Utilization of industrial waste heat for the cultivation and harvesting of microalgae

by

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Abstract

Microalgae sourced lipids that can be transesterified into biodiesel are a promising source of biofuels that can be produced while mitigating industrial carbon dioxide (CO_2) in off-gasses. There are many advantages to microalgae compared to other bio-feedstocks, including their rapid growth rate, their ability to accumulate significant amounts of lipid, and the possibility of year-round production. However, there are significant limitations to achieving wide spread and economic microalgae mass cultivation and two of these are addressed in this research program.

Microalgae cultivation is currently generally limited to climatic zones where temperatures remain above 15°C, which effectively restricts mass cultivation to tropical or sub-tropical regions thereby eliminating the use of a number of worldwide industrial CO_2 sources. However, many of these sources also produce significant amounts of waste heat. The capture and repurposing of waste heat to maintain culture temperature and provide an alterative method for harvesting was explored. A dynamic model was developed to determine the potential of waste streams from a nickel smelter to maintain year-round growth in a cold climate. From this model, it was determined that there is more than enough heat to maintain cultivation temperatures even when the ambient temperature drops well below freezing.

Harvesting of microalgae prior to lipid extraction is, with current approaches, often cited as an area where costs need to be significantly reduced. As a wholly novel approach, the

capture of this waste heat was also explored for the use as a pretreatment for harvesting by flotation. It was determined to be highly effective and crucially avoids the addition and costs of chemical coagulants, which contaminate and restrict the use of the remaining biomass after lipid extraction.

Keywords

Microalgae, Waste heat, Off-gas, Biodiesel, Cold climates, Harvesting, Flotation

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Nomenclature

Symbol	Description
A	pond surface area (m^2)
A_w	pond wall and bottom area (m^2)
b_o	constant
BDAF	ballasted dissolved air flotation
C_{Bowen}	Bowen coefficient (61.3 N m^{-2} °C^{-1})
C_D	drag force coefficient
C_p	specific heat coefficient (J kg^{-1} °C^{-1})
CTAB	cetyl trimethyl ammonium bromide
D	diameter (m)
DAF	dissolved air flotation
DiAF	dispersed air flotation
ECF	elecro coagulation flotation
e_G	vapor pressure in ambient air (N m^{-2})
e_S	saturation vapor pressure of air (N m^{-2})
E	rate of energy variation (W)
f	friction factor
f	frequency of gas bubble formation (s^{-1})
FAME	fatty acid methyl ether
F_b	buoyancy force (N)
F_d	drag force (N)
Fr	Froude number
g	gravitational acceleration (m s^{-2})
h	heat transfer coefficient (W m^{-2} °C^{-1})
H	head loss (m)
H_G	solar radiation (W m^{-2})
I	incident solar radiation (W m^{-2})
IAF	induced air flotation
k	thermal conductivity (W m^{-1} °C^{-1})
K	head loss coefficient
n	number
N	number of ponds
Nu	Nusseult number
P	pressure (N m^{-2})
PEL	low density polyethylene
posiDAF	positively charged dissolved air flotation
PP	polypropylene
Pr	Prandlt number
P_{ref}	reference pressure (N m^{-2})
PVC	polyvinyl chloride

q	heat flux (W)
Q	off-gas volumetric flow rate ($m^3\ s^{-1}$)
R_{Bowen}	Bowen ratio
Re	Reynold's number
S_t	solar insolation over pond surface ($W\ m^{-2}$)
t	time (s)
T	temperature (°C)
TSS	total suspended solids
u	velocity ($m\ s^{-1}$)
W	mass flow rate ($kg\ s^{-1}$)
z	thickness (m)
Z	pond depth (m)

α_L	water adsorptivity (dimensionless)
ε	furnace off-gas holdup (dimensionless)
ρ	density ($kg\ m^{-3}$)
ξ	reflectivity (dimensionless)
τ	transmissivity (dimensionless)
μ	dynamic viscosity (Pa s)
κ	thermal diffusivity ($m^2\ s^{-1}$)
λ	constant ($W\ m^{-2}\ Pa^{-1}\ °C^{-1/3}$)

Subscripts

a	ambient
b	bubble
conc	concrete
cond	conductive
conv	convective
duct	off-gas duct
evap	evaporative
ext	external
f	film condition
F	furnace off-gas
ff	fouling factor
fr	friction
furnace	furnace off-gas
G	gas above pond surface
hf	heating fluid
hx	heat exchanger
i	inlet
in	initial
ins	insulating material
int	internal
L	liquid (water)
o	orifice

out	final
p	pond
pipe	piping material
pump	pump
R, roaster	roaster
solar	solar input
stainless	stainless steel
w	wall
180	180° bend

List of Publications

Eibl JK, Corcoran JD, Senhorinho GNA, Zhang K, Hosseini NS, Marsden J, **Laamanen CA**, Scott JA, Ross GM (2014) Bioprospecting for acidophilic lipid-rich green microalgae isolated from abandoned mine site water bodies. AMB Express 4:7.

Laamanen CA, Shang H, Ross GM, Scott JA (2014) A model for utilizing industrial off-gas to support microalgae cultivation for biodiesel in cold climates. Energy Conversion and Management 88:476-83.

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Senhorinho GNA, Bajwa N, **Laamanen CA**, Ross GM, Scott JA (in progress) Screening fresh water algae from near abandoned mine sites for antimicrobial activity. Journal of Freshwater Biology.

Kennedy AE, Ross M, **Laamanen CA,** Vohra R, Scott JA, Ross GM (in progress) Novel bivalent naphthalamide compound BVNP-0197 identified for nerve growth factor inhibition by means of surface plasmon resonance spectroscopy. Molecular Pharmacology.

Chapter 1

Introduction

1.1 Background

With growing concerns over greenhouse gas production and dwindling fossil fuel reserves, there is a need to develop alternative fuels. One of the most heavily researched options for transportation fuels are biofuels, which can be derived from a large number of feedstocks. Microalgae, a third generation biofuel, has several key advantages compared to more traditional fuel crops. Importantly microalgae, unlike food crops utilized for energy production (first generation) and dedicated energy crops (second generation), do not require arable land to grow and can be grown year-round,

Additionally, microalgae have higher growth rates per unit area the other fuel crops and can accumulate significant amounts of lipid, which can be readily transesterified into biodiesel (Chisti, 2007). This leads to an order of magnitude increase in areal productivity of fuel. These operations can be also coupled with industrial operations to capture carbon dioxide (CO_2) from off-gas (Shang et al., 2010; Yen et al., 2015) and nutrients from wastewater (Lam and Lee, 2012; Assemany et al., 2016). This allows for the double benefit of reducing industrial emissions and producing a sellable product, which includes not only biodiesel, but also food supplements and other value-added bioproducts (Brennan et al., 2010; Vandamme et al., 2013).

Due to this significant potential, there are a number of comprehensive algae literature reviews, covering the capture of CO_2 (Kroumov et al., 2016; Thomas et al., 2016), the factors affecting growth and the potential production (Ho et al., 2014), and different cultivation and processing options (Tan et al., 2015; Misra et al., 2016).

Despite the advantages of microalgal biofuels, there are, however, significant limitations to global microalgae production – two of the most significant being restrictions on the cultivation region due to ambient temperature considerations and economic harvesting of microalgae prior to lipid extraction. This thesis aims to provide options to address both these limitations to global algae production.

The outdoor cultivation of algae, which remains the most economic approach, has traditionally been limited to tropic and sub-tropic climates (Spolaore et al., 2006), due primarily to temperature requirements. Microalgae typically require between 15°C and 30°C (Chisti, 2007), effectively eliminating a large portion of global regions for outdoor production. Many of the industrial operations, whose off-gas CO_2 could be utilized for carbon capture, also produce significant amounts of waste heat. In many cases, this energy is currently dissipated without recovery to atmosphere. However, it is proposed in this work that this heat could be repurposed for the maintenance of microalgae cultivation tank temperature in cold climates. A model was, therefore, developed to determine the potential of this waste heat for microalgae cultivation (Chapters 2 and 3), utilizing both direct and indirect heat capture from a nickel smelter.

At the end of the cultivation phase, microalgae grow to a density in the range of 1 g/L (Hosseini et al., 2015), a level that presents difficult harvesting due to the relatively

dilute culture solution (Brennan and Owende, 2010; Barrut et al., 2013). Bulk harvesting of microalgae is further complicated due to the small size of cells (typically between 2-10 μm (Sharma et al., 2013)), a similar specific gravity to water (Zhang and Hu, 2012) and a negative surface charge (Wang et al., 2015). There are several options of harvesting method, including centrifugation, sedimentation, filtration, and flotation. However, with currently available technology microalgae harvesting accounts for 20-30% of total production costs (Sharma et al., 2013).

Flotation is receiving significant interest as a harvesting technique (and is reviewed in depth in Chapter Four), due to relatively low operating and capital costs while still producing recoveries above 90% (Zhang et al., 2014). However, since both the algae and the bubbles are typically negatively charged, there is the requirement to add some sort of coagulant. In addition to increasing operational costs, this also contaminates the produced biomass and may limit the potential of the remaining biomass after lipid extraction (Laamanen et al., 2016).

Based on a previous study by Scott et al. (1997), utilizing heat-induced flocculation for bacteria recovery, a method for the harvesting of dilute microalgae culture solutions was developed (Chapters Five and Six). While heating of large volumes of these dilute cultures is likely uneconomical if utilized as a stand-alone process, this operation can be utilized as an industrial-coupled separation option. The waste heat from industrial operations can be repurposed for the harvesting of microalgae, an important processing stage that has not traditionally been considered for industrial coupling.

1.2 Thesis Objective

The objective of this thesis is to explore the repurposing of currently waste industrial heat to (a) expand the worldwide cultivation region for year-round microalgae production through heating culture solutions and to (b) provide a novel alternative harvesting method through heat-aided flocculation for flotation. This would allow for industrial operations from traditionally unconsidered climatic zones to be utilized for microalgae production.

The thesis is organized such that Chapters Two and Three provide information on the development and results of the model for culture temperature maintenance. Chapter Four gives a literature review on flotation as a bulk harvesting method for microalgae. This provides background and context for Chapters Five and Six that provide results for heat-aided flocculation prior to flotation harvesting of microalgae.

Chapter 2

Paper #1 – Modeling, Energy Conversion and Management

A model for utilizing industrial off-gas to support microalgae cultivation for biodiesel in cold climates

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Author Contributions

CAL performed the modeling, data analysis and primary manuscript writing. HS developed the previous model and provided assistance in the further development of that model. GMR assisted in some manuscript writing. JAS provided overall direction in project and model development, and manuscript writing.

Abstract

Lipids produced by microalgae are a promising biofuel feedstock. However, as most commercial mass production of microalgae is in open raceway ponds it is generally considered only a practical option in regions where year-round ambient temperatures remain above 15°C. To address this issue it has been proposed to couple microalgae production with industries that produce large amounts of waste heat and carbon dioxide (CO_2). The CO_2 would provide a carbon source for the microalgae and the waste heat would allow year-round cultivation to be extended to regions that experience seasonal ambient temperatures well below 15°C. To demonstrate this concept, a dynamic model has been constructed that predicts the impact on algal pond temperature from both bubbled-in off-gas and heat indirectly recovered from off-gas. Simulations were carried out for a variety of global locations using the quantity off-gas and waste energy from a smelter's operations to determine the volume of microalgae that could be maintained above 15°C. The results demonstrate the feasibility of year-round microalgae production in climates with relatively cold winter seasons.

Keywords

Microalgae, off-gas, biodiesel, cold climates, modeling

2.1 Introduction

The coupling of microalgae production facilities to industrial CO_2 emissions is an attractive concept for carbon capture through photosynthesis (Bilanovic et al., 2012; Chiu et al., 2011; Rickman et al., 2013). Microalgae have also exhibited increased growth rates in the presence of elevated CO_2 levels (Chiu et al., 2011; Jiang et al., 2013; Pires et al., 2012; Sapci and Morken, 2014). Potential sources of off-gas include fossil fuel power stations (5-15% CO_2, Huntley and Redalje, 2006; Hsueh et al., 2007; Wang et al., 2008), cement kilns (15-25% CO_2, Borkenstein et al., 2010; Lara-Gil et al., 2014) and smelters (7% CO_2, Renaud et al., 2010).

Microalgae can produce lipids at between 20-50% of their dry cell weight (Gouveia and Oliveira, 2009) that can be transesterified into biodiesel (Chisti, 2007; Damm and Fedorov, 2008; Wahidin, 2014). As a source of lipids, microalgae are generally considered preferable to terrestrial plants as they reproduce faster, do not require arable land for growth and capture more CO_2 per unit area (Daroch et al., 2013; Rawat et al., 2013; Toledo-Cervantes et al., 2013). When compared to fossil fuel sourced diesel, biodiesel combustion results in a 100% reduction in SO_2, 90% reduction in unburned hydrocarbons, 75-90% reduction in polycyclic aromatic hydrocarbons (Demirbas, 2009a), 14% less CO_2, 17.1% less CO, and a 22.5% reduction in smoke density (Utlu, 2007).

Several methods for integrating microalgae operations to increase carbon capture efficiency into a power plant's flue gas stream are described by Schipper et al. (2013),

while open pond systems have achieved approximately 50% carbon capture with a 10% CO_2 gas stream (Pires et al., 2012). However, current large-scale microalgae production is centred in tropic or sub-tropic locations such as Hawaii, India, Israel, and California (Spolaore et al., 2006). This is due primarily to the tested algal strains requiring water temperatures between 15-30˚C (Chisti, 2007). One consequence is that, as access to freshwater is often limited in these mainly semi-arid regions, operations are restricted to using salt water. Whereas regions that have more abundant freshwater can also experience seasonal periods of cold weather. As a consequence they are not considered suitable for year-round large-scale algae production using relatively inexpensive raceways even though they are not necessarily short of daylight hours.

In Sudbury (Ontario, Canada) for example, the location of two nickel smelters, within the city boundaries there are over 250 freshwater lakes and daylight varies between 8 to 14 hours over the year. Demirbas and Demirbas (2011) state that algae can grow almost anywhere where there is enough sunlight and Sudbury provides an annual average of well above 2800 light hours. This meets the light condition for a favourable growing region as defined by the Sandias National Laboratories (Ziolowska and Simon, 2014). However, average ambient temperatures are below 15°C for 7-8 months of the year. The smelters produce large volumes of off-gas containing significant quantities of heat and CO_2 that is dissipated to the environment without recovery (Shang and Scott, 2011). It has been proposed that opportunity lies in capturing and utilizing this otherwise waste heat and CO_2 to maintain microalgal ponds, for biodiesel production, above 15°C year round (Shang et al., 2010). The clean burning characteristics of biodiesel provide a two-

fold advantage for the mining and mineralogical industry as burning it underground could translate into a decreased ventilation requirement and a better working environment (Mata et al., 2010).

For a nickel smelter, off-gas streams come from furnaces and roasters (Figure 2.1). The roaster off-gas contains around 65% of the total waste heat but is high in sulphur dioxide (SO_2) (11-18%, Loken, 2013). Particulate matter is removed and the SO_2 scrubbed from the off-gas and converted into sulphuric acid (Shang et al., 2007). The off-gas exits the roasters at around 680°C but needs to be reduced to 50°C in order to pass through the SO_2 to sulphuric acid plant (Shang et al., 2007). The scrubbed gas is discharged to atmosphere.

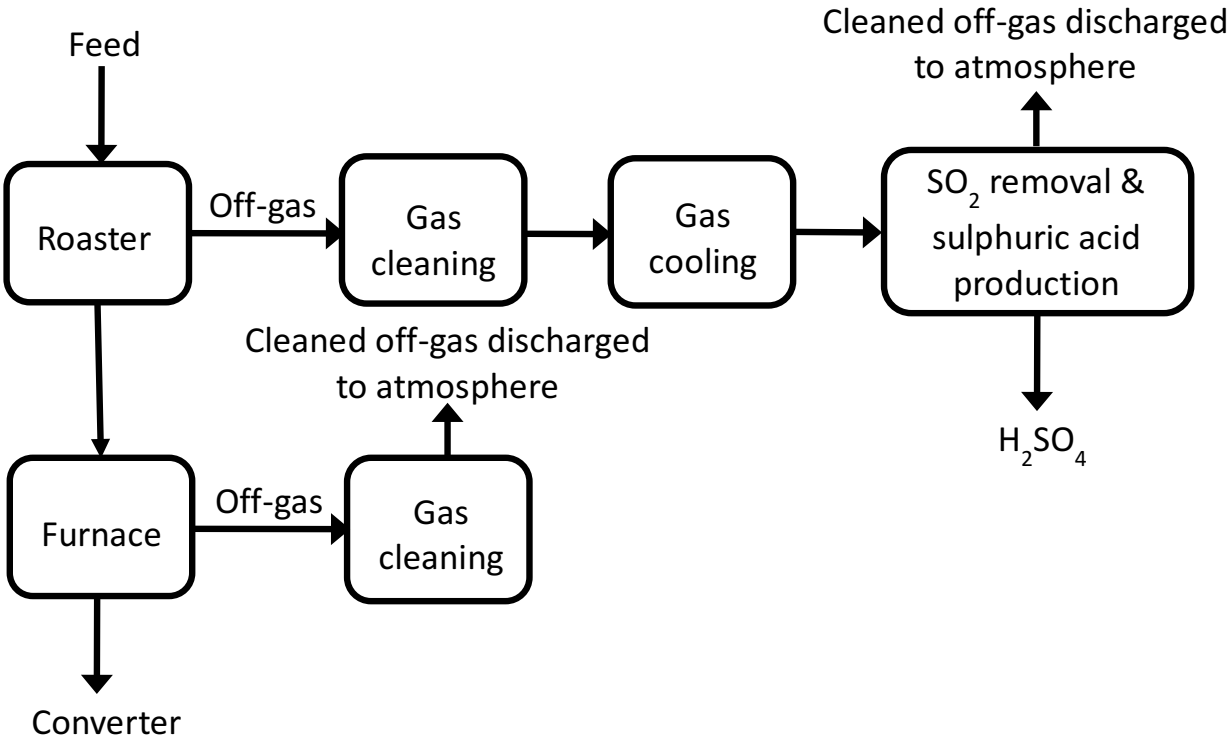

Figure 2.1: Schematic of a smelter off-gas treatment (adapted from Shang et al., 2007)

The off-gas from the furnace exits at around 350°C and contains CO_2 at 6-7% v/v (Renaud et al., 2010), and a lower SO_2 content at approximately 0.4% (Loken, 2013). Particulate matter is also removed from the furnace off-gas before it is exhausted to atmosphere. The NO_x level is not a concern as it is not a significant component of nickel smelter furnace off-gas, and low levels of NO_x (<100 ppm) can be easily tolerated by microalgae (Radmann et al., 2011; Taştan et al., 2012). For both off-gas streams the considerable heat energy they contain is not captured and repurposed.

If an off-gas is bubbled into algal ponds the presence of even relatively low concentrations of acid gas components, such as the 0.4% SO_2 in the furnace off-gas, will adversely impact water pH (Lara-Gil et al., 2014). However, microalgae have adapted to many diverse aquatic environments including low pH environments (Rawat et al., 2013). Microalgae species that have been discovered that can deal with pH 3-4 present significant advantages in comparison with strains that grow in near pH-neutral conditions in terms of reducing the amount of buffer needed for the growth medium to combat the impact of acid gas components (Eibl et al., 2014). Furthermore, in an open pond system a depressed pH would reduce the risk of competition from invasive, low-lipid producing species, which is a common problem (Pires et al., 2012).

As a first step towards demonstrating the potential for using industrial off-gas to support year-round algal production flexible models are needed that can determine the levels of captured waste heat needed for maintaining pond temperatures. To address this need, described below is a dynamic model that incorporates heat contained in both roaster and furnace off-gas and uses the assumption that algal ponds should be maintained above

15˚C throughout the entire year. By taking into account local ambient climate conditions the potential volume of microalgae production per month for a given source of off-gas can be determined. To illustrate this we looked at five global sites (Table 2.1) where nickel/copper smelters are located.

Table 2.1: Worldwide smelting operations (* Platinum group metals)

Location	Latitude	Main Metals Processed
Sudbury, Ontario, Canada	46.5°N	Copper, Nickel, Cobalt, PGM*
Bingham, Utah, USA	33.5°N	Copper, Gold, Silver, Molybdenum
Townsville, Queensland, Australia	19.3°S	Copper
Antofagasta, Antofagasta Province, Chile	23.7°S	Copper
Lanzhou, Gansu, China	36.0°N	Nickel, Cobalt, PGM*

2.2 Process development

With the smelter and other industrial operations the majority of the available heat can be contained within off-gas streams that are not suitable, due to high acid gas components, for bubbling through algal ponds. To maximize the potential pond volume that can be heated during seasonally low ambient temperatures we have, therefore, included in the model heat recovered and utilized indirectly (Figure 2.2).

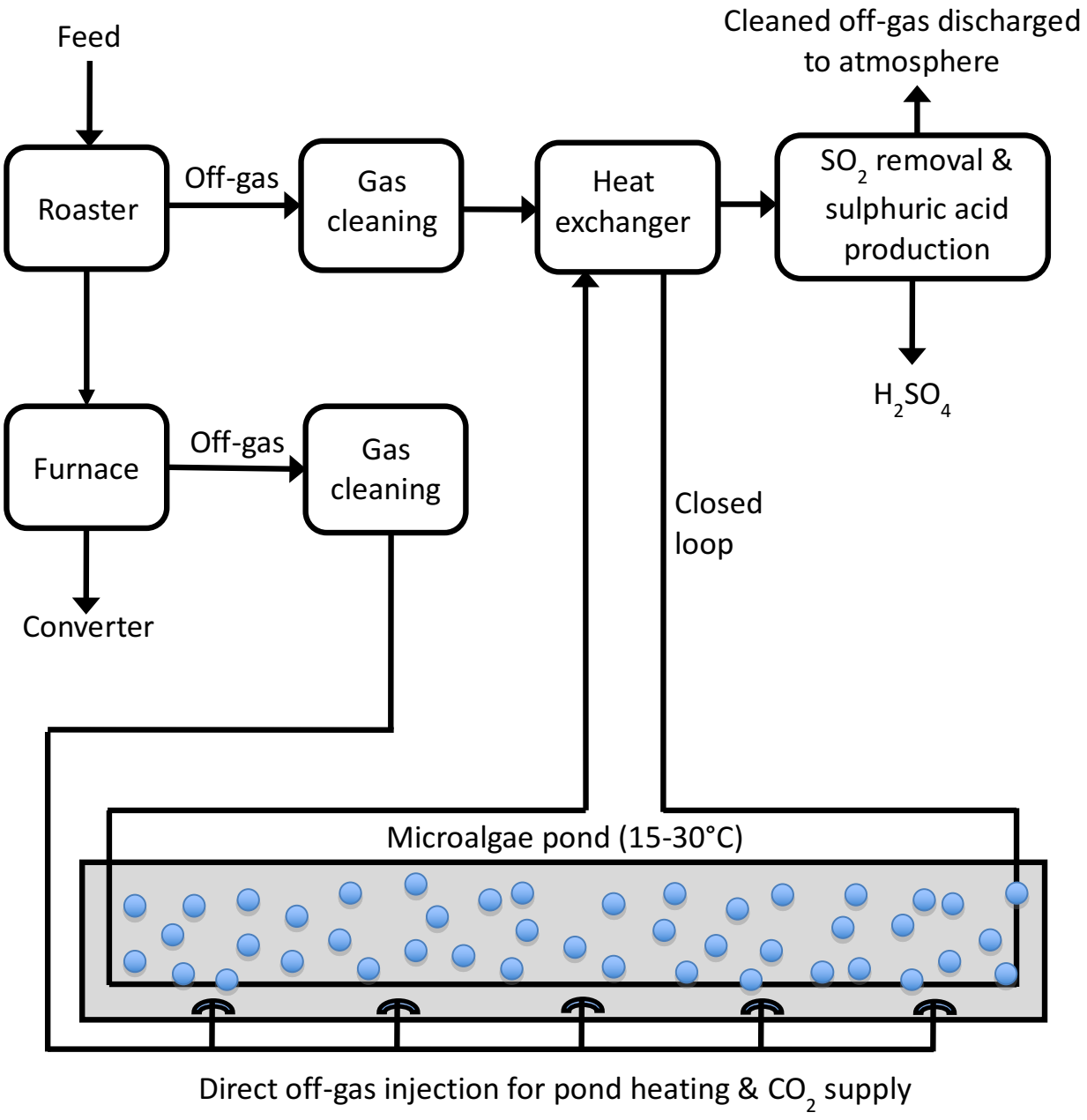

Figure 2.2: Schematic of a smelter coupled microalgae production facility

The modelled ponds are assumed to be covered with a clear roof to reduce contamination from particulate matter and other algal species, and increase CO_2 capture by ensuring a high CO_2 concentration at the tank's water/atmosphere interface. Covers made from the plastic used in commercial greenhouses will also help reduce evaporation by creating 100% humidity above the water surface and minimize the effect of wind velocity (u) on convective heat loss from the surface. In common with existing commercial operations, the concrete tanks are sunk into the ground and have an insulating polyurethane layer along the walls and bottom.

2.3 Model development

The model considers bubbling in of furnace off-gas along with the impact of adding indirect heating from energy recovered from the roaster off-gas. The assumptions used are:

(i) a microalgae growth pond consists of an insulated and covered rectangular concrete tank that is 5 m wide, 50 m long and 1 m deep;

(ii) each pond is a batch operation with no water flow in or out;

(iii) spatial variations of water temperature are negligible due to mixing and turbulence created by sparging in furnace off-gas;

(iv) four 20 cm diameter spargers per square meter of tank bottom are used (i.e., 1000 spargers per tank);

(v) due to relatively low gas transfer, the bubbles of sparged-in furnace off-gas are of constant volume;

(vi) inertial bubble forces are negligible compared to buoyancy and drag forces;

(vii) vertical variations of the density of gas and water are negligible in the system;

(viii) the temperature immediately above the water surface is uniform.

The model utilizes the previous month's temperature to determine the values for the environmental variables that are not measured (e.g., ground temperature). This creates a dynamic association of the climate throughout the year. As a consequence two months of similar environmental data will not necessarily have the same heating requirements as these may vary if the preceding months were colder or warmer.

Using the above qualifications, the overall heat flux (q) can be represented with six terms, as shown in Equation 2.1:

$$q = q_{furnace} + q_{roaster} + q_{solar} - q_{evap} - q_{cond} - q_{conv} \qquad \text{Equation 2.1}$$

On the right hand side of this equation the first three terms represent heat addition from the smelter and solar heating (q_{solar}). The last three terms represent the system's heat flux from evaporation, conduction through the walls and convection at the surface. All these terms are developed below.

2.3.1 Evaporative heat loss (q_{evap})

Evaporative heat loss (q_{evap}) is taken as a function of the saturated vapour pressure of the water (e_S) and the vapour pressure of the water in the atmosphere above the water surface (e_G). The evaporative heat loss was calculated as per Woolley et al. (2011) from:

$$q_{evap} = h_{evap}(e_S - e_G)A \qquad \text{Equation 2.2}$$

where the heat transfer coefficient (h_{evap}) can be estimated from:

$$h_{evap} = 0.0360 + 0.0250u \qquad \text{Equation 2.3}$$

and the vapour pressures, e_S and e_G, representing the saturated vapour pressure and the vapour pressure above the pond surface can be estimated from Troxler and Thackston (1977) by:

$$e_S = 25.37 \exp\left(17.62 - \frac{5271}{T_L+273}\right) \qquad \text{Equation 2.4}$$

$$e_G = R_h \times 25.37 \exp\left(17.62 - \frac{5271}{T_G+273}\right) \qquad \text{Equation 2.5}$$

where R_h is the relative humidity of the gas above the pond's surface.

2.3.2 Heat loss due to convection (q_{conv})

The surface evaporative and convective heat transfer phenomena are related and can be expressed by the ratio defined by Bowen (1926):

$$\frac{q_{conv}}{q_{evap}} = R_{bowen} \cdot \qquad \text{Equation 2.6}$$

Convective heat loss can be then calculated using the Bowen ratio, knowing the Bowen coefficient (C_{Bowen}) and the evaporative heat loss, as calculated in Equations 2-5. The value of R_{Bowen} can be calculated using:

$$R_{bowen} = C_{bowen} \frac{p_G}{p_{ref}} \frac{T_L - T_G}{e_S - e_G}. \quad \text{Equation 2.7}$$

2.3.3 Conduction heat transfer through tank walls and base (q_{cond})

Heat transfer through conduction (q_{cond}) through the tank bottom and walls of the tank with a 5 cm insulating layer of polyurethane between two identical 5 cm layers of concrete is represented by the following equations (Karakilcik et al. 2006):

$$q_{cond} = h_w A_w (T_L - T_{soil}) \quad \text{Equation 2.8}$$

$$h_w = \frac{1}{\frac{z_{conc}}{k_{conc}} + \frac{z_{ins}}{k_{ins}} + \frac{z_{conc}}{k_{conc}}} \quad \text{Equation 2.9}$$

where T_L and T_{soil} are tank liquid and surrounding soil temperatures respectively.

2.3.4 Heat input from furnace off-gas ($q_{furnace}$)

The heating due to bubbling in of furnace off-gas is dependent on the frequency of bubble formation, their size and their velocity. On the assumption that the bubbles are spherical and form at constant intervals (Bhavaraju et al., 1978), bubble diameter (D_b) can be related to the orifice diameter (D_o) (Kang et al., 2002) by:

$$\frac{D_b}{D_o} = 3.23 Re^{-0.1} Fr^{0.21} \quad \text{Equation 2.10}$$

With the Reynolds number (*Re*) and Froude number (*Fr*) expressed as:

$$Re = \frac{4\rho_L Q_o}{\pi D_o \mu_L} \quad \text{Equation 2.11}$$

$$Fr = \frac{{Q_o}^2}{{D_o}^5 g} \quad \text{Equation 2.12}$$

Q_o is the gas flow rate per orifice and can be expressed as a function of furnace off-gas flow rate into the tank (Q_F), the number of orifices per unit area (n), and the tank's surface area (A) by:

$$\mathrm{Q_o} = \frac{\mathrm{Q_F}}{\mathrm{nA}}. \quad \text{Equation 2.13}$$

The frequency of bubble formation (f) can be found by dividing the orifice flow rate by the bubble volume:

$$\mathrm{f} = \frac{6\mathrm{Q_o}}{\pi {\mathrm{D_b}}^3} \quad \text{Equation 2.14}$$

After the bubble detaches from the orifice and assuming negligible inertial forces, the bubble will reach a steady ascent velocity (u_b). This velocity will be a balance between drag force (F_d) and buoyancy (F_b), and these are functions of bubble size and liquid (ρ_L) and gas (ρ_G) densities. Buoyancy and drag force were derived from (Zhang and Shoji, 2001):

$$\mathrm{F_b} = \frac{\pi {\mathrm{D_b}}^3}{6}(\rho_\mathrm{L} - \rho_\mathrm{G})\mathrm{g} \quad \text{Equation 2.15}$$

$$\mathrm{F_d} = \frac{1}{8}\rho_\mathrm{L}\pi {\mathrm{D_b}}^2 \mathrm{C_D}(\mathrm{u_b})^2 \quad \text{Equation 2.16}$$

where C_D is the drag force coefficient and is equal to $18.5/Re^{0.6}$ for $1 < Re < 1000$, and 0.44 for $Re > 1000$ (Zhang and Shoji, 2001). Combining the above two terms and assuming negligible gas density compared to the liquid density, the bubble ascent velocity can be estimated:

$$u_b = \sqrt{\frac{4 d_b g}{3 C_D}} \qquad \text{Equation 2.17}$$

Combining the equations for bubble size, formation frequency, and ascent velocity, the temperature of the gas bubble as it rises through water of depth Z, with the condition $T_b(Z) = T_G$, can be calculated using energy conservation laws:

$$\frac{\partial T_b}{\partial t} - u_b \frac{\partial T_b}{\partial z} = \frac{\pi {D_b}^2 n h_{Lb} f}{\rho_G C_{p,F} \varepsilon u_b} (T_L - T_b) \qquad \text{Equation 2.18}$$

The gas hold up (ε) (the fraction of gas in the liquid by volume) can be represented by:

$$\varepsilon = \frac{n f \pi {d_b}^3}{6 u_b} \qquad \text{Equation 2.19}$$

The energy contribution from the direct bubbling of furnace off-gas is given by:

$$q_{furnace} = Q_F C_{p,F} \rho_G (T_{F,i} - T_G) \qquad \text{Equation 2.20}$$

The furnace off-gas flow to the tank was kept at a constant liquid to gas ratio of 0.0318 v/v/min, based on laboratory tests to determine adequate agitation (unpublished data). This flow rate is similar to the 0.0370 v/v/min used to maximize CO_2 capture at one meter depth (de Godos et al., 2014) and is equivalent to 7.96 m^3/min per 250 m^3 tank.

2.3.5 Solar radiation heat addition (q_{solar})

The quantity of solar radiation H_G, which contributes to the temperature of the atmosphere above the pond's water surface, is a function of adsorptivity (α_L), reflectivity (ξ) and transmissivity (τ), and can be represented as:

$$H_G = (1 - \alpha_L)(1 - \xi)\tau S_t A \qquad \text{Equation 2.21}$$

Examining Equation 21 the quantity of solar radiation that contributes to raising water temperature is:

$$q_{solar} = \alpha_L(1 - \xi)\tau S_t A \qquad \text{Equation 2.22}$$

2.3.6 Temperature of gas above the pond (T_G)

With a covered pond, the temperature of the atmosphere above the water surface is a function of the water temperature, the outside air temperature, and incident solar radiation due to the greenhouse effect (Equation 21) (Pieters and Deltour, 1999; Ganguly and Ghosh, 2009).

There is also an energy contribution (E_{Gb}) from the bubbles when they reach the surface of the pond, which can be determined from:

$$E_{Gb} = \rho_G \frac{\pi {D_b}^3}{6} fnAC_{p,F}(T_b|_0 - T_G) \qquad \text{Equation 2.23}$$

where $T_b|_0$ is the temperature of the bubble when it reaches the water surface.

In addition to energy addition from the bubbles and solar radiation, the temperature of the atmosphere above the water surface will be affected by the heat exchange rate between the atmosphere and the pond surface. These can be combined into the following dynamic model that can be used to estimate the temperature of the gas above the pond:

$$\frac{dT_G}{dt} = \frac{1}{\rho_L C_{p,G} V_G}\left(\rho_G \frac{\pi {D_b}^3}{6} fnAC_{p,F}(T_b|_0 - T_G) - h_{GL}A(T_G - T_L) - h_{Ga}A(T_G - T_a) + (1-\alpha_L)(1-\xi)\tau S_t A\right) \quad \text{Equation 2.24}$$

With this equation, the temperature of the gas above the water can be calculated, and the pond temperature can be determined by examining the heat exchange terms.

2.3.7 Heat input from energy recovered from the roaster off-gas ($q_{roaster}$)

The final consideration is any off-gas heat that can by indirectly added to the tanks, in this case from the smelter's roasters. This leads to considering three sources of heat addition (furnace off-gas bubbling, indirect heating from roaster off-gas, and solar radiation) and three sources of potential heat loss (evaporative loss and convective flux from the pond's surface, and conductive flux from the pond's base and walls).

The energy requirement to keep the cultivation tank at the operating temperature was calculated using the aforementioned heat transfer components. As a result the number of tanks that can be supported in any given month is dependent upon the number that can be agitated and carbon-fed with furnace off-gas as well as heated to at least 15°C with a combination of the off-gases.

The total available heat from the indirect usage of the roaster off-gas is assessed from:

$$q_{roaster,max} = \rho_G C_{p,R} W_R (T_{roaster} - T_{acid\ plant}) \cdot x \qquad \text{Equation 2.25}$$

where W_R is the volumetric flow rate and x is the capture efficiency of the heat exchanger. The capture efficiency was taken as 0.6, based on previous design considerations (Loken, 2013). However, the application of heat exchangers is in a gas stream that is both highly acidic and contains particulates. It is important to note, therefore, that the exact value will be a function of both heat exchanger design and incidence of exchanger surface fouling.

2.3.8 Overall heat transfer model

The resulting overall model, used to evaluate bulk water temperature, is represented by:

$$\frac{dT_L}{dt} = \frac{1}{\rho_L (1-\varepsilon) C_{p,L} AZ} \left(q_{furnace} + q_{roaster} + q_{solar} - q_{evap} - q_{conv} - q_{cond} \right)$$

Equation 2.26

where q_{evap} and q_{conv} are the evaporative and convective heat flux, respectively, from the ponds surface per unit area, and q_{cond} is heat flux through conduction through the bottom and sides of the tank. There are three heat addition terms, q_{solar} representing the heat contribution from solar radiation, $q_{furnace}$ is the heat from bubbling the furnace off-gas and $q_{roaster}$ is the indirect heat from the roaster off-gas. The developed dynamic model allows, therefore, for the determination of the energy required to maintain a single 250 m^3 tank at the required operating temperature.

Table 2.2: Parameters used in the model

	Value	Units	Source
A	250	m^2	This work
b_o	0.032	J m^{-2} Pa^{-1} m^{-1}	Nath and Bolte (1998)
$C_{p,F}$	1007	J kg^{-1} $°C^{-1}$	Ghoshdastidar (2004)
$C_{p,G}$	1007	J kg^{-1} $°C^{-1}$	Ghoshdastidar (2004)
$C_{p,L}$	4180	J kg^{-1} $°C^{-1}$	Ghoshdastidar (2004)
$C_{p,R}$	1330	J kg^{-1} $°C^{-1}$	Shang (2007)
d_o	0.05	m	Shang (2010)
h_{Ga}	12	W m^{-2} $°C^{-1}$	Ghoshdastidar (2004)
h_{Lb}	5000	W m^{-2} $°C^{-1}$	Al-Hemiri and Ahmedzeki (2008)
h_{LG}	22.7	W m^{-2} $°C^{-1}$	Kwon (1995)
h_{Lw}	340	W m^{-2} $°C^{-1}$	Kwon (1995)
k_{conc}	1	W m^{-1} $°C^{-1}$	This work
k_{ins}	0.17	W m^{-1} $°C^{-1}$	This work
n	2500	m^{-2}	Shang (2010)
Q_F	24	m^3 s^{-1}	Renaud (2010)
$T_{F,i}$	90	°C	This work
$T_{roaster}$	665	°C	Shang (2007)
$T_{acid\ plant}$	50	°C	This work
V_G	1125	m^3	Shang (2010)
W_R	36	kg s^{-1}	Shang (2007)
x	0.6	Dimensionless	This work
Z	1	m	Shang (2010)
α_w	0.3	Dimensionless	Sethi (2009)
κ	0.55×10^{-6}	m^2 s^{-1}	Beltrami and Kellman (2003)
λ	0.027	W m^{-2} Pa^{-1} $°C^{-1/3}$	Nath and Bolte (1998)
μ_L	0.0009	Pa s	Ghoshdastidar (2004)
ξ	0.06	Dimensionless	Sethi (2009)
ρ_G	1.2	kg m^{-3}	Ghoshdastidar (2004)
ρ_L	999	kg m^{-3}	This work
T	0.86	Dimensionless	Pieters and Deltour (1999)

2.4 Simulation Results

The annual temperature profiles and solar insolation levels for the five selected global locations where smelters are located are given in Figures 2.3 and 2.4. Taking 15°C as the minimum by which to cultivate suitable microalgae, Townsville (Australia) is the only

one of the five locations that has ambient temperatures above 15˚C for the full year. Antofagasta (Chile) has temperatures that fall below 15˚C from May to October, but remain above 10˚C. The other three locations experience very low temperatures for prolonged periods through the year and would not be considered suitable for year-round cultivation with raceways. However, due to their latitudes they experience reasonably long winter daylight hours. It is proposed, therefore, that by repurposing energy available from normal day-to-day industrial activity year-round microalgal production of biodiesel and CO_2 mitigation may be possible for these areas.

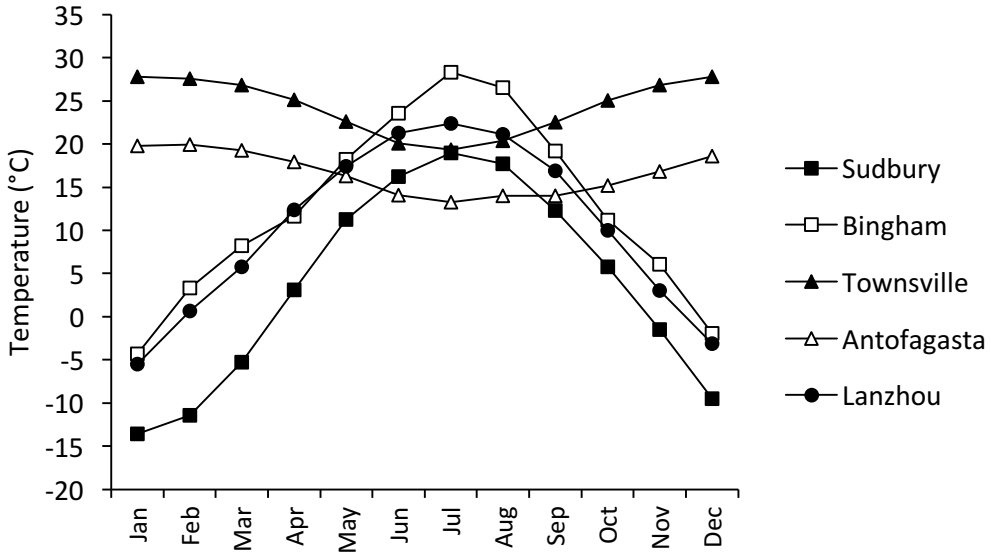

Figure 2.3: Annual temperature profile for example smelter sites

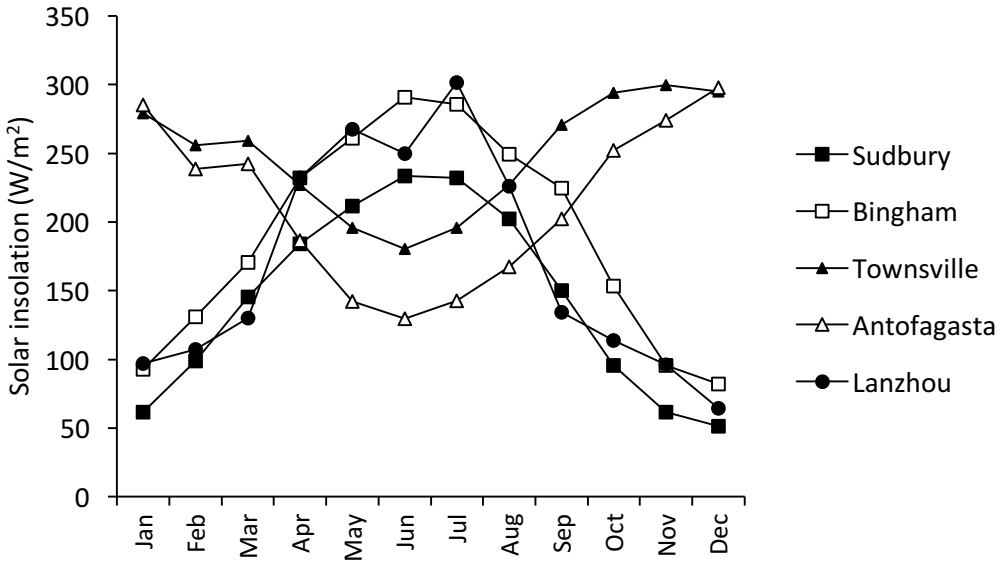

Figure 2.4: Annual solar radiation profile for example smelter sites

To provide a direct comparison between the three locations where ambient temperatures fall below 15°C (Sudbury, Bingham and Lanzhou) simulations were carried out using operating conditions and emissions based on those of the smelter in Sudbury.

The target variable is the volume of algal ponds that can be maintained at or above 15°C by utilizing heat from both furnace and roaster off-gas. However, a limiting factor imposed on the total tank volume is the available quantity of furnace off-gas. This gas not only provides heat and CO_2, but also agitates the tanks. As previously mentioned a suitable gas flow rate per sparger has been found to be 7.96 L/min, which for each 50 m by 5 m tank, and 1000 spargers, is equivalent to a total volumetric flow rate of 133 L/sec. As the volume of furnace off-gas is 24000 L/s (Loken, 2013) in order to provide adequate mixing and assuming sufficient available land, the maximum number of tanks would be 180.

The simulation results give an assessment of the required heat recovered by a heat exchanger from the roaster off-gas stream in order to maintain tank temperatures at 15°C or 30°C (Table 2.3). Bubbling in furnace off-gas at 90°C provides a relatively constant source of heat and contributes approximately 12000 W for 15°C and 9740 W for 30°C pond temperatures. However, it is the volumetric flow rate of the furnace off-gas that provides CO_2 and agitation that will limit the maximum number of tanks that can be supported. A second potential limiting factor is provided by dividing the total energy that can be captured from the roaster off-gas by the indirect heating requirement per tank. That is the "top-up" energy needed above that supplied by the bubbled in furnace off-gas.

The energy available for capture from the roaster off-gas is obtained by cooling it from 680˚C to 300-350˚C before it can be passed through the electrostatic precipitator on its way to being cooled further to 50°C before entering sulphuric acid production. The total roaster off-gas is modelled as 36 kg/s and has a heat capacity of 1330 J/(kg K), which represents an energy removal of 16.3 MW. Due to the elevated temperatures and the presence of particulate matter and the concentration of SO_2, the capture efficiency was taken as a conservative 60% (Stehlík, 2011; Loken, 2013).

The proposed tanks were considered to have insulation layers over the concrete walls and base and a clear roof covering. However, the impact of operating without either the insulating layers or the roof covering was also modelled using Sudbury climate data. With the roof covering removed, the regional average wind speed was taken to be blowing over the tanks and the atmospheric average monthly relative humidity used for assessing evaporative heat loss. The results illustrated in Figures 2.5 and 2.6 display the

energy supply rates from the roaster off-gas needed to supplement that provided by the furnace off-gas (12000 W at 15°C and 9740 W at 30°C) clearly showing the significant benefits obtained from insulation and a roof covering.

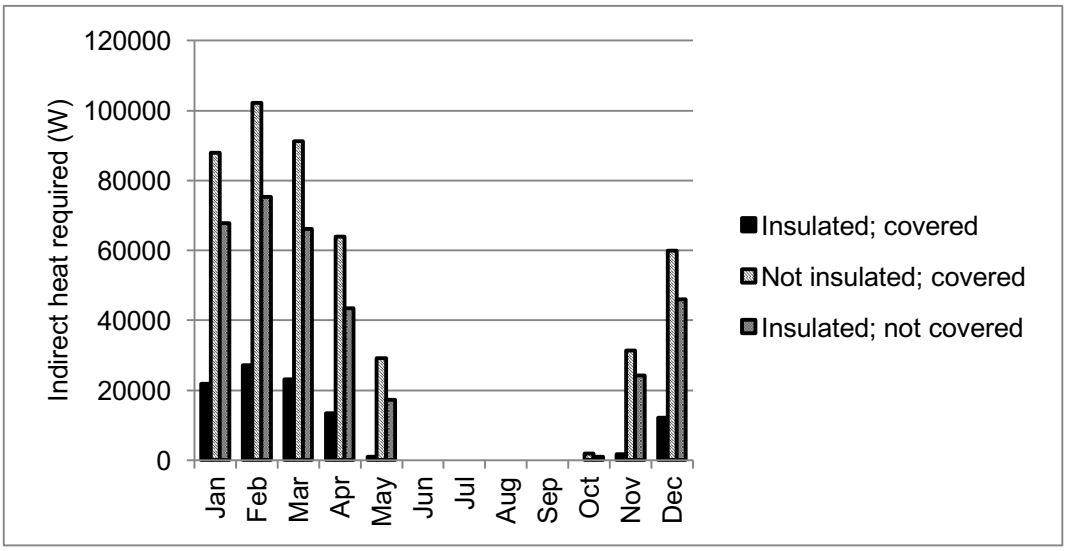

Figure 2.5: Impact on required energy from the roaster off-gas per 250 m^3 tank from removing either the insulation or roof covering from the tanks whilst maintaining water temperature at 15°C in Sudbury

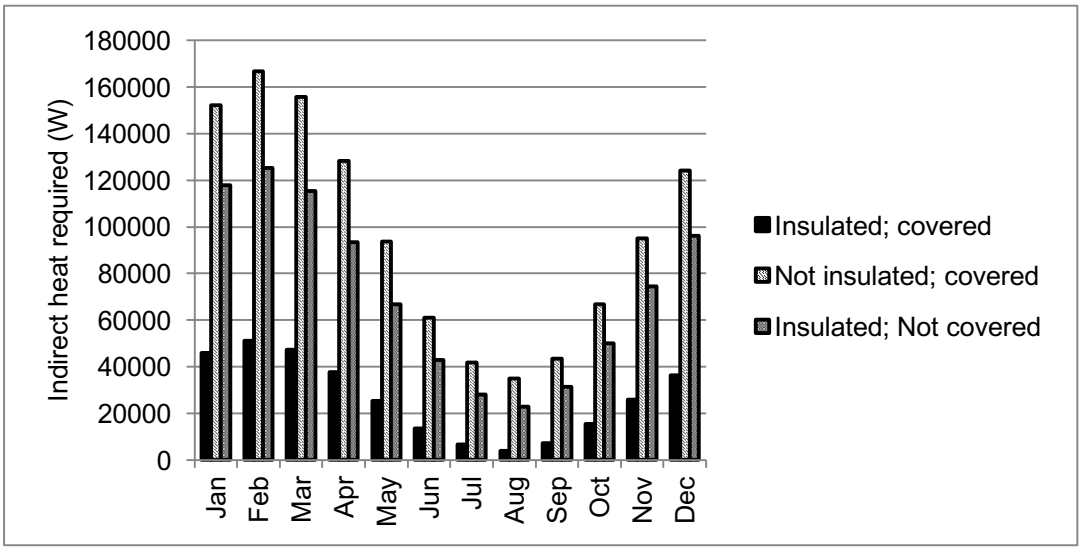

Figure 2.6: Impact on required energy from the roaster off-gas per 250 m^3 tank from removing either the insulation or roof covering from the tanks whilst maintaining water temperature at 30°C in Sudbury

The indirect heating requirements from heat recovered from the roaster off-gas which is added to that from bubbling in the furnace off-gas to maintain a single 250 m^3 tank at 15°C or 30°C are given in Table 2.3. In Sudbury through the coldest month of the year (February) there is still enough indirect energy to heat to 30˚C more than the 180 tanks that can be operated due to agitation by furnace off-gas. The results also illustrate the dynamic nature of the model and the association of historical climate data through the year. For example, the ambient temperature in March in Sudbury (-5.7°C) is similar to that in January in Lanzhou (-5.5°C). However, due the much colder preceding months in Sudbury, the heat needed to maintain tank temperatures is much greater.

Table 2.3: Indirect heating requirements to maintain a 250 m3 tank at 15˚C or 30˚C (empty cells represent no need to supply indirect heat)

Month	Sudbury			Bingham			Lanzhou		
	Ambient Temp. (°C)	Energy for 15˚C (W)	Energy for 30˚C (W)	Ambient Temp. (°C)	Energy for 15˚C (W)	Energy for 30˚C (W)	Ambient Temp. (°C)	Energy for 15˚C (W)	Energy for 30˚C (W)
January	-13.6	21888	46042	10.6		19853	-5.5	12207	36425
February	-11.4	27133	51276	11.1		16685	0.7	13842	37933
March	-5.3	23191	47357	15.4		13979	5.8	6293	30443
April	3.1	13519	37604	18.9		7415	12.4		21875
May	11.3	1051	25236	28.7			17.4		11477
June	16.2		13584	28.6			21.3		4172
July	19.0		6604	34.8			22.4		
August	17.7		4025	32.5			21.1		
September	12.3		7168	30.1			16.9		1870
October	5.8		15582	19.4			10.0		9261
November	-1.5	1768	25922	15.1		3923	3.0		19135
December	-9.5	12230	36285	7.4		11954	-3.1	4822	28885

The available CO_2 contained within the furnace off-gas was determined from an overall flow rate of 24 m^3/s, and a CO_2 content of 7% (Renaud et al., 2010). Combining this total with the commonly used relation that 1.8 kg of captured CO_2 translates into 1 kg of dry algae biomass (Chisti, 2007), maximum microalgae concentrations can be also estimated. This could mean for example, that with 50% carbon capture (Weyer et al., 2010), there could be enough CO_2 in the furnace off-gas to obtain an algal productivity of 48400 kg/day (1.075 $kg/m^3/day$) when using a maximum of 180 tanks. This productivity is not unreasonable in relation to other studies using CO_2-rich industrial gas. Douskova et al. (2009) reported a growth rate of 2.5 $kg/m^3/day$ using an off-gas with 10-13% CO_2 in a 30°C photobioreactor. Similarly, in a bubble column, Jacob-Lopes et al. (2009) achieved a productivity equivalent to 1.250 $kg/m^3/day$ using air enriched to 15% CO_2.

Assuming this biomass achieves a conservative 30% lipid concentration (Chisti, 2007), this translates to 5300000 kg lipid/year. Using an average biodiesel density of 920 kg/m^3, the resulting lipid volume is 5760 m^3 lipid/year. Laboratory scale testing has given conversion efficiencies up to 86% (Wahidin et al., 2014), which would convert this into an annual production of 4954 m^3 of biodiesel.

2.5 Conclusion

Microalgae that can produce lipids for conversion into biodiesel have been previously studied as a CO_2 mitigation technique in tropical and sub-tropical climates. But relatively little research has looked at the methods by which microalgae can be mass-produced in colder climates. Using waste industrial heat and CO_2, such as from a nickel smelter, is one such method. In this paper, the heating value that can be obtained from both direct bubbling in of off-gas from a furnace and indirect capture from roaster off-gas is considered. It was shown through modelling that the smelter's off-gas provides the quantities of off-gas and heat necessary for year round algal production in various cold climates. The results show, therefore, that microalgae production could be expanded into regions that experience extended periods of ambient temperatures well below those currently considered suitable for large-scale growth.

Process-coupled microalgae cultivation creates saleable products in biodiesel and other value-added algal products, reduces CO_2 emissions and can be linked into an existing operation. Indeed, within the smelting process that has been used as an example there is need to significantly cool the roaster off-gas prior to it being passed to a sulphuric acid plant. A microalgae facility would, therefore, represent a positive use of the heat

removed. The same approach could also be adopted for other industrial sectors, such as the fossil-fuel power industry and iron and steel manufacture. The outcomes would be improved sustainability through biodiesel production and CO_2 mitigation.

2.6 Nomenclature

Symbol	Description
A	pond surface area (m^2)
A_w	pond wall and bottom area (m^2)
b_o	constant
C_{Bowen}	Bowen coefficient (61.3 N m^{-2} °C^{-1})
C_D	drag force coefficient
C_p	specific heat coefficient (J kg^{-1} °C^{-1})
d	diameter (m)
e_G	vapor pressure in ambient air (N m^{-2})
e_S	saturation vapor pressure of air at the pond temperature (N m^{-2})
E	rate of energy variation (W)
f	frequency of gas bubble formation (s^{-1})
F_b	buoyancy force (N)
F_d	drag force (N)
Fr	Froude number
g	gravitational acceleration (m s^{-2})
h	heat transfer coefficient (W m^{-2} °C^{-1})
H	solar radiation (W m^{-2})
I	incident solar radiation (W m^{-2})
k	thermal conductivity (W m^{-1} °C^{-1})
n	orifices per unit area (m^{-2})
N	number of tanks
P	pressure (N m^{-2})
P_{ref}	reference pressure (N m^{-2})
q	heat flux (W)
Q	off-gas volumetric flow rate (m^3 s^{-1})
R_{Bowen}	Bowen ratio
S_t	solar insolation over pond surface (W m^{-2})
t	time (s)
T	temperature (°C)
u	wind velocity (m s^{-1})
W	mass flow rate (kg s^{-1})
z	thickness (m)
Z	pond depth (m)

α_L	water adsorptivity (dimensionless)
ε	furnace off-gas holdup (dimensionless)
ρ	density (kg m^{-3})
ξ	reflectivity (dimensionless)
τ	transmissivity (dimensionless)
μ	dynamic viscosity (Pa s)
κ	thermal diffusivity (m^2 s^{-1})
λ	constant (W m^{-2} Pa^{-1} $°C^{-1/3}$)

Subscripts

a	ambient
b	bubble
conc	concrete
cond	conductive
conv	convective
evap	evaporative
G	gas above pond surface
F	furnace off-gas
i	inlet
ins	insulating material
L	liquid (water)
o	orifice
R	roaster
w	wall

Conflict of Interest

The authors declare no conflict of interest.

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Chapter 3

Paper #2 – Modeling, Canadian Institute of Mining

Smelter off-gas waste heat and carbon dioxide sequestration to promote production of biodiesel

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CAL performed the modeling, data analysis and primary manuscript writing. HS developed the previous model and provided assistance in the further development of that model. GMR assisted in some manuscript writing. JAS provided overall direction in project and model development, and manuscript writing.

Abstract

The indirect recovery and use of waste heat contained in smelter off-gas is proposed as a means to significantly expand the regions available for year-round on-site production of microalgae sourced biodiesel, a fuel that could be beneficially used in underground machinery. A dynamic model of an off-gas heat exchanger was developed that describes both the capture and the even distribution of heat into open, externally located rectangular microalgae ponds. In the example used, smelter off-gas is shown to contain sufficient energy to maintain large-scale microalgae cultivation pond temperatures above 15°C, even with winter ambient temperatures below –15°C. The results highlight opportunities that could lie in tapping these types of heat resources to help produce renewable biofuels on-site and sequester carbon dioxide, whilst leaving the industrial process unaffected.

Keywords

Off-gas, smelters, heat recovery, microalgae, biodiesel, clean burning, modeling

3.1 Introduction

Microalgae that grow in water can efficiently convert solar energy and carbon dioxide into biomass. This biomass can be up to 50% oils (lipids), which can be extracted and converted into biodiesel through transesterification (Demirbas, 2009b). Compared to terrestrial plants that produce similar oils (e.g., jatropha, soybean and rapeseed), microalgae represent an order of magnitude increase in areal productivity, do not require arable land and can be continuously harvested (Rawat et al., 2013). The potential advantages through the production of biodiesel from microalgae also include sequestration of carbon dioxide, reduced reliance on fossil fuels and the co-production of other value-added bioproducts.

The burning of biodiesel also allows for a significant reduction in sulphur dioxide production, unburned hydrocarbons, carbon dioxide, carbon monoxide, and smoke density (Utlu, 2007; Demirbas, 2009a). As a consequence, biodiesel can be substituted or blended with diesel in existing equipment, allowing for reduced levels of these emissions. If used in underground mines, this could potentially create a better working environment, however more work needs to be done on the comparative affects of this change in emission profiles. In particular, burning of biodiesel slightly increases production of nitrogen oxides (Tüccar et al., 2014), the elevated levels of which would have to be assessed in a restricted environment. Dependent on this, there would be the possibility to allow for reduced ventilation requirements (Salama et al., 2015). All these advantages combine to encourage the integration of biodiesel into mining operations, not

only from an operational standpoint but also from environmental considerations, including meeting climate change mandates.

Microalgae are an extremely promising source of biodiesel, but water temperature is a dominating parameter in their production as it determines both the growth rate and the extent of the growing season (Davison, 1991). Not surprisingly, therefore, most large-scale microalgae pond systems are located in year-round warm regions such as in Hawaii, India, Israel and southern California (Spolaore et al., 2006). One possible way to open up opportunities for year-round production in colder climates is to exploit waste heat contained within industrial processes.

For low-grade heat, utilizing a supply of warm water was proposed by capturing waste heat in nuclear plant cooling water (Wilde et al., 1991). Baliga and Powers (2010) also proposed the use of low-grade heat with a closed photobioreactor. However, for regions that experience extended cold winters to maintain pond temperatures much higher-grade heat would be needed, such as that contained with industrial off-gas. To meet this need, the use of ore smelter furnace off-gas sparged into microalgae incubator ponds has been proposed for regions that experience prolonged periods of ambient temperatures well below those optimal for microalgae growth (Shang et al., 2010; Laamanen et al., 2014).

The diffusion of CO_2 from the atmosphere into microalgal culture also limits biomass productivity due to the low concentration (approximately 380 ppmv) and the high surface tension of water (Zimmerman et al., 2011). To improve production and economics, it is possible to increase the supply of carbon for the algae (Lam and Lee, 2014; Sapci and Morken, 2014; Zhao and Su, 2014) and, therefore, coupling microalgae plants with

industries, which produce CO_2 rich off-gas, is seen as an attractive economic option (Bilanovic et al., 2012). Many such industries exist, such as natural gas combustion, coal-fired power plants, steel production, iron production, and cement production, which produce 9, 10, 30, and 15–25% CO_2 off-gas, respectively (Bounaceur et al., 2006).

In many countries around the world, potential sources of CO_2-rich industrial off-gas, including from mine and mineral processing sites that could stimulate microalgae growth are located in regions that experience extreme lows in ambient temperatures. Nevertheless these regions can have other beneficial characteristics. In Sudbury, Canada, for example, there are over 300 freshwater lakes within its city limits, and between 8 and 14 hours of solar insolation per day over the year, which provides above the minimum requirement for microalgae production year-round (Figure 3.1).

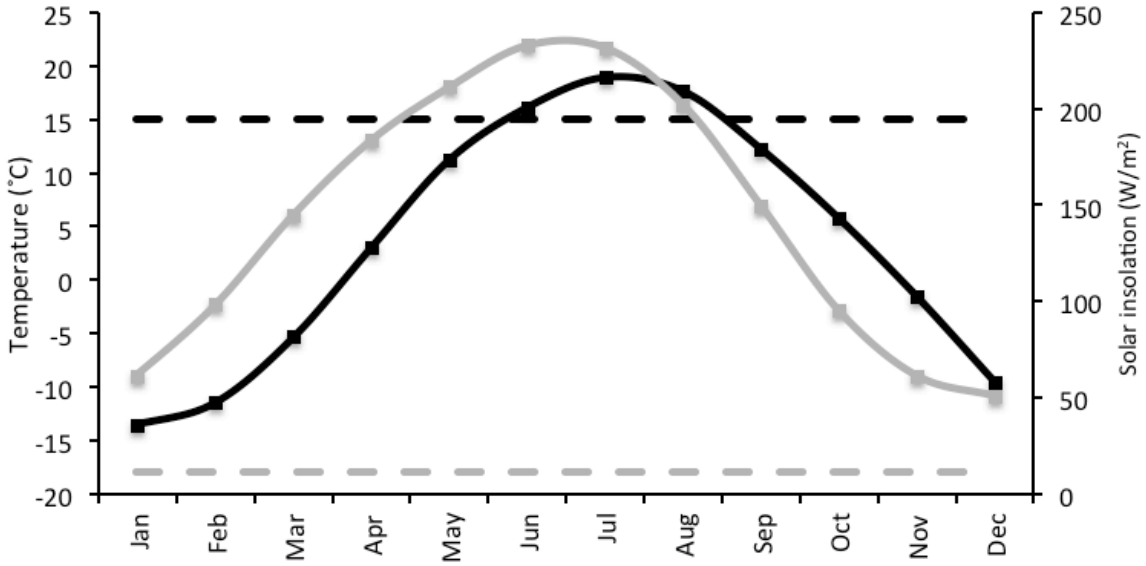

Figure 3.1: Climatic data for Sudbury, ON, Canada, showing average monthly temperatures (black) and solar insolation (grey). The dashed lines represent the minimum of the respective measurements, 15˚C and 11 W/m^2 (Barbosa, Janssen, Ham, Tramper, & Wijffels, 2003), respectively.

The quantity of lakes highlights the ability to operate using freshwater, a limitation in many traditional algae cultivation areas, while the sunlight in the area meets the light requirement to be considered a favourable growing region (Ziolkowska and Simon, 2014). Demirbas and Demirbas (2011) say that open algae cultivation can be done anywhere where there is enough sunlight, and Sudbury provides an annual average of well above 2,800 light hours. The drawback is that for approximately 7–8 months of the year, ambient air temperatures fall well below the 15°C generally regarded as the minimum temperature suitable for microalgae growth (Figure 3.1). For this region the use of smelter furnace off-gas (6–7% CO_2) sparged directly into microalgae incubator ponds has been proposed as a means of providing enhanced CO_2 and also simultaneously heat (Laamanen et al., 2014).

However, many industrial off-gas streams are not suitable for direct application into microalgae ponds. They may contain very large amounts of waste heat, but also significant levels of particulate matter and acid gas components, such as SO_2. For example, for a nickel smelter, 65% of the 60MW of waste heat in the off-gas streams is contained in those from the ore roasters (Loken, 2013). But the off-gas's 11–18% SO_2 content makes it unsuitable for sparging into ponds of microalgae, as they would become too acidic. Furthermore, in 2005 whilst there were more than 50 nickel smelters and Class 2 (<99% Ni) processing facilities worldwide (Eckelman, 2010), they represent only a small portion of the available waste heat from the metallurgical industry and industrial operations in general that may not be suitable for direct use.

To make use of the considerable unexploited energy to support microalgae ponds worldwide it needs to be captured by alternate means. In this paper, using the capture of heat from roaster off-gas as an example, a novel heat exchanger configuration is proposed and modeled which can provide uniform heating of rectangular open microalgae ponds.

3.2 Waste heat in nickel smelter off-gas

For the nickel smelter examined, off-gas from the furnace passes through a cyclone, producing a gas stream, which is relatively clean (SO_2 of approximately 0.4% and dust free), hot (approximately 300°C) and containing 7% CO_2 (Renaud et al., 2010). While the low levels of SO_2 will cause a reduction in pH levels, this can be advantageous by limiting contamination through the use of acidophilic algae (Eibl et al., 2014). Meanwhile negligible amounts of NO_x eliminate a concern that exists with some off-gas

applications, as lNO_x levels higher than present in the smelter furnace off-gas are tolerated by microalgae (Radmann et al., 2011; Taştan et al., 2012).

Direct application of this off-gas through an evenly distributed sparger system over the bottom of the pond has been previously modeled (Shang et al., 2010). The gas bubbles provide supplementary heat for the water and CO_2 to stimulate microalgae growth. They also provide agitation to ensure homogenous vertical mixing of microalgae, which allowed for light-dark cycling for the microalgae cells (Seyed Hosseini et al., 2015).

The roaster off-gas is not feasible for direct application to the culture media due to its high 11–18% SO_2 content (Shang et al., 2011; Loken, 2013). The roaster off-gas passes through cyclones, to remove fine calcine before entering a cooling tower. In the cooling tower an atomized water spray cools the gas from 650–680°C to 300–350°C to prevent heat damage to a downstream electro-static precipitator (ESP). The gas is then cooled further to 50°C and passed to a sulphuric acid plant to remove the SO_2 (Shang et al., 2007). This removed energy is currently not captured and we propose a liquid-gas heat exchanger replacing the existing cooling tower, with heating fluid circulated through microalgae cultivation ponds (Figure 3.2).

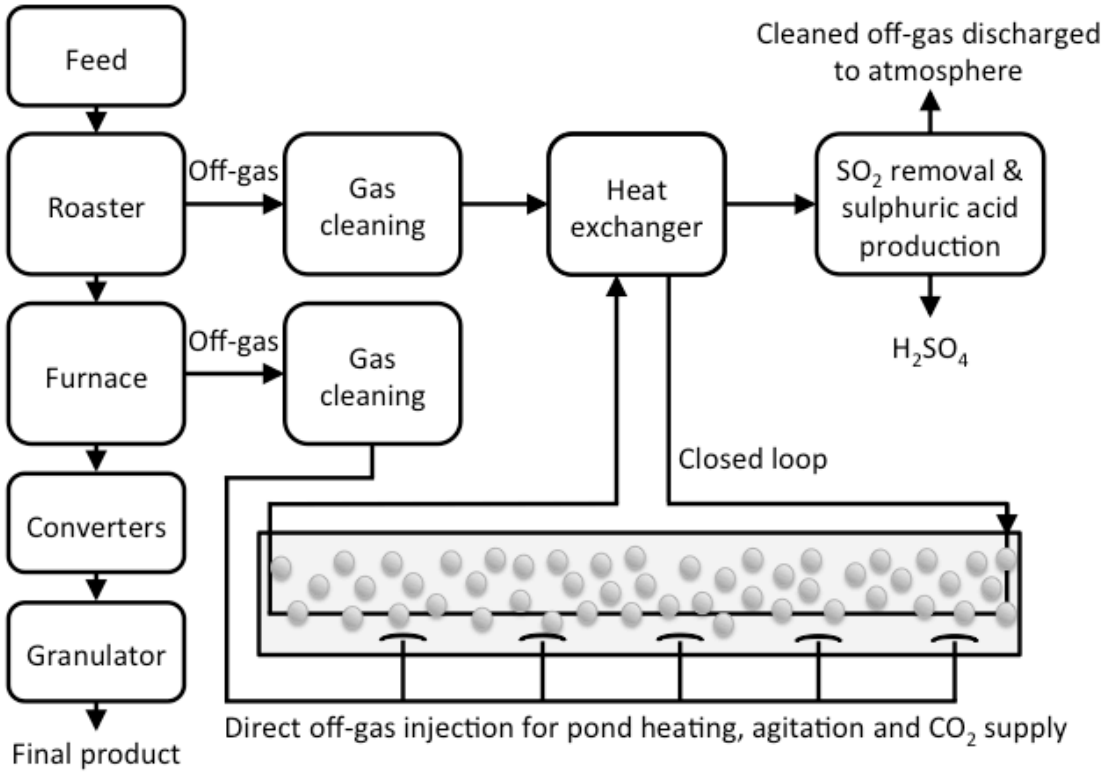

Figure 3.2: Schematic of a smelter coupled microalgae production facility (adapted from Laamanen et al., 2014)

3.3 Heating microalgae ponds using waste off-gas heat

A key requirement is that any heat recovery system must not disrupt the flow of the roaster off-gas and interfere with the smelter's operation. To achieve this a simple jacketed pipe heat exchanger is proposed (Figure 3.3) which typically has a 60% capture efficiency (Stehlík, 2011; Loken, 2013). The heat exchanger consists of a spiral wound coil placed around the outside of the existing off-gas pipe and is, therefore, non-intrusive.

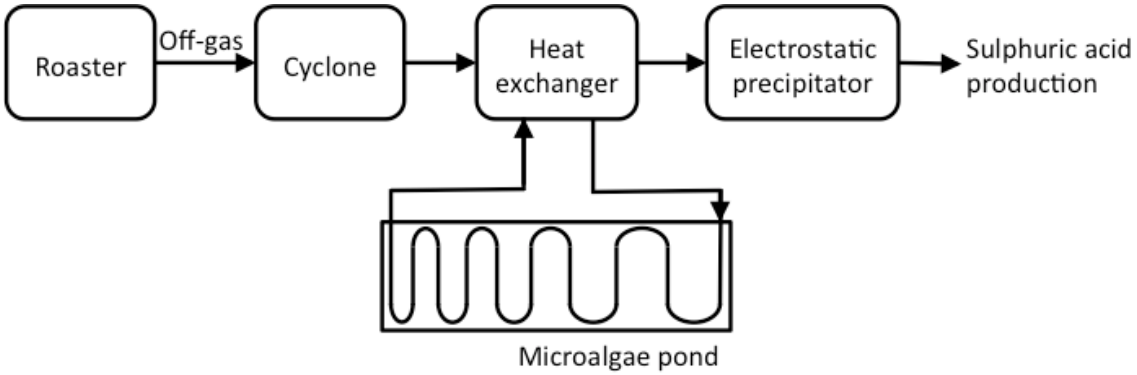

Figure 3.3: Proposed roaster off-gas cooling heat exchanger.

Heat transfer fluid passed through this jacketed pipe heat exchanger would be sent to microalgae ponds and distributed via a coil in the bottom of each pond. We propose that these coils be variably spaced to allow for even heat distribution. The intention is that they get closer together as the fluid passes along the pond and in this way temperature variations in the pond can be minimized. Such a design will allow for the expansion of the algae cultivation from regions with tropical and sub-tropical climates into those with climates traditionally considered too cold.

3.4 Model development

The key determination is the spacing of the heating coil loops placed in the bottom of the ponds. To assess this, a model was constructed that considers a pond divided up into a series of discrete sections over which energy balances can be performed (Figure 3.4). From these balances, the required energy to be supplied from the heating fluid to maintain temperature in each section can be then assessed. This in turn can be used to specify the heat exchanger pipe spacing in each section, which will become closer to compensate for the decreasing temperature difference between the heating fluid and the required bulk pond temperature.

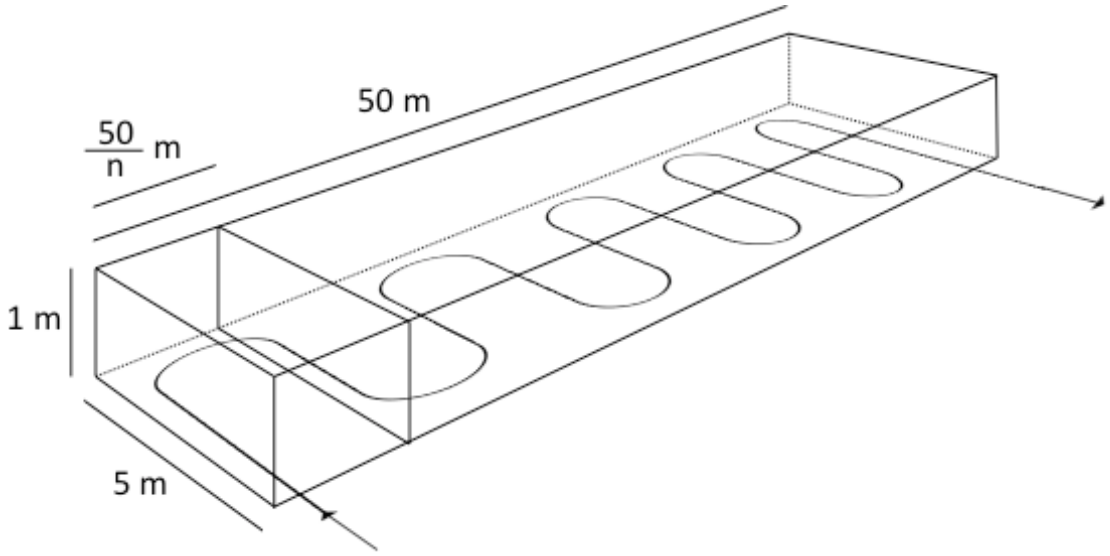

Figure 3.4: Sectioning of pond for heat exchanger spacing determination.

To create the model, the following assumptions were used:

(i) the pond is a batch operation (i.e., no water flow in and out);

(ii) due to the mixing effect of sparged-in furnace off-gas bubbles vertical spatial variations of water temperature in the pond are assumed negligible;

(iii) variations in gas and water density, and heat transfer coefficients are negligible;

(iv) temperature variations in the pipe are dominated by heat convection and the impact of heat diffusivity within the heating fluid is negligible;

(v) the effects of both the furnace off-gas and roaster off-gas heat addition are additive;

(vi) the furnace off-gas heat addition is assumed constant at 12,000 W for 15°C and 9,740 W for 30°C (Laamanen et al., 2014);

(vii) the exit temperature of the heating fluid is 10˚C higher than the pond temperature.

The "standard" pond modeled has a 50 m by 5 m footprint and a water depth of 1 m. The increased depth is possible through bubbling of furnace off-gas providing vertical agitation and light-dark cycling of the algae (Seyed Hosseini et al., 2015). In keeping with commercial raceway designs, the ponds are taken as insulated sunk concrete channels and also covered by a clear roof. The standard pond and base level

thermodynamic principles are given in Laamanen et al. (2014), with the total heat transfer to the pond represented as:

$$q = q_{roaster} + q_{furnace} + q_{solar} - q_{evap} - q_{cond} - q_{conv} \quad \text{Equation 3.1}$$

where $q_{roaster}$ and $q_{furnace}$ represent the energy input from the roaster and furnace off-gas respectively. The remaining four terms make up the environmental heat transfer, namely q_{solar}, q_{evap}, q_{cond}, and q_{conv} representing the solar input, evaporative, conductive and convective energy losses, respectively. For the current work, calculation of the total roaster off-gas heat was obtained from:

$$q_{roaster,\max} = C_{p,roaster} W_{roaster} (T_{duct,in} - T_{duct,out}) \cdot x_{hx} \quad \text{Equation 3.2}$$

where $C_{p,roaster}$ is the heat transfer coefficient of the roaster off-gas, $W_{roaster}$ is the roaster off-gas flow rate, x_{hx} is the heat exchanger efficiency and $T_{duct,in}$ and $T_{duct,out}$ represent the initial roaster temperature in the off-gas duct and the exit temperature from the heat exchanger. While the overall heat transfer model can be represented as:

$$\frac{dT_L}{dt} = \frac{1}{\rho_L (1-\varepsilon) C_{p,L} AZ} (q_{roaster} + q_{furnace} + q_{solar} - q_{evap} - q_{conv} - q_{cond}) \quad \text{Equation 3.3}$$

where T_L is the liquid temperature, ρ_L is the liquid density, ε the furnace off-gas holdup, $C_{p,L}$ the heat transfer coefficient of the liquid, A the surface area of the pond, and Z the depth of the pond.

3.5 Pond sectioning

The requirement is to maintain a constant lateral temperature along the pond despite a falling heat transfer per unit length due to a decreasing temperature gradient between the pond and the heating fluid temperatures. The pond was, therefore, divided into *n* sections in order that the pipe length per section, based on energy requirements to maintain a specified water temperature, can be determined. Certain heat transfer terms are the same for each section, including the addition from sparged-in furnace off-gas, solar irradiation, and evaporative and convective heat transfer from the surface. As the conductive heat loss is a function of the wall area, this will result in increased energy requirements for the first and last sections due to the end walls. As the goal is to maintain the pond temperature at steady state, total heat transfer (Equation 3.1) can be set to zero.

The required energy from roaster off-gas for a section, i, along the pond can be calculated from:

$$q_{roaster,i} = \frac{q_{furnace} + q_{solar} - q_{evap} - q_{cond}}{n} - q_{conv,i} \qquad \text{Equation 3.4}$$

where $q_{conv,i}$ is the convective loss in section i, and is a function of the wall surface area. This can be used to find the heat exchanger pipe length for each section:

$$q_{roaster,i} = \int_{s=0}^{l_i} U_{hf} \dot{m}_{hf} \left(T_i(s) - T_p \right) A_i \, ds \qquad \text{Equation 3.5}$$

where U_{hf} is the overall heat transfer coefficient (calculated in Equation 3.15) and $T_i(s)$ is the temperature of the heating fluid in the pipe (for the first section, $T_i(0)$ is the inlet temperature of the heating fluid into the pond and for every other section, $T_i(0)$ is the exit temperature from the previous section).

3.6 Heat transfer coefficient for pond heat exchanger

To determine the length of heat exchanger pipe required in the pond for each pond section the overall heat transfer coefficient (U_{hf}) must be calculated. U_{hf} is a function of convection through the heat transfer fluid in the pipe, conduction through the pipe wall, and forced convection from the outer surface of the pipe.

To calculate the internal heat transfer component, the fluid velocity in the pipe is a determining factor and is found from the required mass flow rate:

$$\dot{m}_{hf} = \frac{\sum_{i=1}^{n} q_{roaster,i}}{C_{p,hf}(T_{p,in} - T_{p,out})} \qquad \text{Equation 3.6}$$

where $T_{p,in}$ and $T_{p,out}$ are the initial and final temperatures of the heat fluid in the pond, respectively, and from which the velocity of the heating fluid can be calculated:

$$v_{hf} = \frac{\dot{m}_{hf}}{\rho_{hf} \frac{\pi}{4} D_{int}^2} \qquad \text{Equation 3.7}$$

Calculation of fluid velocity allows determination of the common heat transfer values, Reynolds number (Re) and Prandtl number (Pr):

$$\mathrm{Re} = \frac{D_{int} u_{hf} \rho_{hf}}{\mu_{hf}}$$ Equation 3.8

$$\mathrm{Pr} = \frac{C_{p,hf} \mu_{hf}}{k_{hf}}$$ Equation 3.9

As for all cases considered in this work, Re > 6,000 and 0.7 < Pr < 16,000, the heating fluid flow will be turbulent and the Nusselt number (Nu) can be calculated from (Sieder and Tate, 1936):

$$Nu = 0.027 \mathrm{Re}^{0.8} \mathrm{Pr}^{1/3} \left(\frac{\mu_{hf}}{\mu_{f,hf}} \right)^{0.14}$$ Equation 3.10

from which, the internal convective heat transfer coefficient, h_{int}, can be found:

$$h_{int} = \frac{Nu \cdot k_{hf}}{D_{int}}$$ Equation 3.11

The calculation of the external forced convective heat transfer coefficient (h_{ext}) also requires the Reynolds number (Re_{ext}) and Prandtl number (Pr_{ext}) for the exterior of the pipe:

$$\mathrm{Re}_{ext} = \frac{D_{ext} u_{ext} \rho_{f,L}}{\mu_{f,L}}$$ Equation 3.12

$$\mathrm{Pr}_{ext} = \frac{C_{p,L} \mu_{f,L}}{k_{f,L}}$$ Equation 3.13

where u_{ext} is the circulation velocity of the microalgae culture medium and is taken as the gas bubble rise velocity (0.04 m/s ; Zhang, 2011) and can be used for calculating h_{ext} (Hilpert, 1933):

$$h_{ext} = C_{h,ext} \mathrm{Re}_{ext}^{m_{h,ext}} \mathrm{Pr}_{ext}^{1/3} \frac{k_{f,L}}{D_{ext}} \qquad \text{Equation 3.14}$$

where $C_{h,ext}$ and $m_{h,ext}$ are coefficients, equal to 0.193 and 0.618 (Geankoplis, 2003), respectively, as the $Pr_{ext} > 0.6$ and $4{,}000 < Re_{ext} < 40{,}000$.

The combination of these two heat transfer terms (h_{int} and h_{ext}) and the pipe conductivity gives the overall heat transfer coefficient, U_{hf}:

$$U_{hf} = \left(\frac{1}{h_{int}} + \frac{D_{int}}{2k_{pipe}} \log\left(\frac{D_{ext}}{D_{int}}\right) + \frac{1}{h_{ext}} \frac{D_{int}}{D_{ext}} \right)^{-1} \qquad \text{Equation 3.15}$$

which is a determining factor for the heat exchanger pipe length in each section (Equation 3.5).

3.7 Pond pumping requirements

To pump the required heating fluid through a pond, there is an energy requirement, which is determined by the head loss, H, in the system. This head loss is a function of both the friction in the pipe (H_f) and the number and type of bends along the he length of the pond. For the pipe material, various plastic materials (polyvinyl chloride, polypropylene, low density polyethylene) were chosen based on favorable costs, low coefficient of friction, and chemical resistance. The internal roughness of the pipe,

$k_{fr,pipe}$, can be used in the Colebrook-White equation (Colebrook, 1939) to relate it to the friction factor, f:

$$\frac{1}{\sqrt{f}} = -2\log\left(\frac{k_{fr,pipe}}{3.7D_{int}} + \frac{2.51}{\mathrm{Re}\sqrt{f}}\right) \qquad \text{Equation 3.16}$$

Equation 3.16 can iteratively be solved to find f, and once calculated the head loss due to friction (H_{fr}) can be obtained from:

$$H_{fr} = f\left(\frac{\sum_{i=1}^{n} L_i}{D_{int}}\right)\left(\frac{V_{hf}^2}{2g}\right) \qquad \text{Equation 3.17}$$

where L_i is the length of pipe in each tank section. Additional head losses come from the bends in the tank, these are taken as 180° and the head loss from them is a product of their number (n_{180}) and the equivalent piping distance (K_{180}) for each bend (Beij, 1938):

$$H_{total} = H_{fr} + n_{180}K_{180}\frac{V_{hf}^2}{2g} \qquad \text{Equation 3.18}$$

The total pumping energy requirement for the entire pond (E_{pump}) can be then calculated:

$$E_{pump} = \frac{\dot{m}_{hf} \cdot H_{total} g}{x_{pump}} \qquad \text{Equation 3.19}$$

where x_{pump} is the pump efficiency and is taken as a 70% (Haman et al., 1994). The total energy required for pumping through the pond system can be taken as a multiple of this value. Since 180 ponds are the maximum that can be supported based on furnace off-gas

(Laamanen et al., 2014), this number will be utilized for the sizing of the heat exchanger used to extract heat from the roaster off-gas prior to it entering the electrostatic precipitator.

3.8 Roaster heat exchanger

As previously mentioned the roaster off-gas heat exchanger is assumed to be a jacketed pipe and must handle the required flow rate, as given by:

$$\dot{m}_{hf,duct} = \frac{180\dot{m}_{hf}(T_{p,in} - T_{p,out})}{\Delta T} \qquad \text{Equation 3.20}$$

where ΔT is the average temperature gradient between the roaster off-gas and the heating fluid, and can be calculated from:

$$\Delta T = \frac{(T_{duct,in} - T_{duct,out}) + (T_{duct,out} - T_{p,out})}{2} \qquad \text{Equation 3.21}$$

This flow rate can be used to calculate the fluid velocity, Reynolds number and Prandtl number, in a similar manner to the heat exchanger pipe in the pond, with the additional requirement of calculating the hydraulic diameter as the heat exchanger coil surrounding the off-gas duct is semi-circular:

$$D_{hx} = \frac{\pi D_{int,hx}}{2} \qquad \text{Equation 3.22}$$

The calculation of the roaster off-gas heat exchanger is a combination of various heat transfer values:

$$U_{duct} = \left(\frac{1}{h_{hx}} + \frac{x_{duct}}{k_{duct}} + \frac{1}{h_{roaster}} + \frac{1}{h_{ff}} \right)^{-1} \quad \text{Equation 3.23}$$

where x_{duct} and k_{duct} are respectively the thickness and thermal conductivity of the roaster off-gas pipe, and h_{offgas} is the convective transfer through the roaster off-gas. The convective heat transfer in the heating fluid in the heat exchanger, h_{hx}, can be calculated from (Sharratt, 1997):

$$h_{hx} = \frac{0.023 \mathrm{Re}_{hx}^{0.8} \mathrm{Pr}_{hx}^{1/3} \left(\frac{\mu_{hf}}{\mu_{f,hf}} \right)^{0.14} k_{hf} x_{roaster}}{D_{int,hx}} \quad \text{Equation 3.24}$$

With the overall heat transfer coefficient calculated, the required heat exchanger area, A_{duct}, is:

$$A_{duct} = \frac{180 \sum_{i=1}^{n} q_{roaster,i}}{U_{duct} \Delta T} \quad \text{Equation 3.25}$$

And from this area requirement, the length of the roaster off-gas heat exchanger, L_{duct}, can be determined based on the existing off-gas duct diameter, D_{duct}:

$$L_{duct} = \frac{A_{duct}}{\pi D_{duct}} \quad \text{Equation 3.26}$$

By using the length and the diameter of the coils used previously, the number of coils around the pipe can be determined which allows for calculation of pumping requirements in the same manner as outlined for the in-pond heat exchanger pipe.

3.9 Simulation results

The standard pond used for these simulations was 50 m long, 5 m wide and 1 m. It was sunk into the ground, insulated and covered by an A-frame of transparent polyethylene, as described in Laamanen et al. (2014). Based on previous work, there is sufficient volume of furnace off-gas to sparge-in and provide agitation and CO_2 for 180 of these standard ponds (Laamanen et al., 2014).

Climate data from Sudbury, Ontario, Canada (Figure 3.1) were used for the calculation of heating requirements. The parameters used in the model are given in Table 3.1, and simulations were completed at a microalgae cultivation pond temperature of 30°C (Table 3.2). Model parameters varied included the diameter of heat exchanger pipe in the pond, inlet heating fluid temperature, and the type of pipe material.

Table 3.1: Model parameters.

	Value	Units	Source
A_p	250	m^2	Laamanen et al. (2014)
b_o	0.032	J/m^3 Pa	Nath and Bolte (1998)
$C_{p,furnace}$	1,007	J/kg °C	Ghoshdastidar (2004)
$C_{p,G}$	1,007	J/kg °C	Ghoshdastidar (2004)
$C_{p,L}$	4,180	J/kg °C	Ghoshdastidar (2004)
$C_{p,roaster}$	1,330	J/kg °C	Shang et al. (2007)
d_o	0.05	m	Shang et al. (2010)
D_{duct}	4.88	m	Loken (2013)
$D_{int,hx}$	0.121	m	Loken (2013)
h_{ff}	1/0.00018	W/m^2 °C	Loken (2013)
h_{Ga}	12	W/m^2 °C	Ghoshdastidar (2004)
h_{Lb}	5,000	W/m^2 °C	Al-Hemiri and Ahmedzeki (2008)
h_{LG}	22.7	W/m^2 °C	Kwon (1995)
h_{Lw}	340	W/m^2 °C	Kwon (1995)
$h_{roaster}$	6.94	W/m^2 °C	Loken (2013)
k_{conc}	1	W/m °C	Laamanen et al. (2014)
k_{ins}	0.17	W/m °C	Laamanen et al. (2014)
K_{180}	0.15	Dimensionless	This work
n_o	2,500	$/m^2$	Shang et al. (2010)
$Q_{furnace}$	24	m^3/s	Renaud et al. (2010)
$T_{duct,in}$	665	°C	Shang et al. (2007)
$T_{duct,out}$	300	°C	This work
$T_{furnace,in}$	95	°C	Laamanen et al. (2014)
V_G	1,125	m^3	Shang et al. (2010)
$W_{roaster}$	36	kg/s	Shang et al. (2007)
x_{hx}	0.6	Dimensionless	Laamanen et al. (2014)
x_{pump}	0.7	Dimensionless	This work
Z	1	m	Shang et al. (2010)
α_L	0.3	Dimensionless	Sethi (2009)
κ	0.55×10^{-6}	m^2/s	Beltrami and Kellman (2003)
λ	0.027	W/m^2 Pa^1 $°C^{1/3}$	Nath and Bolte (1998)
μ_L	0.0009	Pa s	Ghoshdastidar (2004)
μ_{PVC}	0.0000015	m	This work
$\mu_{stainless}$	0.000015	m	This work
ξ	0.06	Dimensionless	Sethi (2009)
ρ_G	1.2	kg/m^3	Ghoshdastidar (2004)
ρ_L	999	kg/m^3	Laamanen et al. (2014)
τ	0.86	Dimensionless	Pieters and Deltour (1999)

Table 3.2: Off-gas and energy requirements for microalgae ponds maintained at 30°C.

Month	Furnace off-gas flow rate per tank (m^3/h)	Furnace off-gas energy input (W)	Roaster off-gas energy input (W)	For all tanks (180)		
				Total roaster off-gas heating (MW)	Roaster off-gas energy use (%)	Excess roaster off-gas energy (MW)
January	480	9,740	42,060	7.57	72.2	2.91
February	480	9,740	43,700	7.87	75.0	2.62
March	480	9,740	38,380	6.91	65.9	3.58
April	480	9,740	28,580	5.14	49.1	5.34
May	480	9,740	17,600	3.17	30.2	7.32
June	480	9,740	8,530	1.54	14.6	8.95
July	480	9,740	3,320	0.60	5.7	9.89
August	480	9,740	2,650	0.48	4.5	10.01
September	480	9,740	7,230	1.30	12.4	9.18
October	480	9,740	15,270	2.75	26.2	7.74
November	480	9,740	24,800	4.46	42.6	6.02
December	480	9,740	34,260	6.17	58.8	4.32

The results for February, the coldest month of the year, indicate that 75% of the energy from the required cooling of the roaster off-gas before in enters the electrostatic precipitator is enough to maintain the 180 ponds at 30°C. This means that not only can these ponds be supported year round, there is also an additional 2.62 MW of energy which is available for use. This excess energy can be allocated elsewhere, such as for the required drying of harvested microalgae.

Harvesting of the microalgae is commonly achieved by centrifugation or flotation (Laamanen, Ross, & Scott, 2016). If, for example, centrifugation is used a product of approximately 12% solids is obtained (Molina Grima et al., 2003), which is usually then dried to 90–95% solids (Sharma et al., 2013). This drying has an energy requirement of 3556 kJ per kilogram of water evaporated (Sheehan et al., 1998), which can have significant implications on the cost of biomass production, (Sander and Murthy, 2010).

For 180 ponds operating 300 days/year, algae production based on a production rate of 0.060 g/L/day (Seyed Hosseini et al., 2015) would be 810,000 kg/year, which would require an average 807 kW to dry. Even with this requirement there is more than enough heat all year to cover both the pond heating and harvested algae drying energy demands. It is, however, interesting to note that if diesel fuel was used to dry this biomass there would be a need for an approximate 458,500 kg/year of additional diesel. This would result in the requirement for algae to accumulate 65.8% lipids, at 86% conversion efficiency (Wahidin et al., 2014), to break even on the drying stage alone. Therefore, the drying method is proposed as an industrially-coupled waste heat capture method and not as a stand alone option. The avoidance of the need for additional fossil fuel consumption to aid drying serves to enforce the potential for repurposing currently wasted off-gas heat.

From a model run using polyvinyl chloride (PVC) pipe (D_{ext} = 0.089 m), $T_{p,in}$ = 70°C and the pond divided into five 10 m sections (n = 5), to maintain a working temperature of 30°C through February, a total of 160 m of heat exchanger pipe is required in each pond. This was distributed from 20 m in the first section to 56 m in the fifth and final section. If, however, the sections were assumed to be separate from each other (no thermal conduction between sections) and the pipe was evenly distributed throughout the pond (i.e., 32 m of pipe in each section), then the first pond section would be heated to 50°C and the last section to only 16°C. This highlights the value of the variably spaced heat exchanger in the ponds in maintaining an even temperature along the pond length.

As the first and last sections have end walls and hence higher conductive loses, they require more energy input to maintain temperature than the other sections. Figure 3.5 shows the annual profile of energy requirement for each section.

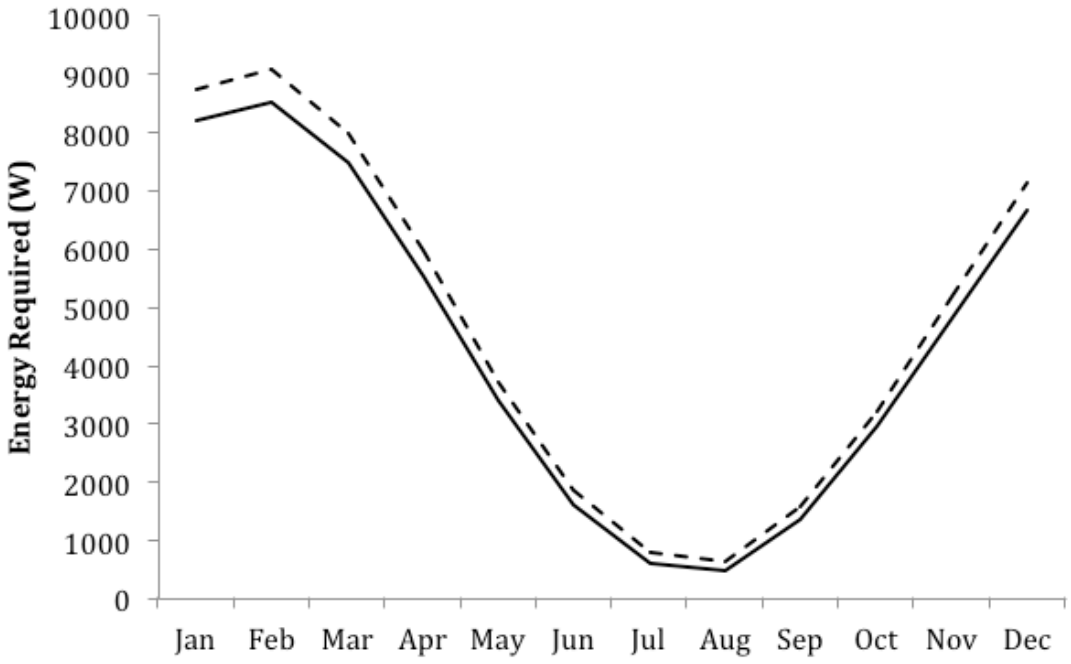

Figure 3.5: Energy requirements to maintain 30°C for sections of the pond (n = 5). Dashed line represents the energy requirement for the end sections and the solid line the energy requirement for the middle sections.

Three common plastic pipes were compared (Table 3.3) with regards to the required length and energy to pump the heating fluid. Since the roughness is similar for all of these materials, the pumping energy differences are a result of the different required pipe lengths.

Table 3.3: Comparison of different plastic piping materials, with an inlet temperature of 70°C and an exit temperature of 40°C (PVC = polyvinyl chloride, PP = polypropylene, PEL = low density polyethylene)

	OD (m)	ID (m)	U_{hf} (W/m^2 °C)	Length in section (m)					Total (m)	Pump (W)
				1	2	3	4	5		
PVC	0.089	0.083	48.437	19.51	21.94	27.12	35.53	55.83	159.93	0.48
PP	0.089	0.083	58.869	16.05	18.06	22.32	29.23	45.94	131.60	0.39
PEL	0.089	0.083	70.532	13.40	15.07	18.63	24.40	38.35	109.85	0.33

Using PVC as the piping material, inlet temperatures of 60, 70, and 80°C, and the pipe diameters of 0.040, 0.060, 0.089, 0.114, and 0.141 m were modeled (Table 3.4). The smallest pipe tested showed an order of magnitude rise in the pumping energy requirement due to increases in velocity and frictional losses. Increasing the outer diameter from 0.060 to 0.089 m increased the required pipe length as the greater pipe wall thickness (4–6 mm) results in higher thermal resistance.

Table 3.4: Experimental results based on inlet temperature and pipe size.

T_{in} (°C)	T_{out} (°C)	OD (m)	ID (m)	U_{hf} (W/m^2 °C)	Length in section (m)					Total (m)	Pump (W)
					1	2	3	4	5		
60	40	0.040	0.036	83.949	34.26	37.65	45.03	56.04	79.89	252.87	122.29
60	40	0.060	0.056	76.541	24.16	26.55	31.76	39.52	56.34	178.33	10.56
60	40	0.089	0.083	50.802	24.56	26.99	32.28	40.17	57.27	181.27	1.68
60	40	0.114	0.108	46.399	20.67	22.71	27.16	33.80	48.19	152.53	0.41
60	40	0.141	0.135	41.958	18.28	20.09	24.03	29.90	42.63	134.93	0.13
70	40	0.040	0.036	82.470	26.42	29.71	36.73	48.11	75.60	216.57	33.55
70	40	0.060	0.056	73.864	18.96	21.33	26.36	34.53	54.26	155.44	2.96
70	40	0.089	0.083	48.437	19.51	21.94	27.12	35.53	55.83	159.93	0.48
70	40	0.114	0.108	43.297	16.77	18.87	23.32	30.55	48.01	137.52	0.12
70	40	0.141	0.135	38.255	15.19	17.08	21.12	27.66	43.47	124.52	0.04
80	40	0.040	0.036	81.134	21.61	24.66	31.14	42.29	71.96	191.66	13.27
80	40	0.060	0.056	71.528	15.76	17.99	22.71	30.84	52.49	139.79	1.19
80	40	0.089	0.083	46.418	16.39	18.70	23.61	32.07	54.58	145.35	0.19
80	40	0.114	0.108	40.752	14.34	16.37	20.67	28.07	47.77	127.22	0.05
80	40	0.141	0.135	35.340	13.23	15.10	19.07	25.89	44.06	117.35	0.02

Based on the system parameters, with respect to the heat exchanger for the roaster off-gas ducting, the overall heat transfer coefficient ($U_{roaster}$) is 6.924 W/m^2 °C, and the total length of the coil around the duct is 237 m based on the existing off-gas duct diameter (4.88 m). Using a pond inlet temperature of 60°C and an exit temperature of 40°C, there is a required heating fluid flowrate of 15.7 kg/s, which is approximately 8.3% of the total heating fluid required for the operation of all 180 tanks. This gives a head loss of 20.9 m, or 4.0 kW of required pumping power. Only a portion of the total heating fluid flow is circulated through the roaster off-gas ducting heat exchanger to reduce pumping requirements. After heating, the two streams of heating fluid (high temperature exiting the heat exchanger and the remaining heating fluid) are mixed and distributed to the ponds. For distribution of the heating fluid, it was assumed the ponds were located 200 m from the roaster off-gas heat exchanger, and arranged in a 30 by 6 grid of ponds. The distribution of the heating fluid was determined to require 33.7 kW of energy for pumping.

The total energy required for pumping the heating fluid is 38.4 kW, of which 87.8% would be used for distribution of the heating fluid to and from the cultivation ponds, 12.0% for the roaster off-gas heat exchanger and the remainder coming from the circulation in the ponds. Assuming the plant is operational for 300 days per year, total biomass production is 810,000 kg/year, biodiesel density is 920 kg/m^3 (Zemke et al., 2010) and conversion efficiency is 86% (Wahidin et al., 2014), this translates to 144 m^3/year of biodiesel at 19% lipid (Seyed Hosseini et al., 2015). This in turn gives an energy consumption of 1,227 kW/kg of biomass produced, or US$0.031/kg at a regional electricity pricing of US$0.09/kWh. To be economical, it has been suggested that

production of algae biomass for biofuel must be US$0.25/kg (Chisti, 2012), and therefore, the estimated pumping requirements for the heat exchangers of the described system would contribute approximately 12.3% of this total cost.

Microalgae biomass production allows for the capture of carbon dioxide emissions. This can either be considered as an environmental consideration and/or help off-set any future direct carbon dioxide emission taxes. Using a stoichiometric carbon capture of 1.88 kg of CO_2 per kilogram (dry weight) of algae (Chisti, 2007), an algae production of 810,000 kg/year would result in the direct capture of 1,522.8 tonnes of CO_2. Based on a proposed tax on CO_2 emissions of US$100/tonne in 2020 to reach governmental goals in Canada (M. K. Jaccard and Associates Inc., 2009), this would be a direct savings of US$152,280/year.

3.10 Conclusion

Microalgae present a promising source of biofuel for the mining industry and its local communities, and have been also shown to effectively capture carbon dioxide from off-gas emissions. By looking at opportunities to capture and repurposing otherwise industrial waste heat, microalgal biodiesel and production in relatively inexpensive open external ponds could be expanded into mining regions, such as in Canada, currently considered too cold. This can be achieved through use of non-intrusive heat exchangers to capture energy from smelter off-gas streams.

The developed model determines the amount of waste energy needed to operate a full-scale microalgae production facility coupled to nickel smelter off-gas. The modeled heat exchanger located in microalgae growing ponds provides an even temperature

distribution by utilizing variable spacing heating loops along the pond length. This represents a positive use of heat that in the case of the smelter must be removed to satisfy existing production requirements. Furthermore, the concept can be easily extended to other industrial sectors with significant waste heat.

3.11 Nomenclature

Symbol	Description
A	surface area (m^2)
C_p	specific heat coefficient (J/kg °C)
D	diameter (m)
E	energy requirement (W)
f	friction factor
Fr	Froude number
g	gravitational acceleration (m/s^2)
h	heat transfer coefficient (W/m^2 °C)
H	head loss (m)
k	thermal conductivity (W/m °C)
K	head loss coefficient
n	number
N	number of ponds
Nu	Nusseult number
P	pressure (N/m^2)
Pr	Prandlt number
q	heat flux (W)
Q	volumetric flow rate (m^3/s)
Re	Reynold's number
t	time (s)
T	temperature (°C)
u	velocity (m/s)
V	volume (m^3)
W	mass flow rate (kg/s)
Z	pond depth (m)
α_L	water adsorptivity (dimensionless)
ε	furnace off-gas holdup (dimensionless)
ρ	density (kg/m^3)
ξ	reflectivity (dimensionless)
τ	transmissivity (dimensionless)
μ	dynamic viscosity (Pa s)
κ	thermal diffusivity (m^2/s)
λ	constant (W/m^2 Pa $°C^{1/3}$)

Subscripts

b	bubble
conc	concrete
cond	conductive
conv	convective
duct	off-gas duct
evap	evaporative
ext	external
f	film condition
ff	fouling factor
fr	friction
furnace	furnace off-gas
G	gas above pond surface
hf	heating fluid
hx	heat exchanger
in	initial
ins	insulating material
int	internal
L	liquid (water)
o	orifice
out	final
p	pond
pipe	piping material
pvc	polyvinyl chloride
pump	pump
roaster	roaster off-gas
solar	solar input
stainless	stainless steel
w	wall
180	180° bend

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Chapter 4

Paper #3 – Literature Review, Renewable and Sustainable Energy Reviews

Flotation harvesting of microalgae

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CAL performed the literature survey and primary manuscript writing. GMR assisted in some manuscript writing. JAS provided overall direction in project and manuscript writing.

Abstract

Microalgae are a promising source of third generation renewable fuels. However, the biofuel production process from microalgae growth through to fuel production is still generally regarded as not economically viable. One area of particular consideration, for requiring more cost effective methods, is the recovery or harvesting stage. Among the several harvesting methods that have been proposed and used, flotation is emerging as one of significant promise. This review highlights why flotation can offer better harvesting characteristics than other methods by looking at work that has been carried out to date, as well as discussing the need for further developments in key areas.

Keywords

Microalgae, biofuel, harvesting, flotation

4.1 Introduction

Currently initiatives are being taken in many areas to move from fossil fuel to a biodiesel-based economy (Vandamme et al., 2013). However for a biofuel to be viable, it needs to be produced at a competitive price, require low or no land usage, use minimal water and ideally have a reduced environmental impact (Brennan and Owende, 2010).

Microalgae are efficient at converting solar energy into triglycerides suitable for transesterification into biodiesel (Borges et al., 2011) and also have the potential for coproduction of nutraceuticals, foods and other value-added products (Chisti, 2007; González-Fernández and Ballesteros, 2013). Microalgae-sourced biodiesel in comparison to terrestrial sourced biofuels has higher productivities, requires no arable land and can purify wastewater (Amaro et al., 2011; Lam and Lee, 2012). Another notable advantage is their ability to be used in process-coupled sequestration of CO_2 from industrial off-gas such as power stations, cement factories and smelters (Shang et al., 2010; Chiu et al., 2011; Pires et al., 2012; Jiang et al., 2013; Laamanen et al., 2014). The typical microalgae production process is given in Figure 4.1.

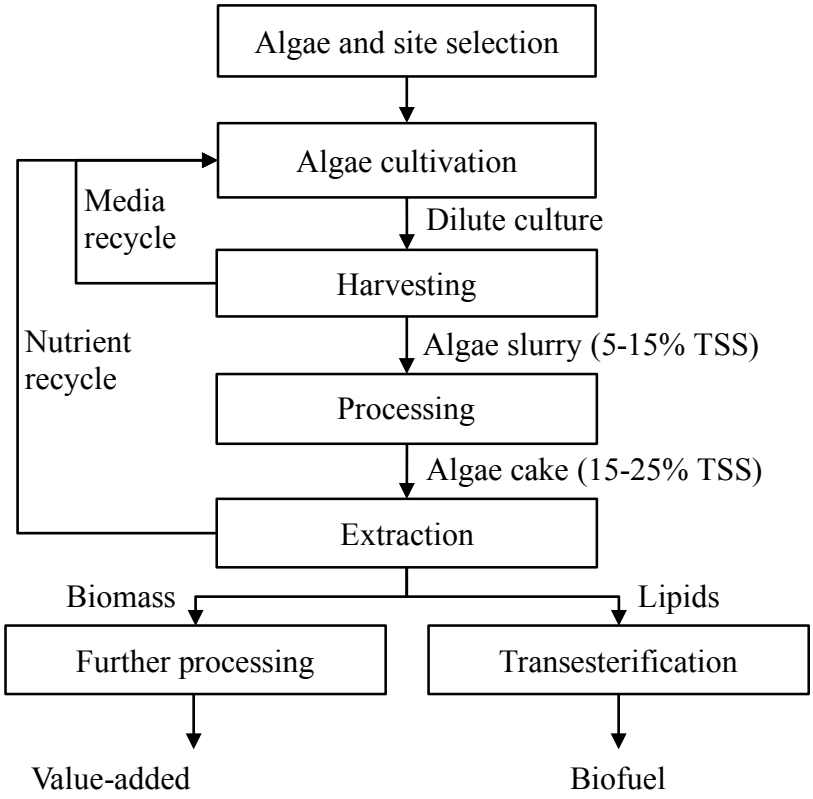

Figure 4.1: Flow sheet of algae production (TSS = total suspended solids) (adapted from Mata et al. (2010)).

Extensive research has been done on different microalgae species with regards to productivity and lipid production (Chen et al., 2011), but the resulting biodiesel remains more expensive than fossil fuels (Mata et al., 2010). A major economic hurdle is the separation (harvesting) of the microalgae from their growth medium (Danquah et al., 2009).

A reliable and cost effective method of bulk harvesting has not been developed. Difficulties arise arises from harvesting being affected by microalgal strain selection and their growth characteristics (Danquah et al., 2009), and impacts on downstream processing (Christenson and Sims, 2011). The development of such a technology has,

however, been highlighted as of prime importance in achieving economic production of microalgae sourced biofuels (Amaro et al., 2011; Lam and Lee, 2012; Farid et al., 2013).

As the microalgae harvesting stage is of significant technical and economic importance, this review briefly highlights current methods and their limitations, which have led to flotation recently emerging as a promising alternative. This promise is based on good scale-up potential due to technical and economic parameters, such as lower energy and maintenance costs. In this review, results and trends from microalgae and other bioseparations utilizing flotation are discussed.

4.2 Microalgae harvesting

Harvesting requires microalgae to be separated from the growth medium and then concentrated (Amaro et al., 2011). Bulk harvesting usually results in 100-800 times concentrating, producing a 2-7% solid slurry (Brennan and Owende, 2010; Sharma et al., 2013). This slurry must then be concentrated, as industrial conversion requires 300-400 g/L dry weight of microalgae (Coward et al., 2013). The bulk harvesting method plays an important role in the energy requirement for the thickening process (Lam and Lee, 2012). As a consequence, there has been significant research into different bulk harvesting methods, namely: centrifugation, filtration and membrane separation, gravity sedimentation, flocculation and flotation (Phoochinda and White, 2003; Uduman et al., 2010).

Algae require light to undergo photosynthesis and produce biomass, however as cultures become dense mutual shading occurs and limits productivity at approximately 0.5 g/L dry weight in an open system and 5 g/L in a photobioreactor (Vandamme et al., 2013).

Subsequently, this dilute concentration creates a considerable separation challenge (Milledge and Heaven, 2013). Additional challenges arise from the small cell size, similar specific gravities of microalgae and the aqueous medium, negative surface charges, and the requirement for frequent harvesting (Bare et al., 1975; Teixeira and Rosa, 2006; Milledge and Heaven, 2013). The separation process may also need to take into account the strain to be used in production (González-Fernández and Ballesteros, 2013).

There are currently no universal techniques for harvesting (Brennan and Owende, 2010), so it is important that the constraints of each separation method are examined in biofuel production (Kröger and Müller-Langer, 2012). In addition to the considerations with regards to microalgae's characteristics, the technique also depends on other considerations including water composition and salinity (Barrut et al., 2013), and process development, as the method will affect downstream processes (Christenson and Sims, 2011). The harvesting method must also produce an acceptable level of moisture in the product (Molina Grima et al., 2003). Most current harvesting methods have either economic or technical limitations, which include high energy costs, flocculant toxicity, or non-feasible scale-up (Oh et al., 2001; Rawat et al., 2013).

Despite research into different methods, current bulk harvesting remains energy extensive and expensive (Wiley et al., 2009), and methods are both species and final product specific (González-Fernández and Ballesteros, 2013). Separation from the aqueous growth medium is difficult as microalgae are small (3 – 15 μm), have a specific gravity similar to that of their medium and are in dilute suspension (Bare et al., 1975). In

addition, separation is also influenced by hydrophobicity, microalgal density, medium composition and salinity (Barrut et al., 2013).

Based on the difficulties of microalgae harvesting, there have been several methods developed and each method has advantages and limitations (Kröger and Müller-Langer, 2012). A feasible harvesting method should have low energy consumption, allow for the recycle of water and nutrients, avoid the additions of harmful chemicals and have a small footprint (Uduman et al., 2010). The optimal method should in addition to these considerations, be species independent and allow for the release of intracellular materials (Chen et al., 2011). The main methods that are researched for microalgae separation are centrifugation, flocculation, filtration, gravity sedimentation and flotation (Phoochinda and White, 2003; Uduman et al., 2010; Milledge and Heaven, 2013). The main characteristics of these methods are summarized in Table 4.1.

Centrifugation is well characterized and is commonly used at the laboratory scale production stage. An advantage of centrifugation is that it avoids the addition of chemicals, which can contaminate the biomass and limit further production. However, due the energy requirement to spin the cells out of suspension, the operation is costly (Banerjee et al., 2014) and makes the harvesting unfeasible at scale (U.S. DOE, 2010). Filtration can also avoid the addition of chemicals, but it requires relatively high operating and maintenance costs (Lam and Lee, 2012). Furthermore, filters clog quickly (Aulenbach et al., 2010; Banerjee et al., 2014), the operation is slow (Molina Grima et al., 2003) and it can be abrasive to the microalgal cells (Coward et al., 2013).

In certain systems, sedimentation can avoid chemical addition. However with microalgae, due to their small size and negative surface charge, the processing time is too long to make it a feasible for harvesting option (Vandamme et al., 2013). To get around this, cells can be flocculated by either chemical addition or a pH shift. Utilizing pH changes allows for the medium to be reused after neutralization as well as magnesium addition, which is depleted through precipitation (Besson and Guiraud, 2013). Flocculation, in combination with sedimentation or flotation, is one of the most economic bulk harvesting techniques and produces 2-7% solids (Brennan and Owende, 2010)

Table 4.1: Comparison of algae separation techniques

Type	Mechanism	Coagulant	Cost	Output (%)[1]	Recovery (%)[1]	Footprint [2]	Efficiency [2]	Drawback
Centrifugation	High-speed rotation	No	High	12-22	>90	Medium	++	Energy requirement, cell composition may change
Gravity Sedimentation	Gravity settling	Sometimes	Low	0.5-3	10-90	Large	-	Time requirement, cell composition may change
Flotation (DAF)	Bubble attachment	Sometimes	Medium	3-6	50-90	Small	+	Electrical flocculation: Electrode replacement, energy requirement, cell composition may change Chemical flocculation: Flocculant cost, potential contamination
Tangential filtration	Crossflow membrane	Sometimes	High	5-27	70-90	Medium	+	Membrane cleaning and replacement

References: [1] Christenson and Sims (2011), [2] Danquah et al. (2009)

Due to the requirement for frequent harvesting, flotation is preferred for higher overflow rates as microalgae cells move upward rather than downward (Edzwald, 1993; Amaro et al., 2011). Flotation originated in the mineral industry (Coward et al., 2014) and is prevalent in water treatment (Bare et al., 1975; Edzwald, 1993; Edzwald, 2010). The main difference for harvesting of microalgae for biofuels is that the method must not contaminate the biomass or create a toxic medium for recycle (Uduman et al., 2010). Water treatment research can be used as a platform for method development, while some studies even look at a combined method for both treatment and biofuel production (Hamawand et al., 2014). Additionally for flotation, the microalgae must be destabilized, which are the same requirements for flocculation and sedimentation (Edzwald, 1993).

Currently no universal technique exists, but flotation has shown particular promise. To support its development, technology from other industries can act as a framework and provide potential solutions (Brennan and Owende, 2010; Kröger and Müller-Langer, 2012). In the following sections the development of flotation as a method of harvesting microalgae and cyanobacteria for biofuel production are explored. The benefits of flotation, the different methods of flotation and the operational parameters are discussed. It should be noted that microalgae will be used in reference to both green microalgae and cyanobacteria in the following sections.

4.3 Flotation

With separation by flotation, small bubbles attach to destabilized particles and cause them to rise to the surface and concentrate. Combined with the use of a flocculant to destabilize the cells, flotation has emerged as a major harvesting option for microalgae

(Amaro et al., 2011; Coward et al., 2013). Flotation has been shown to be more effective than sedimentation under the same conditions for removal of microalgae from water (Edzwald, 1993). Furthermore, gravitational drainage of water from the foam creates an increased concentration factor (Besson and Guiraud, 2013).

Flotation can be viewed as inverted sedimentation (Hanotu et al., 2012), and is advantageous due to the tendency of microalgae to float instead of settle (Phoochinda and White, 2003). Flotation can provide high overflow rates, low detention periods, a small footprint, and produces a thicker concentrate than sedimentation (Liu et al., 1999; Rubio et al., 2002). Flotation typically creates a sludge that is 2-7% solids (Brennan and Owende, 2010; Milledge and Heaven, 2013). Reports on the economic feasibility of flotation range from high capital and operational costs (Milledge and Heaven, 2013) to low initial and operating costs, low energy input, and easy operation (Phoochinda and White, 2003). However, despite these differences, flotation has been assessed as the most economic method for bulk harvesting of microalgae (Sharma et al., 2013).

While extensively used in the treatment of water (Table 4.2), it has been shown for sometime to be a flexible treatment for microalgae and other microorganisms (Edzwald, 1993; French et al., 2000). However, flotation has been referred to as difficult if different species of microalgae are present (Henderson et al., 2008). Despite this, an advantage of flotation is its ability to harvest a diverse number of species once the operation is optimized (Henderson et al., 2010).

Table 4.2: Results from algae flotation for water treatment

Type of flotation	Algae species	Algae concentration	Coagulant	Coagulant dose	pH	Flotation time (min)	Removal (%)	Zeta potential (mV)	Reference
DAF	*Microcystis aeruginosa*	$6\times10^5 \pm 1.5\times10^4$ cells/ml	Aluminum sulfate	0.0014 ng Al/cell	7	10	--	1.9×10^{-6} (neq/cell)	(Henderson et al., 2008)
DAF	*Chlorella vulgaris*	$5\times10^5 \pm 5\times10^4$ cells/ml	Aluminum sulfate	0.0057 ng Al/cell	7	10	--	1.1×10^{-5} (neq/cell)	(Henderson et al., 2008)
DAF	*Asterionella formosa*	$5\times10^4 \pm 1.2\times10^4$ cells/ml	Aluminum sulfate	0.0314 ng Al/cell	7	10	98.9	6.8×10^{-5} (neq/cell)	(Henderson et al., 2008)
DAF	*Melosira sp.*	$2\times10^3 \pm 2\times10^2$ cells/ml	Aluminum sulfate	0.29 ng Al/cell	7	10	99.7	1.88×10^{-3} (neq/cell)	(Henderson et al., 2008)
DAF	*Chlorella vulgaris*	$5\times10^5 \pm 5\times10^4$ cells/ml	Aluminum sulfate	4.3 pg/cell	7	10	94.8	0.011 (peq/cell)	(Henderson et al., 2010)
DAF	*Microcystis aeruginosa*	$6\times10^5 \pm 1.5\times10^4$ cells/ml	Aluminum sulfate	1.1 pg/cell	7	10	97.3	0.002 (peq/cell)	(Henderson et al., 2010)
DAF	*Asterionella Formosa*	$5\times10^4 \pm 1.2\times10^4$ cells/ml	Aluminum sulfate	31.4 pg/cell	7	10	98.8	0.062 (peq/cell)	(Henderson et al., 2010)
DAF	*Melosira sp.*	$1.9\times10^3 \pm 550$ cells/ml	Aluminum sulfate	290 pg/cell	7	10	99.7	1.88 (peq/cell)	(Henderson et al., 2010)
DiAF	*Scenedesmus quadricauda*	7.4×10^4 cells/ml	CTAB	40 mg/L	8±0.1	20	90	~ -20	(Chen et al., 1998)
DiAF	*Scenedesmus quadricauda*	7.4×10^4 cells/ml	SDS	20 mg/L (+10 mg/L chitosan)	8±0.1	20	95	~ -20	(Chen et al., 1998)
DiAF	Mixed	$<1.08\times10^7$ cells/ml	PAC	1.25-1.65 mg/L	--	--	92.7	--	(Guiqing et al., 2011)
DiAF	Mixed	4.0×10^{-3} g/min	Methylated egg albumin	3.2×10^{-3} g/min	--	--	94	--	(Maruyama et al., 2009)
DiAF	*Scenedesmus quadricauda*	1×10^5 cells/ml	CTAB	100 mg/L	7.8	15	85 (graph)	12.5 (graph)	(Phoochinda and White, 2003)
DiAF	*Scenedesmus quadricauda*	1×10^5 cells/ml	SDS	100 mg/L	3.5	25	78 (graph)	-7.5 (graph)	(Phoochinda and White, 2003)
DiAF	*Scenedesmus quadricauda (live)*	1×10^5 cells/ml	CTAB	100 mg/L	7.8	20	85	--	(Phoochinda et al., 2005)
DiAF	*Scenedesmus quadricauda (dead)*	1×10^5 cells/ml	CTAB	100 mg/L	7.8	20	93	--	(Phoochinda et al., 2005)
ECF	*Microcystis aeruginosa*	$0.55\text{-}1.55\times10^9$ cells/L	Aluminum electrode	1 mA/cm^2	4-7	--	100	--	(Gao et al., 2010)
PosiDAF	*Microcystis aeruginosa*	$7.5\times10^5 \pm 1.5\times10^4$ cells/ml	OTAB	0.0022 – 0.0042 mequiv/L	7	10	65 ± 3	-20.2 ± 1.5	(Henderson et al., 2008)
PosiDAF	*Microcystis aeruginosa*	$7.5\times10^5 \pm 1.5\times10^4$ cells/ml	CTAB	0.0022 – 0.004 mequiv/L	7	10	64 ± 5	-20.2 ± 1.5	(Henderson et al., 2008)

PosiDAF	*Chlorella vulgaris*	$5.0\times10^5 \pm 5\times10^4$ cells/ml	CTAB	0.005 mequiv/L	7	10	54 ± 0.4	-32.3 ± 0.6	(Henderson et al., 2008)
PosiDAF	*Asterionella formosa*	$1.7\times10^5 \pm 2.5\times10^4$ cells/ml	CTAB	0.0008 mequiv/L	7	10	89 ± 4.1	-20.7 ± 2.4	(Henderson et al., 2008)
PosiDAF	*Melosira sp.*	1900 ± 550 cells/ml	CTAB	0.0005 mequiv/L	7	10	97 ± 2.7	-12.9 ± 0.2	(Henderson et al., 2008)
PosiDAF	*Microcystis aeruginosa*	$7.5\times10^5 \pm 2.3\times10^4$ cells/ml	PolyDADMAC	0.32 – 0.44 mg/L	7	10	95	-20 – -25	(Henderson et al., 2009)
PosiDAF	*Microcystis aeruginosa*	5.6×10^5 cells/ml	PolyDADMAC (low MW)	0.0024 meq/L	7	10	97	-19.8 ± 1.5	(Henderson et al., 2010)
PosiDAF	*Chlorella vulgaris*	$9.2\times10^5 \pm 7\times10^3$ cells/ml	PolyDADMAC (low MW)	0.034 – 0.042 meq/L	7	10	76.2 ± 2	-32.3 ± 0.6	(Henderson et al., 2010)
PosiDAF	*Asterionella formosa*	$3.7\times10^5 \pm 500$ cells/ml	PolyDADMAC (low MW)	>0.00536 meq/L	7	10	49.1 ± 1	-20.7 ± 2.4	(Henderson et al., 2010)
PosiDAF	*Melosira sp.*	1100 ± 50 cells/ml	PolyDADMAC (low MW)	6.7×10^{-5} meq/L	7	10	99.7 ± 0.5	-12.9 ± 0.2	(Henderson et al., 2010)
PosiDAF	*Microcystis aeruginosa*	7.5×10^5 cells/ml	PolyDADMAC	0.3 mg/L	7	10	99	-31.6 ± 1.6	(Yap et al., 2014)
IAF	*Microcystis aeruginosa*	400675 cells/ml	Iron chloride	10 mg Fe/L	9.2	--	98.8	-25 – -30	(Jameson, 1999)
Ballasted	*Microcystis*	$0.5–1\times10^6$ cells/L	Ferric sulfate	3.5 mg Fe/L	5.5	10	97	--	(Jarvis et al., 2009)
Ballasted	*Melosira*	$0.5–1\times10^6$ cells/L	Ferric sulfate	3.5 mg Fe/L	5.5	10	81	--	(Jarvis et al., 2009)
Ballasted	*Chlorella*	$0.5–1\times10^6$ cells/L	Ferric sulfate	3.5 mg Fe/L	5.5	10	63	--	(Jarvis et al., 2009)
BDAF	*Melosira*	$0.5–1\times10^6$ cells/L	Ferric sulfate	3.5 mg Fe/L	5.5	10	96	--	(Jarvis et al., 2009)
BDAF	*Chlorella*	$0.5–1\times10^6$ cells/L	Ferric sulfate	3.5 mg Fe/L	5.5	10	94	--	(Jarvis et al., 2009)

4.4 Coagulants

Microalgae are hydrophilic and have a negative surface charge (Cheng et al., 2010), which keeps them in suspension. While untreated microalgae will separate to a small degree (10%), it is not enough to avoid the use of coagulant (Bare et al., 1975; Teixeira and Rosa, 2006). That is, for effective flotation to occur the cells must be destabilized (Wiley et al., 2009), in order to make them hydrophobic and to neutralize the surface charge. This is commonly done through the addition of a coagulant (Chen et al., 2011; Schlesinger et al., 2012). Typically microalgae hydrophobicity increases with coagulant dosage (Garg et al., 2012).

The addition of a coagulant causes the formation of flocs (Vandamme et al., 2013; Besson and Guiraud, 2013), which are separated preferentially due to the larger surface area providing greater bubble formation at the surface, bubble entrapment and bubble entrainment (Hanotu et al., 2012). There are four approaches to induce flocculation, namely: charge neutralization, electrostatic patch mechanisms, bridging and sweeping (Vandamme et al., 2013). Any microalgae remaining after dissolved air flotation (DAF), where the water is recycled and pressurized to produce small air bubbles, are commonly single, non-flocculated cells (Bare et al., 1975).

The electrostatic interaction between the microalgae and the coagulant is crucial (Chen et al., 1998; Liu et al., 1999). Less than 10% removal was achieved for non-ionic and anionic collectors (Chen et al., 1998) and less than 8% removal for anionic sodium dodecyl sulfate (SDS) (Liu et al., 1999). As around 10% removal can be achieved without coagulation (Bare et al., 1975; Henderson et al., 2008; Henderson et al., 2009),

the addition of these coagulants, that do not have an electrostatic interaction with the microalgae, provide no additional separation. However, good cell removal (94-99%) was achieved for all microalgae tested provided sufficient cationic coagulant was added (Henderson et al., 2010).

A potential disadvantage arising from the use of common coagulants is when the chemicals, such as metal ions, become part of the recovered biomass and affect potential end uses (Coward et al., 2013). Therefore, coagulant selection is crucial, as it must not impact on subsequent processes or products (Ahmad et al., 2011; Rashid et al., 2013; Vandamme et al., 2013). Coagulants should be selected that are inexpensive, non-toxic, and effective in low concentrations, as well as not effect downstream production or final products (Molina Grima et al., 2003).

4.4.1 Metallic salts

Inorganic metal salts, in particular aluminum and ferric sulfate or chloride are commonly used as coagulants (Aulenbach et al., 2010; Banerjee et al., 2014). It is their 3^+ cationic charge that allows them to be effective at neutralization (Christenson and Sims, 2011). They also have proven cost-effective in comparison to other coagulant options, such as polymers, which has led them to be commonly used in water treatment (Ahmad et al., 2011).

The obtained separation is dependent on the concentration of coagulant used. In one microalgae separation report, the highest concentration tested (150 mg/L) gave the highest recovery for each coagulant tested (Hanotu et al., 2012). However, high concentrations (1.5 and 2 g/L) of aluminum sulfate showed reduced coagulation, due to

reactions with alkalinity reducing the medium pH (Kwon et al., 2014). Conversely, lower dosages of coagulant (0.1 ml/L of Ecover©) created polyhedral bubbles, while higher dosages (0.2 ml/L of Ecover©) created spherical bubbles. The polyhedral bubbles gave a lower water content in the collected algal biomass and hence a higher concentration factor (Coward et al., 2013).

Aluminum (particularly alum) is used for microalgae flotation more commonly than ferric salts as it generally forms more stable flocs and has a higher percentage recovery (Bare et al., 1975). Aluminum polyhydroxichlorosulphate (WAC) has been found to perform even better than alum giving a higher removal level, lower pH decrease and lower optimal dosage (Teixeira and Rosa, 2006). Aluminum coagulants were able to remove over 80% of 18 types of microalgae when using DAF in water treatment (Yuheng et al., 2011), while over 90% was achieved for collecting *Chlorella zofingiensis* for biofuel regardless of the growth stage (Zhang and Hu, 2012).

The major drawback for aluminum or ferric salts is that residual chemicals could pose environmental or health problems (Sharma et al., 2013). These metal coagulants are toxic (Schlesinger et al., 2012) and alum in particular has been shown to have involvement with carcinogenesis and Alzheimer's disease (Ahmad et al., 2011). Additional limitations arise from the relatively large concentrations required, sensitivity to pH levels, and not being universally applicable to all microalgae (Chen et al., 2011). In general, it has been concluded that these salts, whilst extremely useful in general water treatment, have limited application in harvesting microalgae (Schlesinger et al., 2012; Banerjee et al., 2014).

4.4.2 pH-induced

pH induced flocculation can be caused by precipitation of substances from the medium (autoflocculation) and/or by changing the surface physiology of the microalgae (bioflocculation) (Besson and Guiraud, 2013). In general, an increase in pH results in spontaneous aggregation (Zhang and Hu, 2012). The medium pH rises naturally during cultivation due to the consumption of carbon dioxide and the resulting formation of calcium and/or magnesium precipitates (Uduman et al., 2010). These precipitates result in charge neutralization and sweeping mechanisms, where the inherent increased size of agglomerated precipitate and cells in turn cause more cellular interactions, resulting in flocculation. While the resulting biomass is high in these components, it is less concerning than the contamination resulting from metal salts (Vandamme et al., 2013).

The pH threshold to induce autoflocculation is species specific (González-Fernández and Ballesteros, 2013). Some species, such as *D. salina*, did not reach the autoflocculation point naturally. However with the addition of a base to increase pH, flocculation could be achieved (Besson and Guiraud, 2013). The natural pH increase can, therefore, be used to decrease chemical requirements and improve the economics of the process (Schlesinger et al., 2012).

4.4.3 Polymers

Polymers (typically PolyDADMACs) can act as coagulants through a number of different mechanism. The most common being long chain polymers acting as particle connectors and sweeping collectors (Henderson et al., 2009). Polymers also neutralize charges if they are cationic in nature. Anionic polymers can be also used but require the addition of

bridging ions to connect with the cells (Borges et al., 2011). The extent of each coagulation mechanism is based on the charge density and length of the polymer (Uduman et al., 2010).

Whilst polymers are generally more expensive than metal ions, issues of contamination and influences on downstream production and end uses are largely avoided. It has been shown that polymer treatment did not affect lipid levels or the lipid extraction process (Borges et al., 2011). It did, however, lower the levels of unsaturated fatty acids, which was attributed to the polymers attaching to the cell surface and acting as a trap for complex lipids after extraction. This would result in a biodiesel with higher oxidative stability and a higher cetane number (Borges et al., 2011).

4.4.4 Chitosan

Chitosan is an abundant naturally sourced organic compound with a high cationic charge density and long polymer chains, which allow for charge neutralization and bridging (Ahmad et al., 2011). It is also biodegradable, has low toxicity and has little influence on culture pH (Rashid et al., 2013; Banerjee et al., 2014; Kwon et al., 2014). Chitosan can be obtained from fungi or through the treatment of chitin (the main component of crustacean shells), making waste from the seafood industry a potential source of the coagulant (Farid et al., 2013). Chitosan is commercially available, but is currently considered cost prohibitive to purchase for use as an microalgae coagulant (Harun et al., 2010).

The high charge density of chitosan allows for strong adsorption to negative microalgae cells and results in destabilization through neutralization (Chen et al., 1998). The result is the effective coagulation of microalgae with low concentrations of chitosan (Ahmad et

al., 2011). Since the coagulant works as a function of surface charge, the required dosage increases proportionately to microalgae concentration (Xu et al., 2013). Chitosan concentration should be monitored, therefore, as a concentration that is too high will result in restabilization due to excess cationic charge (Ahmad et al., 2011).

The range of culture conditions that can be treated is also expanded, as organic coagulants are less sensitive to pH changes than metal salts (Pragya et al., 2013). The optimal pH varied according to different studies and was found to be 11 (Oh et al., 2001) and 9 (Farid et al., 2013). The flocculation achieved was more effective than aluminum sulfate or polyacrylamide (Oh et al., 2001). However, there is a significant difference in dosage for different conditions. For example, the dosage required was doubled in nitrogen-replete medium compared to nitrogen-limited medium (Xu et al., 2013).

Chitosan has been shown to coagulate microalgae cells effectively, and to produce larger flocs than Polyaluminum Chloride (PACl). The PACl flocculation also interfered with biodiesel conversion due to diffusion resistance in the flocs, a problem that was not evident in chitosan-treated cells (Tran et al., 2013). An additional advantage compared to metal salts is the avoidance of having to remove the salt contamination if the biomass after lipid extraction is going to be processed (Banerjee et al., 2014). However, the reduced cost of not having to remove the salt is counteracted by the increased cost of chitosan (Borges et al., 2011).

Additional limitations of chitosan include that as it is not water-soluble, it requires a weak acid treatment to be dissolved (Kwon et al., 2014). The dissolution in different acids (0.1 M) has been examined, giving the following results for flocculation efficiency:

hydrochloric acid > phosphoric acid > nitric acid > citric acid (Rashid et al., 2013). While chitosan is effective and developments are being researched to increase the effectiveness (like using nano-chitosan (Farid et al., 2013)), the cost limitations still exist. Furthermore, the method is not universal to all microalgae types as it was found effective for green microalgae, but gave poor results for cyanobacteria (Oh et al., 2001).

4.4.5 Cetyl trimethyl ammonium bromide (CTAB)

Cetyl trimethyl ammonium bromide (CTAB) can be used as an microalgae coagulant and allows for simultaneous harvesting and cell membrane disruption (Huang and Kim, 2014). The cell surfaces become more hydrophobic and thus easier to harvest when treated with CTAB (Chen et al., 1998). While research regarding the use of CTAB for a microalgae coagulant is limited, it is known to be a cationic molecule that results in effective collection using flotation (Kurniawati et al., 2014).

There are significant advantages from using CTAB, including that it also does not contaminate the resulting biomass with any salts. In addition, CTAB increases the total lipid by solubilizing the phospholipids from the cell membrane. While these lipids are of little interest for biofuel production, potential markets exist for certain phospholipids (Coward et al., 2014), namely as nutritional supplements.

4.5 Types of flotation

Traditionally flotation is done either by air addition through a diffuser (dispersed air flotation) or through pressurization (dissolved air flotation) (Chug et al., 2000; Aulenbach

et al., 2010). A similar result can be achieved through the use of electrodes, which is known as electrolytic flotation (Pragya et al., 2013). These methods are discussed below.

4.5.1 Dispersed air flotation (DiAF)

In dispersed air flotation (DiAF) air is introduced to the system through either a mechanical agitator or air injection through a porous medium (Uduman et al., 2010). This is less energy intensive than dissolved air flotation (DAF), but has limited uses due to the relatively large bubble size (Hanotu et al., 2012) in the range of 700-1500 μm (Rubio et al., 2002). It has been shown that smaller bubbles result in higher capture efficiency (Hanotu et al., 2012; Garg et al., 2014).

If smaller bubbles are required, the usual method of reducing their size is through addition of surfactants (Phoochinda et al., 2005). However, with microalgae harvesting this is undesirable, as any chemicals added will likely be found in the recovered biomass. This is a significant disadvantage as uncontaminated biomass can be used as an animal feed or a food supplement (Draaisma et al., 2013). However, DiAF can have increased effectiveness in highly saline waters as salinity can significantly reduce bubble size due to decreased surface tension (Barrut et al., 2013).

Dispersed air flotation does have significant advantages from an economic and operational standpoint. The operation has lower energy requirements, few mechanical parts and can easily be scaled up (Maruyama et al., 2009).

4.5.2 Dissolved air flotation (DAF)

In dissolved air flotation (DAF) a portion of the water that has been through separation is recycled and pressurized (Jameson, 1999). This recycle ratio governs the amount of bubbles in the operation and is typically 5-15% (Jarvis et al., 2009) and is pressurized in the range of 400-650 kPa (Edzwald, 1993). When the saturated water depressurizes back to atmospheric pressure, it releases excess air, due to the new reduced saturation level.

The bubbles produced are in the range of 10-100 μm (Cassell et al., 1975; Phoochinda et al., 2005; Uduman et al., 2010) and are over an order of magnitude smaller than the bubbles produced in dispersed air flotation (Cassell et al., 1975). This creates a more efficient separation.

An additional advantage to DAF is that air which is not converted to bubbles in the inlet will nucleate into small bubbles at the surface of the algal cells. This allows for flotation of these hydrophilic particles (Rubio et al., 2002). DAF separation is more efficient than dispersed air flotation, is more commonly used (Chen et al., 1998), and is also proven on a large scale (Christenson and Sims, 2011).

However, in comparison to DiAF, DAF is relatively expensive due to the compression stage, which requires around 7.6 kWh/m^3 (Wiley et al., 2009; Hanotu et al., 2012). These costs are compounded due to the relatively small amount of air per unit volume, which increases the volume of water recycled and pressurized. For example, pressurization at 400 kPa results in only 5.6 milliliters of air per liter water (Jameson, 1999).

4.5.3 Electro coagulation flotation (ECF)

Electro coagulation flotation (ECF) is a four stage process in which: (i) a reactive anode dissolves creating coagulants, (ii) these coagulants interact with the microalgae to destabilize the suspension, (iii) the destabilized particles form flocs and (iv) gas bubbles formed at the electrodes adhere to the flocs and cause them to float (Gao et al., 2010; Kim et al., 2012; Uduman et al., 2012).

The coagulants are formed through the dissolution of either iron or aluminum electrodes, which produce Al^{3+} and Fe^{3+}, respectively. It has been shown that aluminum has a higher current efficiency (Zongo et al., 2009). The bubbles are created through the splitting of water to form H_2 and O_2 bubbles in the range of 22-50 μm (Phoochinda et al., 2005).

The amount of the flocculants dissolved at any time is correlated with current density (Xu et al., 2010) and the time to reach a certain collection level is current density dependent (Gao et al., 2010). However, while a high current density results in quick flotation, it also increases costs (González-Fernández and Ballesteros, 2013).

Advantageously ECF does not introduce sulfate or chloride anions usually attached to metal salts added as coagulating agents. Additionally, ECF produces high efficiency coagulants and performs over a large pH range (4-10, with lower pH being beneficial) (Gao et al., 2010). Furthermore, if more bubbles and increased collection efficiency is required, the method can be combined with DiAF (Xu et al., 2010).

Whilst the energy required for freshwater microalgae harvesting is relatively low, the high conductivity of seawater makes ECF impractical (Schlesinger et al., 2012). Another

limitation is that an oxide film forms on the electrodes during operation, which reduces the energy efficiency. Although this can be avoided through use of polarity exchange (Kim et al., 2012). The main disadvantages of ECF are considered the emission of H_2 gas bubbles as a health and safety concern and the electrode costs (Rubio et al., 2002).

4.5.4 Modifications

4.5.4.1 Microflotation

Microflotation uses DiAF in combination with fluidic oscillation to produce microbubble clouds that have been shown to efficiently remove colloidal particles (Cassell et al., 1975). Fluidic oscillation utilizes the Coanda effect to transform a stream of air into an oscillating flow at a specific frequency. The oscillation provides an additional force helping the bubbles detach from the sparger (Hanotu et al., 2012). These microbubbles are an order of magnitude smaller than produced through traditional DiAF (Zimmerman et al., 2008). Hanotu et al. (2012) found that the resulting bubbles are approximately twice the size of the sparger pore, compared to 28 times the pore size for regular DiAF. While being able to produce bubbles in the same range as DAF, for microalgae separations this method utilizes significantly less energy and has a lower capital cost (Zimmerman et al., 2008; Hanotu et al., 2012).

4.5.4.2 PosiDAF

With the goal of removing the coagulation stage from DAF, PosiDAF is a bubble modification technique in which chemicals are added to the saturator. As the bubbles form due to the pressure decrease, they are coated with these chemicals (Henderson et al.,

2009). This technique has shown potential using commercial polymers or surfactants to alter bubble surface charge (Yap et al., 2014). PosiDAF has the added advantages of reducing the operational cost, by decreasing coagulant demand and removing the flocculation tank (Henderson et al., 2008), and that it is a simple retrofit of existing DAF technology (Henderson et al., 2010).

Polymers can be used in the PosiDAF operation to protrude from bubbles and increase capture efficiency (Henderson et al., 2009). PolyDADMACs, for example, are large molecular weight polymers, which are hydrophilic and project from a bubble's surface to increase the swept area (Henderson et al., 2010).

The use of polyDADMAC in PosiDAF was found to give similar removal efficiencies to DAF, but did not require pH modification or a coagulation stage (Henderson et al., 2010). Similar to DAF technologies, a significant difference in harvesting efficiency was found when used with different microalgae species (Henderson et al., 2010).

4.5.4.3 Ozone flotation

In a control test using DiAF oxygen aeration, flotation harvesting did not occur, but through the use of ozone, separation was achieved (Cheng et al., 2010). This method still produces the 2-7% sludge, but enhanced bubble-cell interactions and allowed for cell lysis. Combining harvesting with cell lysis can be desirable to allow for the extraction of lipids (Cheng et al., 2011). However, there is a significant additional cost associated with using ozone compared to ambient air for the flotation process.

4.5.4.4 Ballasted flotation

The generation of bubbles accounts for a significant fraction of the cost of DAF and ballasted flotation was introduced to avoid this cost (Jarvis et al., 2009). Small particles of low-density material are added to the solution and are incorporated into flocs. This effectively reduces the density of the flocs and causes them to float. The microspheres used in this process can then be recovered using a hydrocyclone and reused (Jarvis et al., 2009; Ometto et al., 2014). In effect, the saturator is removed while two pumps (for new and recycled beads) and a hydrocyclone for recovery are added, resulting in at least 50% reduction in energy usage (Jarvis et al., 2009).

This method has been also examined in combination with DAF (known as BDAF) rather than as a replacement. This approach was able to capture up to 96% of *Melosira* and 94% of *Chlorella,* which was better recovery and less coagulant demand than the use of beads or DAF (Jarvis et al., 2009). BDAF has been shown to be able to reduce coagulant demand by 95% in comparison to DAF (Cheng et al., 2011). This combined method has been also shown to given similar removal efficiencies compared to DAF with a 60-80% reduction in energy demand and the production of a more concentrated microalgae product (Cheng et al., 2011).

4.5.4.5 Other methods of increasing efficiency

To improve microalgae collection efficiency, microbubbles can be generated in a number of different ways. These methods include using a spinning disk to pull atmospheric air down a shaft and into the liquid in a process known as cavitation air flotation (Rubio et al., 2002). Alternatively, jet microbubble generators can be used to produce smaller

bubbles without the economic shortcomings of DAF (Lin et al., 2011). The use of jet flotation allows for high throughput with high efficiency and it also requires low energy consumption and low maintenance (Rubio et al., 2002).

Another potential harvesting method is induced air flotation (IAF), which has been used to remove oil droplets from water. It works through inducing air with an impeller-based system, which avoids the need for blowers or compressors. While IAF produces larger bubbles than DAF, it requires a smaller footprint and allows for the ability to add far more air than the 5.6 ml/L of water recycled in DAF (Jameson, 1999).

Whilst there are modifications that aim to avoid the use of DAF, some methods have been developed to improve DAF efficiency. These include a gas aspiration nozzle to draw air into the recycled water (Rubio et al., 2002). This has the effect of reducing capital costs, maintenance costs and energy requirements below the levels for IAF. Similarly, the use of column flotation is an alternative, in which the liquid moves countercurrent to the gas (Rubio et al., 2002).

Research has been also carried out to explore modifications to the process that aim to avoid other problems associated with harvesting, albeit they are unlikely to improve the economics. For example, flotation can be done under a vacuum to harvest dilute cultures without harming the microalgae cells. This approach creates a large interface between liquid and gas phases (Barrut et al., 2013).

4.6 Operational Parameters

The type of flotation and coagulant used largely determine the effectiveness of flotation recovery (Table 4.3). There are, however, operational parameters which can influence the effectiveness and required dosages, and hence the feasibility of the operation as a method for microalgae harvesting.

Table 4.3: Results from algae flotation for biofuels

Type of flotation	Algae species	Algae concentration	Coagulant	Coagulant dose	pH	Flotation time (min)	Removal (%)	Concentration factor	Zeta potential (mV)	Additional information	Reference
DAF	*Dunaliella salina*	0.4 – 0.6 g/L	pH-induced (NaOH)	--	10.2 – 10.5	--	95 – 99+	4 – 6	--	Abrupt injection of NaOH	(Besson and Guiraud, 2013)
DAF	*Dunaliella salina*	0.4 – 0.6 g/L	pH-induced (NaOH)	--	9.8 – 10.2	--	48 – 64	19 – 26	--	<0.0005 mol/L/min NaOH	(Besson and Guiraud, 2013)
DAF	*Tetraselmis sp.*	3 g/L	Aluminum sulfate	1.2 g/L	5 – 6	--	85.6	--	--	--	(Kwon et al., 2014)
DAF	*Tetraselmis sp.*	3 g/L	Ferric sulfate	0.7 g/L	4 – 8	--	92.6	--	--	--	(Kwon et al., 2014)
DAF	*Tetraselmis sp.*	3 g/L	Chitosan	4.0 mg/ml	7 – 8	--	93	--	--	--	(Kwon et al., 2014)
DAF	*Chlorella zofingiensis*	1.5 g/L	Aluminum sulfate	--	7 – 8.2	10	91.5	--	-20.6 ± 0.9	Exponential phase, with DOM	(Zhang and Hu, 2012)
DAF	*Chlorella zofingiensis*	1.5 g/L	Aluminum sulfate	--	7 – 8.2	10	91.9	--	-20.6 ± 0.9	Exponential phase, no DOM	(Zhang and Hu, 2012)
DAF	*Chlorella zofingiensis*	1.9 g/L	Aluminum sulfate	--	7 – 8.2	10	90.5	--	-13.2 ± 3.0	Stationary phase, with DOM	(Zhang and Hu, 2012)
DAF	*Chlorella zofingiensis*	1.9 g/L	Aluminum sulfate	--	7 – 8.2	10	93.3	--	-13.2 ± 3.0	Stationary phase, no DOM	(Zhang and Hu, 2012)
DAF	*Chlorella zofingiensis*	2.1 g/L	Aluminum sulfate	--	7 – 8.2	10	90.9	--	-12.2 ± 0.5	Declining phase, with DOM	(Zhang and Hu, 2012)
DAF	*Chlorella zofingiensis*	2.1 g/L	Aluminum sulfate	--	7 – 8.2	10	95.2	--	-12.2 ± 0.5	Declining phase, no DOM	(Zhang and Hu, 2012)
DAF (jet)	*Chlorella sp.*	300 mg/L	Ferric chloride	100 mg/L	--	--	89.57	--	--	+ 20 mg/L polyacrylamide and 2.5 ml/L ethanol	(Lin et al., 2011)
DiAF	*Chlorella vulgaris*	--	CTAB	60 mg/L	6.89 ± 0.4	20	>93.7	--	-30.3 ± 2.4	--	(Kurniawati et al., 2014)
DiAF	*Scenedesmus obliquus*	--	CTAB	60 mg/L	7.77 ± 0.05	20	>93.7	--	-13.43 ± 0.4	--	(Kurniawati et al., 2014)
DiAF	*Chlorella vulgaris*	--	Chitosan	20 mg/L	6.89 ± 0.4	20	97 (graph)	--	-30.3 ± 2.4	+20 mg/L saponin	(Kurniawati et al., 2014)
DiAF	*Scenedesmus obliquus*	--	Chitosan	20 mg/L	7.77 ± 0.05	20	99 (graph)	--	-13.43 ± 0.4	+20 mg/L saponin	(Kurniawati et al., 2014)
DiAF	*Chlorella sp.*	--	CTAB	3 ppm	9.5	6	99.6 (calc)	--	--	--	(Garg et al., 2012)
DiAF	*Tetraselmis sp.*	--	CTAB	80 ppm	9.5	6	84.7 (calc)	--	--	--	(Garg et al., 2012)

DiAF	*Tetraselmis sp.*	--	DAH	25 ppm	6	6	85.0	5.6	--	--	(Garg et al., 2014)
DiAF	*Chlorella sp.* (high temperature)	--	pH-induced (HCl)	--	~ 2	18	88	--	--	'Typical results'	(Levin, 1962)
DiAF	*Chlorella sp.*	6.8×10^5 cells/ml	CTAB	40 mg/L	7 ± 0.1	20	92 (graph)	--	--	--	(Liu et al., 1999)
DiAF	*Chlorella sp.*	6.8×10^5 cells/ml	SDS +Chitosan	20 mg/L SDS, 10 mg/L Chitosan	7 ± 0.1	20	89 (graph)	--	--	--	(Liu et al., 1999)
DiAF	*Botryococcus braunii*	1.6 g/L	Aluminum electrode	60V, 0.101A	11	14	98.9	--	--	--	(Xu et al., 2010)
ECF (polarity exchange)	*Nannochloris oculata*	1 g/L	Aluminum electrode	0.25A	8	15	95.8	--	--	--	(Kim et al., 2012)
Microflotation	*Dunaliella salina*	--	Aluminum sulfate	150 mg/L	5	--	95.2	--	--	Lowest pH tested	(Hanotu et al., 2012)
Microflotation	*Dunaliella salina*	--	Ferric sulfate	150 mg/L	5	--	98.1	--	--	Lowest pH tested	(Hanotu et al., 2012)
Microflotation	*Dunaliella salina*	--	Ferric chloride	150 mg/L	5	--	99.2	--	--	Lowest pH tested	(Hanotu et al., 2012)
Vacuum DiAF	Mixed	0.386 g/L	None	--	--	60	6.5 ± 0.54	130.6 ± 8.51	--	Collected = 1L	(Barrut et al., 2013)
Vacuum DiAF	Mixed	0.389 g/L	None	--	--	60	49.5 ± 6.37	9.9 ± 1.63	--	Collected = 100L	(Barrut et al., 2013)
Foam flotation	*Chlorella sp.*	$4.1\times10^7 \pm 9.6\times10^6$ cells/ml	CTAB	10 mg/L	--	15	2.3 (calc)	230.4	--	Column height = 1.5 m	(Coward et al., 2013)
Foam flotation	*Chlorella sp.*	$4.1\times10^7 \pm 9.6\times10^6$ cells/ml	CTAB	15 mg/L	--	15	18.1 (calc)	8.8	--	Column height = 0.29 m	(Coward et al., 2013)
Foam flotation	*Chlorella sp.*	~27×10^7 cells/ml (graph)	CTAB	10 mg/L	--	30	--	306.89 ± 31.6	--	--	(Coward et al., 2014)
Foam fractionation	*Chaetoceros spp.*	6×10^6 cells/ml	pH-induced (CO_2)	--	7.5	30	94 (graph)	8.9 (calc)	--	--	(Csordas and Wang, 2004)
BDAF	*Scenedesmus obliquus*	$2\times10^6 \pm 1\times10^5$ cells/ml	Aluminum sulfate	0.1 mg Al/mg TSS (graph)	5	10	>99	--	-34.6 ± 6.0	--	(Ometto et al., 2014)
BDAF	*Chlorella vulgaris*	$2\times10^6 \pm 1\times10^5$ cells/ml	Aluminum sulfate	0.015 mg Al/mg TSS (graph)	5	10	>99	--	-30.5 ± 1.2	--	(Ometto et al., 2014)
BDAF	*Arthrospira maxima*	$2\times10^4 \pm 1\times10^3$ cells/ml	Aluminum sulfate	0.07 mg Al/mg TSS (graph)	5	10	>99	--	-44.2 ± 7.8	--	(Ometto et al., 2014)

Important considerations for the operation of a flotation system for the recovery of microalgae include hydraulic loading rate, initial algal concentration, air to solids ratio, coagulant type, coagulant dosage, pH, salinity and the type of flotation (Bare et al., 1975; Aulenbach et al., 2010; Coward et al., 2013).

The height of a flotation column and the residence time of the microalgae in the foam have been shown to have significant impact on the concentration factor (Coward et al., 2013). The fact that the foam phase plays an important role in recovery and concentration has been noted for other applications such as mineral processing (Neethling, 2008). The concentration factor has also been found to be inversely dependent on the volume harvested (Barrut et al., 2013).

The effects of some variables are inconclusive. For example, changes in airflow rate has been said to not affect the recovery of microalgae (Chen et al., 1998; Coward et al., 2013). Conversely when airflow is increased for vacuum flotation, the harvesting efficiency and concentration decreased, which was attributed to turbulence causing resuspension from the foam (Barrut et al., 2013). The same inverse relationship was seen for dispersed air flotation (Levin, 1962).

4.6.1 pH

The pH of the solution can have a significant effect on the coagulation of microalgae due to interfacial properties and reaction mechanisms (Liu et al., 1999). Each coagulant generally has a peak performance at a certain pH. Thus, through the choice of coagulant, a large pH range can be covered (Gao et al., 2010).

Changing the pH between 5-8 is seen to have little effect on separation (Chen et al., 1998; Liu et al., 1999). However, as pH moves away from neutral in either direction, the separation efficiency generally increases for metal salts. At lower pH, excess H^+ reacts with the salt to further release metal cations, and at high pH, the metals form oxides and create larger gelatinous flocs (Hanotu et al., 2012). It should be noted, however, that flocs can be too large for microbubbles to float which will reduce recovery (Kim et al., 2012). If pH is increased to 12, cell lysis occurs which also serves to decrease recovery (Xu et al., 2010).

Other flotation operations have been shown to be most effective at different pH ranges. CTAB coagulation was found to be the most effective at pH 7.8, while separation efficiency using anionic sodium dodecyl sulfate (SDS) was poor until the pH was depressed to 3.5 (Phoochinda and White, 2003). This is attributed to a change in surface charge resulting in an electrochemical interaction. In ECF separation, lower pH levels were found to be most beneficial (Gao et al., 2010).

The influence of pH can be significant enough that pH alone can be used for the coagulation of cells. If the pH was depressed to nearly 2 (from a culture of pH 7.5 to 8) 88% of microalgae could be recovered in 18 minutes (Levin, 1962). Below a pH of 2, microalgae began to decompose, but cells could be maintained at pH 2.05 for 10 to 60 minutes with no significant difference in growth after neutralization. pH-induced flocculation maintains the integrity of non-harvested microalgae (Besson and Guiraud, 2013). This allows for culture recycle as it does not contaminate the produced biomass. The cost of pH modification, however, is significant.

4.6.2 Salinity

Rather than a condition that is changed for harvesting, salinity is determined by the nature of the microalgae cultivated. It has, however, been shown to have a significant impact on flotation. For example, with DiAF, the bubble size is heavily dependent on salinity. The higher the salinity, the smaller the resulting bubbles which lead to a higher recovery and concentration factor (Barrut et al., 2013). This is due to salts inhibiting the merger of bubbles and thereby preventing coalescence during flotation (Lin et al., 2011).

Salinity is also significant with regards to ECF, although the literature is contradictory on its impact. ECF has been reported to require relatively little energy for processing freshwater microalgae, but due to the high conductivity of seawater, its use with marine microalgae is impractical (Schlesinger et al., 2012). Conversely, a significant reduction in electrical demand for seawater compared to freshwater was found (Vandamme et al., 2013).

4.6.3 Bubbles

Bubbles without any modifications exert a negative surface charge (Cheng et al., 2010; Edzwald, 2010), which limits interaction with the negatively charged microalgae. This lead to the development of the PosiDAF bubble modification technique.

Each flotation method produces different bubble sizes and this has significant implications on separation effectiveness. Smaller bubbles have a higher surface area to volume ratio, which leads to higher probabilities of collision and attachment, a lower

detachment probability, lower ascending rate and higher free surface energy (Hanotu et al., 2012; Garg et al., 2014).

The optimal bubble size has been reported as approximately 50 μm, and efficiency drops significantly with larger bubbles (Cassell et al., 1975). This was attributed to the reduced number of bubbles, and thus each bubble is required to remove more cells resulting in decreased efficiency (Henderson et al., 2008). Bubble size was also said to determine the shape and rise pattern of the bubbles (Edzwald, 2010).

4.6.4 Microalgae cells

Microalgae strain selection has a significant effect on the harvesting stage (Brennan and Owende, 2010). Many characteristics of the cell can play a role, including morphology, size, shape, surface area, motility, hydrophobicity, cell concentration, extracellular organic matter and zeta potential (Henderson et al., 2010; Kröger and Müller-Langer, 2012; Barrut et al., 2013).

Microalgae cell size (Uduman et al., 2010), cell density (Lin et al., 2011), hydrophobicity (Garg et al., 2012) and growth phase (Kim et al., 2005) are important. Cell size determines the cell surface to biomass ratio, which means that smaller cells require more coagulant per unit mass of biomass harvested (Schenk et al., 2008). Cell density is closely linked with coagulant demand and it was shown that with higher densities in ECF, removal efficiency was decreased. This was attributed to insufficient coagulant availablity due to a short electrolysis time in the experiment (Gao et al., 2010).

Hydrophobicity is a major factor for all microalgae (Garg et al., 2012), with some species being naturally more hydrophobic than others. For example, *Chlorella* is naturally more hydrophobic than *Tetraselmis* sp. (Garg et al., 2014). As cell surfaces become more hydrophobic, they are more likely to be collected by rising bubbles and hence easier collection is possible (Chen et al., 1998).

The growth phase of microalgae also appears to have an effect on the harvesting efficiency. Microalgae have been shown to be more efficiently concentrated when harvested in the exponential phase compared to the stationary phase (Kim et al., 2005; Zhang and Hu, 2012; Coward et al., 2013). Maximum lipid content is commonly found in the stationary phase (Huerlimann et al., 2010; Salim et al., 2013) and as lipids are lighter than the culture medium, it would be expected that this phase would experience the easiest flotation, which is contrary to experimental results (Tran et al., 2013). Furthermore, cells in the exponential phase are also less likely to undergo natural flocculation. For example, *Chlorella vulgaris* showed natural flocculation of 22±2% of cells in the stationary phase and only 0.25±0.02% in the exponential phase (Rashid et al., 2013). However, regardless of growth phase over 90% of *Chlorella zofingiensis* could be recovered by flotation (Zhang and Hu, 2012).

Dissolved organic matter (DOM) or extracellular algogenic organic matter (AOM) excreted during algal growth are thought to be a potential link between growth phase, coagulant demand and harvesting efficiency (Edzwald, 1993). They have been identified as a significant component of the microalgae system (Henderson et al., 2008) and in determining coagulant demand and floc formation (Ometto et al., 2014). With DOM removed, it was found that the ratio of Al^{3+} determined the harvesting efficiency, but

regularly DOM in the culture medium consumes some of the coagulant (Zhang and Hu, 2012).

Zeta potential is the measure of the electric potential at the plane of shear of the electric double layer and represents the best measure of microalgae surface charge (Henderson et al., 2008). Zeta potential is linked to cell phase and is determined by the amount of surface functional groups (polysaccharides and proteins) (Zhang and Hu, 2012). It is most negative in the exponential phase and increases in the stationary and death phases (Danquah et al., 2009; Coward et al., 2014).

As the zeta potential approaches the point of zero charge, coagulation is generally improved (Taki et al., 2008). In harvesting, this can be affected by pH and coagulant dosage (Heinänen et al., 1995). Increasing pH causes zeta potential to become more negative, which is attributed to OH^- ions adhering to the surface (Phoochinda and White, 2003). Different microalgae show different overall changes in zeta potential as a function of pH. Some have been found to be negatively charged for all pH values between 2.5 and 11.5 (Edzwald, 1993), whilst other species had a point of zero charge at pH 4 (Phoochinda and White, 2003).

In combination with pH, coagulants cause an increase in surface charge (Banerjee et al., 2014). The result is that for effective coagulation to occur, coagulant demand is more strongly affected by charge density than surface area. The zeta potential should be between -10 and +2 mV (Henderson et al., 2008) and as long as zeta potential is within the optimal range, coagulant dosage and pH are unimportant (Sharp et al., 2006). For example, 95% of *Melosira* sp. could be recovered without coagulation, which was

attributed to a near neautral zeta potential in combination with a large cell size (Henderson et al., 2008).

4.7 Economics

Whilst microalgae such as *Dunaliella salina* that produce high value products, namely β-carotene (Zhu et al., 2008; Kleinegris et al., 2011), can be grown and harvested economically (Besson and Guiraud, 2013). The economic harvesting of high volume, low value products such as biofuels is more problematic (Sheehan et al., 1998). For microalgae biofuels to be economically viable, the biomass must cost between 0.4 and 0.75 $/kg (Williams et al., 2010). While this is a significant reduction from the estimated biofuel production cost in 2007 of 2.80$/L (Chisti, 2007), there are significant improvements that can be developed, making this a potentially attainable reduction. The cost of separation has ben cited as 20-30% of the biomass production costs (Gudin and Therpenier, 1986). Therefore, the harvesting costs are required to be less than 0.08 (Farid et al., 2013) or 0.25 $/kg, depending on the estimate used, for biofuels to be produced economically (Barrut et al., 2013).

Whilst the choice of harvesting method is an important economic consideration (González-Fernández and Ballesteros, 2013), it has been also shown to have significant influence on the final product (Coward et al., 2014). While flotation is a promising technique, there remains little reported work as to its economic feasibility (Brennan and Owende, 2010). Also, there is no method with proven economics at the large-scale (Coward et al., 2013).

The most economic method of microalgae harvesting by flotation appears to be DiAF (Garg et al., 2012). While the highest cost for DiAF is air injection, the need for coagulant addition also significantly increases the operation cost (Barrut et al., 2013). The most effective coagulants reported are aluminum sulfate and an organic cationic polyelectrolyte, but their costs were considered prohibitive (Coward et al., 2013). Additionally, all methods that involve the addition of a chemical run the risk of costs from a potential loss of market opportunities due to contamination of the biomass (Henderson et al., 2010).

The operation itself can have significant effects on the cost of coagulants. For example, when using chitosan, it was shown that chemical cost increased from 18 to 191 US$/kg when the pH was changed from 6 to 9 (Tran et al., 2013). Electrical based systems avoid the costs associated with coagulant addition, but high energy requirements and electrode replacement costs limit the economic feasibility of the techniques (Uduman et al., 2010).

4.8 Conclusions

The use of flotation for the recovery of microalgae is a promising technique that can achieve good recovery and concentration. Several flotation techniques have been researched, along with different methods to destabilize microalgae cultures to encourage them to flocculate. However, whilst flotation recovery shows potential, most work to date is still at the laboratory scale.

At the operational level, however, there is significant research that can be done to make the separation process more efficient and economically feasible. Foremost is obtaining a better understanding how different microalgae and their medium affect flotation and

recovery (Zhang and Hu, 2012; Vandamme et al., 2013). It is currently not possible to specify a universal method due to the little understood impacts arising from differences between microalgae species (Uduman et al., 2010). From a better understanding it would be possible to determine the minimum surfactant dosage, perhaps through zeta potential measurements (Coward et al., 2013).

Work is required to help address the need for development of cost-effective full-scale process designs (Kröger and Müller-Langer, 2012). These designs will need to consider the influence of cultivation and upstream production on separation, and the influence of harvesting on subsequent downstream production (Milledge and Heaven, 2013).

Conflict of Interest

The authors declare no conflict of interest.

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Chapter 5

Paper #4 – Separation, Algal Research

Heat-aided flocculation for flotation harvesting of microalgae

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CAL performed the experiments, data analysis and primary manuscript writing. GNAS assisted in the isolation and cultivation of microalgae strains. GMR conducted environmental sampling and assisted in some manuscript writing. JAS provided overall direction in the project and experimental design, and manuscript writing.

Abstract

Microalgae biofuels are a promising renewable fuel that can be produced whilst mitigating industrial CO_2. However, their production is still not economically comparable to fossil fuels, with microalgae harvesting recognized as an area requiring development. Flotation is emerging as a promising harvesting method, but typically requires addition of flocculating chemicals to allow a foam concentrate to be formed and collected. In addition to adding to process costs, these additives contaminate the biomass and limit applications, such as for animal feed, for the non-biofuel component. An alternative method to achieve efficient harvesting is proposed that could use waste industrial heat to aid the flotation process and avoids the need for chemical additives. The best separation was achieved at 85°C, where the *Scenedesmus* sp. culture was concentrated to 2.78 g/L from an initial density of 0.13 g/L. The result was a concentration factor of 25.8 and a recovery of 83%.

Keywords

Microalgae, harvesting, separation, flotation, waste heat

5.1 Introduction

Microalgae with high lipid content have the potential to produce biofuel whilst also producing food supplements and other value-added products (Vandamme et al., 2013; Brennan and Owende, 2010; Chisti, 2007). There are many other advantages to microalgae-based production, including that they do not compete with food crops (Lam and Lee, 2012), are capable of year-round production, and do not require pesticides or herbicides (Brennan and Owende, 2010). Microalgae production can be also coupled to industrial emissions for carbon capture (Yen et al., 2015; Laamanen et al., 2014; Shang et al., 2010) and wastewater treatment (Assemany et al., 2016; Lam and Lee, 2012).

However, despite these advantages process development is required to improve production economics (Molina Grima et al., 2013), including harvesting of microalgae prior to lipid extraction. It has been estimated that 20-30% of total production costs lie in harvesting (Sharma et al., 2013; González-Fernández and Ballesteros, 2013) due to difficult separation processes (Wiley et al., 2009; Bare et al., 1975).

The difficulty in harvesting arises from the nature of microalgae cells, namely; low concentrations (Pavez et al., 2015), small sizes (typically 2-10 μm (Sharma et al., 2013)), a specific gravity similar to water (Zhang and Hu, 2012), a negative surface charge (Wang et al., 2015; González-Fernández and Ballesteros, 2013), and a requirement for frequent harvesting due to high growth rates (Milledge and Heaven, 2013).

The primary harvesting techniques currently available for microalgae separation are centrifugation, filtration, flocculation, sedimentation and flotation (Laamanen et al.,

2016; Milledge and Heaven, 2013), electrophoresis (Coward et al., 2013) and membrane filtration (Phoochinda and White, 2003).

Flotation has received significant attention due relatively low capital and operating costs, and the possibility for 90-99% recovery (Ndikubwimana et al., 2016; Zhang et al., 2014). However, the process typically requires the addition of a surface-active chemical to make the microalgae cells hydrophobic so that they attach to rising bubbles (Hanotu et al. 2012; Phoochinda and White, 2003). Bubble surfaces and microalgae cells are typically both negatively charged, so recovery without chemical addition would otherwise be low (Coward et al., 2014; Henderson et al., 2008; Edzwald, 1993). Ferric chloride, aluminum sulphate, sodium dodecyl sulfate, chitosan, and acetyl trimethyl ammonium bromide are common chemical additives (Sharma et al., 2013). The addition of these chemicals unfortunately contaminates the biomass, whilst also contributing to the cost of the operation (Laamanen et al. 2016; Smith and Davis, 2012). Contamination with metal salts can significantly limit application of the biomass remaining after lipid extraction for uses such as animal feed, fertilizer and in aquaculture (Vandamme et al., 2013; Ahmad et al., 2011).

In this study, heat-aided flotation without the use of any chemical additives that was originally developed for bacteria recovery (Scott et al., 1997) is examined as a potential new alternative separation method for dilute microalgae suspensions. As a stand-alone process, the heating of large volumes of microalgae culture is likely to be too expensive, but through utilization of waste heat from industry this approach could be used for on-site separation of process-coupled microalgae. The parameters examined include the

influence of temperature and microalgae strain, as well any impacts on recovered lipid quantity and quality.

5.2 Materials and Methods

5.2.1 Algae cultivation

Scenedesmus dimorphus #1237 (UTEX culture collection, University of Texas at Austin, TX, USA) and wild strains of microalgae were grown in Bold Basal medium (Andersen, 2005). The culture was incubated in a flask, in an Infors HT Multitron Standard (Montreal, QC, Canada) at 25°C, continuously agitated at 125 rpm, under photosynthetic light conditions of ~70-80 μmol photon $m^{-2}s^{-1}$ (Sylvania Gro-Lux F15W / Gro T8, Infors) using a 12:12 hour light:dark cycle.

5.2.2 Algae collection

Microalgae strains were collected and screened as described in Eibl et al. (2014). The samples were subject to purification by serial dilution and then transferred to Bold's Basal Medium agar plates (Bold and Wynne 1985). Identification to the genus level was performed using morphological analysis, as described by Bellinger and Sigee (2010).

5.2.3 Temperature modification

Prior to separation, the temperature of each sample was raised in a water bath, taking 30±2 minutes to reach 65°C and 66±2 minutes to reach 95°C. After reaching the run temperature, the samples were immediately transferred to an ice bath and rapidly brought back to room temperature (21±2°C).

5.2.4 Flotation column design

A laboratory scale dispersed air flotation column (Figure 5.1) was made using a clear acrylic tube with a porous stone sparger at the bottom (mean pore size of 15 μm, Refractron Technologies Corp., NY, USA). A collection chamber was located at the top with a weighted deflection plate to force the bubbles to concentrate. A side port was connected to an external water reservoir to maintain a constant level in the tube. Individual flotation tests were carried out with 500 ml of culture and a headspace of 1.5 cm. Separations were conducted with a run time of 5 minutes.

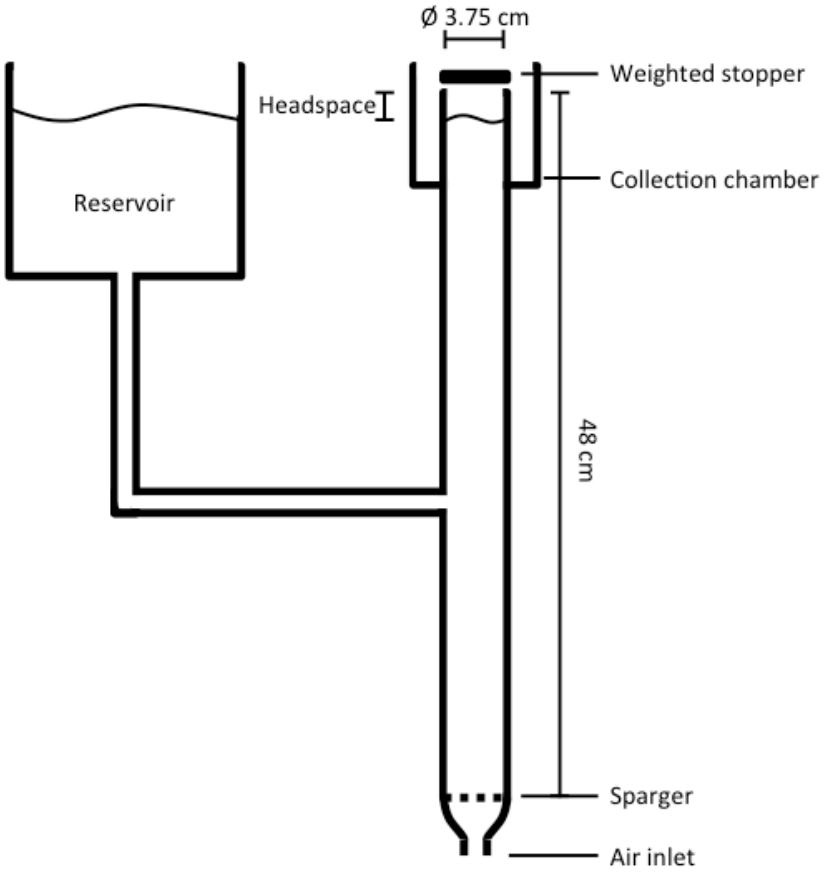

Figure 5.1: Laboratory flotation column design

5.2.5 Separation analysis

Biomass concentration was measured with an Ahlstrom 151 glass microfiber filter according to Equation 5.1:

$$C_{algae} = \frac{m_{final} - m_{filter}}{V_{filter}} \quad \text{Equation 5.1}$$

where C_{algae} (g/L) is the biomass of the measured algae. m_{final} (g) and m_{filter} (g) are the weights of dried sample and filter paper, respectively, and V_{filter} (L) the volume of sample filtered.

The volume and the biomass concentration of concentrate was measured, along with the initial biomass of the culture, in order to calculate the concentration factor and collected (%), as shown in Equations 5.2 and 5.3:

$$Concentration\ factor = \frac{C_{concentrate}}{C_{initial}} \quad \text{Equation 5.2}$$

$$Collected\ (\%) = \frac{C_{concentrate} \cdot V_{concentrate}}{C_{initial} \cdot V_{initial}} \cdot 100\% \quad \text{Equation 5.3}$$

The concentration factor is the ratio of concentrate biomass concentration (g/L) to initial medium biomass concentration (g/L). The recovery (%) is the comparison of mass in the concentrate (g) to the mass initially in the column (g). These masses are calculated as concentration (g/L) multiplied by their respective volumes (L).

5.2.6 Lipid extraction and total lipid analysis

A modification of the lipid extraction described by Folch et al. (1957) was performed. Microalgae samples (100 mg) were freeze-dried and mixed with 3 ml of

chloroform:methanol (2:1 v/v) and sonicated using a Sonic Dismembrator Model 500 (Fisher Scientific, Ottawa, Ontario, Canada) for approximately 1 minute. Samples were then centrifuged using an Allegra X-15R Centrifuge (Beckham, Palo Alto, CA, USA) and the solvent was removed to a weighted vial. Extraction was repeated in triplicate and the resulting extracts were combined. The combined extract was dried using a Savant DNA120 SpeedVac Concentrator (Thermo Electron Corporation (Milford, MA, USA).

5.2.7 Direct transesterification

Direct transesterification of the extracted lipid was performed as described by Velasquez-Orta et al. (2012). Microalgae samples (100 mg) were freeze dried and placed in a glass tube, where they were mixed with 2 ml of methanol:hexane (1:1 v/v). The reaction was initiated with the addition of sodium methoxide (100 µl) as a catalyst. The reaction was allowed to continue for 1 hour, while being well mixed and maintained at 80°C. After an hour, 0.5 ml of hydrochloric acid was added to neutralize the catalyst. The samples were centrifuged and the hexane layer containing the fatty acid methyl esters (FAME) extract was transferred to a gas chromatography vial for analysis.

5.2.8 Gas chromatography

The fatty acid methyl ester (FAME) composition was analyzed via gas chromatography using a Thermo Trace 1300 (Thermo Canada, Ottawa, Ontario, Canada) that was equipped with a flame-ionization detector (FID) and a SGE SolGel-Wax capillary column (30 m x 0.25 mm x 0.25 µm, Canadian Life Sciences, Peterborough, Ontario, Canada). Samples (dissolved in hexane) were spiked with C17:0 as an internal standard. Helium was used as the carrier gas at a flow rate of 1.6 ml/min. Standard split/splitless

injection was used with a split ratio of 80 and an injector temperature of 250°C. The column temperature was ramped from 140°C to 240°C at a rate of 4°C/min. The detector temperature was 280°C. An external standard, using a C4-C24 FAME mix, was used to identify peaks based on retention time, whilst peak area was used to quantify each FAME relative to the internal standard.

5.3 Results and discussion

The capture of industrial waste heat, such as from ore smelters, to maintain year-round microalgae cultivation temperatures in cold climates has potential (Laamanen et al., 2014; Shang et al., 2010). Furthermore, the heat could be utilized elsewhere the production cycle, such as in biomass drying and of interest here, to aid floatation. Application of heat has been previously shown to aid the separation of bacteria from wastewater without the need to add flocculating agents (Scott et al., 1997). A similar concept has been investigated for microalgae, where the exposure to an elevated temperature prior to flotation increased hydrophobicity and aided separation.

While the heating of cultures for the bulk harvesting of algae is likely not economical if purchasing energy to heat, the ability to couple with existing industry largely avoids this hurdle. Industries that are commonly coupled with algae cultivation for CO_2 capture, such as fossil fuel power plants and cement production, also produce large amounts of waste heat that is often just dispersed to atmosphere. This method proposes the utilization of current industrial coupling approaches to utilize this waste heat, in addition to the CO_2 for cultivation.

5.3.1 Temperature

A significant change in the percentage collected and concentration factor when *Scenedesmus dimorphus* (UTEX #1237) samples were pre-heated to 65°C and above prior to dispersed air flotation was indeed seen (Figure 5.2). As the temperature increases up to 85°C, the recovery and concentration factor increased to 83% and 25.8, respectively. The application caused the quartets of *Scenedesmus dimorphus* to form into small clumps, (Figure 5.3A,B). This clumping emulates the addition of a flocculating agent in traditional bubble flotation systems, but without the resulting contamination of metal salts or other additives (Besson and Guiraud, 2013; Vandamme et al., 2013; Hanotu et al., 2012).

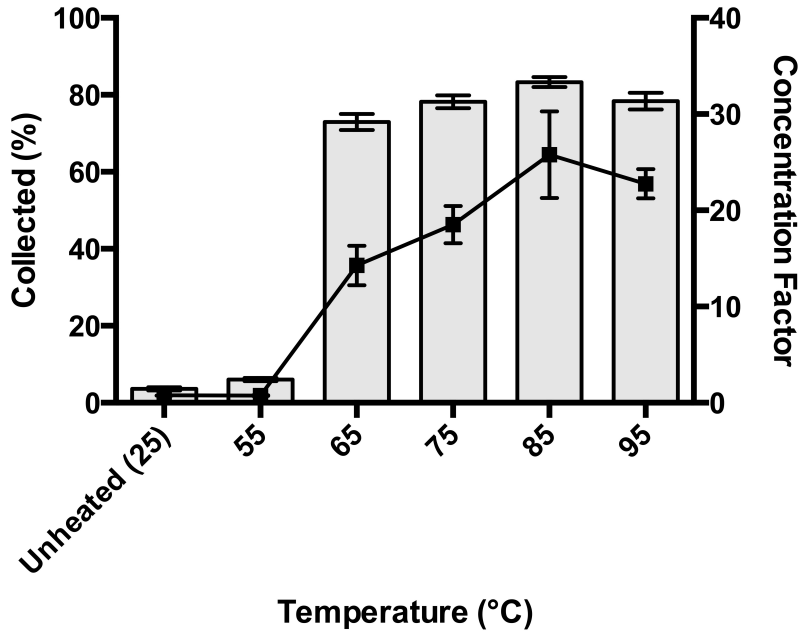

Figure 5.2: Recovery (bars) and concentration factor (solid squares) of *Scenedesmus dimorphus* (UTEX #1237) as a function of heating temperature. The initial microalgae concentration was 0.13 g/L and the error bars represent the standard error of the mean (n = 3).

It is also important to note that the initial algae concentrations used in these studies are significantly lower than those commonly found in published harvesting studies. This was done deliberately, as open pond algae cultivation has been shown to produce concentrations at minimum in this 0.1 g/L range (Brennan and Owende, 2010). Through the ability to prove a harvesting method at these dilute concentrations, there is the potential to optimize the harvesting schedule.

The concentrated microalgae recovered at 85°C had a resulting concentration of 2.78 g/L, which is in the common range for bulk harvesting (2-7% TSS (Sharma et al., 2013)) despite the relatively dilute initial concentration. While a concentration factor of 25.8 puts this operation slightly above the values published in other flotation studies. On the other hand, 83% is on the lower end of reported recovery values (Laamanen et al., 2016). This highlights the potential for possible trade off of concentration factor for recovery, if more desirable for the proposed operation.

The decrease in collection above 85°C was a function of cells being destroyed and lysing in the heating stage, which resulted in a 14% decrease of collectable biomass at 95°C. However, as can be seen from Figure 5.2 and Figure 5.3C, 90% of the remaining microalgae can be captured after heating to 85°C and subsequent flotation, a percentage that falls within the range of chemical aided flotation recovery (Phoochinda and White, 2003).

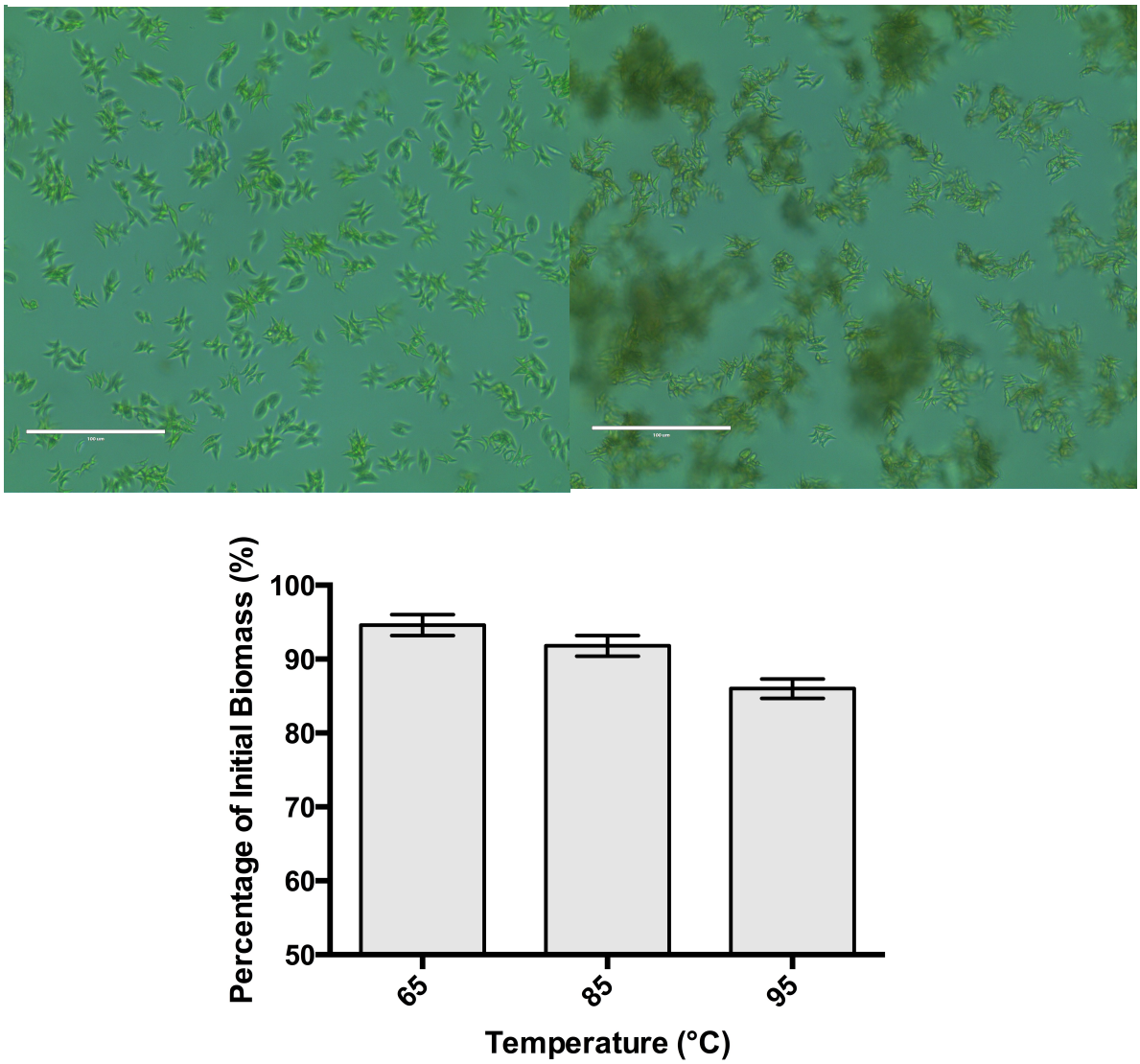

Figure 5.3: (A) *Scenedesmus dimorphus* (UTEX #1237) before and (B) after heating to 95°C. Clumping may be attributed to cell lysing, for which mass loss in the heating stage was measured (C). Error bars represent the standard error of the mean (n = 3).

After heating, the subsequent cooling stage prior to flotation was also found to have an effect on collection efficiency. Using the same *Scenedesmus dimorphus* strain (UTEX #1237), the cooling temperatures were varied after heating to 85°C and as seen in Figure 5.4, cooling to 30°C results in significantly less recovery than if cooled to 25°C. Whereas, as cooling to between 25°C and 10°C offered no significant advantage, the cooling temperature was, therefore, maintained as 21±2°C for all further experiments.

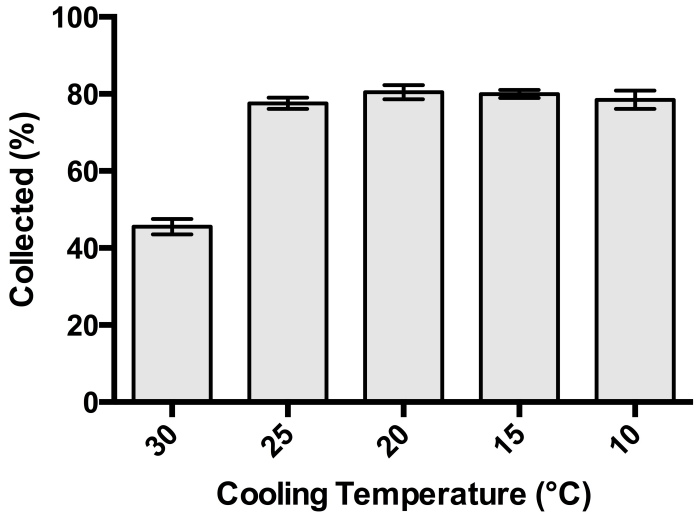

Figure 5.4: Recovered biomass (*Scenedesmus dimorphus* (UTEX #1237)) as a function of post-heating cooling temperature. Error bars represent the standard error of the mean (n = 3).

While cooling was done in the laboratory for these experiments, there is the possibility that the culture could be cooled without the addition of energy. Ambient cooling would bring the algae back to low temperature, however longer periods of elevated temperature may run a higher risk of damaging components of the residual biomass. These residues are commonly cited as having the potential for the feed industry, among other products, and contribute to the economic viability of the operation (Markou and Nerantzis, 2013). However, this is not necessarily a large concern, as the degradation of biomass at 70°C

took 12 hours to be a significantly different than the initial sampling (Napan et al., 2015). It could affect specific components, but further studies would be needed to determine the exact changes.

5.3.2 Microalgae strain

Another important consideration for any harvesting technique is its ability to harvest a number of different microalgae species. The use of heat was initially successfully demonstrated with *Scenedesmus dimorphus* #1237, and six wild microalgae strains were also compared for their response to thermal treatment before flotation. The wild strains included *Scenedesmus* spp. and the results of their separations after heating to 85°C are given in Figure 5.5.

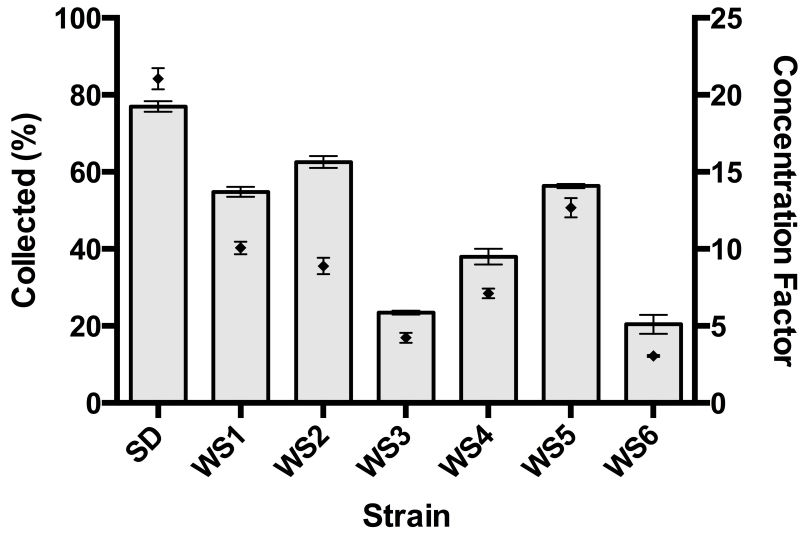

Figure 5.5: Recovery (bars) and concentration factor (solid diamonds) as a function of microalgae strain (initial concentration = 0.20 g/L), at a temperature of 85°C. SD is *Scenedesmus dimorphus* (UTEX #1237), and the wild strains were WS1 (*Chlorococcum* sp.), WS2 (*Coccomyxa* sp.), WS3 and WS4 (*Scenedesmus* sp.), and WS5 and WS6 (*Chlamydomonas* sp.), Error bars represent the standard error of the mean (n = 3).

As seen in Figure 5.5, the culture collection *Scenedesmus dimorphus* strain (UTEX #1237), provided the best separation. However, with the wild strains there was a diverse range of responses, even within the same genus. Nevertheless, WS1 (*Chlorococcum* sp.), WS2 (*Coccomyxa* sp.) and WS5 (*Chlamydomonas* sp.) all recovered over 50% of the initial biomass, which indicates potential for further optimization of the process for specific strains, such as the applied heating temperature.

The bubbles formed in the column and the resulting foam were observed to vary. For example, WS3 (*Scenedesmus* sp.) produced the least stable bubbles, creating at most a 2 cm thick stable foam in the column, whereas the *Chlamydomonas* spp. (WS5 and WS6) produced smaller more stable bubbles during flotation, allowing for foam height to increase beyond 10-15 cm. WS2 (*Coccomyxa* sp.) also produced a number of small stable bubbles, comparable to those with the *Chlamydomonas* sp. samples. This could be due to the mucilage of these strains, which is not seen in *Scenedesmus* sp. strains.

These strain-based experiments were done as a proof of concept, showing that the effect is not specific to *Scenedesmus* sp. cultures. The results of this study showed that the heating allowed for the capture of different strains, but also that the strains reacted differently to heating. Not only proving that harvesting through this method is possible, but also showing that there is the potential for the optimization for different strains.

5.3.3 Lipid content and composition

For biodiesel production, microalgal lipids are the target and, therefore, any separation method must not adversely impact on lipid quantity and quality. To test the applicability

of heat-induced flotation for harvesting of microalgae for biofuel, the lipid profile of *Scenedesmus dimorphus* (UTEX #1237) was analyzed prior to, and after heating.

The lipid content of the microalgae prior to heating was 21.1 ± 1.1% and it was found that heating did not have a significant impact. Additionally, with a separation completed at 65°C, whilst only 47.5% of the initial biomass was recovered, the lipid content in this biomass was higher (27.5 ± 2.2%) (Figure 5.6), resulting in the recovery of 63.9% of the total lipids before flotation. This suggests a useful functionality, where this process preferentially recovers lipids.

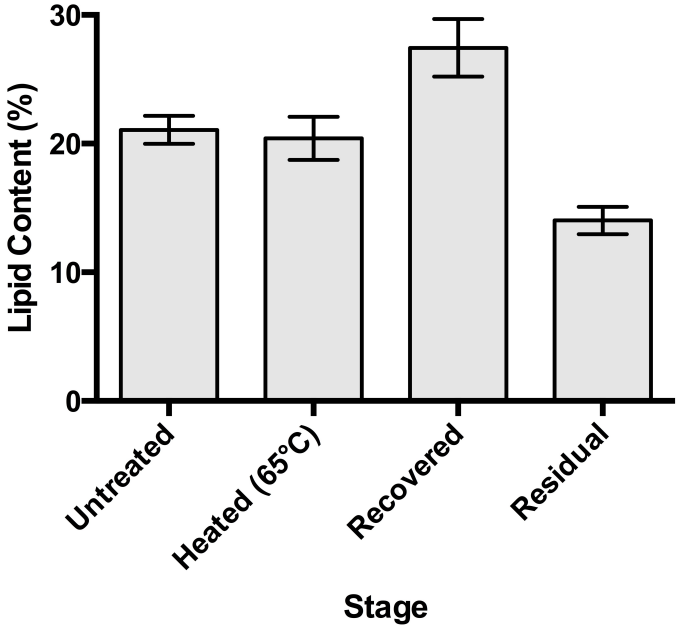

Figure 5.6: Total lipid content throughout the separation process of *Scenedesmus dimorphus* (UTEX #1237). Error bars represent the standard error of the mean (n = 3).

The method for this lipid enhancement is largely unknown, however the increased lipid content has been seen in other flotation harvesting methods. Coward et al. (2014) found that CTAB-aided flotation caused an increase in extractable lipids, through both solubilizing the phospholipid bilayer and some surfactant entering the extraction process.

While Naghdi and Schenk (2016) reported that, if cells were ruptured, the lipids and cell debris were not harvested at the same efficiency. For heat-aided flocculation for flotation it is likely to be the latter, the preferential recovery of lipids from ruptured cells.

The lipid quality, in terms of the distribution of carbon chain lengths was found to remain unaffected by the heating process (Table 5.1). As a consequence the biodiesel quality arising from transesterification of these lipids into fatty acid methyl esters (FAME) should not be adversely affected by this separation technique. But the enhanced overall lipid content should provide a more base material for conversion.

Table 5.1: Lipid composition of unheated and heated Scenedesmus dimorphus (UTEX #1237), average and the standard error of the mean (n = 3).

	Residence time (min)	**Lipid Composition (%)**		
		Unheated (25°C)	65°C	95°C
C15:0	11.25	0.05 ± 0.01	0.06 ± 0.01	0.09 ± 0.01
	12.68	10.87 ± 0.29	10.83 ± 0.07	10.58 ± 0.05
	13.04	2.49 ± 0.53	3.77 ± 0.07	3.86 ± 0.02
C16:0	13.47	0.70 ± 0.03	0.75 ± 0.03	0.71 ± 0.02
	13.84	2.78 ± 0.14	2.09 ± 0.03	3.02 ± 0.01
C16:1	14.01	1.10 ± 0.22	1.27 ± 0.04	0.60 ± 0.01
	14.95	7.80 ± 0.26	8.64 ± 0.50	9.75 ± 0.34
	15.40	3.62 ± 0.06	3.47 ± 0.01	3.49 ± 0.04
	16.04	11.10 ± 053	12.16 ± 0.44	10.51 ± 0.04
C18:1n9c	17.50	9.03 ± 0.10	9.19 ± 0.09	8.88 ± 0.03
	18.44	8.26 ± 1.47	9.77 ± 1.41	10.70 ± 1.90
	19.76	15.57 ± 0.93	14.06 ± 1.41	13.13 ± 1.48
	19.82	2.98 ± 0.04	3.06 ± 0.02	3.03 ± 0.02
	20.35	9.58 ± 0.24	9.36 ± 0.09	8.68 ± 0.29
C20:0	20.97	0.03 ± 0.02	0.03 ± 0.01	0.04 ± 0.01
	22.33	1.47 ± 0.02	1.71 ± 0.04	1.90 ± 0.04
Others		12.55	9.78	11.02

5.4 Conclusion

Heating microalgae cultures prior to flotation can create noticeable cell clumping, which aids recovery. This harvesting method could, therefore, be significant by the avoiding costs and contamination associated with adding chemical flocculants. Furthermore, lipid analysis showed that the applied elevated temperatures had no adverse effect on the biodiesel potential of the microalgae. The microalgae strain used is, however, shown to influence overall biomass recovery, which suggests that strain specific optimization, such as the applied temperature may be required.

The best separation was achieved at 85°C, where the *Scenedesmus* sp. culture was concentrated to 2.78 g/L from an initial density of 0.13 g/L. The result was a concentration factor of 25.8 and a recovery of 83%.

This method as a standalone separation may not be economical due to energy purchase costs. However, the repurposing of otherwise waste heat from industrial operations could make this a very feasible approach, especially if microalgae production is linked to CO_2 sequestration from off-gas.

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Chapter 6

Paper #5 – Separation, Biomass and Bioenergy (submitted)

Development of heat-aided flocculation for flotation harvesting microalgae

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Author Contributions

CAL performed the experiments, data analysis and primary manuscript writing. GMR assisted in some manuscript writing. JAS provided overall direction in the project and experimental design, and manuscript writing.

Abstract

Biofuel from microalgae has significant potential, but the economics of production are still not on par with fossil fuels. A stage of production commonly cited as requiring improvement is harvesting of microalgae from dilute culture solutions. Flotation has emerged as a promising harvesting method and a novel derivative, heat-aided flocculation, is examined. By potentially using waste heat from industry, flotation can be achieved without addition of the chemicals commonly utilized and which limit the usage of the non-biofuel component.

Keywords

Microalgae, harvesting, separation, flotation, waste heat

6.1 Introduction

Microalgae are a promising biological feedstock for both biofuels and other bioproducts. Microalgae's high lipid content can be converted into fuels that can be utilized as drop-in replacements in traditional diesel engines (Garg et al., 2012; Zhang and Hu, 2012). Compared to terrestrial plant sourced biofuels, microalgae biofuel has several advantages including that it does not compete for agricultural land, has higher areal productivity, and can be produced year-round. Furthermore, microalgae production can be coupled to industrial carbon dioxide (CO_2) off-gas emissions for carbon capture and mitigation (Brennan and Owende, 2010; Lam and Lee, 2012). This can provide for increased growth rates through utilizing the CO_2 as a carbon source (Wang et al., 2008; Chiu et al., 2011; Pires et al., 2012; Rickman et al., 2013; Schipper et al., 2013; Seyed Hosseini et al., 2015).

The possible industrial CO_2 sources for algae cultivation are significant worldwide, but there utilization is currently limited due to ambient temperature considerations. This has lead to large-scale microalgae cultivation being mainly in tropic and sub-tropic areas. To expand the potential of these technologies, the use of industrial waste heat in off-gas emissions to allow for year-round cultivation in cold climates has been also advocated (Shang et al., 2010; Laamanen et al., 2014).

A common theme with all proposed industrially coupled operations is that the utilization of CO_2 and heat in off-gas emissions is considered only in the cultivation stage. However, it has been demonstrated that the use of heat can be also used to promote flotation harvesting. Such an approach would allow for bulk harvesting of algae while avoiding the

high energy costs of centrifugation or the contamination from the addition of traditional flotation flocculants (Laamanen et al., 2016a; 2016b). This contamination can significantly limit the usage of the residual biomass after lipid extraction, especially for common uses such as animal feed or fertilizer (Ahmad et al., 2011; Vandamme et al., 2013).

In this study, a heat-aided flotation process, originally used for bacteria recovery (Scott et al., 1997), is developed for the harvesting of microalgae. Elevating the culture temperature to at least 65°C prior to gas flotation allows for efficient microalgae harvesting without the addition of chemicals (Laamanen et al., 2016). This is an important development as chemical addition is a common problem in flotation, as it increases cost and contaminates the resulting biomass, possibly limiting the applications of the final product. The method is presented as a process-coupled system to utilize otherwise waste heat from industrial operations as an economic means by which to elevate the temperature of large volumes of microalgae culture. The parameters examined in this study include the initial algae concentration, pH modification and effects on the growth media in terms of its value for recycling back into the cultivation stage.

6.2 Materials and Methods

6.2.1 Algae cultivation

Scenedesmus dimorphus #1237 (UTEX culture collection, University of Texas at Austin, TX, USA) and other wild algae samples were grown in Bold Basal medium (Andersen, 2005). The cultures were incubated in a flask, in an Infors HT Multitron Standard (Montreal, QC, Canada) at 25°C, continuously agitated at 125 rpm, under photosynthetic

light conditions of ~70-80 μmol photon $m^{-2}s^{-1}$ (Sylvania Gro-Lux F15W / Gro T8, Infors) using a 12:12 hour light:dark cycle.

6.2.2 Temperature and pH modification

Prior to separation, the temperature of each sample was raised in a water bath over for 30±2 minutes to reach 65°C and for 66±2 minutes to reach 95°C. After attaining the experimental run temperature, the samples were immediately transferred to an ice bath and rapidly brought back to room temperature (21±2°C).

6.2.3 Flotation column design

A laboratory scale dispersed air flotation column (Figure 6.1) was made using a clear acrylic tube with a porous stone sparger at the bottom (mean pore size of 15 μm, Refractron Technologies Corp., NY, USA). A collection chamber was located at the top with a weighted deflection plate to force the bubbles to concentrate. A side port was connected to an external water reservoir to maintain a constant level in the tube. Individual flotation tests were carried out with 500 ml of culture and a headspace of 1.5 cm. Separations were conducted with a run time of 5 minutes.

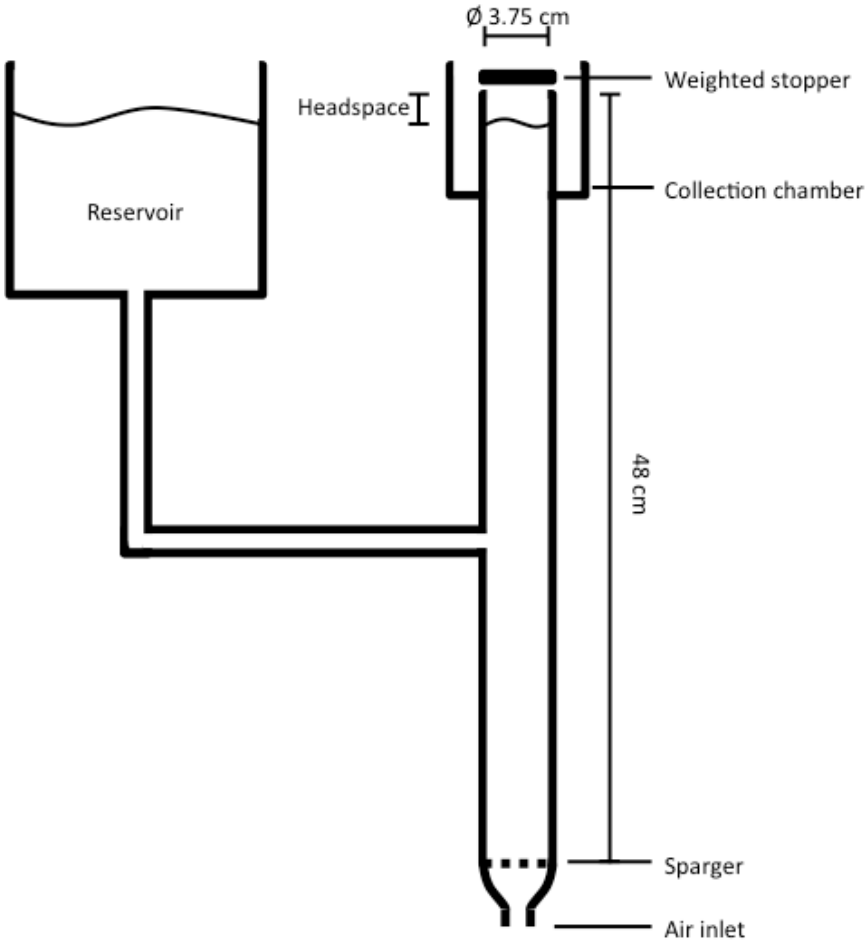

Figure 6.1: Laboratory flotation column design

6.2.4 Separation analysis

Biomass concentration was measured with an Ahlstrom 151 glass microfiber filter according to Equation 6.1:

$$C_{algae} = \frac{m_{final} - m_{filter}}{V_{filter}} \qquad \text{Equation 6.1}$$

where C_{algae} (g/L) is the biomass of the measured algae. m_{final} (g) and m_{filter} (g) are the weights of dried sample and filter paper, respectively, and V_{filter} (L) the volume of sample filtered.

The volume and the biomass concentration of concentrate was measured, along with the initial biomass of the culture, in order to calculate the concentration factor and recovery efficiency, as shown in Equations 6.2 and 6.3:

$$Concentration\ factor = \frac{C_{concentrate}}{C_{initial}} \quad \text{Equation 6.2}$$

$$Collected\ (\%) = \frac{C_{concentrate} \cdot V_{concentrate}}{C_{initial} \cdot V_{initial}} \cdot 100\% \quad \text{Equation 6.3}$$

The concentration factor is the ratio of concentrate biomass concentration (g/L) to initial medium biomass concentration (g/L). The recovery (%) is the comparison of mass in the concentrate (g) to the mass initially in the column (g). These masses are calculated as concentration (g/L) multiplied by their respective volumes (L).

6.3 Results and discussion

6.3.1 Algae concentration

Microalgae harvesting is difficult as even when grown to the maximum concentration, the solution is still relatively dilute. For example, for outdoor raceway ponds, the most common method for microalgae mass production, the typical biomass concentration is around 0.5 g/L (Vandamme et al., 2013). This makes the processing of large volumes of culture for the harvesting of microalgae a necessity. However, the time taken to grow to the maximum culture concentration may not be economical, meaning that even lower concentrations of microalgae could require harvesting.

A series (Figure 6.2) of experiments were completed to show the ability of the thermal flotation method to harvest very dilute culture conditions. The “full” initial culture

concentration was 0.545 g/L, that is similar to commercial raceways, and subsequent dilutions of 1/2, 1/4, 1/8, and 1/16 were used. The recovery after flotation decreased from 79.4% at full initial concentration, to 79.0, 75.7, 75.1 and 68.1% at 1/2, 1/4, 1/8, and 1/16 of the full concentration, respectively. Even at the lowest concentration tested (0.034 g/L), the recovery was a reasonable 68.1%, with a final concentration of 0.70 g/L.

The harvested separations (concentrate) from initial culture levels of 0.545 to 0.068 g/L all produced 2-7% total biomass solids, which is in line with other bulk harvesting operations (Sharma et al., 2013). The concentration factors were 4.84, 12.21, 22.92, and 29.84, for full concentration, 1/2, 1/4, and 1/8 concentration, respectively. The maximum final product concentration produced was for the 1/2 concentration run, and was 3.33 g/L. Therefore, thermal aided separation could be performed at early stages of growth and/or concentration levels, thereby allowing optimization as to the best time to harvest with respect to economic considerations.

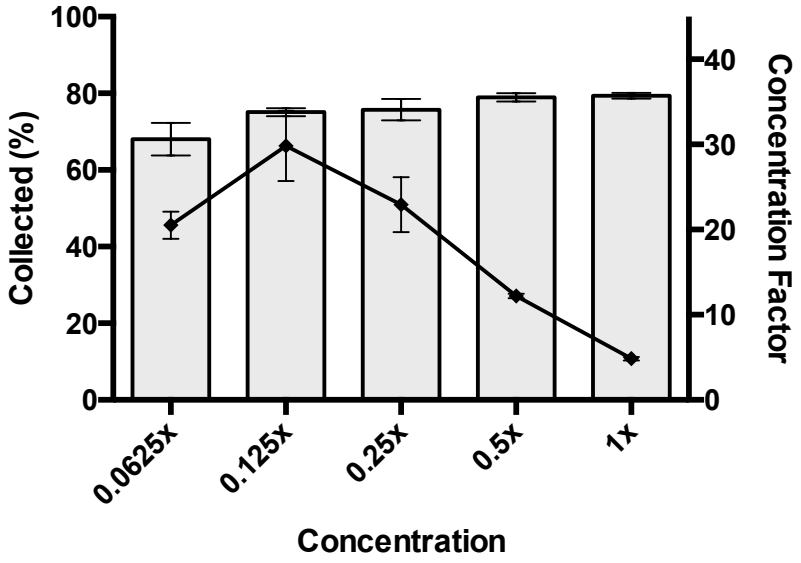

Figure 6.2: Recovery (bars) and concentration factor (diamonds) as a function of algae biomass concentration (1x = 0.545 g/L), at a temperature of 85°C. Error bars represent the standard error of the mean (n = 3).

6.3.2 pH alteration

Levin et al. (1962) originally showed that microalgae flotation could be achieved through the depression of the culture pH, in a similar manner to the heat-induced separation developed here. Aljuboori et al. (2016) also showed that decreasing pH in the microalgae culture caused flocculation, which started to have an effect with a change of as little as from 7 to 6.5, and increasing down to pH 3.

While having similar advantages, namely the avoidance of flocculating agent addition and the resulting metal contamination, the two methods are not necessarily exclusive. Heat-induced flotation is proposed as an industrially coupled approach to harvesting by using otherwise waste heat in off-gas, such as from power stations or ore smelters. As

these off-gasses are typically acidic (Shang et al., 2007), they could be utilized for pH alteration as well as for heating.

Therefore, before testing the combined effects of pH and heating, the effect of pH alone was tested (Figure 6.3). The results show that for *Scenedesmus dimorphus*, pH can have a positive effect on separation. However, a recovery of only 50% was achieved, even when the pH was decreased to 2, which was similar to that observed by Levin et al. (1962).

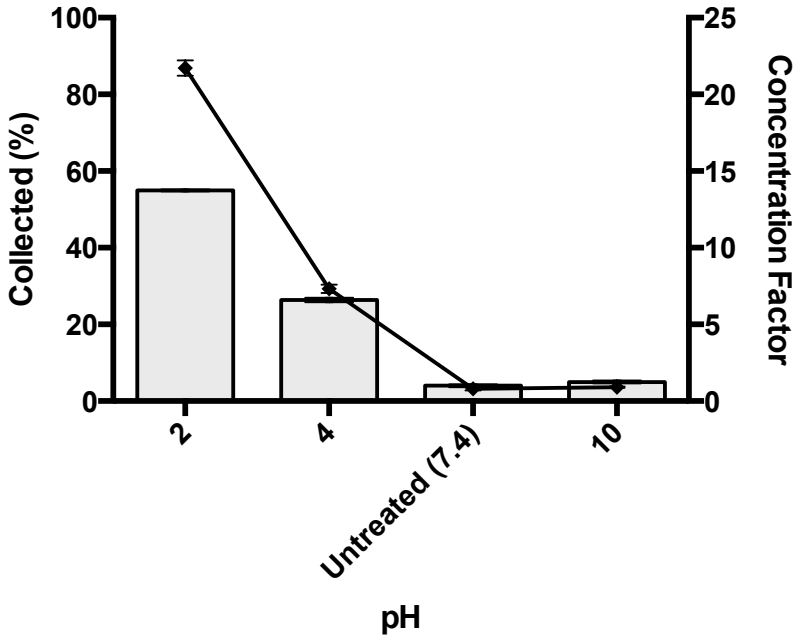

Figure 6.3: Recovery (bars) and concentration factor (diamonds) as a function of pH alteration (Initial concentration = 0.12 g/L). Error bars represent the standard error of the mean (n = 3).

6.3.3 Combination with pH alteration

As mentioned in Section 6.3.2, the industrial off-gas coupled approach is promising not only in heat-induced flotation, but also as a combined approach utilizing acid gases to also allow pH alteration. To examine this, a series of experiments were completed to see

the affects of altering both temperature and pH prior to separation. The results are shown in Figure 6.4.

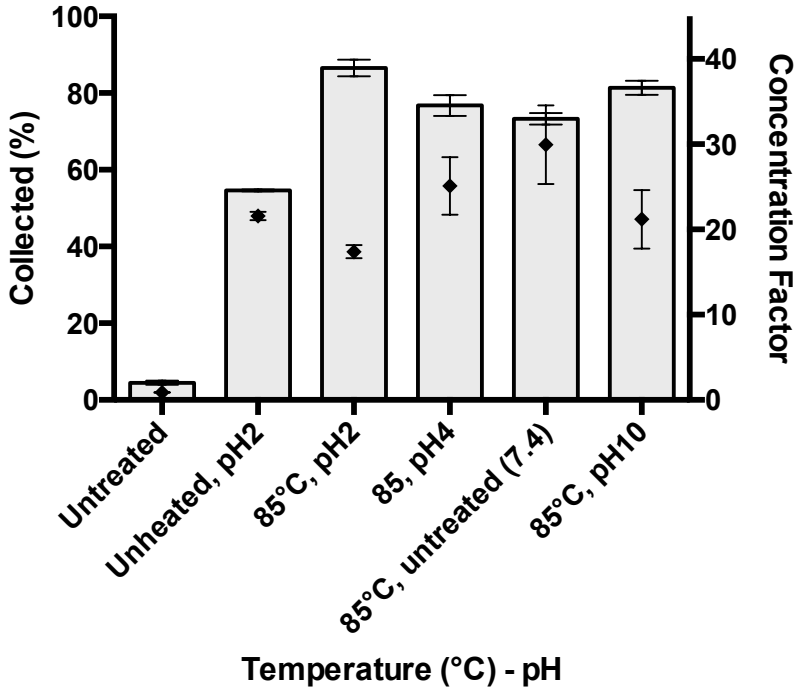

Figure 6.4: Recovery (bars) and concentration factor (diamonds) as a function of combined pH alteration and heating (Initial concentration = 0.12 g/L). Error bars represent the standard error of the mean (n = 3).

As seen in Figure 6.4, pH deviations from the untreated pH (7.4) in either direction resulted in an increased recovery of biomass. This is likely attributed to the formation of metal oxides from the media at higher pH levels (Laamanen et al., 2016), and charge neutralization at lower pH levels. Furthermore, in comparison to results with pH alteration alone, increased pH requires the heating stage to have an affect on the recovery, whereas the lower pH levels produce an effect with or without heating. The maximum recovery occurred at 85°C with a pH of 2, showing that there is potential for the combined effects of both pH alteration and thermal treatment.

Whilst there was an increased recovery at both lower and higher pH values, only the increased pH produced a marginal rise in the concentration factor. A pH of 2 seemingly resulted in a worse separation based on the concentration factor, but this was due to the volume of concentrate produced. When utilizing the 85°C and pH 2 combined experiment, the separation produced a more stable structure, with smaller bubbles in the culture medium. This foam increased in height significantly more than the foams produced in other experimental runs. With the laboratory separator design used for these experiments, and the amount of foam increasing significantly, resulted in the poorer result. While this is not advantageous, there would be the possibility of optimizing the separator design for this bubble production. One possibility of this is through increasing headspace, to produce a more concentrated product for the trade-off of a marginal reduction in recovery.

6.3.4 Media considerations

One of the economic considerations for any proposed separation technique is the ability to recycle media after the microalgae have been harvested (Mata et al., 2010). If a separation method negatively affects the media quality, it could present an additional major economic hurdle, as well as a bottleneck for large-scale production (Farooq et al., 2015; Zhang et al., 2016). Therefore, major nutrients were tested before and after heating (to 65 and 95°C), using both a microalgae culture and the culture medium (Bold's Basal media) alone (Table 6.1).

Table 6.1: Media concentrations before and after heating (a) with microalgae (Scenedesmus dimorphus) and (b) Bold's Basal media alone.

Component	With microalgae						
	Unheated	55°C		65°C		95°C	
	(ppm)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
NO_3-N	29.5	29.8	101.0	29.6	100.3	30.0	101.7
PO_4-P	47.2	47.0	99.6	48.4	102.5	48.6	103.0
SO_4	35.1	35.7	101.7	35.1	100.0	36.6	104.3
Fe	0.452	0.460	101.8	0.472	104.4	0.479	106.0
Cu	0.427	0.420	98.4	0.419	98.1	0.420	98.4
Zn	2.38	2.35	98.7	2.32	97.5	2.42	101.7
Ca	6.51	6.42	98.6	6.12	94.0	5.86	90.0

Component	Without microalgae						
	Unheated	55°C		65°C		95°C	
	(ppm)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
NO_3-N	43.6	44.0	100.9	43.6	100.0	44.8	102.8
PO_4-P	53.3	53.1	99.6	51.4	96.4	53.3	100.0
SO_4	38.4	38.6	99.5	38.2	99.0	39.3	101.8
Fe	0.994	0.949	95.5	0.985	99.1	1.016	102.2
Cu	0.459	0.452	98.5	0.468	102.0	0.478	104.1
Zn	2.46	2.42	98.4	2.52	102.4	2.58	104.9
Ca	6.90	6.90	100.0	6.90	100.0	7.02	101.7

Heating the media alone showed little variation in all of the components tested, as expected due to the relatively short period and temperature change. While 10% of calcium in solution was depleted when algae and media were heated together. The formation of calcium precipitates in autoflocculation at high pH has been proposed as a mechanism for charge neutralization and sweeping collection (Vandamme et al., 2013). Based on the media analysis in heat-aided flocculation for flotation it is likely that the formation of calcium precipitates perform a similar role as proposed for autoflocculation at high pH.

Further experimentation, where the calcium levels were increased in both heated and unheated samples, produced no change in recovery or concentration factor, there was no significant difference from 83% collected and a concentration factor of 25.8 at 85°C. Therefore, if calcium does play a role in the flotation mechanism, the levels in the media were not a limiting factor. It has been previously found by Oh et al. (2001) that the addition of Ca^{2+} increased flocculation efficiency, while Kim et al. (2005) found the addition of Ca^{2+} still caused flocculation, but did not increase flotation efficiency. Aljuboori et al. (2016), however, showed that there was no increase in flocculation efficiency for any metal ion other than zinc. For our heat-induced flocculation method, zinc did not appear to have a significant affect and did not change significantly in concentration in media when heated with or without microalgae.

6.4 Conclusion

The utilization of heat to avoid chemical flocculant addition for microalgae flotation harvesting from dilute solutions has been demonstrated. In this method, microalgae concentrations as low as 0.068 g/L produced a concentrate in the common concentration range (2-7% TSS) for bulk harvesting. This method provides the potential to allow for cost optimization of the production process. This technique allows for harvesting of industrially coupled algae production systems, through capturing the waste heat in off-gas in addition to CO_2 emissions. Additionally, the alteration of pH is shown to have synergistic effects when combined with the heating stage.

During this process, the media composition is left largely unaffected, showing a significant decrease in only calcium levels after heating a microalgae culture. The media,

therefore, is left largely unaffected and available for recycle back to the cultivation stage. The utilization of calcium for charge neutralization during heating is proposed as the mechanism for the flocculation step, similar to the proposed method for autoflocculation.

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Chapter 7

Conclusions

Conclusion

The capture of industrial carbon dioxide for microalgae production has been well established in literature, however the capture of waste heat produced by many of the same industrial processes has been largely unexplored. This waste heat can be utilized to maintain culture temperatures in cold climates, effectively expanding the possible cultivation area based on climatic zones. While the example of a nickel smelter in Sudbury, ON, Canada was used for modeling purposes, this novel method can be utilized by any industrial operation producing relatively large quantities of waste heat.

The model for cultivation temperature maintenance showed that there is indeed potential for the capture of waste heat to expand the worldwide climatic cultivation zone. While the same source of waste heat can be utilized for the harvesting of microalgae, through heat-aided flocculation for flotation. This avoids the addition of chemical flocculants, avoiding the additional cost of these chemicals and the contamination issues of the same chemicals. The heat-induced flocculation allows for the capture of up to 83% with a concentration factor of 25.8, when heated to 85°C. This same method can be utilized in combination with pH alteration, allowing for the utilization of acid gases, to provide a synergistic effect on the flotation process.

Future Work

There are several important directions in which this research can be continued, including but not limited to:

- The continued development of an industrially linked pilot plant to verify model parameters;

    The novel analyses in this thesis show that there is significant potential for utilizing waste heat to very significantly expand the cultivation zone for microalgae to cold climates. Therefore, verification of these numbers at a pilot scale is important. This would provide a significant next step towards exploiting this technology at an industrial scale.

- A civil engineering analysis of proposed pond construction;

    While the results are very positive with regards to temperature maintenance and algal production, there is still an important study to be carried out on design, construction and operation of large buried tanks in cold climates. This would provide insight into the costs associated with installations subject to extreme ambient temperature variations.

- Analysis of heat loss distribution for directed design considerations;

    Results from thesis look at temperature maintenance, but do not look directly at the distribution of heat loss through the different heat transfer methods considered. A more detailed look at heat loss mechanisms would allow for further refinement of both the model and a pilot plant to improve suitability for cold climate production.

- The optimization of pond design;

  The standard ponds used in this thesis are sized based on laboratory experiments and literature review, and are designed to provide adequate sunlight, CO_2 and circulation for the system. These numbers could change based on a more thorough optimization process for tank design – specifically looking at fluid and heat flow within the tank and CO_2 capture rates.

- The optimization of flotation parameters for different algae species;

  Whilst novel heat-aided flocculation for flotation provides excellent separation for *Scenedesmus dimorphus*, the results for the other algae strains tested gave mixed results. The further optimization of this method, in particular looking at temperature, pH, and column design, could allow for enhanced separation of different microalgae. This could also provide further insights into the flotation mechanism. For example, the reduction of calcium levels after the separation stage suggests that calcium may play a role in the heat-aided harvesting method – but further research into the exact mechanism is needed. By determining the exact mechanism, there is the potential to improve the process.

- A worldwide screening of industrial operations that can be utilized for these cultivation and harvesting processes.

  The proposed method is for the utilization of waste heat from industry uses a Nickel smelter as an example. To determine the worldwide potential for these operations, a broader screening of industries producing CO_2 and waste heat using the approaches developed in this thesis could be of significant benefit.

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