassing unit and algae is removed at photobioreactor exit. Diameter of the photobioreactor tubes is restricted by the mutual shading of algal cells and the associated light penetration; degassing unit volume is also wanted to be kept at minimum to maximize time spent in the more

⁵Calculated using a conversion factor of 0.75 € to USD

⁶See Section 3.4.4



(a) Raceway pond, depicted from above



(b) Tubular photobioreactor

Figure 3.2: Schematic representations of major algal cultivation systems (Chisti 2007)

illuminated photobioreactor tubes (Chisti 2007). Mixing of the culture is important: it prevents algae sedimentation, ensures uniform distribution of light and nutrients among cells and ensures good gas and heat transfer within the growth medium (Wang, Lan and Horsman 2012). Therefore, flow in the photobioreactor tubes is kept in turbulent region; yet too intense shear stress can damage algal cells (Chisti 2007).

Upon harvesting, typical algal dry matter concentration in cultures is 0.25 kg/m^3 to 1 kg/m^3 in raceway ponds and 1.5 kg/m^3 to 1.7 kg/m^3 in tubular reactors (Christenson and Sims 2011). In order to process the algae further, water has to be removed from the stream. Possible harvesting and dewatering options include chemical (flocculation) and mechanical methods (centrifugation, filtration, sedimentation, flotation) and to lesser extent biological (autoflocculation, bioflocculation, microbial flocculation) and electrical methods (Christenson and Sims 2011). The choice over harvesting and dewatering technologies needs to be done based on the algal strain and its properties, for example cell size (Uduman et al. 2010): there is no single method that would be superior under all circumstances (Molina Grima, Belarbi et al. 2003; Christenson and Sims 2011). Dewatering of algae requires significant energy input and thus it has to be designed carefully to keep biomass production viable (Uduman et al. 2010).

Water removal can be done in one or several stages. Chemical flocculation is often performed as a first stage (Christenson and Sims 2011; Cooney, Young and Nagle 2009); circa 1 % total solids content is usually achieved (Cooney, Young and Nagle 2009). Downstream processes have to be taken into account when choosing the flotation chemicals, for instance as metal salts that can be used as coagulants can upset digestion processes that might follow (Christenson and Sims 2011). Sedimentation is a low-cost harvesting option that can reach 1.5 % solids concentration, but it is considered unreliable (Uduman et al. 2010; Christenson and Sims 2011).

Centrifugation is seen as very efficient, rapid and reliable dewatering method (Molina Grima, Belarbi et al. 2003; Uduman et al. 2010; Christenson and Sims 2011), but it is also very energy intensive and has high investment costs (Uduman et al. 2010; Christenson and Sims 2011). 12 % to 22 % solids concentration is achievable with centrifugation (Molina Grima, Belarbi et al. 2003; Christenson and Sims 2011) and over 90 % of the algae can be recovered in the solids fraction (Christenson and Sims 2011). Similar concentrations, 5 % to 27 %, can be attained with filtration (Molina Grima, Belarbi et al. 2003; Christenson and Sims 2011) with 70 % to 90 % algae recovery in solids fraction (Christenson and Sims 2011). Higher cell size enables larger flow rates through filter material and hence lower filtration costs (Uduman et al. 2010) — consequently filter presses are considered adequate

for relatively large microalgal species but unsuitable for ‘organisms approaching bacterial dimensions’ (Molina Grima, Belarbi et al. 2003). If still higher total solids concentration is desired, thermal drying can be applied (Molina Grima, Belarbi et al. 2003; Cooney, Young and Nagle 2009).

Actual algae production costs depend very much on processes and external conditions, but actual costs of 2.6 €/kg to 3.8 €/kg in open ponds have been reported and estimations of 0.5 €/kg to 5.0 €/kg in open ponds and 0.4 €/kg to 4.2 €/kg in photobioreactors have been made⁷ (Christenson and Sims 2011). Meanwhile, 69 €/kg levelized cost of production has been calculated for a site that produces 3.8 t/a algae in photobioreactors and it was evaluated that this could decrease to 12.6 €/kg with 200 t/a production (Acién et al. 2012).

3.3.3 Lipid extraction and refining

After microalgae has been cultivated and harvested, lipids may be extracted and purified. There are multiple methods for lipid extraction, which include at least traditional solvent extraction, accelerated solvent extraction, subcritical water extraction, supercritical CO₂ or methanol extraction, milking and direct transesterification (C.-H. Cheng et al. 2011; Cooney, Young and Nagle 2009). Mechanical disruption of cells may be used before extraction to allow less restricted flow for solvents — for instance grinding, microwave or ultrasound treatment (Cooney, Young and Nagle 2009). Most extraction methods require total solids content greater than 90 %, but some work with wet biomass (Dejoye Tanzi, Abert Vian and Chemat 2013). Generally, the most appropriate extraction technology depends on microalgal species and its cultivation (Cooney, Young and Nagle 2009).

There are many purification methods that can be used to extract a certain fatty acid, including winterization, molecular distillation, urea complexation, AgNO₃-complexation, supercritical CO₂ extraction, enzymatic purification, membrane techniques, transesterification and chromatography (Tang et al. 2011; Kune 2002). Urea complexation is regarded as one of the most efficient methods for ω -3 fatty acid enrichment due to use of simple equipment, inexpensive solvents and mild operating conditions (Robles Medina et al. 1995; Mendes, Lopes da Silva and Reis 2007; Tang et al. 2011). However, it is considered to be ‘of limited value’ in commercial EPA purification, where silica gel chromatography, membrane-based selective enrichment, supercritical chromatography, kinetic resolution and winterization are conceived more appropriate (Molina Grima, Belarbi et al. 2003).

Actual extraction and refining yields vary significantly depending on the algal strain and the extraction process, but as much as over 90 % of the desired fatty acids

⁷Calculated using a conversion factor of 0.75 € to USD, where applicable

have been recovered in some studies (Robles Medina et al. 1995; Molina Grima, Sánchez Pérez et al. 1995; Dong et al. 2013).

3.4 Anaerobic digestion

3.4.1 Theory of operation

Anaerobic digestion is a biological conversion process, in which organic matter is transformed into methane (CH_4) and carbon dioxide (CO_2) in the absence of oxygen. It is a naturally occurring process, but it can also be engineered — examples of such processes are found in waste treatment and power generation systems. In the context of wastewater treatment, the term anaerobic process is used to describe various biological treatment systems that operate in conditions in which there are no dissolved oxygen or nitrate (NO_3^-) present (Grady et al. 2011, Chapter 14). Anaerobic processes are mostly used to stabilize biodegradable organic matter and to simultaneously reduce odours, pathogen concentration and the mass of the incoming solid organic material (Parkin and Owen 1986; Grady et al. 2011, Chapter 14). The engineered processes can be fed either in batch or in continuous mode.

A schematic representation of the different reactions in an anaerobic digester is shown in Figure 3.3, as proposed by Gujer and Zehnder (1983). The incoming biological matter is first hydrolysed to organic monomers that can be utilized by fermentative organisms or anaerobic oxidizers. These organisms then use the monomers to produce either acetic acid, hydrogen (H_2) or intermediate compounds such as propionic, butyric or valeric acid. The intermediate compounds can be further oxidized to hydrogen or acetic acid (CH_3COOH). These products of acidogenic reactions are then used by methanogenic organisms to produce methane. (Gujer and Zehnder 1983; Parkin and Owen 1986; Grady et al. 2011, Chapter 2)

Six separate processes may be identified in an anaerobic digester, which are enumerated in Figure 3.3 (Gujer and Zehnder 1983):

1. Hydrolysis of biopolymers
 - 1A. Hydrolysis of proteins
 - 1B. Hydrolysis of carbohydrates
 - 1C. Hydrolysis of lipids
2. Fermentation of sugars and amino acids
3. Anaerobic oxidation of alcohols and long-chain fatty acids
4. Anaerobic oxidation of intermediate products

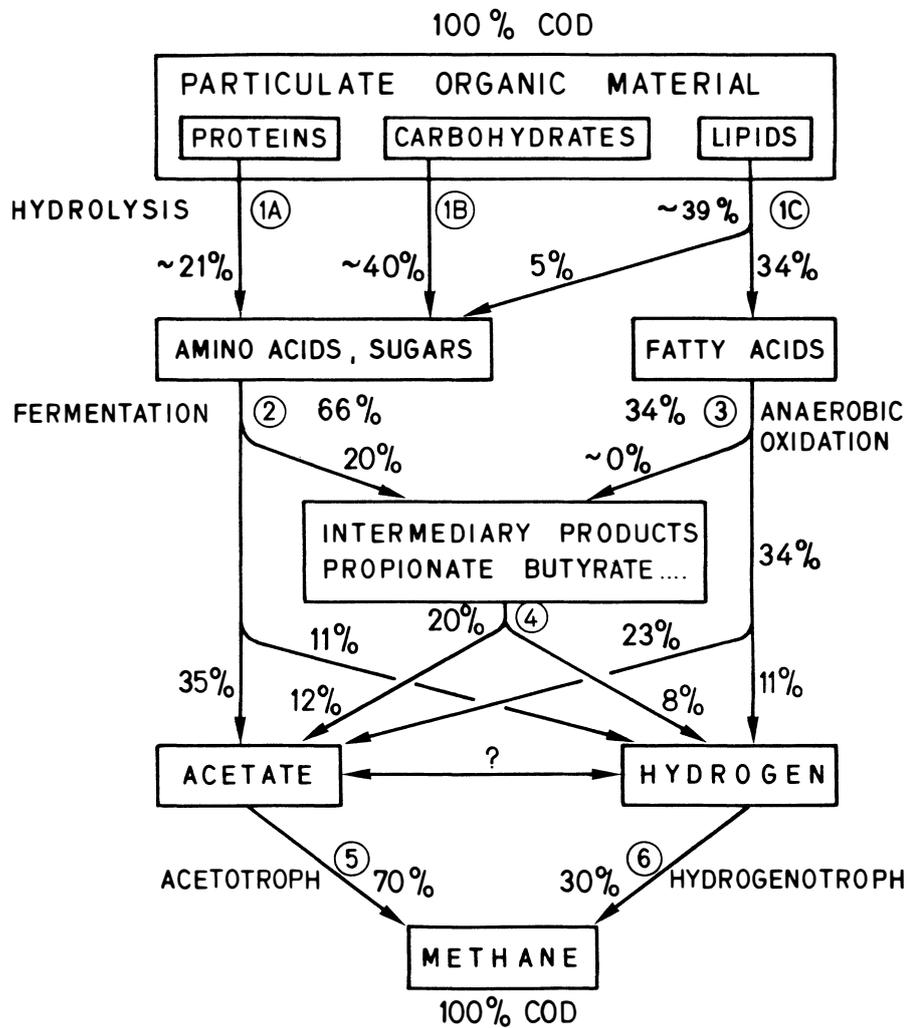


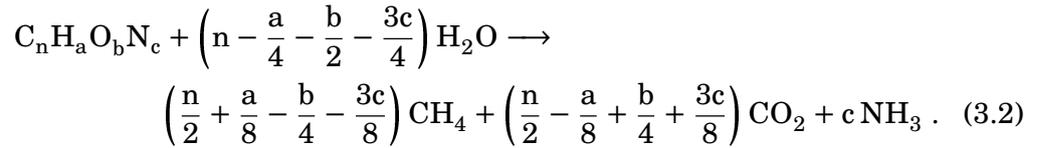
Figure 3.3: Reaction scheme for anaerobic digestion of waste activated sludge, modified from the work of Kaspar and Wuhrmann (1978) by Gujer and Zehnder (1983). The percentages indicate the theoretical fraction of total chemical oxygen demand (COD) or methane flow that undergoes the respective reaction. (Gujer and Zehnder 1983)

5. Conversion of acetate to methane

6. Conversion of hydrogen to methane .

These are often grouped into four stages: hydrolysis (process 1), acidogenesis (processes 2 and 3), acetogenesis (process 4) and methanogenesis (processes 5 and 6). The balance between these reactions in a steady state will only depend on the feed material, operating conditions and the stoichiometry of the reactions (Gujer and Zehnder 1983). Hydrogen has a key role in governing the organic acid production and consumption: a partial pressure of hydrogen greater than 10 Pa will inhibit reactions that result in production of hydrogen and acetic acid — this will in turn limit the hydrogen content. The production of methane allows the previously mentioned reactions to continue further due to reduction in hydrogen concentration. (Grady et al. 2011)

Altogether, biogas production requires anaerobic conditions, aforementioned micro-organisms and organic substrates. Theoretical methane yield in digestion can be calculated from the substrate composition with equation first presented by Symons and Buswell (1933) and thereafter modified by others (Parkin and Owen 1986):



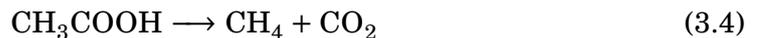
Theoretical yield is generally not met: incomplete reaction can be caused by for example inadequate residence time in reactor or inability to break down the substrate.

If the carbon (and not sulphur or nitrogen) in the reactor is the dominant sink of electrons (Gujer and Zehnder 1983) and if the change in chemical oxygen demand (COD) during the process is known, the methane production may also be calculated from the COD equivalent of methane (Parkin and Owen 1986; Gujer and Zehnder 1983). This can be determined from the oxidizing reaction of methane:



Hence, every mole of produced CH_4 corresponds to 2 mol reduction in COD (Parkin and Owen 1986; Grady et al. 2011, Chapter 2).

Methane in the anaerobic reactor is produced primarily from reactions



and



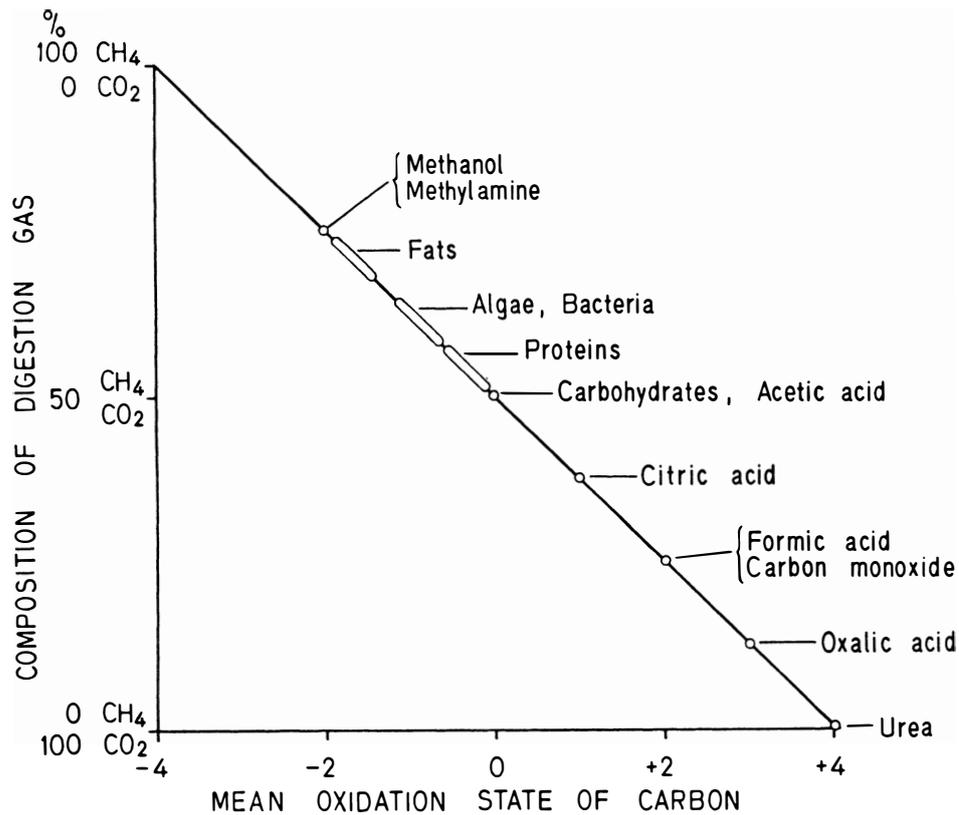


Figure 3.4: Composition of the digester gas as a function of the mean oxidation state of carbon in the feedstock, assuming complete mineralization of the feedstock (Gujer and Zehnder 1983)

which correspond to processes 5 and 6 in Figure 3.3, respectively (Parkin and Owen 1986; Grady et al. 2011; Gujer and Zehnder 1983). The carbon dioxide content in the product gas will hence be affected by the balance between the methane-forming reactions. Some of the formed CO₂ may remain dissolved in the digester or — depending on the ammonia concentration in the reactor — it can be converted to bicarbonate (Gujer and Zehnder 1983). In total, the composition of product gas will depend on the mean oxidation state of the carbon in the organic matter, the amount of dissolved CO₂ in the digester liquid and the nitrogen content of the feedstock (Gujer and Zehnder 1983). The dependency of the digester gas composition on the mean oxidation state of carbon is illustrated in Figure 3.4.

In addition to gas production, the breakdown of organic compounds releases some of the nutrients into dissolved form that were originally present in the digester feed. The nutrient-rich digester effluent can hence be used to replace additional nutrients that are used elsewhere in the process. (Karlsson et al. 2011)

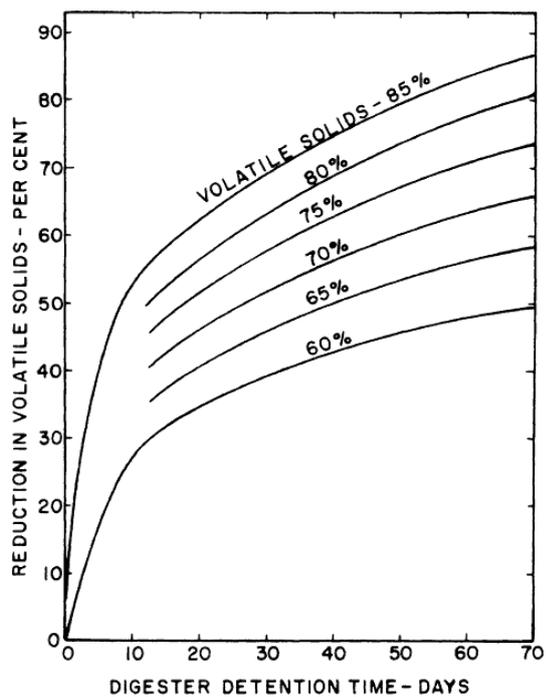
3.4.2 Factors that affect the performance of anaerobic digestion

The performance of anaerobic digestion process and hence the yield of produced methane are affected by numerous factors, including solids retention time (SRT) and the closely related volumetric organic loading rate, total hydraulic loading in the reactor, temperature, pH, inhibitory and toxic materials such as light metal cations and ammonia, availability of nutrients, mixing and waste type (Grady et al. 2011, Chapter 14).

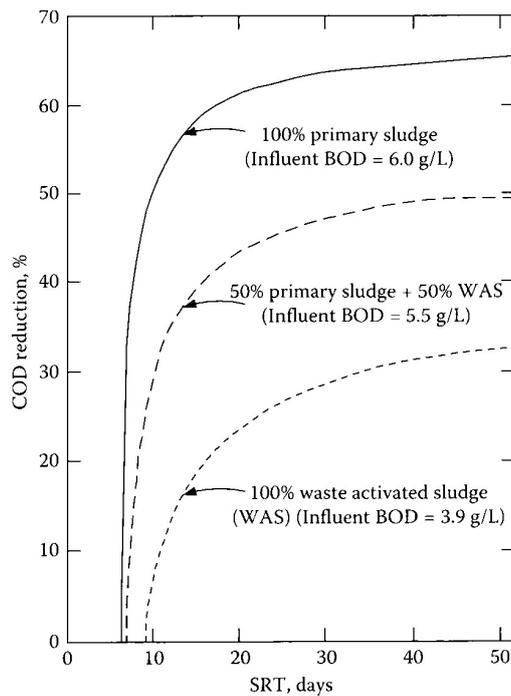
Firstly, the SRT — the average time a solid particle spends in the process — must be kept high enough to maintain sufficient quantity and concentration of bacteria in the reactor (Parkin and Owen 1986). The fraction of degraded solids will increase with growing SRT, as Figure 3.5 suggests, and the produced methane amount will grow accordingly. However, as the methane production rate decreases with time but reactor size and the related investment costs will keep increasing, the final SRT will be subject to optimization. A 20-day SRT would be a rather typical value for an anaerobic digester (Parkin and Owen 1986), while a SRT of 30 to 40 days is not uncommon in pilot-scale treatment systems (Grady et al. 2011, Chapter 14). If there is no recycling of solids, the solids retention time of a digester will be equal to the hydraulic retention time (HRT) in the digester, which is the digester volume digester divided by the flow rate (Parkin and Owen 1986; Grady et al. 2011, Chapter 14).

Temperature has a significant effect on the anaerobic process and the best performance is generally reached in the optimal region of two possible temperature ranges: 30 °C to 40 °C for mesophilic and 50 °C to 60 °C for thermophilic methanogenic organisms. Even though methane production can be sustained in approximately 10 °C, the practical lower temperature limit for operations is about 20 °C to 25 °C. The temperature affects also hydrolytic and acidogenic reactions. Consequently, if the influent is simple-structured and readily biodegradable, the effect of temperature on methanogenesis is the primary concern and if the solids in the feed are complex, then the effect of temperature on hydrolysis and acidogenesis is of more importance. Temperature gradients may disturb the organisms' growth, and it is typically recommended to restrict the temperature variations to ± 1 °C per day. Thermophilic operations exhibit some benefits over mesophilic, but there are numerous drawbacks — decreased process stability and increased odours among others. (Grady et al. 2011, Chapter 14)

The pH in the reactor must lie between 6.8 to 7.4 (Grady et al. 2011, Chapter 14) to meet the optimum conditions for methanogens, which are the most sensitive organisms to pH variation in the digester. The pH is controlled primarily by the bicarbonate buffering system, where alkalinity is produced during digestion of nitrogen-containing organic material. (Grady et al. 2011, Chapter 14; Parkin and Owen 1986)



(a) Effect of varying influent volatile solids concentrations (Pfeffer 1968)



(b) Effect of waste type (Grady et al. 2011, Chapter 14)

Figure 3.5: Examples of volatile solids and chemical oxygen demand (COD) reduction as a function of solids retention time (SRT)

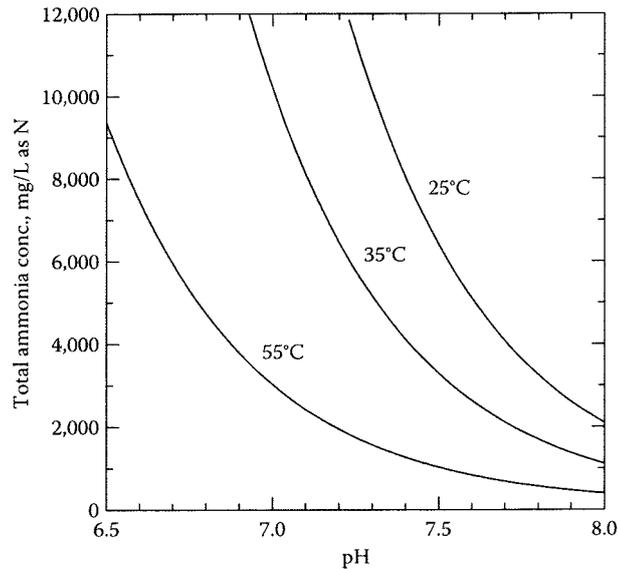


Figure 3.6: Total ammonia-N concentration that is required to give 100 gN/m^3 free ammonia concentration at different temperature and pH levels (Grady et al. 2011, Chapter 14)

There are various substances, which are stimulatory to digestion, but can upset the process in excessive amounts: these include ammonia and light metal cations such as sodium, potassium, calcium and magnesium. Ammonia in the reactor is produced as a result of breakdown of nitrogen-containing organic material, or it may be present in the influent wastewater. Ammonia-N⁸ is a required nutrient for digestion and concentrations between 50 g/m^3 to 200 g/m^3 are regarded as beneficial. However, free ammonia (NH_3) is considered toxic at concentrations of approximately 100 gN/m^3 . (Grady et al. 2011, Chapter 14; Parkin and Owen 1986) Figure 3.6 shows the required total ammonia-N concentration that is needed to meet the 100 g/m^3 NH_3 concentration limit; for instance at 35°C and pH 7.0 the total ammonia-N concentration can be approximately 10 kg/m^3 .

There are also other substances that are inhibitory to anaerobic reactions: these include sulphide (S^{2-}), heavy metals and a wide range of organic compounds. Sulphide is produced in anaerobic conditions from sulphate (SO_4^{2-}) in the influent or during degradation of sulphur-containing compounds. Soluble sulphides are inhibitory and concentrations above 200 g/m^3 cause notable decrease in methane production. (Grady et al. 2011, Chapter 14; Parkin and Owen 1986) Sulphates themselves are

⁸Nitrogen in NH_3 and NH_4^+

not inhibitory, but they compete with methanogens as electron acceptors, which has various negative effects to digestion (Grady et al. 2011, Chapter 14).

Heavy metals are particularly harmful to anaerobic systems (Parkin and Owen 1986) and they can be present in significant amounts in municipal sewage (Y. Chen, Y. J. Cheng and Creamer 2008). The toxicity of heavy metals varies very much, for example 50 % inhibition is achieved with Fe^{2+} at a concentration of 1 g/m³ to 10 g/m³, whereas with Cu^{2+} the same effect is achieved with 10⁻¹⁶ g/m³ concentration. However, as only soluble metal ions are inhibitory and metal sulphides are extremely insoluble, the sulphides in the digester reduce the risk of metal ion inhibition. Vice versa, iron addition can be used to keep sulphidity at a low level. (Grady et al. 2011, Chapter 14)

Nutrients are essential to anaerobic digestion, similarly to other biochemical operations. The nutrient requirements are nevertheless quite low: approximately 4 % to 10 % of incoming COD is consumed in the production of new biomass and consequently adequate nutrients will generally be available when complex wastes are being treated. (Grady et al. 2011, Chapter 14)

Adequate mixing must also be provided to the reactor in order to ensure good contact between the micro-organisms and their substrates, to reduce resistance to mass transfer, to minimize the buildup of inhibitory substances and to stabilize environmental conditions. Volumetric power inputs in anaerobic digesters are often in the range of 5 kW/m³ to 8 kW/m³. (Grady et al. 2011, Chapter 14)

Lastly, waste type and content has a significant effect on the digester performance. Not all organic matter can be converted into such forms that it can be utilized by the organisms in the reactor and the composition of incoming matter can vary greatly. For example, the non-biodegradable portion of municipal primary sludge can range from 35 % to 80 %. (Parkin and Owen 1986) Figure 3.5b illustrates the difference between digestion properties of waste activated sludge (WAS) and municipal primary sludge: COD removal in WAS digestion is much less efficient and hence the CH₄ production is also lower. Some soluble organic matter decomposes readily and for some it takes more time to decompose. Examples of slowly biodegradable matter include polymers such as hydrocarbons and proteins and complex organic compounds that can be found in many industrial wastewaters. (Grady et al. 2011, Chapter 14)

Digester feed concentration can vary widely: in low solids digestion dry matter content is maintained generally below 10 %, but high solids digestion is performed at 18 % to 35 % total solids content. Higher concentrations lead to increased solids retention time for a given loading rate and reactor volume; consequently higher conversion efficiency and gas production can be reached. Inversely, if the SRT is maintained constant, smaller reactors can be used at the same loading rate. Sewage

Table 3.2: Organic constituents in waste activated sludge samples from four Finnish pulp and paper mills, on dry ash-free basis (Kyllönen et al. 1988)

Component	Share (%)	
	Minimum	Maximum
Lipids	2	10
Proteins	22	52
Carbohydrates	0	23
– of which cellulose	0	8
Lignin	20	58

sludge has been conventionally digested around 7 % solids content due to pumping and mixing limitations. (Jewell, Cummings and Richards 1993)

3.4.3 Anaerobic digestion of pulp and paper mill waste activated sludge

The degradable fraction of waste activated sludge (WAS) from clarification stage of aerobic digestion consists mostly of active bacterial cells, whose biodegradability is approximately 68 %. The net biodegradability of chemical oxygen demand (COD) and volatile solids (VS) in WAS is estimated to range from 30 % to 50 %, depending on the activated sludge process: the longer the solids retention time is in the activated sludge process, the lower is the biodegradable fraction in WAS. (Parkin and Owen 1986)

Based on WAS analyses at four Finnish pulp and paper mills, dry WAS has been measured to contain 53 % to 76 % volatile substances and 10 % to 40 % ash. Organic component fractions in dry ash-free content are shown in Table 3.2; nitrogen accounted for 3 % to 7 % of the dry matter. (Kyllönen et al. 1988)

Table 3.3 shows specific methane yields from previous WAS digestion experiments: production potentials of $50 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS added}}$ to $220 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS added}}$ have been demonstrated with 29 % to 40 % volatile solids reduction and 36 % to 56 % CH_4 content. Differences in methane yields have been accounted to low volatile solids content in sludges caused by high amount of inorganic material from paper machines (Jokela et al. 1997) and lignin in the sludges (Bayr and Rintala 2012). Lignin is known to be non-biodegradable in anaerobic conditions (Puhakka, Alavakeri and Shieh 1992; Bayr and Rintala 2012).

There are only few experiments made about the differences of thermophilic and mesophilic digestion in pulp and paper mill sludge handling. Bayr and Rintala (2012) concluded that the yield of methane is increased in thermophilic conditions when compared to thermophilic: WAS digestion in mesophilic conditions showed potential

Table 3.3: Specific methane yield, methane content in produced gas and volatile solids (VS) reduction in pulp and paper mill waste activated sludge (WAS) digestion, in varying temperature conditions

Substance	Temp. °C	CH ₄ yield m ³ /t _{VS added}	CH ₄ content %	VS reduction %	Source
WAS ¹	37	100 ... 200			a
WAS ²	36	220	56	40	b
WAS		85			c
Mixed sludge ³	37	190	58 ... 59	27 ... 40	d
WAS	35	50			e
WAS	55	100			e
Mixed sludge ⁴	55	150 ... 170		29 ... 32	e
Mixed sludge ⁴	35	90		41	f
Mixed sludge ⁴	55	50		36	f

¹ WAS from six chemical and mechanical pulp mills

² WAS from a chemical pulp mill

³ Primary and secondary sludge from a pulp and paper mill, municipal sewage sludge

⁴ Primary and secondary sludge from a chemical pulp mill

^a Karlsson et al. (2011)

^b Puhakka, Alavakeri and Shieh (1992)

^c Jokela et al. (1997)

^d Jokela et al. (1997)

^e Bayr and Rintala (2012)

^f Puhakka, Viitasaari et al. (1988)

of $50 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS added}}$ whereas in thermophilic conditions the yield was $100 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$. For fibre sludge the results were similar; $210 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$ in 35°C and $230 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$ in 55°C . The findings of Puhakka, Viitasaari et al. (1988) show the opposite: volatile solids (VS) reduction was lower for thermophilic than for mesophilic digestion (36 % versus 41 %) and gas production was significantly lower ($50 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS added}}$ vs. $90 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS added}}$). Experience in municipal primary sludge and WAS digestion shows that methane yield is greater in thermophilic digestion when compared to mesophilic digestion⁹.

In digestion tests loading rates of $1.2 \text{ kg}_{\text{VS}}/\text{m}^3 \text{ d}$ to $5.2 \text{ kg}_{\text{VS}}/\text{m}^3 \text{ d}$ and hydraulic retention times of 8 d to 32 d have been tried (Karlsson et al. 2011; Puhakka, Alavakeri and Shieh 1992; Bayr and Rintala 2012). Optimal process performance has been detected at $2.2 \text{ kg}_{\text{VS}}/\text{m}^3 \text{ d}$ (Puhakka, Alavakeri and Shieh 1992), while pH control and sludge recycling might be necessary when loading rate exceeds $1.5 \text{ kg}_{\text{VS}}/\text{m}^3 \text{ d}$ (Puhakka, Alavakeri and Shieh 1992; Bayr and Rintala 2012). Hydraulic retention times as low as 14 to 16 days are considered as feasible if proper pH levels can be maintained (Bayr and Rintala 2012). Optimum total solids concentration for input sludge is typically between 5 % to 6 % (Elliott and Mahmood 2007).

There are many ways of enhancing degradability of feedstock and methane production in digestion: thermal, chemical, enzymatic, ultrasonic, microwave or mechanical pretreatments can be used to enhance the process performance. These pretreatment methods accelerate the hydrolysis of influent matter and thus address the main rate-limiting step in anaerobic digestion (Kim et al. 2003).

There are conflicting results about whether all aforementioned pretreatment methods improve pulp and paper mill WAS solubilization: some studies indicate that ultrasonic pretreatment does not increase solubilization (Karlsson et al. 2011; Wood, Tran and Master 2009), while others have detected positive effect (Saha, Eskicioglu and Marin 2011; Elliott and Mahmood 2012) and some have found that solubilization is increased when ultrasonic treatment is used with alkaline treatment (N. D. Park, Helle and Thring 2012). Similarly, enzymatic pretreatment has been shown to have no effect (Karlsson et al. 2011) and to increase solubilization (Bayr, Kaparaju and Rintala 2013). Some studies examine mesophilic and some thermophilic digestion and the WAS properties differ, which may explain some differences. Alkaline¹⁰, thermal¹¹, mechanical¹², chemi-mechanical¹³, thermochemical¹⁴ and microwave¹⁵ pretreatments have been shown to increase solubilization of pulp and paper mill

⁹See e.g. Gavala et al. 2003; Záborská et al. 2000; Moen et al. 2003.

¹⁰Lin et al. 2009; Bayr, Kaparaju and Rintala 2013.

¹¹Bayr, Kaparaju and Rintala 2013; Wood, Tran and Master 2009.

¹²Elliott and Mahmood 2012.

¹³Saha, Eskicioglu and Marin 2011.

¹⁴Wood, Tran and Master 2009.

¹⁵Saha, Eskicioglu and Marin 2011.

WAS. With some pretreatment methods, similar methane production has been obtained with three-day solids retention time in digester as was reached with untreated sludge at 20 days digestion period (Elliott and Mahmood 2012).

Methane yield can also be increased with pretreatment methods: thermal¹⁶, thermochemical¹⁷ and microwave¹⁸ treatment have been shown to increase methane production from 30 % to 280 %. Meanwhile, tests on alkaline¹⁹ and ultrasound²⁰ pretreatments show conflicting results. Acidic pretreatment has been shown to decrease methane production in thermophilic digestion (Bayr, Kaparaju and Rintala 2013).

There are not many sources about how nutrients are distributed during WAS digestion, but Zhang, Itakura and Matsuto (2012) provide some data about nutrient flows in 'sewage sludge' digestion. From this data, it can be calculated that (57 ± 4) % of nitrogen and (64 ± 8) % of phosphorus in the WAS is in dissolved form after anaerobic digestion. In the same study, average CH₄ concentration in biogas from nine plants was (57 ± 3) %. (Zhang, Itakura and Matsuto 2012)

3.4.4 Anaerobic digestion of algal biomass

If only some parts of algae are utilized, digesting the remaining components allows production of methane and possibly reuse of nutrients if those are present in the digested fraction. The released nutrients enable positive feedback for algal growth if digester effluent is used as growth medium for algae. Recycling of nitrogen and phosphorus in this way is considered to be a key element in keeping external fertilizer use in algae cultivation at sustainable level (Sialve, Bernet and Bernard 2009). Comparatively high nitrogen content in algae and the associated release of ammonia during digestion can however inhibit digestion (Sialve, Bernet and Bernard 2009), as was described in Section 3.4.2.

Degradability of microalgae is rather low, which is greatly affected by the resistance of cell walls (Golueke, Oswald and Gotaas 1957; Afi et al. 1996; P. H. Chen and Oswald 1998). Volatile solids reduction in anaerobic digestion of algae has been measured to be approximately 35 % to 55 % (Golueke, Oswald and Gotaas 1957; Yuan et al. 2012); or in other units approximately 50 % chemical oxygen demand (COD) reduction has been attained (Ras et al. 2011; Zamalloa et al. 2012). Greater volatile solids reduction has been achieved with thermophilic digestion than with mesophilic digestion (Golueke, Oswald and Gotaas 1957). Co-digestion of algae

¹⁶Wood, Tran and Master 2009; Bayr, Kaparaju and Rintala 2013.

¹⁷Wood, Tran and Master 2009.

¹⁸Wood, Tran and Master 2009.

¹⁹Lin et al. 2009; Bayr, Kaparaju and Rintala 2013.

²⁰Saha, Eskicioglu and Marin 2011; Bayr, Kaparaju and Rintala 2013; Wood, Tran and Master 2009.

with waste activated sludge has been evaluated: results indicate that co-digestion enhances volatile solids reduction in WAS digestion to same levels as in pure algae digestion (47 % to 57 %), beginning from 32 % share of algae in total mass (Yuan et al. 2012).

Methane yield in algae digestion has been measured to be between $180 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$ and $410 \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$ (Ras et al. 2011; Alzate et al. 2012; Keymer et al. 2013; Frigon et al. 2013). In tests with 20 different algal strains, gas production was in average $(329 \pm 43) \text{ m}^3_{\text{CH}_4}/\text{t}_{\text{VS}}$ and no significant differences were found between marine and freshwater strains; it was also observed that final ammonium concentration in batch operation stayed well below inhibitory concentrations (Frigon et al. 2013).

Lipid extraction before digestion increases biomass solubilization, methane yield and methane production rate substantially: in comparison to raw algae digestion, digestion of residual algal mass after hexane-based lipid extraction shows a 2.5-fold increase in COD solubilization, 33 % increase in specific methane production per volatile solids added and 33 % increase in digestion rate. This is accounted for cell disruption and possible biomass degradation. (Keymer et al. 2013)

Similarly, different pretreatment methods can be utilized to enhance digestion properties: Thermal pretreatment has been shown to increase methane yield in algae digestion by 46 % to 62 % (Alzate et al. 2012), while only 33 % increase has been detected with thermochemical treatment (P. H. Chen and Oswald 1998). High-pressure thermal pretreatment has been demonstrated to increase methane yield by 81 % over digestion of untreated raw algae and 58 % over lipid-extracted algal matter (Keymer et al. 2013). 6 % to 24 % methane yield increase has been achieved with ultrasound treatment, whereas biological treatment showed no significant effect (Alzate et al. 2012).

There are few studies about nutrient distribution after anaerobic digestion of microalgae: Alcántara, García-Encina and Muñoz (2013) illustrate that 59 % of nitrogen and 89 % of phosphorus in the algae are converted to dissolved form during digestion and the rest remain in solid phase; then again Keymer et al. (2013) observe that 43 % of nitrogen and 25 % of phosphorus are soluble after digestion. Lipid extraction and high-pressure thermal pretreatment both increased the amount of soluble nitrogen after digestion to 56 % and combination of the aforementioned to 66 %; high-pressure thermal pretreatment decreased dissolved phosphorus fraction after anaerobic digestion to 20 %, lipid extraction increased it to 33 % and both manipulations together to 40 % (Keymer et al. 2013). The large differences in phosphorus distribution to solid and aqueous form might be partially explained with possible pH differences, as phosphate solubility is dependent on pH (Wahal 2010; Keymer et al. 2013).

3.5 Fertilizer production

A great majority of plants require sixteen elements for balanced growth: carbon (C) from the air, hydrogen (H) and oxygen (O) from the water and nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo) and chlorine (Cl) from the soil. The elements that are acquired from soil can be grouped to *macronutrients*, which are needed in large amounts and *micronutrients* or *trace elements* that are only required in minute amounts. Macronutrients are further divided to *primary nutrients* (N, P, K) and *secondary nutrients* (Ca, Mg, S). In addition to these, other elements are taken up, which may be beneficial nutrients for some plants but are not essential to all. (FAO and IFA 2000)

To optimize growth conditions, all nutrients must be present in correct amounts for the crop. A nutrient cannot be substituted by any other and the nutrient that is most deficient will limit yield or affect quality. On the other hand, if some nutrient is present in excessive amounts, it will not promote further growth but it is likely to be lost to the environment. (FAO and IFA 2000)

Fertilizers are additives that are used to replenish or enhance nutrient stock in agricultural soil. By definition, they contain at least 5 % of one or more of the three primary nutrients (FAO and IFA 2000). Fertilizers can be divided to organic and inorganic (mineral) fertilizers that might have fossil or renewable inputs. The main source of nitrogen present in fertilizers is urea, followed by ammonium sulphate and calcium ammonium nitrate (FAO and IFA 2000). Nitrogen fertilizers are most often made from ammonia, whose production covers 87 % of the fertilizer industry's total energy consumption; as a whole 1.2 % of world's energy is consumed in fertilizer production (IFA 2009). The production of ammonia occurs usually via ammonia synthesis or *Haber-Bosch process*:



where the hydrogen comes usually from synthesis gas — a mixture of carbon monoxide and hydrogen — and nitrogen is separated from air. In Europe, synthesis gas for ammonia production originates mainly from steam reforming of natural gas or other light hydrocarbons, or gasification of heavy fuel oil. (EFMA 2000) Raw materials for majority of phosphate and potassium fertilizers occur in natural deposits; phosphate rock and potash are first mined and then further processed to commercial products (UNIDO 1988, Chapter 3). Multi-nutrient fertilizers are produced either in chemical reactions between substances containing the desired nutrients or are mixtures of single-nutrient fertilizers (FAO and IFA 2000).

Due to large energy requirement in fertilizer production and increasing scarcity of minerals — particularly phosphate rock — there is growing interest in renewable

and organic fertilizers. Substituting conventional fertilizers may also result in significant economic and ecological benefits. (Vaneekhaute et al. 2013) Organic fertilizers are derived from animal or vegetable matter and their composition can vary a lot, depending on the feedstock. The nutrient content in organic fertilizers is generally lower in comparison to mineral fertilizers²¹, but for instance solid residue from biomass digestion can also be used as a soil conditioner (Collet et al. 2011).

3.6 Biogas cleaning and upgrading

Biogas that originates from anaerobic digestion may contain multiple trace components in addition to the main constituents methane (CH₄) and carbon dioxide (CO₂). In order to use the biogas in demanding applications, some or all of these trace components have to be removed and the carbon dioxide amount reduced. Different methods for gas cleaning and upgrading are used, depending on the final use of the product and original impurity content of the gas. Biomethane — as the end product may be called — can be used as a replacement for natural gas; it contains typically 95 % to 97 % CH₄ and 1 % to 3 % CO₂. (Ryckebosch, Drouillon and Vervaeren 2011)

Biogas cleaning usually includes removal of water, hydrogen sulphide (H₂S), siloxanes, halogenated carbon hydrates, oxygen and ammonia (NH₃) or some of the aforementioned, after which upgrading is performed by removing the CO₂. Water can be condensed out of the gas or it can be removed with chemical methods. H₂S can be removed during digestion by controlling air dosage or by adding iron chloride, or after digestion using chemical, physical or biological methods. Similarly, there are many ways to remove siloxanes: absorption, adsorption and cryogenic separation can be used. Halogenated carbon hydrates can be removed with activated carbon, while oxygen and nitrogen can be removed using membrane separation or low temperature pressure swing adsorption (PSA). However, gas removal with these methods is costly and preventing air introduction to digester is much cheaper than treating the gas. In large-scale cleaning processes, NH₃ is usually removed by scrubbing, but in smaller scale the removal may also be done with activated carbon. Some CO₂ removing processes, such as absorption and adsorption processes with water, also eliminate NH₃ and hence separate removal is not necessary. (Ryckebosch, Drouillon and Vervaeren 2011)

Carbon dioxide content can be reduced in multiple ways: physical and chemical absorption, pressure swing adsorption (PSA) and vacuum swing adsorption (VSA), cryogenic separation, membrane separation and biological enrichment may be used in the upgrading process. Many of these also remove some trace components and thus reduce the number of required cleaning steps: water scrubbing removes H₂S

²¹See for example Palm, Myers and Nandwa 1997; Zublena, Baird and Lilly 1997.

and scrubbing with polyethylene glycol²² removes organic sulphur components, H₂S, NH₃ and water. Pressure swing adsorption and vacuum swing adsorption can remove water vapour, oxygen and nitrogen from the methane; selectivity for different impurities is adjusted by varying mesh sizes and pressure levels. Because gases and impurities liquefy at different temperature and pressure conditions and because liquid CO₂ acts as a solvent, cryogenic separation can be used to remove practically all unwanted components. Membrane separation selectivity is dependent on the membrane material and operating conditions; similarly efficiency and selectivity of biological treatment systems vary with the utilized organism and operating conditions. (Ryckebosch, Drouillon and Vervaeren 2011)

In many cases, scale of operation will partly determine most appropriate process combination, since investment and operational costs need to be taken into account. Processes that are currently used in large-scale plants have prohibitive prices for small installations (Mann et al. 2009; Warren 2012), but for example microalgae is researched as a low-cost option to remove carbon dioxide and H₂S from biogas (Mann et al. 2009; Sialve, Bernet and Bernard 2009). Water scrubbing and pressure swing adsorption are the most common upgrading methods at least in German (Urban, Girod and Lohmann 2009) and in Swedish market (Persson 2003), while in the Netherlands membrane technology is used in addition to the two aforementioned techniques (Ryckebosch, Drouillon and Vervaeren 2011).

²²Sold with trade name Selexol™

4 Materials and methods

4.1 Case study

In this thesis, one biorefinery process will be analysed thoroughly. The process units and their coupling are based on previous concepts on the process as well as other biorefinery processes and project partners' experience on relevant processes. The proposed process is in its development stage and further research has to be conducted in order to find an optimal configuration.

4.1.1 Description of proposed biorefinery process

The proposed process is presented in Figure 4.1. Wastewaters enter the wastewater treatment plant and are treated as was described in Section 2.3. In this case however, primary and secondary sludge are not mixed after settling, but dewatered and removed separately. Primary sludge is directed to thermal drying and burning, while secondary sludge or waste activated sludge (WAS) is taken to anaerobic digestion.

In the digestion stage a part of waste activated sludge (WAS) is converted to methane and some of the nutrients in the incoming matter are released into soluble form. After digestion the stream is taken to hygienization due to the organic wastewaters and the desire to produce food grade products in the process. Biogas that is produced during digestion is collected and upgraded.

After hygienization the digested stream is directed to dewatering, where the water content is reduced and the dewatered stream is taken to fertilizer production via thermal drying. Fly ash from boilers is separated into fine and coarse fractions and the heavy-metal rich fine fraction is removed as reject. Accept is mixed with the digested solids in order to produce fertilizer.

Liquid effluent from dewatering is used as growth medium for algae in photobioreactors. The algae consume nitrogen and phosphorus in the effluent and carbon dioxide in flue gases that come from the boilers. As the algae grow, they produce oxygen, which is removed from the reactors and which is then used in the bleaching process at the chemical pulp mill.

A more detailed diagram of the algae production is presented in Figure 4.2. Here, digester effluent, algae and eventual additional nutrients are mixed and carbon

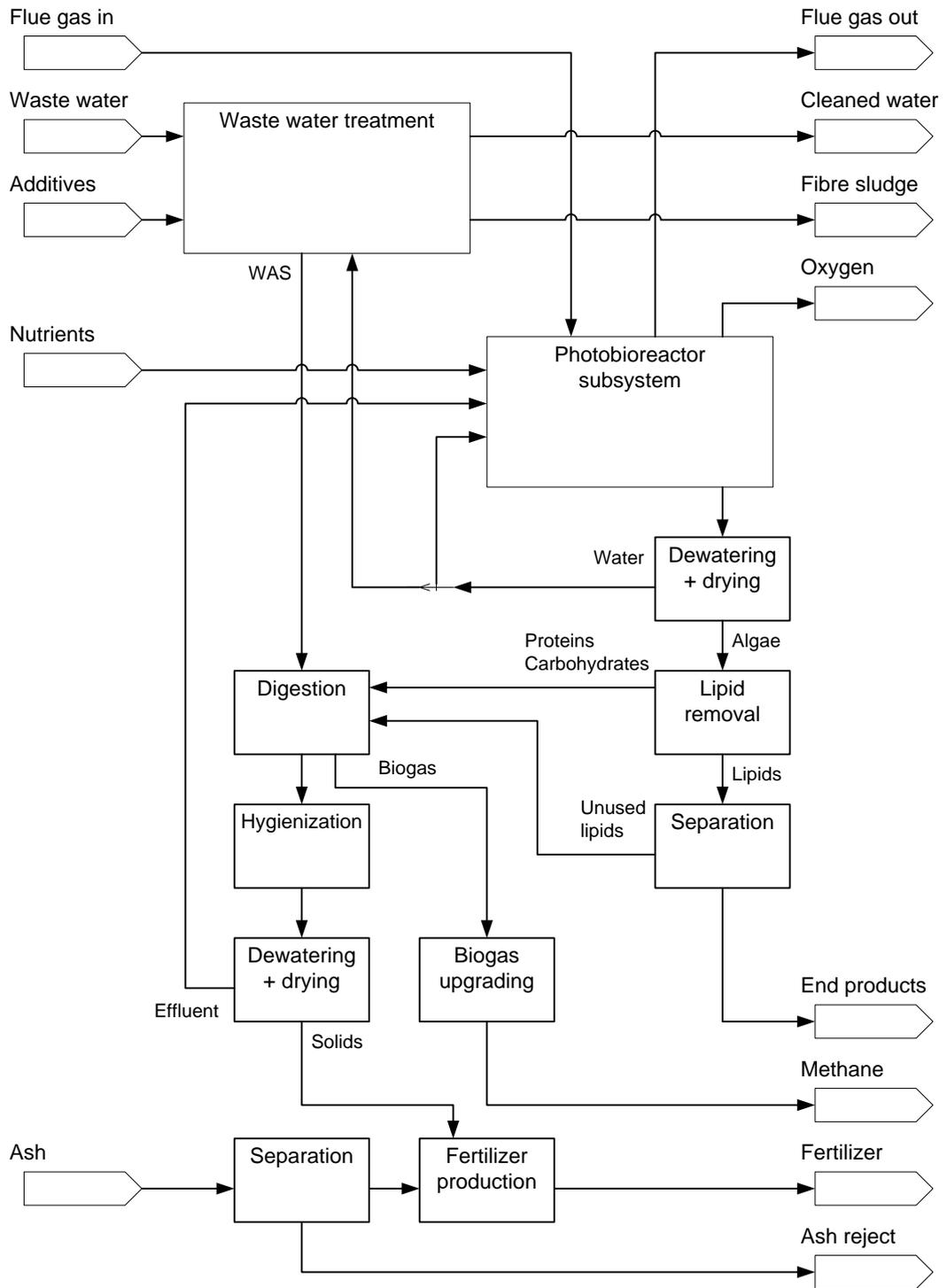


Figure 4.1: Schematic process diagram of proposed biorefinery process

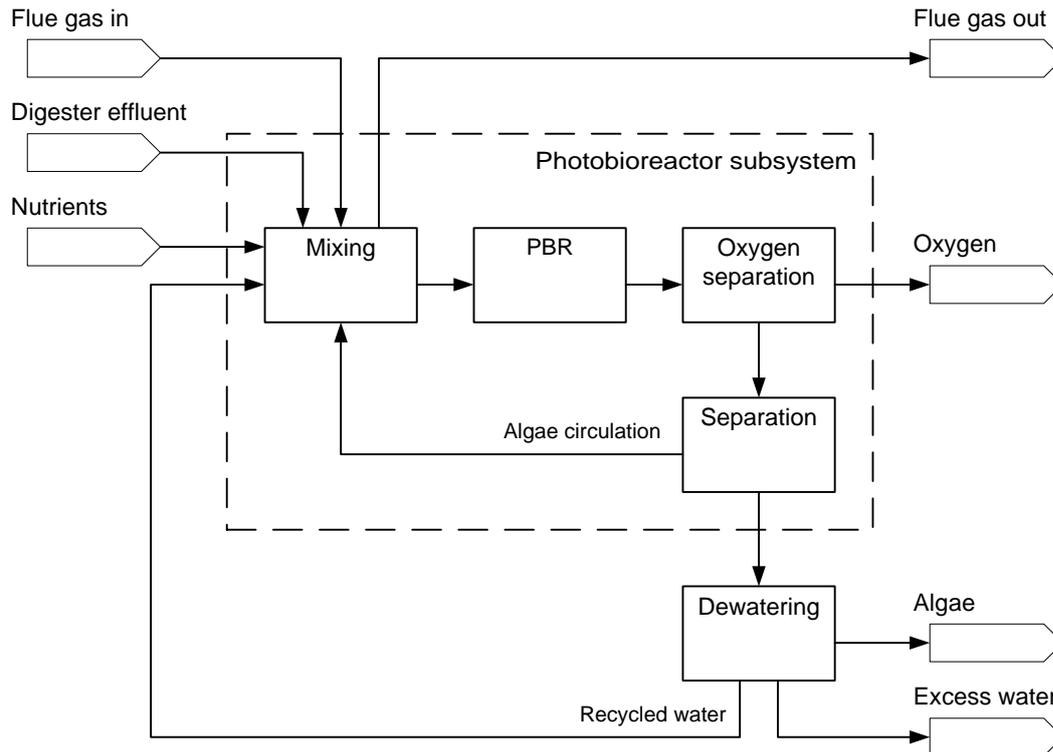


Figure 4.2: Schematic process diagram of photobioreactor (PBR) subsystem.

dioxide is added to the stream by bubbling flue gases through the liquid. The stream is directed into the photobioreactors, where algae is grown until some nutrient is depleted from the initial stream. At this stage, oxygen produced by algae is removed from this stream. Some of the stream is now directed to dewatering while most is taken back to circulation to ensure continuous algal growth.

After the grown algae is removed from the photobioreactor, excess water is removed from the stream. Some water is directed back to the growth cycle to dilute the digester effluent stream and to balance the algal growth target concentration after photobioreactors; the rest is taken to wastewater treatment plant. Now, lipids are removed from the algal stream and after this ω -3 fatty acids are separated from lipids. The remaining components are returned to digestion.

4.1.2 Motivation for the chosen process scheme

The biorefinery is designed to produce as many valuable products as possible. The most desired products are algae-derived goods, such as ω -3 fatty acids, then biofertilizers and finally biogas or biomethane. It is anticipated that digester

effluent will provide a good substrate for the algae and little or none additional nutrients are needed. Excess heat from the pulp and paper integrate can be used in photobioreactor, digester, hygienization and other stages that require heat input and thus the process economy would be enhanced when compared to a stand-alone process. Photobioreactors are chosen instead of other algae cultivation methods in order to prevent contamination, increase controllability and to allow capture of produced oxygen.

In the process all streams are used to their full extent: algae residue is taken back to digestion in order to maximize methane production, fibre sludge is burned in boilers and ash reject is intended to be used as an additive in concrete production. Integration enhances process economy compared to existing situation: for example, fibre sludge can be dewatered to higher total solids content than mixed sludge and thus its heating value will be higher; ashes on the other hand can be used as a valuable product instead of disposing of them when they can be no more used in the current land filling application.

4.2 Process calculations

4.2.1 Digester

Biogas output is calculated based on measured volumetric methane production potential per mass unit of waste activated sludge (WAS) (V_{CH_4}/m_{VS}):

$$\dot{V}_{CH_4} = \dot{m}_{WAS} \cdot x_{VS} \cdot \frac{V_{CH_4}}{m_{VS}}, \quad (4.1)$$

where \dot{V} is volumetric flow rate, \dot{m} mass flow rate and $x_{VS} = m_{VS}/m_{WAS}$ measured volatile solids (VS) content in WAS. The total gas amount is calculated based on biogas composition,

$$\dot{V}_{biogas} = \frac{\dot{V}_{CH_4}}{x_{CH_4}}, \quad (4.2)$$

where x_{CH_4} is volume fraction of methane in the biogas.

For the algae components that are recirculated back to the digester, methane and carbon dioxide production are calculated with Equation (3.2), under the assumption that only some percentage of the algal mass has time to react and the remainder will pass through. When mass flow rates of each algae component are known, the molar flow rates \dot{n}_i are calculated as

$$\dot{n}_i = \frac{\dot{m}_i}{M_i}, \quad (4.3)$$

where M_i is the molar mass of component i . The molar flow rates of gaseous products that are calculated with Equation (3.2) are then converted back to mass and volumetric flow rates with Equation (4.3) and ideal gas law

$$pV = nRT , \quad (4.4)$$

where p is pressure, $R = 8.314 \text{ J/mol K}$ universal gas constant and T temperature. When calculating gas volumes, standard temperature and pressure¹ are used.

Volatile solids reduction percentage in WAS digestion can be calculated based on assumed WAS composition, theoretical methane production potential from Equation (3.2) and measured methane production in digestion tests². The measured methane yield is converted to mass units with Equation (4.4) and the theoretical yield becomes

$$\frac{m_{\text{CH}_4}}{m_{\text{VS}}} = \frac{M_{\text{CH}_4}}{M_{\text{WAS}}} \cdot \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right) , \quad (4.5)$$

where coefficients n , a , b and c come from the composition of WAS, $\text{C}_n\text{H}_a\text{O}_b\text{N}_c$ — similarly to Equation (3.2). As the theoretical yield describes how much methane would be produced if all volatile solids were reacted, VS reduction percentage in digestion can be expressed as a fraction of actual and theoretical production:

$$x_{\text{VS red.}} = \frac{(m_{\text{CH}_4}/m_{\text{VS}})_{\text{actual}}}{(m_{\text{CH}_4}/m_{\text{VS}})_{\text{theoretical}}} . \quad (4.6)$$

The distribution of nutrients in WAS digestion can be calculated based on the data on nutrient content of the WAS and on measured nutrient content in digester effluent from digestion tests. Assuming that all nutrients will go to the liquid effluent or solid residue, the mass balance for nutrient i becomes

$$\begin{aligned} m_{i,\text{in}} &= m_{i,\text{aq}} + m_{i,\text{s}} \\ \iff m_{\text{WAS}} \cdot x_{i,\text{WAS}} &= \frac{m_i}{V_{\text{effluent}}} \cdot \frac{V_{\text{effluent}}}{m_{\text{WAS}}} \cdot m_{\text{WAS}} + m_{i,\text{s}} , \end{aligned} \quad (4.7)$$

where $x_{i,\text{WAS}}$ is the mass fraction of nutrient i in WAS and m_i/V_{effluent} measured content of nutrient in effluent. Abbreviation ‘aq’ stands for aqueous phase and ‘s’ for solid phase. Volume of the effluent is calculated according to what is written later in this section, but it will be very close to the amount of liquid in the incoming WAS. Hereby the fraction of nutrients that go with the liquids and solids are following:

$$x_{i,\text{aq}} = \frac{m_{i,\text{aq}}}{m_{i,\text{in}}} \quad (4.8)$$

$$x_{i,\text{s}} = \frac{m_{i,\text{s}}}{m_{i,\text{in}}} . \quad (4.9)$$

¹ $T = 273.15 \text{ K}$, $p = 10^5 \text{ Pa}$ (IUPAC 1997)

²See Section 4.3.2

For algae digestion, published data about nutrient distribution is used instead of Equations (4.8) and (4.9).

In order to calculate the potential algae growth and fertilizer composition, the absolute nutrient flows in the digester have to be analysed. It is assumed that there is no loss of nitrogen and phosphorus and they will be distributed in the solid and dissolved phases according to the previously calculated ratios. The nutrient content in algal streams is calculated based on the assumed chemical composition.

All solid matter is assumed to be transferred into the solid fraction during dewatering of the digested sludge, except for the portion which is converted to gas in the digester. For algae that amount is estimated based on Equation (3.2) and volatile solids reduction percentage in digestion. For WAS the reduction of mass is calculated in a similar way, assuming a chemical composition for the organic fraction and calculating the changes in mass with Equation (3.2) under the assumption that the mass portion of reduced WAS is equal to previously calculated VS reduction percentage in digestion.

In addition to the solids, some liquids and consequently also dissolved nutrients will go with the solids — their amount is determined by the achievable solids content in dewatering. Because total solids content is defined as

$$y = \frac{m_{\text{solids}}}{m_{\text{total}}} = \frac{m_{\text{solids}}}{m_{\text{solids}} + m_{\text{water}}} , \quad (4.10)$$

water flow rate in solid stream can be expressed as

$$\dot{m}_{\text{water}} = \dot{m}_{\text{solids}} \frac{1 - y}{y} . \quad (4.11)$$

Mass flow of dissolved nutrient i in solid stream is then

$$\dot{m}_i = \dot{m}_{i, \text{total dissolved}} \frac{\dot{m}_{\text{water, solid stream}}}{\dot{m}_{\text{water, total}}} , \quad (4.12)$$

where total mass flow rate of nutrient i is calculated with estimated nutrient distributions for WAS and algae digestion as well as incoming nutrient amounts, mass flow rate of water in solid stream is calculated with Equation (4.11) and total mass flow rate of water is calculated based on the amount of influent water to the digester. In the total water flow calculation, reduction in water amount is calculated similarly to solids reduction in digestion, using Equation (3.2) and the VS reduction percentages.

The water and nutrient amounts that go with the liquid effluent are simply calculated as the difference of incoming water and nutrient flows and the respective flows exiting with solid residue that were calculated with Equations (4.11) and (4.12).

4.2.2 Photobioreactor

Algae is considered to consist of lipids, carbohydrates and proteins. The amount of each element i in algal mass can be calculated based on the composition of component j and the fraction of that component in dry matter of algae, x_j :

$$\begin{aligned}
 \frac{m_i}{m_{\text{algae}}} &= \frac{\sum_j (m_j m_{i/m_j})}{m_{\text{algae}}} \\
 \Leftrightarrow \frac{m_i}{m_{\text{algae}}} &= \frac{\sum_j (m_{\text{algae}} x_j m_{i/m_j})}{m_{\text{algae}}} \\
 \Leftrightarrow \frac{m_i}{m_{\text{algae}}} &= \sum_j \left(x_j \frac{m_i}{m_j} \right) \\
 \Leftrightarrow \frac{m_i}{m_{\text{algae}}} &= \sum_j \left(x_j \frac{n_{ij} M_i}{\sum_i (n_{ij} M_i)} \right), \quad (4.13)
 \end{aligned}$$

where n_{ij} stands for number of atoms of element i in the stoichiometric formula of component j and M_i for the molar mass of element i .

It is assumed that algae will use nutrients in their growth according to their composition; consumption of nutrient i can be thus expressed with algae growth rate \dot{m}_{algae} and proportion of nutrient i to algae dry matter:

$$\dot{m}_i = \dot{m}_{\text{algae}} \frac{m_i}{m_{\text{algae}}}. \quad (4.14)$$

Hence maximum growth rate of algae can be determined when mass flows of nutrients and carbon are known:

$$\dot{m}_{\text{algae}} = \max_i \left(\frac{\dot{m}_i}{m_i/m_{\text{algae}}} \right). \quad (4.15)$$

Nutrients originate from digester effluent and eventual nutrient addition; carbon originates from carbon dioxide in flue gas. Only nitrogen and phosphorus are used in determining the possible growth rate; other nutrients are not taken into account. Some amount of carbon could be attained from organic compounds in the digester effluent and readily dissolved carbonates, but their effect is neglected as the aim is to estimate the upper limit for flue gas consumption and to assess flue gas sufficiency. In steady state operation algal growth rate from Equation (4.15) equals mass flow rate of biomass that is removed from the system.

Photobioreactor volume V_{PBR} is estimated from volumetric growth rate μ of algae:

$$\begin{aligned}
 \mu &= \frac{\dot{m}_{\text{algae}}}{V_{\text{PBR}}} \\
 \Leftrightarrow V_{\text{PBR}} &= \frac{\dot{m}_{\text{algae}}}{\mu}. \quad (4.16)
 \end{aligned}$$

Algal growth rate can also be expressed with the algae mass concentration γ before and after photobioreactor and the volumetric flow rate of water in the reactor:

$$\dot{m}_{\text{algae}} = \dot{V} (\gamma_{\text{out}} - \gamma_{\text{in}}) , \quad (4.17)$$

where $\gamma = m/V$ and ‘in’ and ‘out’ refer to algae concentration at photobioreactor inlet and outlet. Thus volumetric flow rate of water in the reactor is

$$\dot{V} = \frac{\dot{m}_{\text{algae}}}{\gamma_{\text{out}} - \gamma_{\text{in}}} . \quad (4.18)$$

As this can be formulated with inner cross-sectional area A_i of each photobioreactor tube, flow speed v in reactor tubes and number of tubes N :

$$\dot{V} = NA_i v , \quad (4.19)$$

the number of tubes can be obtained as

$$N = \frac{\dot{V}}{A_i v} . \quad (4.20)$$

The area is expressed with the internal diameter d_i of the tubes:

$$A_i = \pi \left(\frac{d_i}{2} \right)^2 . \quad (4.21)$$

Correspondingly the length of the photobioreactor tubes can be calculated when the relationship between volume of the reactor V_{PBR} , number of tubes, inner cross-sectional area and length l of individual tube is known:

$$\begin{aligned} V_{\text{PBR}} &= NA_i l \\ \iff l &= \frac{V_{\text{PBR}}}{NA_i} . \end{aligned} \quad (4.22)$$

Photobioreactor can be approximated as an ideal plug flow reactor, where residence time in reactor would be

$$\tau = \frac{V_{\text{PBR}}}{\dot{V}} = \frac{l}{v} . \quad (4.23)$$

This assumption implies that there is no mixing in axial direction. However, in a real photobioreactor good mixing is desired and residence time distribution will not be as uniform as it is in the ideal model.

A flow can be characterized as turbulent or laminar based on Reynolds number, a dimensionless number that indicates a ratio of inertial forces to viscous forces in the flow. For $Re < 2000 \dots 2300$, the flow is considered to be laminar and for approximately $Re > 10\,000$ fully turbulent; between those the flow is called to be

transitional (Suryanarayana 1995, Chapter 4). For circular pipe, Reynolds number is defined as

$$\text{Re} = \frac{vd_i}{\nu} , \quad (4.24)$$

where ν is kinematic viscosity of the fluid.

The mass concentration of element i in the photobioreactor liquid can be expressed as a function of time with Equations (4.14) and (4.16):

$$\gamma_i(t) = \gamma_{i,0} - \mu \frac{m_i}{m_{\text{algae}}} t , \quad (4.25)$$

assuming that growth rate of algae can be maintained at a constant level throughout the reactor. Here γ is mass concentration and μ volumetric growth rate of algae. For oxygen that is produced in the photosynthesis according to Equation (3.1), Equation (4.25) can be transformed to

$$\gamma_{\text{O}_2}(t) = \gamma_{\text{O}_2,0} + \mu \frac{m_{\text{C}}}{m_{\text{algae}}} t . \quad (4.26)$$

The growth rate of algae is very likely to decrease with increasing oxygen concentration and increasing algal concentration, but Equations (4.25) and (4.26) will likely hold true for small oxygen and algae concentrations. At photobioreactor output the previous equations can be written out as

$$\gamma_i(t=\tau) = \gamma_{i,0} - (\gamma_{\text{out}} - \gamma_{\text{in}}) \frac{m_i}{m_{\text{algae}}} \quad (4.27)$$

and

$$\gamma_{\text{O}_2}(t=\tau) = \gamma_{\text{O}_2,0} + (\gamma_{\text{out}} - \gamma_{\text{in}}) \frac{m_{\text{C}}}{m_{\text{algae}}} . \quad (4.28)$$

Hence, if maximum oxygen concentration at photobioreactor output is fixed, algae concentration at photobioreactor input can be solved:

$$\gamma_{\text{in}} = \gamma_{\text{out}} - \frac{\gamma_{\text{O}_2, \text{max.}} - \gamma_{\text{O}_2,0}}{m_{\text{C}}/m_{\text{algae}}} . \quad (4.29)$$

Flow rate of recycled water can be calculated from water balance for photobioreactor system:

$$\dot{m}_{\text{recycled water}} = \dot{m}_{\text{water flow to dewatering}} - \dot{m}_{\text{effluent}} , \quad (4.30)$$

where

$$\dot{m}_{\text{water flow to dewatering}} = \dot{m}_{\text{algae}} \frac{\rho_{\text{water}}}{\gamma_{\text{out}}} \quad (4.31)$$

and notations refer to Figure 4.2. Excess water flow rate is similarly

$$\dot{m}_{\text{excess water}} = \dot{m}_{\text{effluent}} - \dot{m}_{\text{water with dewatered algae}} \quad (4.32)$$

and $\dot{m}_{\text{water with dewatered algae}}$ can be calculated with Equation (4.11) where y is total solids content of algae after mechanical dewatering.

The amount of water that needs to be removed with thermal drying can be calculated from the known total solid target concentrations: water mass flow is

$$\dot{m}_{\text{evaporated}} = \dot{m}_{\text{water with dewatered algae}} - \dot{m}_{\text{water with dried algae}} , \quad (4.33)$$

where $\dot{m}_{\text{water with dried algae}}$ is again calculated with Equation (4.11). Required heat input is then

$$\Phi = \dot{m}_{\text{evaporated}} q , \quad (4.34)$$

where q is specific heat consumption in drying.

4.2.3 Fertilizer production

Solids flow rate of fertilizer is simply a sum of digester solid residue flow rate that was calculated in Section 4.2.1 and flow rate of ash accept fraction. Water contents in each stream are calculated with Equation (4.11) and the total flow rate of water at assumed fertilizer total solids content is also calculated with the same equation. If the total solids content of ready fertilizer product would be lower than given 80 %, water has to be removed thermally at a rate of

$$\dot{m}_{\text{evaporated}} = \dot{m}_{\text{water, actual}} - \dot{m}_{\text{water, optimal}} . \quad (4.35)$$

The heat input is then calculated with Equation (4.34).

Nutrient content in a fertilizer is often expressed as a N–P–K rating, which describes the mass fractions of elemental nitrogen, phosphate (P_2O_5) and potash (K_2O) in a fertilizer (Maguire, Alley and Flowers 2009). The fertilizer that is produced in this process does not have those inputs, but the content of elemental nitrogen, phosphorus and potassium are known, since nutrient content in solid digestion residue and fly ash are available. Thus, the P and K in a N–P–K rating are calculated by computing the masses of P_2O_5 and K_2O that correspond to the existing nitrogen and potassium content and calculating the share of those masses from total mass flow of produced fertilizer.

4.2.4 Calculation program

A calculation program is written using Python programming language³ to conduct process calculations. The calculations are performed in following order:

1. calculate digester outputs (biogas, solid residue, effluent)

³Python Software Foundation 2010.

Table 4.1: Properties of waste activated sludge from the examined mill

Dry matter flow rate	30 t/d
Total solids content	8 %
Nitrogen content in dry matter	5 %
Phosphorus content in dry matter	0.6 %

2. calculate possible algal growth rate based on composition of algae and growth medium
3. calculate flow rates for ω -3 fatty acids, unused lipids and lipid-extracted algal matter
4. iterate over items 1 to 3, until relative difference in algae growth rate between iteration rounds is less than 10^{-6}
5. calculate photobioreactor properties
6. calculate fertilizer flow rate and composition.

Iteration is necessary, because possible algal growth rate is affected by addition of algal matter to digestion and the related nutrient circulation. The value of relative difference, which indicates that iteration has reached its end, has been chosen as a small enough value that is substantially smaller than error margin for input values but still allows calculation to be done in tolerable time.

4.3 Initial data used in process calculations

4.3.1 Data from the integrate

In these calculations waste activated sludge (WAS) flow is considered to have properties outlined in Table 4.1. The total solids content is higher than what it is after settling in the wastewater treatment plant, but the solids content is assumed to be raised with a separate dewatering stage.

Flue gases from two different boilers can be used; properties of the available flue gases are presented in Table 4.2. Total flow of ash from the same boilers is 32 000 t/a dry matter and there is 0.4 % moisture in the ash. In the accept fraction that will be used for fertilizer production, there is 1.17 % phosphorus and 1.21 % potassium by weight in dry matter.

Table 4.2: Available flue gas flows from fluidized bed boilers at the combined heat and power plant in standard temperature and pressure conditions. Carbon dioxide content in Boiler 5 flue gases is not measured.

		Boiler 5	Boiler 6
Wet flue gas flow rate	m ³ /s	102	57
Temperature	°C	63	155
NO _x content	mg/m ³	165	217
SO ₂ content	mg/m ³	58	95
CO ₂ content	%	–	11
H ₂ O content	%	23	24

4.3.2 Digestion tests of waste activated sludge

Anaerobic digestion of WAS was tested by Metener Oy in autumn 2012. A WAS sample from the forest industry integrate wastewater treatment plant was digested in a 2.2 m³ mesophilic, continuously stirred tank reactor (CSTR) for 24 days at (37 ± 1) °C. Total solids content of the WAS was measured to be 1.5 % of the influent and volatile solids (VS) content 77.7 % of the total solids. In the experiments volumetric organic loading rate was kept at approximately 0.5 kg_{VS}/m³ and the hydraulic retention time was hence 22 days. Methane content of the product gas was 64 % to 67 % and the yield of methane was 2.1 m³/t of wet WAS, corresponding to 172 m³/t of VS added. (Luostarinen 2012)

Liquid effluent from digestion experiment was also measured for various properties. The measurements showed phosphorus content to be 26 mg/l and total soluble nitrogen content 570 µg/l. (Hokkanen 2013)

4.3.3 Assumptions

Many estimations are made in the calculations about how processes work, how high is their conversion efficiency and what is the input streams' composition. The main numerical assumptions for calculations are listed in Table 4.3 and are briefly presented in current section.

In the existing wastewater treatment plant the WAS exits in approximately 1 % total solids content. This is rather low and it is anticipated that digestion would be more efficient if the solids content of the influent would be 6 % to 8 %: the loading rate of the digester would be higher and thus smaller reactor size can be achieved while holding the throughput constant (Luostarinen 2012). Consequently, the solids content for WAS flowing into the digester has been chosen to be at 8 %. This will be

Table 4.3: Numerical assumptions for the calculations

WAS solids content	8 %
WAS composition	$C_5H_7NO_2$
Digested solids dry matter content after dewatering	30 %
Heat consumption in thermal drying	3500 $\text{kJ}/\text{kg}_{\text{water}}$
Fertilizer total solids content	80 %
Ash accept fraction in classification	75 %
Algae VS reduction percentage in digestion	50 %
Component share of algae dry mass	
– carbohydrates	30 %
– lipids	15 %
– proteins	55 %
Algae component composition	
– carbohydrates	$C_6H_{10}O_5$
– lipids	$C_{57}H_{104}O_6$
– proteins	$C_6H_{13.1}ON_{1.6}P_{0.1}$
Lipid recovery percentage	80 %
ω -3 fatty acid share of lipids	30 %
Nutrient released to aqueous form during algae digestion	
– nitrogen	50 %
– phosphorus	60 %
Reynolds number in photobioreactor tubes	10 000
Photobioreactor tube diameter	32 mm
Volumetric growth rate of algae	2 $\text{kg}/\text{m}^3 \text{ d}$
Maximum concentration of algae in photobioreactor	6 kg/m^3
Oxygen concentration at photobioreactor input	8 g/m^3
Maximum oxygen concentration in photobioreactor	24 g/m^3
Algal stream solids content after dewatering	25 %
Algal stream solids content after thermal drying	90 %

achieved with additional mechanical dewatering or rearranging existing dewatering equipment in the wastewater treatment plant.

While the chemical composition of WAS is not necessary to know for gas production calculations, it can be used in estimating the solid matter flow out of the digester. For these calculations, it is presumed that the volatile solids (VS) fraction of WAS consists of microbial matter, whose computational composition is $C_5H_7NO_2$. This composition was first presented by Hoover and Porges (1952) and it appears to be widely used⁴.

To calculate the water and nutrient flow after digestion, some dryness has to be supposed for outflowing solids. The total solids content is assumed to be 30 % — same as for the combined sludge from current wastewater treatment process. If there is excess water in the solid residue stream so that the total solids content of ready fertilizer would decrease under 80 %, thermal drying is applied to the dewatered digested sludge in order to achieve the desired dryness. Water that is removed in thermal drying stage is assumed to exit the system. Heat consumption in thermal drying is considered to be 3500 kJ/kg for removed water. It is assumed that 75 % of the fly ash mass can be recovered as heavy-metal poor coarse fraction in classification and can thus be used in fertilizer production. Design criteria in fertilizer production is to utilize all available ash accept and digester residue.

All matter that goes into the digester is not fully digested but a part stays unreacted. The amount is dependent on the solids retention time and other parameters, but for recycled algae components the fraction of degraded solids is estimated to be 50 % of the incoming mass. For WAS the reduction percentage of volatile matter will be calculated based on theoretical and realized methane yield.

The algae composition is very much dependent on the species. At this stage of the project no specific algal strain is yet chosen, and hence assumptions have to be made regarding the composition. Based on published gross chemical composition of different algae (Becker 1994, Chapter 12), it is roughly estimated that the dry matter of algae consists of 30 % carbohydrates, 15 % lipids and 55 % proteins. It is assumed that 80 % of the lipids can be recovered in separation stage and 30 % of the lipids are ω -3 fatty acids. The stoichiometric composition of the components, as presented in Table 4.3, are taken from Sialve, Bernet and Bernard (2009), but nitrogen and phosphorus amount in proteins are corrected in order to have a carbon to nitrogen to phosphorus (C:N:P) molar ratio of 106:16:1 in dry algal mass. This ratio — so called 'Redfield ratio', named after Redfield (1934) — is commonly regarded as the average element distribution in marine biomass. These components of algae and their composition are used in calculations because different end products are anticipated to be separated from the algae.

⁴See e.g. Grady et al. 2011, Chapter 3.

It is assumed that all nutrients that come into digestion with the streams are distributed in solid and aqueous phase and that the proportion of these is dependent on the feed. How they are actually distributed depends on many factors — including algal species and solids retention time in the digester — but for these purposes it is assumed that 50 % of nitrogen and 60 % of phosphorus in algae are dissolved after digestion. These are rough averages of results obtained by Alcántara, García-Encina and Muñoz (2013) and Keymer et al. (2013). It is also assumed that nutrients in aqueous phase are in their inorganic form and nutrients in undissolved fraction are in organic compounds.

In the photobioreactor flow is kept at the lower limit of turbulent region to promote mixing but to limit shear stress to algae. Hence, Reynolds number of the flow is fixed at 10 000. To calculate the flow velocity, properties for pure water at 25 °C are used. Internal diameter of photobioreactor tube is chosen to be 32 mm. It is assumed that algae can grow at a rate of 2 kg/m³ d in the photobioreactors and that the final concentration will be 6 kg/m³ at maximum when the mass is extracted from the reactors. Oxygen concentration at photobioreactor inlet is assumed to be 8 g/m³ — the equilibrium concentration that will be achieved in contact with air at 25 °C. Maximum allowable oxygen concentration in photobioreactor is set at three times the value, 24 g/m³, which seems to be a decent limit⁵.

After cultivation, algae is first dewatered mechanically to 25 % solids content and the removed water is recycled; the algae is then dried thermally to 90 % solids content. All algae is considered to go into the solids fraction and the water that is removed in thermal drying is assumed to exit the system. The remaining water in the algal stream is presumed to go into digestion after lipid removal.

⁵See for instance Molina et al. 2001.

5 Results

During the analysis it was observed that calculated nitrogen concentration in waste activated sludge (WAS) digestion effluent is low in comparison to expected levels. The difference is assumed to be caused by volatilization of nitrogen in the effluent before measurement of nutrient levels. The lack of nitrogen in algae growth medium leads to minimal algal growth and hence also another case is analysed, in which nitrogen content is considered to be more reasonable. Investigated cases are the following:

Base case Assumptions and given values in Section 4.3 are used.

Modified case Similar to the base case, apart from solubility of nitrogen after WAS digestion, which is set at 28 %. This level allows all phosphorus that is released to effluent to be consumed by the algae without lack of nitrogen hindering growth. Similar effect could be achieved with 310 kg/a external nitrogen input to the photobioreactor.

5.1 Digestion

Based on data from WAS digestion tests, assumed WAS composition and Equation (4.6), volatile solids (VS) reduction in WAS digestion is determined to be 34 %. This is fairly well in line with previous pulp and paper mill WAS digestion experiments: for example Puhakka, Alavakeri and Shieh (1992) and Puhakka, Viitasaari et al. (1988) have experienced approximately 40 % VS reduction in thermophilic conditions and Bayr and Rintala (2012) achieved 29 % to 32 % reduction in VS.

Nutrient distribution in WAS digestion is calculated from Equation (4.8). The results are shown in Table 5.1: only 0.1 % of incoming nitrogen and 28 % of incoming phosphorus appear to be transferred into digester effluent. This is remarkably different from the distribution that can be calculated based on published nutrient flows in municipal WAS digestion (Zhang, Itakura and Matsuto 2012): 57 % of nitrogen and 64 % of phosphorus is dissolved according to that data. Assumptions for nutrient distribution in algae digestion are also presented for reference in Table 5.1.

Due to feedback of algal matter into the digester and the consequent nutrient recirculation, mass flows in digester–photobioreactor system have to be iterated until

Table 5.1: Share of dissolved nutrients after waste activated sludge (WAS) and algae digestion, as a proportion of total element mass in digester output.

Element		WAS ¹	WAS ²	Algae ³
N	%	0.1	57	50
P	%	28	64	60

¹ Based on calculations in Section 4.2.1.

² Based on Zhang, Itakura and Matsuto (2012)

³ Assumptions for calculations

the mass flows reach steady state. Table 5.2 shows outcomes of digestion without algal input and at the end of iteration. Potential algal growth rate in Table 5.2 was calculated based on nutrient flows in digester effluent and composition of algae, Equation (4.15).

It is obvious that algal growth that is enabled by released aqueous nutrients in the base case is substantially lower than the WAS input and thus algae recycling has no remarkable effect to digestion outcome. The only significant difference between no algal input and steady state digester operation lies in nitrogen flow rate within digester effluent, which is explained by the assumed larger nitrogen solubility after digestion of algae — in these calculations it was assumed that nutrient distribution in digestion is dependent only on the digested matter and separate percentages were used for WAS and algal mass.

Results for the modified case are also shown in Table 5.2. Most importantly, possible algal growth rate is substantially larger than in the base case; methane output is also somewhat larger and the amount of solid residue has increased slightly. The effect of nutrient recycling can be seen in nitrogen and phosphorus balance: because most of N and P in the effluent are metabolized by the algae and they are recirculated back to digestion, the total nutrient amount in digester output has increased in comparison to the base case.

Energy content in the methane that is produced in digesters is small compared to propane usage in paper machines at the site: daily 2.8 t/a production covers approximately 7% of the energy requirement and 4.0 t/a is equivalent to 10% of what is currently used. Specific methane and biogas productions in algal residue digestion are 230 kg_{CH₄}/t and 520 m³/t, respectively. In the modified case, algal residue digestion accounts for 28% of produced methane.

Table 5.2: Digestion outcome without algal input and during steady state operation. Solid substance mass flow rates are reported on dry matter basis.

		Base case		Modified case	
		No algae	Steady	No algae	Steady
WAS input	t/d	30	30	30	30
Biogas output	m ³ /d	6200	6200	6200	8800
– CH ₄ output	t/d	2.8	2.8	2.8	4.0
– CH ₄ content	vol-%	0.65	0.65	0.65	0.64
Solid residue	t/d	22	22	22	24
– N flow rate	kg/d	1500	1500	1200	1500
– P flow rate	kg/d	140	140	140	180
Effluent	t/d	270	270	270	260
– N flow rate	kg/d	0.87	1.4	330	500
– P flow rate	kg/d	40	40	40	69
Possible algal growth	kg/d	9.0	15	3000	5100

5.2 Photobioreactor

Nitrogen concentration in digester effluent is very low in the base case and therefore target algal concentration of 6 kg/m³ cannot be reached: nutrient availability limits maximum algae concentration to 0.055 kg/m³, or practically zero. It is evident that algae production would be unfeasible with this concentration and 15 kg/d total algal growth, but the outcomes are calculated and shown for reference.

If nutrient and algae concentrations were at normal levels that are used in algae cultivation systems, algae concentration at photobioreactor input would be restricted by maximum allowable oxygen concentration in the photobioreactor, as was formulated in Equation (4.29). However, calculations indicate that oxygen concentration will not be limiting in this case, because algal growth and associated oxygen production is low compared to water flow rate. Hence, minimum algae concentration at reactor input is set at arbitrary 80% of output concentration to show indicative results.

Algae production key numbers and photobioreactor configuration are presented in Table 5.3. Nutrient concentrations in photobioreactor circulation are shown in Figure 5.1 for the base case and in Figure 5.2 for the modified case. Product flows and input requirements are very small in the base case, but in the modified case the amounts are similar to current algae production plants: United States based company Alltech claims to own one of the largest algae production plants in the

Table 5.3: Algae production key numbers and photobioreactor configuration in standard conditions

		Base case	Modified case
Flue gas requirement	m ³ /d	180	61 000
– CO ₂ requirement	kg/d	30	11 000
Oxygen production	kg/d	16	5500
Algae growth	kg/d	15	5100
ω -3 lipid yield	kg/d	0.53	190
Heat input in algae drying	kW	1.7	600
Reactor volume	m ³	7.4	2600
Water flow rate	m ³ /s	0.016	2.1
Average flow speed	m/s	0.29	0.29
Residence time	s	470	1200
Tube length	m	140	350
Number of tubes		68	9100

world (Alltech 2013), whose reactor volume is 1200 m³ (Geiver 2011). Nevertheless, daily algae production would be little in comparison to paper production of the mill: algae production in the modified case is well under 1 % of the daily paper production capacity. Daily oxygen production in the photobioreactors would equal to 6 % of current oxygen production at the integrate air separation plant and the carbon dioxide utilization equals 0.7 % of what would be available from Boiler 5 at 11 % CO₂ content. See Table 4.2 for properties of available flue gases.

Estimated nutrient concentrations at the photobioreactor input are very low in comparison to general algae growth medium concentrations — apart from phosphorus concentration in the base case which is significantly higher. In BG-11 medium (University of Texas 2009) there is $250 \cdot 10^{-3}$ kg/m³ nitrogen and $6.8 \cdot 10^{-3}$ kg/m³ phosphorus, whereas anticipated nitrogen concentration in the base case is 0.4 % of this and phosphorus concentration 2200 % of what is in BG-11. In the modified case, where nitrogen solubility was altered in order to have right concentration of nitrogen in comparison to phosphorus, nitrogen concentration is 8 % and phosphorus concentration is 5 % of what it is in BG-11. The concentrations in the latter case are supposedly reasonable since they result from the assumption that algae will deplete the growth medium from some nutrient at the end of the growth cycle. However, the imbalance between nutrient concentrations in the base case is likely to cause problems and the stream would have to be diluted even more to reduce phosphorus

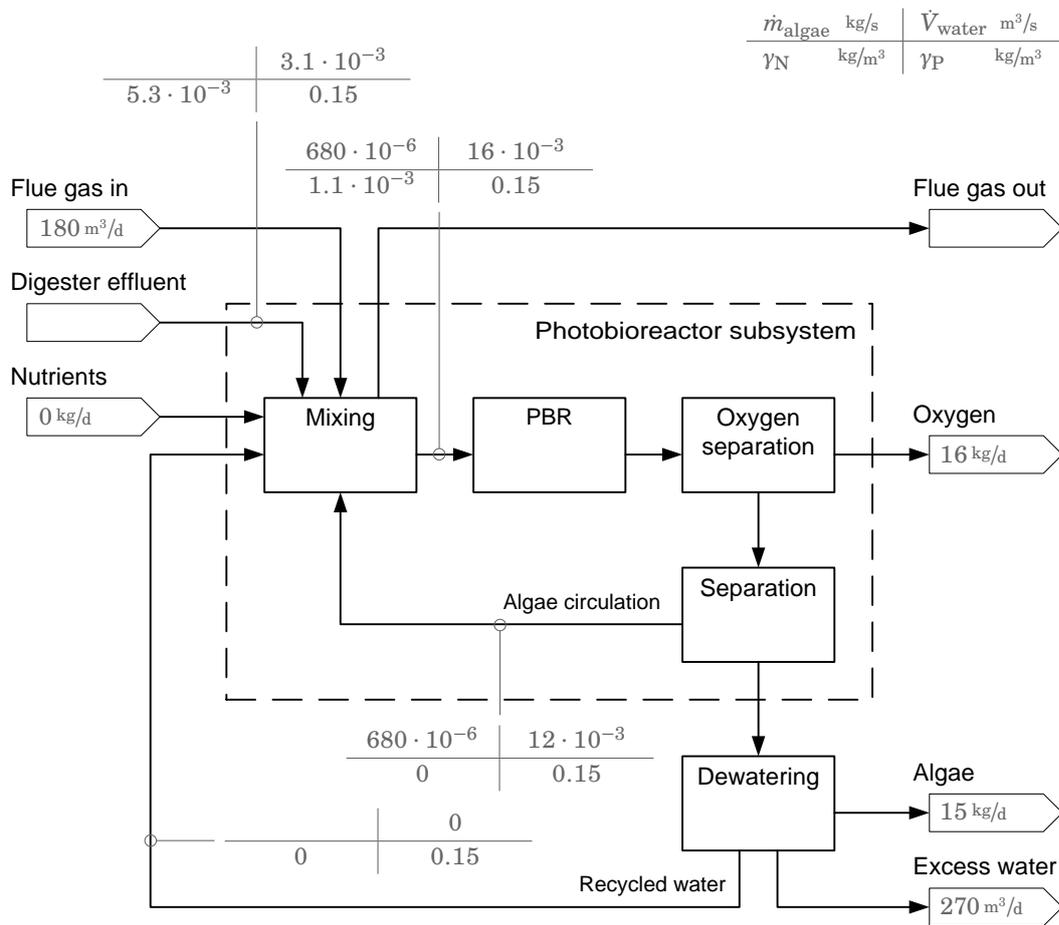


Figure 5.1: Photobioreactor flows (\dot{m} , \dot{V}) and nutrient mass concentrations (γ_i) in the base case

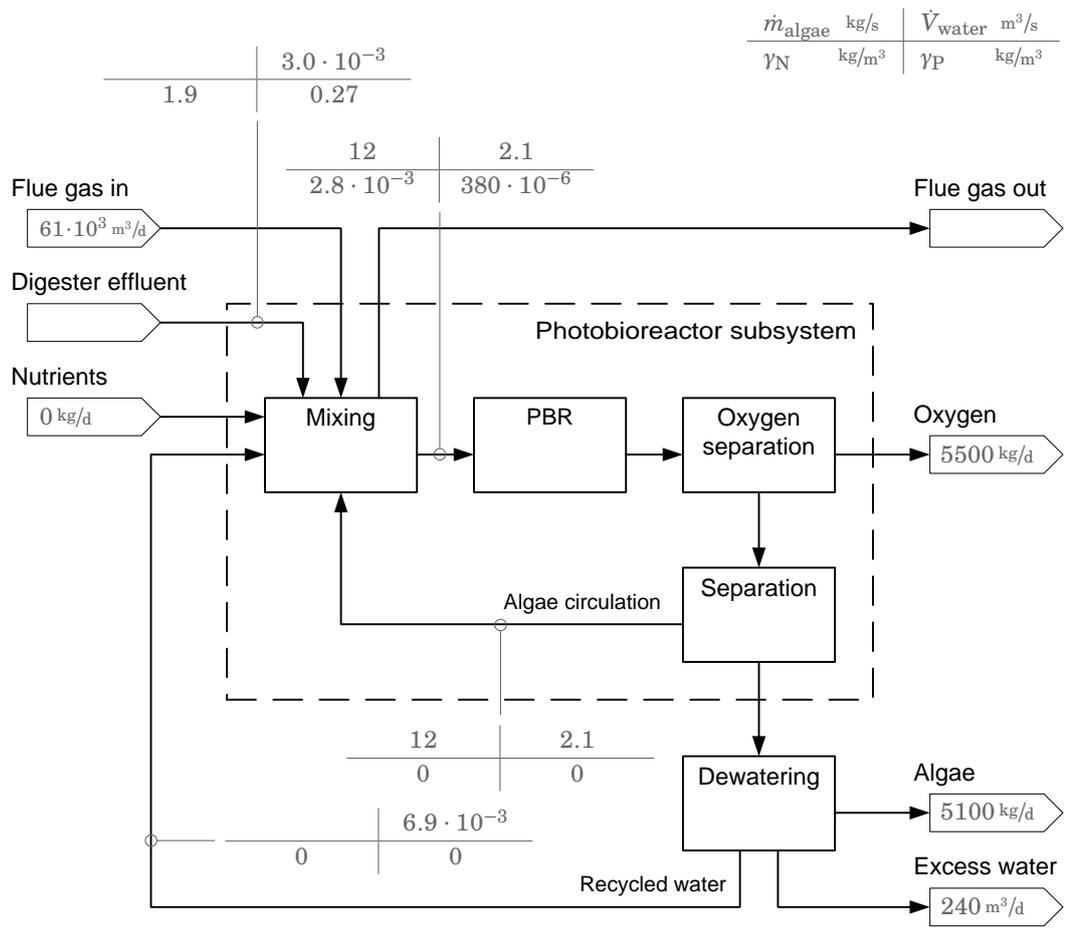


Figure 5.2: Photobioreactor flows (\dot{m} , \dot{V}) and nutrient mass concentrations (γ_i) in the modified case

concentration to an acceptable level. In the modified case, algae concentration at photobioreactor input was calculated to be 5.97 kg/m^3 .

Heat requirement in algae drying appears to be rather large in comparison to algae production, but small in comparison to availability of excess heat at the pulp and paper mill. Even though secondary heat is intended to be used in drying, a comparison to biogas and algae energy content gives an impression of the magnitude: the required heat input in the modified case is 26 % of the energy content in produced methane and 56 % of energy content in dry algae¹.

5.3 Fertilizer production

Fertilizer production seems to be quite stable and independent on the algae production. Because ash flow rates are constant and solid residue amount and composition are not altered much with algal input to digestion², the mass flow rate and composition of produced fertilizer are fairly static. Main calculation results of fertilizer production are displayed in Table 5.4. where nutrient content in produced fertilizer is presented as mass ratio to total fertilizer amount. In terms of N–P–K rating — as described in Section 4.2.3 — the nutrient content is 1.7–2.4–1.1 for both base case and modified case. All nitrogen in the fertilizer has its origin in waste activated sludge (WAS) and all potassium in ash; 16 % of phosphorus comes from WAS in the base case and 19 % in the modified case while the rest comes with the ash.

N–P–K rating for the produced fertilizer is lower but comparable to organic fertilizers that are currently on market: for example Biolan organic fertilizer that consists of composted chicken manure and powdered seaweed has a rating of 4–1.2–2 (Biolan Oy 2013a). Table 5.5 lists ratings for some fertilizers that are allowed in organic farming in Finland (Evisa 2012). A more elaborate summary of Finnish organic fertilizers, their composition and pricing from 2012 can be viewed in Finnish at agricultural magazine Käytännön Maamies website (Käytännön Maamies 2012).

Only values that differ notably between the cases are share of organic nutrients in the fertilizer and heat input to thermal drying of solid digester residue. The former is due to the assumption that all nutrients in aqueous form are inorganic while nutrients in solid phase are organic; in the base case practically no soluble nitrogen was present but in the modified case 28 % of nitrogen in WAS was released during digestion in soluble form. A part of soluble nitrogen enters the solid stream because dryness of solid residue was assumed to be 30 % after dewatering. The difference in heat requirement is mostly due to increased amount of solid residue that needs to be dried.

¹Assumed lower heating value of 18 MJ/kg for general dry biomass

²See Table 5.2

Table 5.4: Fertilizer production key numbers, dry matter

		Base case	Modified case
Ash flow rate	t/d	87	87
– accept	t/d	65	65
– reject	t/d	22	22
Fertilizer flow rate	t/d	88	90
Fertilizer composition			
– N	%	1.7	1.7
– P	%	1.0	1.1
– K	%	0.91	0.88
Share of organic compounds			
– N	%	100	89
– P	%	14	17
Heat input in drying	kW	1200	1400

Table 5.5: N–P–K ratings for some Finnish organic fertilizers (Berner Oy 2013a,b; Biokasvu Oy 2013a,b; Biolan Oy 2013a,b; Novarbo Oy 2013)

Marketer	Brand name	N	P	K
Berner Oy	GreenCare Luomu Yleislannoite	4	1	2
Berner Oy	GreenCare Luonnonlannoite	4	1	2
Biokasvu Oy	BioGreen 3–1–6	3	1	6
Biokasvu Oy	BioPelto 8–5–1	8	5	1
Biolan Oy	Biolan Luonnonlannoite	4	1.2	2
Biolan Oy	Biolan Yleislannoite	4	1	6
Novarbo Oy	Arvo 4–1–2	4	1	2
Novarbo Oy	Arvo 6–3–5	6	3	5
Novarbo Oy	Viljo 8–5–2	8	5	2

Heat requirement in digester residue drying is even larger than in algae drying: in the base case it corresponds to 73 % of energy content in produced methane and in the modified case heating power equals 61 % of energy content in produced methane and 130 % of energy content in produced dry algae. However, the heat requirement is low in comparison to available secondary heat at the site.

5.4 Total balance

Figure 5.3 shows a total balance for the proposed biorefinery in the base case; results for the modified case are depicted in Figure 5.4.

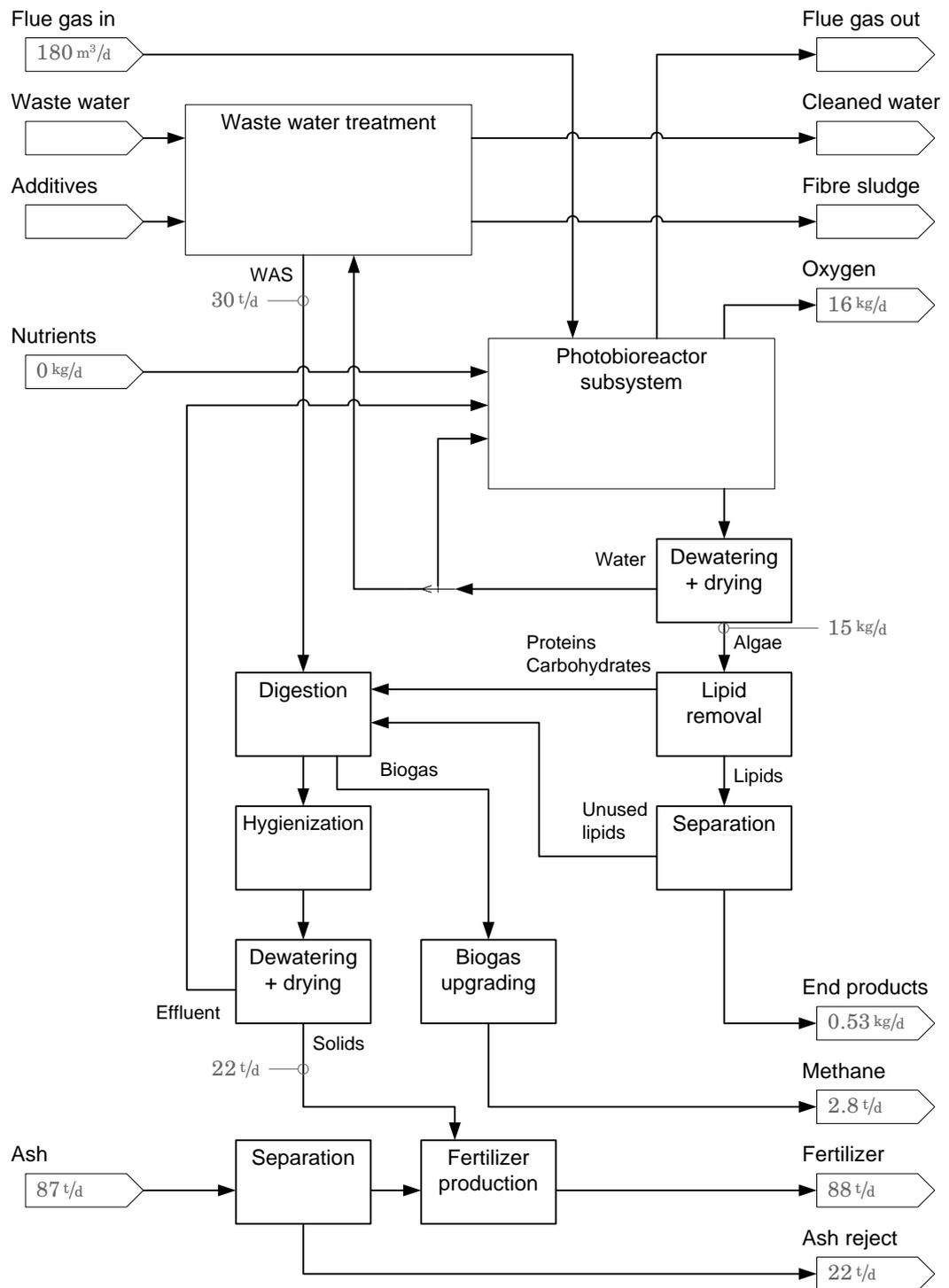


Figure 5.3: Biorefinery mass flows in the base case

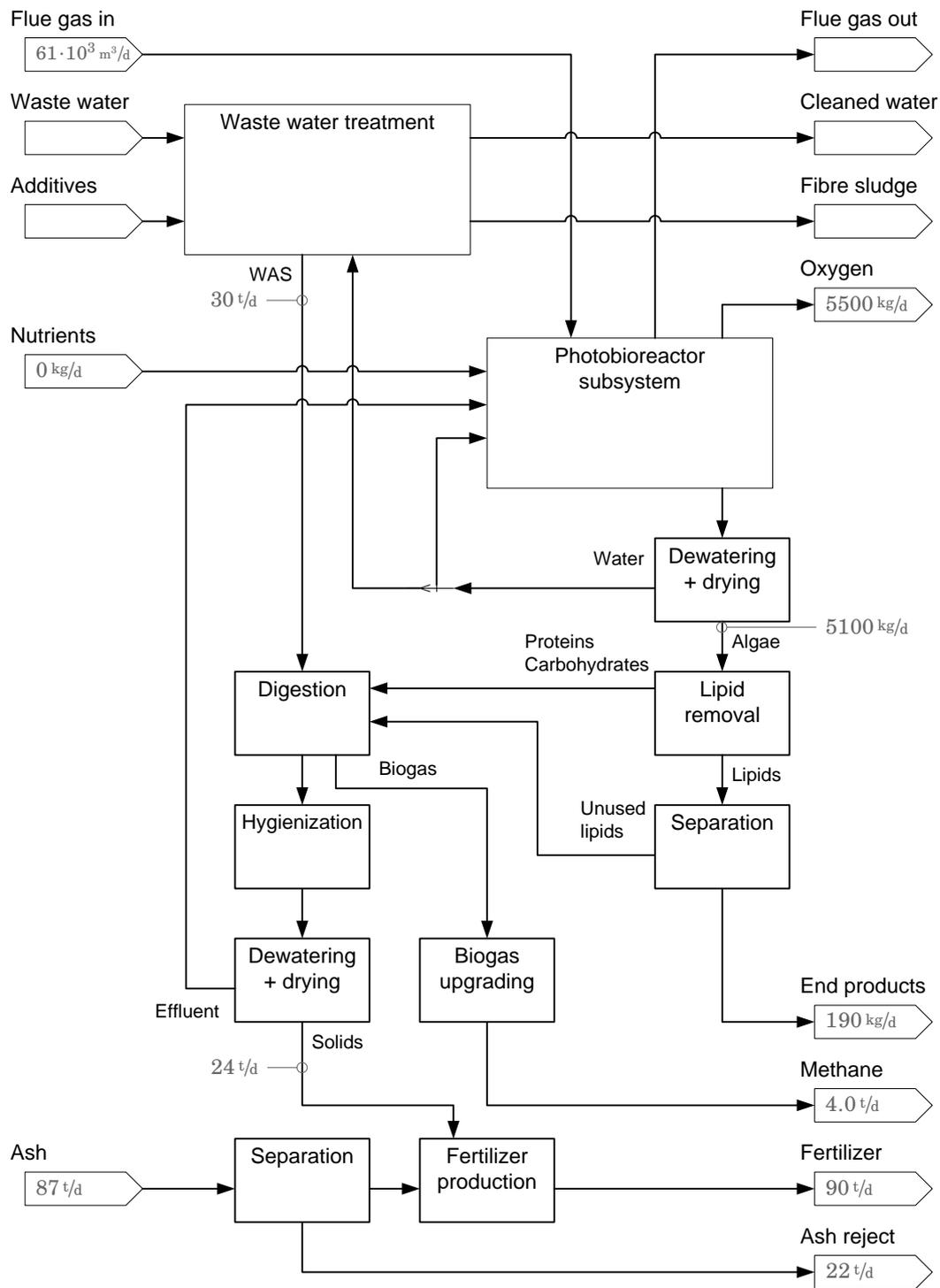


Figure 5.4: Biorefinery mass flows in the modified case

6 Discussion

A microalgae-utilizing biorefinery process was analysed in Chapter 5. Computational results indicate that the presented process is technically feasible and expected products are obtained. However, the outcome is seemingly sensitive to variations in digester effluent nutrient content. Algae cultivation is a constituent part of the proposed process and due nutrient composition in algal growth medium appears to be important for maximizing algae growth. Fertilizer output is quite stable regardless of algae production, but ω -3 fatty acid production is linearly dependent on algae yield and a significant amount (28 % in the modified case) of generated methane originates from digestion of lipid-extracted algal matter.

Although waste activated sludge (WAS) digestion residue was examined with accredited methods, there is a belief that determined nitrogen concentration in digester effluent is erroneous: because nutrients in WAS are mostly in the microbial matter, it would be odd if solubilization would differ so vastly between nitrogen and phosphorus compounds (0.1 % and 28 %), and from the reduction of volatile solids during digestion (34 %). It is considered likely that ammonia has volatilized from the effluent during transportation and storage before the measurements have been made. Higher shares of dissolved nutrients that were calculated for municipal WAS digestion¹ also support these doubts.

There are few key values that can be directly compared to literature, but at least methane production in algal residue digestion and volatile solids reduction in WAS digestion agree with published data. None of the presented results were found to conflict with previous research — even nitrogen distribution after WAS digestion could not be verified or determined incorrect, because no published data could be found.

A sensitivity analysis was not conducted, but it appears that nutrient distribution after anaerobic digestion has a significant influence on the process outcome: great differences in algae production were calculated between computed and assumed nitrogen content in digestion residue. Apart from WAS digestion, there are not many possible error sources in input data: availability of flue gases will not be limiting algal growth and variation in ash amount will only be reflected in fertilizer mass flow and composition. Differences in input for boilers may result in variation of fertilizer

¹See Section 3.4.3

composition, but the nutrient content seems to be not much influenced by algal growth variation. Fluctuations in wastewater treatment plant activated sludge process will likely have an effect on WAS flow and composition, and correspondingly will probably affect digestion and indirectly algal production.

Assumptions that have most influence on the results are presumably algae composition, its growth rates and behaviour in the digestion process. Because no strain has been chosen yet, the preliminary assumptions can be quite far off. Nevertheless, accuracy of results could be improved by a few measurements: when the algal strain has been chosen and its properties are known, mass flows may be estimated more precisely. Similarly, re-evaluating WAS digestion with and without algal input would remove uncertainties about nutrient flow rates. Tests on dewatering and thermal drying would help to determine energy requirement in water removal processes quite precisely.

The effect of biorefinery implementation to existing processes has not been taken into account in this study. Taking WAS to digestion instead of burning it is one cause of such effects, which should lead to decrease in heavy metal content in fuel mix and consequently ash, but the heavy metals would then be passed to the fertilizer among digestion residue. Other external effects include operation of sludge dewatering equipment in wastewater treatment plant and possible rearrangements in existing heat exchange network. Requirements of other nutrients except nitrogen and phosphorus were not taken into account in determining algal growth potential. Those may or may not be present in digester effluent; their requirement needs to be yet assessed.

In most calculations, daily averages were used and thus daily or seasonal variations were not taken into account. These variations will have a remarkable influence on the real process economy and plant operations: algae will not grow during dark hours and climate conditions will also place their restrictions on algal growth. Excess heat may be used to keep algal growth medium in appropriate temperatures during winter months, but availability of light might be a bigger problem. If ashes and sludges from the mill are stored during the times at which photobioreactors are not operational, their properties will likely change and additional space will be needed for the storage. On the other hand, if they are not stored, some substitute use will have to be developed for these streams.

Results of the study might be generalized to other similar systems, but the optimal biorefinery configuration is likely to vary with different boundary conditions. For instance, a part of the presented process is well applicable to biological wastewater treatment plants with an aerobic treatment process, but if other inputs such as ash, heat and carbon dioxide are not present, the process economy and feasibility might differ remarkably from the studied case.

Examined process configuration has been chosen based on knowledge of similar biorefinery processes and an impression of how waste streams and by-products could be used in an efficient way at the mill. This is probably not the optimal configuration in a technical or economic perspective and hence the alternative options would yet need to be examined in order to have a proper understanding of integration possibilities. Alternative process options include at least

- pre-treating WAS and lipid-extracted algal matter before digestion
- producing different algae-based substances
- removing lipid-extracted algal matter and unused portion of the lipids as separate end products
- leading fibre sludge into the digester
- producing bioethanol from fibre sludge or combined sludge from the wastewater treatment plant and taking the residue to digestion
- using carbon dioxide within produced biogas as a carbon source for algae
- adding supplementary nutrients to photobioreactor in order to ensure optimal nutrient levels and/or to maximize algae production
- growing the algae in total effluent from the wastewater treatment plant
- using the algae as a replacement for the aerobic wastewater treatment.

However, before any of these investigations are made, WAS digestion tests should be redone and nutrient content should be measured before and after digestion in every fraction. Without verified digestion results there will be too much room for error, as nutrient flow to algae cultivation is essential to the process. When the algal strain has been selected, co-digestion tests also need to be performed and digester parameters need to be optimized to maximize methane production and nutrient distribution. Conducting a sensitivity analysis and a calculation with fluctuating algal growth rates would be important in order to understand the dynamics of the process and to compute yearly utilization time for the plant. Before the latter study can be made, it will be necessary to determine possible algal growth rate as a function of light and temperature conditions. The calculation program that was written to do the computations for this thesis will serve as a basis for evaluating alternative processes and outcome sensitivity.

Energy balances and heat integration analysis need to be done in order to attain a comprehension of the production economy. After this, investment costs and economic performance of the biorefinery should be assessed, market analysis of

products should be conducted and best process configuration should be selected based on the aforementioned. After these analyses, conclusions may be made about feasibility of the biorefinery and the optimal product combination. Additionally it would be good to assess the environmental effects of this plant, including greenhouse gas mitigation potential in the whole value chain.

7 Conclusion

Based on this study, pulp and paper mill appears to be a suitable place for algae production and the associated biorefining activities. Nutrients, heat and water for growing are all present even though availability of the latter two were not confirmed with calculations.

The proposed biorefinery seems technically feasible: calculations indicate that ω -3 fatty acids, fertilizer and methane can be produced in the process. However, there are still major uncertainties concerning algae production: calculated nitrogen distribution after waste activated sludge digestion allows only minimal algal growth. This highlights the importance of correct nutrient mixture in algae cultivation. Due to uncertainties in input values, possible algal product yields cannot be determined reliably.

Further investigations on sludge digestion and algae production will facilitate more exact definition of biorefinery production potentials. Analyses on alternative processes as well as their energy input and investment requirements will allow the most economical biorefinery process to be determined. Once clearer understanding of the process economy has been reached, investment decisions may be made.

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