CARBON DIOXIDE UTILISATION BY INTEGRATED MICROALGAE CULTIVATION PROCESS IN MEMBRANE PHOTOBIOREACTOR

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ABSTRACT

The CO_2 emission has encouraged the research on CO_2 mitigation by microalgae. However, low carbonation and high dissolved oxygen (DO) of microalgal media in bioreactor were identified as major drawbacks of this technique, besides low CO_2 uptake by microalgae. Thus, this study aimed to increase the carbonation by integrating bioreactor with two types of membrane so that CO_2 uptake by microalgae can be increased during the CO_2 mitigation process. This study used indirect membrane-based bubbling as an alternative to increase carbonation of microalgae, while the selected microalga was evaluated in term of its suitability for CO_2 mitigation. It was found that the selected microalgae, which is a local isolate *Chlorella* sp. is suitable for CO_2 mitigation and as biomass producer. This microalga is also capable of performing a carbon concentrating mechanism (CCM), which can be manipulated to increase the CO_2 utilisation. The carbonation by using membrane on the other hand was successfully evaluated in term of fouling, bubbling, and dissolved CO_2 (DCO_2). The effect of membrane to remove the dissolved O_2 (DO) was evaluated in term of DO efficiency and CO_2 uptake by microalgae. It was found that the membrane integration resulted in DCO_2 up to 82%. This is 4 times higher than typical direct bubbling, which only reached 29%. The result of carbonation efficiency was supported by the correlation of CO_2 inlet and accumulated CO_2 concentration with DCO_2. Based on the developed correlation, overall mass transfer coefficient of CO_2 in the membrane was 4.35×10^{-2} cm^2s^{-1}, making the selected membrane and technique suitable for CO_2 mitigation by microalgae. However, large bubbles were identified as the main reason for low DCO_2. This causes low CO_2 uptake by microalgae. Thus, the decrease in bubble size decreased CO_2 escape into the bioreactor headspace. The most suitable bubble size for CO_2 mitigation is in the range of 1 mm to 5 mm. The use of membrane for deoxygenation resulted in up to 43% of DO removal. However, the membrane integration removed the DCO_2 up to 11% compared to non-integrated. The membrane also resulted in microalgae accumulation of 3% of the total microalgae concentration when pumped through the membrane. It may be concluded that overall CO_2 uptake by microalgae can be increased up to 10% through the aid of a membrane. The experimental results show that membrane integration aiding the CO_2 utilisation by microalgae is possible by controlling both operating conditions and CO_2 supply concentration.

ABSTRAK

PENGGUNAAN KARBON DIOKSIDA OLEH PROSES YANG DIINTEGRASI DENGAN PENANAMAN MIKROALGA DI DALAM MEMBRAN FOTOBIOREAKTOR

Pelepasan CO_2 telah menggalakkan penyelidikan mengenai penggunaan CO_2 oleh mikroalga. Walau bagaimanapun, pengkarbonan yang rendah atau terlalu berasid dan tinggi kandungan O_2 di dalam bioreaktor telah dikenalpasti sebagai kelemahan utama teknik ini selain pengambilan CO_2 yang rendah oleh mikroalga. Oleh itu, kerja ini bertujuan untuk meningkatkan kadar pengambilan CO_2 oleh mikroalga dengan menggunakan dua jenis membran yang diintegrasi dengan bioreaktor. Kerja ini telah menggunakan teknik pengelembungan secara tidak langsung berdasarkan membran sebagai alternatif meningkatkan CO_2 mitigasi ole mikroalga. Hasil penyelidikan mendapati bahawa mikrolaga tempatan sesuai untuk pengurangan CO_2 dan sebagai pengeluar biojisim. Mikroalga ini juga dikenal pasti dapat melaksanakan mekanisma pengunnan carbon (CCM) untuk meningkatkan pengunaan CO_2 secara tidak langsung. Kajian ini telah mendapati bahawa integrasi membran boleh mencapai sehingga 82% DCO_2 iaitu 4 kali lebih tinggi berbanding dengan yang tidak diintegrasi yang hanya mencapai sehingga 29%. Pengkarbonan bergantung kepada penyebaran CO_2 dan boleh dinilai menggunakan model. Model tersebut bertujuan untuk meramal hubungan diantara CO_2 dan DCO_2 dengan CO_2 yang terkumpul. Model yang telah dicipta tersebut telah disahkan sesuai untuk mengkaji pemindahan jisim dari bahagian gas ke bahagian cecair, dengen ralat kurang daripada 20%. Kedua-dua model dan keputusan ujikaji menunjukkan bahawa pengumpulan terendah CO_2 di dalam membran boleh dicapai apabila beroperasi pada nisbah gas kepada cecair diantara 0.6:1 dan 6:01. Keseluruhan pemindahan jisim CO_2 di dalam membran adalah 4.35×10^{-2} cm^2/s. Nilai ini boleh dianggap sesuai untuk pemindahan CO_2 di dalam membran. Keputusan ini menunjukan integrasi membran adalah sesuai untuk meningkatkan penyerapan CO_2 didalam bioreaktor. Kajian ini juga mendapati bahawa pembentukan gelembung gas yang berpunca daripada ketidakseimbangan kadar aliran masuk bendalir atau cecair dan gas boleh menyebabkan DCO_2 rendah dan meningkatkan nisbah di antara ruang legar dan DCO_2. Ini boleh menyebabkan pengambilan CO_2 yang rendah oleh mikroalga. Penurunan saiz gelembung dapat mengurangkan nisbah ruang legar dan DCO_2. Gelembung yang paling sesuai untuk penyerapan CO_2 adalah dalam lingkungan 1 mm sehingga 5 mm. Integrasi oleh membran kedua telah berjaya mengurangkan pengumpulan O_2 dalam bioreaktor sehingga 43% tetapi menyebabkan pengurangan DCO_2 sehingga 11%. Integrasi membran juga menyebabkan pengurangan biojisim mikroalga sebanyak 3%. Pengambilan CO_2 secara keseluruhan oleh mikroalga boleh meningkat sehingga 10% dengan bantuan integrasi membran kedua. Kajian ini juga mendapati bahawa keupayaan Chlorella sp. untuk melaksanakan CCM meningkatkan penyerapan CO_2. Keputusan ujikaji menunjukkan bahawa integrasi membran dapat meningkatkan penyerapan CO_2 oleh mikroalga.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ADP	-	Adenosine diphosphate
ATP	-	Adenosine triphosphate
ASTM	-	American Society for Testing and Materials
BP	-	British Petroleum
BV	-	Ball valve
BOD	-	Biochemical oxygen demand
CCM	-	Carbon concentrating mechanism
CCS	-	Carbon capture and storage
CO_2	-	Carbon dioxide
C:E	-	Ratio of consumption to emission
COD	-	Chemical oxygen demand
CO_3^-	-	Carbonate ion
CI	-	Confidence interval
DCO_2	-	Dissolved carbon dioxide
DO	-	Dissolved oxygen
DIC	-	Dissolved inorganic carbon
DHA	-	Docosahexaenoic acid
EOR	-	Enhanced Oil Recovery
EPA	-	Eicosapentaenoic acid
EPICs	-	Equilibrium partitioning in closed systems
GFM	-	Gas flow metre
GC	-	Gas chromatography
GHG	-	Greenhouse gas
GPRV1	-	Gauge pressure regulator
HS:DCO_2	-	Ratio of headspace to dissolved CO_2
IEA	-	International Energy Agency
JM	-	Jaworski's media
LDL	-	Low-density lipoprotein
LFM	-	Liquid flow metre
MT	-	Million tonnes
N/A	-	Not applicable

NADPH	-	Nicotinamide adenine dinucleotide phosphate-oxidise
NaOH	-	Natrium hydroxide
OD	-	Optical density
PHI	-	Photosystem 1
PHII	-	Photosystem 2
PGA	-	Phosphoglycerate
PGAL	-	Glyceraldehyde 3-phosphate
PP	-	Polypropylene
PTFE	-	Polytetrafluoroethylene
PVDF	-	Polyvinylidenefluoride
PBR	-	Photobioreactor
PVC	-	Polyvinylchloride
PG	-	Pressure gauge
PAR	-	Photosynthetically active radiation
SEM	-	Scanning Electron Method
WMO	-	World Meteorological Organisation

LIST OF NOMENCLATURES

α	-	Function of inlet and outlet liquid flow rate (dimensionless)
C_{il}	-	Initial concentration of CO_2 in liquid phase (kgm^{-3})
$C_{il(std)}$	-	Initial concentration of CO_2 in standard solution (kgm^{-3})
$C_{il(unk)}$	-	Initial concentration of CO_2 in unknown solution (kgm^{-3})
C_{ig}	-	Initial concentration of CO_2 in gas phase (kgm^{-3})
$C_{ig(std)}$	-	Initial concentration of CO_2 in standard gas phase (kgm^{-3})
$C_{ig(unk)}$	-	Initial concentration of CO_2 in unknown gas phase (kgm^{-3})
C_{g1}	-	Concentration of CO_2 in gas phase at first point (kgm^{-3})
C_{g2}	-	Concentration of CO_2 in gas phase at final point (kgm^{-3})
C_g	-	Gas dissolved at constant temperature (kgm^{-3})
$C_{o_2}^{i}$	-	Initial concentration of O_2 gas (kgm^{-3})
$C_{o_2}^{*}$	-	Concentration of O_2 at equilibrium (kgm^{-3})
$C_{o_2}^{l}$	-	Concentration of in bulk liquid (kgm^{-3})
C	-	Molar concentration ($molm^{-3}$)
D	-	Diffusion coefficient (m^2s^{-1})
D_e	-	Effective diffusion coefficient (m^2s^{-1})
D_k	-	Knudsen diffusion coefficient (m^2s^{-1})
df	-	Degree of freedom
H	-	Henry constant
H_i	-	Initial Henry gas constant
$J_{CO_2(m)}$	-	Diffusion flux of CO_2 gas in the membrane ($kgm^{-2}s^{-1}$)
I_{avg}	-	Average light intensity ($\mu Es^{-1}m^{-2}$)
I_o	-	Initial light intensity ($\mu Es^{-1}m^{-2}$)
I	-	Light intensity ($\mu Es^{-1}m^{-2}$)
l_d	-	Light path length (m)

l_{di}	-	Light path length at initial point (m)
K	-	Overall mass transfer coefficient (m^2s^{-1})
K_m	-	Overall mass transfer coefficient (m^2s^{-1})
K_g	-	Overall mass transfer coefficient of gas phase (m^2s^{-1})
K_l	-	Overall mass transfer coefficient of bulk liquid (m^2s^{-1})
K'	-	Growth rate (per day)
K_n	-	Knudsen number
m	-	Slope of value at Y-axis divide over value of X-axis
$\dot{m}$	-	Biomass of microalgae per unit time (kgs^{-1})
$\dot{\mathbf{m}}$	-	Mass flow rate ($gmin^{-1}$)
M	-	Molarity ($moll^{-1}$)
n	-	Biomass (kg)
$\mathbf{n}$	-	Number of sample
N_g	-	Molar flux in gas phase ($molm^{-2}s^{-1}$)
N_l	-	Molar flux in liquid phase ($molm^{-2}s^{-1}$)
P	-	Pressure at constant temperature (Pa)
$p^g_{o_2}$	-	Partial pressure at gas phase (Pa)
$p^i_{o_2}$	-	Partial pressure at interphase (Pa)
$P^*_{o_2}$	-	Partial pressure of gas at the equilibrium (Pa)
R	-	Gas constant ($JK^{-1}mol^{-1}$)
t	-	Time (s)
V_g	-	Volume of gas (m^3)
V_{g2}	-	Volume of gas at second point (m^3)
V_{g1}	-	Volume of gas at first point (m^3)
V_l	-	Volume of liquid (m^3)
V_{l1}	-	Volume of liquid at first point (m^3)
V_{l2}	-	Volume of liquid at second point (m^3)

$\dot{V}$	-	Volumetric flow rate (m^3s^{-1})
x	-	Travel length of diffusion solute (m)
x	-	Sample
$\bar{\mathrm{x}}$	-	Mean
$x1$	-	Constant value of gas inlet
$y1$	-	Constant value of liquid inlet

Greeks

τ	-	Tortuosity
λ	-	Mean free path (m)
ε	-	Molar absorptivity or absorption coefficient (m^2mol^{-1})
δ_m	-	Membrane thickness (m)
k_H	-	Henry constant
d	-	Derivative
k_g	-	Individual Mass transfer coefficient in gas phase (m^2s^{-1})
k_l	-	Individual Mass transfer coefficient in liquid phase (m^2s^{-1})

Subscripts

il	-	Initial liquid
i	-	Initial
l	-	Liquid phase
$\mathrm{l1}$	-	Liquid at first point
$\mathrm{l2}$	-	Liquid at second point
ig	-	Initial gas
g	-	Gas
std	-	Standard
unk	-	Unknown
gl	-	Gas at first point

g2	-	Gas at second point
O_2	-	Gas oxygen
e	-	Effective
k	-	Knudsen
avg	-	Average
n	-	Number
m	-	Membrane
H	-	Henry constant

Superscripts

i	-	Initial
*	-	Equilibrium
l	-	Liquid

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

1.1 Background

Carbon dioxide emissions are the second largest contributor to climate change, making up 30% of the greenhouse gases (GHG). The GHG causes global warming and threaten ecological systems. Antarctic and arctic sea ice also show declines caused by increasing global temperature (Stroeve *et al.*, 2007; Swingedouw *et al.*, 2008). Sea level, on the other hand, rose about 17 cm over the last century; this forced some communities to relocate, including those in Fiji, Papua New Guinea, Panama and Vanuatu (Mattson, 2010). The global warming also expected to increase the sea level in Malaysia about 13 cm over the next 100 years.

The effect of global warming shows that CO_2 emissions are likely to harm the environment than to provide benefits. For this concern, many approaches to overcome the issue of CO_2 emissions have been proposed, which mostly involve high and expensive technology such as carbon capture and storage technology (CCS) and conventional methods. Both CCS and conventional methods are used to prevent the release of CO_2 into the atmosphere. However, safety, capital cost and storage capacity are the major issues that hinders the successful of this technique.

One concern often raised because of the CCS application was leaking of the CO_2 reservoir. The leaking can cause sudden increased acidity in the ocean that is lethal to marine life. Therefore, low cost techniques, which applies a biological approach for CO_2 sequestration is needed. One of these approaches is by using microalgae for CO_2 mitigation and at the same time producing biomass for low CO_2-emitting energy source. The microalgae research also desires to be used for CO_2 sequestration in the future.

Microalgae are microscopic unicellular organisms with cell diameter range from 1 μm to 50 μm. Microalgae can be found naturally in freshwater saline lakes,

aquatic environment and marine environment. Microalgae have an ability to conduct photosynthesis 40 times higher compared to terrestrial plant (based on $0.09d^{-1}$ to $0.58d^{-1}$ relative growth rate estimation of terrestrial plant (Garnier, 1992; Hunt and Cornelissen, 1997) compared with $0.11d^{-1}$ to $0.55d^{-1}$ specific growth rate estimation of microalgae (Aleya *et al.* 2011; Suali *et al.*, 2012). Thus, microalgae have a high potential as a biological approach for CO_2 mitigation. However, CO_2 mitigation by microalgae is a species dependent as reported by researchers (Zhang *et al.*, 2011; Doucha *et al.*, 2005; Yoo *et al.*, 2010). Thus, selection of microalga for the purpose of CO_2 mitigation is a very crucial step.

In this study, a local isolate microalga species known as *Chlorella* sp. was selected as a test subject for CO_2 mitigation. The selection was based on the growth and characteristics of this microalga, which primarily was investigated suitable for CO_2 mitigation and biomass production, which has potential to be processed into low CO_2 emitted energy source such as biodiesel. The investigation on this microalga will give benefit to the local community as it was never mentioned in any publication.

The use of microalgae for CO_2 mitigation is a step-by-step process. This includes transferring CO_2 into microalgal culture through the process of carbonation, followed by CO_2 fixation by the microalgae. CO_2 mitigation must be carried out in a closed cultivation system to prevent the release of unutilised CO_2 into the atmosphere. The closed cultivation system typically used is known as a photobioreactor (PBR) or bioreactor (BR).

In this study, the term PBR has been used to define a system that consists of mini bioreactor which was made up of tubular acrylic pipes. The bioreactor unit is equipped with white cool fluorescent lamps as a light source for the photosynthesis, stirrer, and aeration system. The other unit making up the PBR system include gas exchange unit and a CO_2 supply unit. The gas exchange unit consists of two types of hydrophobic membranes. Carbon dioxide uptake does not occur inside the membrane, but rather inside the tubular bioreactor.

The main purpose for the integration of a membrane was to address the issue of direct bubbling to the bioreactor. Membrane technology was applied due to its flexibility and selective properties which only allows certain type of substance or compound to pass through the membrane wall. In addition, membrane is known as a device that is versatile and can be integrated into many devices and processes.

The integration of PBR with membrane technology for the purpose of gas transfer was not well researched. To date, literature has reported that only hydrophobic membrane can be used to aid the gas transfers into the bioreactor (Cheng *et al.*, 2006; Fan *et al.*, 2007). Many others issue such as fouling by microalgae, bubbling and generated O_2 were reported caused the low CO_2 uptake. These issues discussed in the following subsections.

1.2 Problem statement

1.2.1 Issue of microalgae selection for CO_2 mitigation

Each microalga species was reported to have various capabilities to mitigate CO_2. According to Sydney *et al.* (2001), *Botryococcus braunii* is tolerable to CO_2 concentration up to 5% of overall air composition. Others species include *Scendemus* sp., *Spirulina* sp. and *Dunaliella* sp. were reported tolerant to CO_2 concentration up to 10% of overall air, which were used to carbonise microalgae media for the purpose of CO_2 utilisation and biomass production (Sydney *et al.*, 2001; Yoo *et al.*, 2010). The tolerant concentration of CO_2 is important to prevent CO_2 excess, which is lethal to microalgae. Thus, any microalgae species for CO_2 mitigation must be analysed for both CO_2 tolerant and growth rate before further use in CO_2 mitigation. Besides the issue of CO_2 tolerance, other microalgae issues in terms of CO_2 mitigation in a membrane bioreactor include fouling and accumulation of microalgae, as detailed in the following subsection.

1.2.2 Fouling and accumulation of microalgae in membrane

The typical process of CO_2 mitigation by microalgae involves carbonation and deoxygenation. During carbonation, the microalgal media, which composed of a medium and microalgae cell crosses over the hollow fibre as shown in Figure 1.1. The CO_2 first contacts the microalgae cells in media that crossed over the hollow