

**CARBON DIOXIDE UTILISATION BY
INTEGRATED MICROALGAE CULTIVATION
PROCESS IN MEMBRANE
PHOTOBIOREACTOR**

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OF THE DEGREE OF DOCTOR OF
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ABSTRACT

The CO₂ emission has encouraged the research on CO₂ 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 CO₂ uptake by microalgae. Thus, this study aimed to increase the carbonation by integrating bioreactor with two types of membrane so that CO₂ uptake by microalgae can be increased during the CO₂ 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 CO₂ mitigation. It was found that the selected microalgae, which is a local isolate *Chlorella* sp. is suitable for CO₂ mitigation and as biomass producer. This microalga is also capable of performing a carbon concentrating mechanism (CCM), which can be manipulated to increase the CO₂ utilisation. The carbonation by using membrane on the other hand was successfully evaluated in term of fouling, bubbling, and dissolved CO₂ (DCO₂). The effect of membrane to remove the dissolved O₂ (DO) was evaluated in term of DO efficiency and CO₂ uptake by microalgae. It was found that the membrane integration resulted in DCO₂ 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 CO₂ inlet and accumulated CO₂ concentration with DCO₂. Based on the developed correlation, overall mass transfer coefficient of CO₂ in the membrane was $4.35 \times 10^{-2} \text{ cm}^2\text{s}^{-1}$, making the selected membrane and technique suitable for CO₂ mitigation by microalgae. However, large bubbles were identified as the main reason for low DCO₂. This causes low CO₂ uptake by microalgae. Thus, the decrease in bubble size decreased CO₂ escape into the bioreactor headspace. The most suitable bubble size for CO₂ 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 DCO₂ 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 CO₂ uptake by microalgae can be increased up to 10% through the aid of a membrane. The experimental results show that membrane integration aiding the CO₂ utilisation by microalgae is possible by controlling both operating conditions and CO₂ supply concentration.

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

*Pelepasan CO₂ telah menggalakkan penyelidikan mengenai penggunaan CO₂ oleh mikroalga. Walau bagaimanapun, pengkarbonan yang rendah atau terlalu berasid dan tinggi kandungan O₂ di dalam bioreaktor telah dikenalpasti sebagai kelemahan utama teknik ini selain pengambilan CO₂ yang rendah oleh mikroalga. Oleh itu, kerja ini bertujuan untuk meningkatkan kadar pengambilan CO₂ oleh mikroalga dengan menggunakan dua jenis membran yang diintegrasikan dengan bioreaktor. Kerja ini telah menggunakan teknik pengelembungan secara tidak langsung berdasarkan membran sebagai alternatif meningkatkan CO₂ mitigasi oleh mikroalga. Hasil penyelidikan mendapati bahawa mikroalga tempatan sesuai untuk pengurangan CO₂ dan sebagai pengeluar biojisim. Mikroalga ini juga dikenal pasti dapat melaksanakan mekanisme penggunaan carbon (CCM) untuk meningkatkan penggunaan CO₂ secara tidak langsung. Kajian ini telah mendapati bahawa integrasi membran boleh mencapai sehingga 82% DCO₂ iaitu 4 kali lebih tinggi berbanding dengan yang tidak diintegrasikan yang hanya mencapai sehingga 29%. Pengkarbonan bergantung kepada penyebaran CO₂ dan boleh dinilai menggunakan model. Model tersebut bertujuan untuk meramal hubungan diantara CO₂ dan DCO₂ dengan CO₂ yang terkumpul. Model yang telah dicipta tersebut telah disahkan sesuai untuk mengkaji pemindahan jisim dari bahagian gas ke bahagian cecair, dengan ralat kurang daripada 20%. Kedua-dua model dan keputusan ujikaji menunjukkan bahawa pengumpulan terendah CO₂ di dalam membran boleh dicapai apabila beroperasi pada nisbah gas kepada cecair diantara 0.6:1 dan 6:01. Keseluruhan pemindahan jisim CO₂ di dalam membran adalah 4.35×10^2 cm²/s. Nilai ini boleh dianggap sesuai untuk pemindahan CO₂ di dalam membran. Keputusan ini menunjukkan integrasi membran adalah sesuai untuk meningkatkan penyerapan CO₂ didalam bioreaktor. Kajian ini juga mendapati bahawa pembentukan gelembung gas yang berpunca daripada ketidakseimbangan kadar aliran masuk bendalir atau cecair dan gas boleh menyebabkan DCO₂ rendah dan meningkatkan nisbah di antara ruang legar dan DCO₂. Ini boleh menyebabkan pengambilan CO₂ yang rendah oleh mikroalga. Penurunan saiz gelembung dapat mengurangkan nisbah ruang legar dan DCO₂. Gelembung yang paling sesuai untuk penyerapan CO₂ adalah dalam lingkungan 1 mm sehingga 5 mm. Integrasi oleh membran kedua telah berjaya mengurangkan pengumpulan O₂ dalam bioreaktor sehingga 43% tetapi menyebabkan pengurangan DCO₂ sehingga 11%. Integrasi membran juga menyebabkan pengurangan biojisim mikroalga sebanyak 3%. Pengambilan CO₂ 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 CO₂. Keputusan ujikaji menunjukkan bahawa integrasi membran dapat meningkatkan penyerapan CO₂ oleh mikroalga.*

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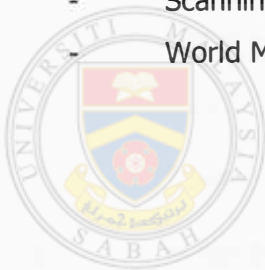
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LIST OF ABBREVIATIONS

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
CO₂	-	Carbon dioxide
C:E	-	Ratio of consumption to emission
COD	-	Chemical oxygen demand
CO₃⁻	-	Carbonate ion
CI	-	Confidence interval
DCO₂	-	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:DCO₂	-	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	-	Polyvinylidene fluoride
PBR	-	Photobioreactor
PVC	-	Polyvinylchloride
PG	-	Pressure gauge
PAR	-	Photosynthetically active radiation
SEM	-	Scanning Electron Method
WMO	-	World Meteorological Organisation



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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 ² s ⁻¹)
D_e	-	Effective diffusion coefficient (m ² s ⁻¹)
D_k	-	Knudsen diffusion coefficient (m ² s ⁻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 (μEs ⁻¹ m ⁻²)
I_o	-	Initial light intensity (μEs ⁻¹ m ⁻²)
I	-	Light intensity (μEs ⁻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{m}	-	Mass flow rate ($gmin^{-1}$)
M	-	Molarity (mol^{-1})
n	-	Biomass (kg)
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)
$p_{O_2}^g$	-	Partial pressure at gas phase (Pa)
$p_{O_2}^i$	-	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{x}	-	Mean
x_1	-	Constant value of gas inlet
y_1	-	Constant value of liquid inlet

Greeks

τ	-	Tortuosity
λ	-	Mean free path (m)
ε	-	Molar absorptivity or absorption coefficient ($\text{m}^2\text{mol}^{-1}$)
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
l_1	-	Liquid at first point
l_2	-	Liquid at second point
ig	-	Initial gas
g	-	Gas
std	-	Standard
unk	-	Unknown
g_1	-	Gas at first point

g_2	-	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



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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 CO₂ emissions are likely to harm the environment than to provide benefits. For this concern, many approaches to overcome the issue of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ sequestration is needed. One of these approaches is by using microalgae for CO₂ mitigation and at the same time producing biomass for low CO₂-emitting energy source. The microalgae research also desires to be used for CO₂ 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 CO₂ mitigation. However, CO₂ 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 CO₂ 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 CO₂ mitigation. The selection was based on the growth and characteristics of this microalga, which primarily was investigated suitable for CO₂ mitigation and biomass production, which has potential to be processed into low CO₂ 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 CO₂ mitigation is a step-by-step process. This includes transferring CO₂ into microalgal culture through the process of carbonation, followed by CO₂ fixation by the microalgae. CO₂ mitigation must be carried out in a closed cultivation system to prevent the release of unutilised CO₂ 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 CO₂ 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 O₂ were reported caused the low CO₂ uptake. These issues discussed in the following subsections.

1.2 Problem statement

1.2.1 Issue of microalgae selection for CO₂ mitigation

Each microalga species was reported to have various capabilities to mitigate CO₂. According to Sydney *et al.* (2001), *Botryococcus braunii* is tolerable to CO₂ concentration up to 5% of overall air composition. Others species include *Scenedemus* sp., *Spirulina* sp. and *Dunaliella* sp. were reported tolerant to CO₂ concentration up to 10% of overall air, which were used to carbonise microalgae media for the purpose of CO₂ utilisation and biomass production (Sydney *et al.*, 2001; Yoo *et al.*, 2010). The tolerant concentration of CO₂ is important to prevent CO₂ excess, which is lethal to microalgae. Thus, any microalgae species for CO₂ mitigation must be analysed for both CO₂ tolerant and growth rate before further use in CO₂ mitigation. Besides the issue of CO₂ tolerance, other microalgae issues in terms of CO₂ 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 CO₂ 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 CO₂ first contacts the microalgae cells in media that crossed over the hollow