Carbon dioxide diffusion: A molecular dynamics study for Microalgae Biofixation Technology

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Abstract. Global warming has been a very critical issue for the past decades which is primarily due to carbon emissions brought by rapid industrialization. To address this, various strategies have been introduced to lessen environmental impacts and reduce carbon dioxide emission. Biological approach using microalgae is one of the most promising methods for the direct conversion of carbon dioxide. An atomic scale analysis is of great importance as it provides information beyond what traditional experiments can offer. The present study involves an atomic level of analysis on the carbon dioxide absorption intended for the development of microalgae biofixation method. The study was conducted using Molecular Dynamics simulations to analyze the effects of temperature and salinity on the dynamics and transport of carbon dioxide into the microalgae lipid bilayer. A total of 20 simulation sets equilibrated at temperature from 300 to 330 K and salinity level of 0.18 to 0.55 M was undertaken. The permeation coefficient of carbon dioxide molecules was calculated using the inhomogeneous solubility diffusion model while the force auto correlation function was used to estimate the diffusion coefficient. The resulting transport mechanisms of carbon dioxide showed an increasing pattern with increasing temperature and salinity despite membrane pathway compression. The highest calculated diffusion coefficient of 7.7101x10^-5 cm²/s was at 330 K and 0.05 M salinity level while the permeation coefficient was 2.3994x10^-16 cm⁻¹ s⁻¹ at 330 K and 0.55 M. Hence, the study suggests that the mobility of carbon dioxide molecule increases with linearly with temperature.

1. Introduction

Greenhouse gases (GHGs) trap the earth’s infrared radiation that is supposed to escape through space which consequently causes global temperature rise. Since the start of industrial revolution, its concentration changes over time and continue to increase until present. As a response, the international community established a protocol to remedy its worsening effects through The Paris Agreement [1]. The said protocol is one of the major steps intended to battle climate change that generally aims to limit the temperature rise to two degrees from the pre-industrial level by reducing CO₂ concentrations from the atmosphere. This brought CO₂ removal technologies to the forefront which drive the scientific community to design and develop technologies to mitigate the persistent increase of carbon emissions. One of the most extensively investigated methods to address carbon sequestration is through the biological approach using microorganisms such as microalgae. It has long been recognized as a sustainable means to capture anthropogenic carbon dioxide via photosynthesis, that is, the fundamental process that generated the fixed carbon in today’s fossil fuels.

Microalgae are among the fastest growing photosynthetic microorganisms with carbon fixation rates relatively higher than those of terrestrial plants [2]. Many types of microalgae species are capable of accumulating carbon under different concentration levels of CO₂ [3]. Earlier reports showed that 1 kg of dried algae biomass can fix up to 1.88 kg of CO₂ [4]. Also, a number of microalgae studies showed promising results in treating flue gas emissions coming from different sources. Kao et al., (2014) cultured Chlorella sp in a photobioreactor supplied with flue gas collected from hot stove, coke oven and power plant [5]. Moheimani (2016) cultured Tetraselmis suecica and studied its growth conditions...
by exposing with untreated flue gas coming from coal-fired power plant [6]. Both studies showed biomass growth and efficient utilization of CO$_2$, NO$_x$ and SO$_2$. While present and past studies [7]–[9] demonstrate potential of microalgae to sequester CO$_2$ from atmosphere and flue gases, further developments are still needed especially on the cultivation stage to assess long-term growth potential.

Optimal cultivation condition is of great importance and generally aimed by researchers to realize sustainable production. However, microalgae cultivation involving biofixation involves a complex process that has not been fully understood, as experimental studies have limited observation only up to macroscopic scale. The current study aims to contribute in the development of biofixation by investigating the CO$_2$ transport across the microalgae lipid membrane in the atomic scale using Molecular Dynamics (MD) simulation. At this level, information not accessible using the current experimental techniques can be demonstrated, particularly the mechanism and dynamics of CO$_2$ molecule.

MD has consistently provided significant insights on the dynamics of biological molecules particularly on the transport mechanisms. The very first MD simulation successfully demonstrated the permeation process of water molecule across the lipid membrane using the inhomogeneous solubility diffusion model [10]. This brought progress on other permeation studies involving different solutes. The transport of other small molecules was later on demonstrated showing the free energy barrier [11] and other dynamics involved in the process. This was followed by elucidating the permeation across other types of lipids with varying size of hydrocarbon tails [12]. The most recent works demonstrates the effects of salinity on both the lipid membrane structure and the transport mechanisms of CO$_2$ molecules [13]. The present study analyzed the CO$_2$ transport by calculating the diffusion coefficient and permeability coefficient at different levels of temperature and salinity. The said parameters are mainly responsible for the transformation of lipid membrane structure to undergo phase transition. The mechanism of CO$_2$ transport during this occurrence is poorly understood and is very important for the development of the biofixation capability of microalgae.

2. Computational details

Microalgae cells are outlined with rigid layers of cell walls and semi permeable membrane composed of various lipids, glycolipids and protein channels which are mainly responsible for the transport of nutrients from its surrounding to support their metabolic needs. The transport mechanisms that takes place in the membrane are of great importance in the field of cellular biology [14] and drug delivery [15], [16]. The model of the microalgae lipid membrane used for this study is composed of dipalmitoyl phosphatidylcholine (DPPC) lipids. The said lipid contains palmitic acid chains that is known to be the dominant fatty acids present in several species of microalgae [17]–[19]. The present study adopted the lipid membrane structure from the author’s previous works [20] that consists of 128 DPPC phospholipids, water and flue gas molecules [21], [22] as shown in figure 1. The interaction parameters for lipids were taken from the GROMOS53a6 [23] library while the Simple Point Charge (SPC) model [24] was used for the water molecules. From the structure, partition (black lines) 0 to −1.7 nm represents the lipid membrane, −1.7 to −2.7 nm for the aqueous region (H$_2$O and NaCl molecules) while −2.7 to 4.0 nm for the flue gas molecules (N$_2$, CO$_2$, O$_2$, SO$_2$ and NO$_2$).

The experimental space was determined using the Space Filling Design method. The said method is very useful for deterministic system such as MD simulation with the aim to minimize the difference between the fitted model and the true mathematical model (bias) by spreading the sampling points (simulation sets) evenly to cover the design region. The temperature range chosen for this study covers below and above the reported phase transition of DPPC lipids (315 K)[25], while the range of salinity was limited up to 600 mM (seawater). A total of 20 simulation sets were generated that covers the range of temperature (300 – 330 K) and salinity (0 – 550 mM) using the JMP software ®.
To calculate the Permeability coefficient $P$ of CO$_2$ molecules, the inhomogeneous solubility diffusion model [26-28] was used given by the equations below:

$$\frac{1}{P} = \int_{z_1}^{z_2} R(z) \, dz = \int_{z_1}^{z_2} \frac{\exp\{\Delta G(z)/k_B T\}}{D_z(z)} \, dz$$

(1)

**Figure 1.** Microalgae lipid membrane molecular structure. The green lines represent the lipid membrane while the red-white lines are the water molecules. The gray balls represent nitrogen while the cyan-red balls are CO$_2$ molecules. SO$_2$ molecules are represented by yellow-red balls while NO$_2$ are blue-red balls.

In here, $P$ is the defined as the inverse of $R(z)$ which is the total local resistance to permeation at different depths in the membrane, and is a function of the excess free energy and the local diffusion coefficient of the solute molecule permeating the membrane. The calculated free energies ($\Delta G$) were taken from the author’s previous works [20]. Moreover, the diffusion coefficient was estimated using the force auto correlation function (FACF) method [10], [12]:

$$D(z) = \frac{(RT)^2}{\int_0^\infty \langle \Delta F(z, t) \cdot \Delta F(z, 0) \rangle \, dt}$$

In here, the $\Delta F(z, t)$ represents the deviation of the instantaneous force acting on the CO$_2$ molecules at given depth $z$ while $R$ is the gas constant and $T$ for temperature. The said method can estimate diffusion at locations where high free energy barrier exists (i.e. lipid bilayer).

3. **Results and discussion**

**Local Diffusion Coefficient**

Diffusion coefficient $D(z)$ profiles for CO$_2$ molecule are plotted in figure 2, error bars are omitted for clarity. These errors are standard errors calculated from the difference of the diffusion coefficients.
from the repeated simulation sets. A general trend was observed among all the simulation sets, $D(z)$ are uniform along the aqueous region (−1.7 to −2.7 nm) and it decreases significantly as it enters the phosphate groups with an average drop of $1.916 \times 10^{-5}$ cm$^2$s$^{-1}$. The sudden drop demonstrates abrupt decrease in the mobility of the CO$_2$ molecule as it penetrates the inter-lipid spacing of the membrane while crossing towards the intra cellular part of the cell. For comparison, other data of CO$_2$ diffusivity were also plotted. The orange ($2.18 \times 10^{-5}$ cm$^2$s$^{-1}$) [29], violet ($2.29 \times 10^{-5}$ cm$^2$s$^{-1}$) [30], blue ($3.68 \times 10^{-5}$ cm$^2$s$^{-1}$) and green ($4.4 \times 10^{-5}$ cm$^2$s$^{-1}$) [31] lines were all obtained from experimental studies while the dark blue line ($8.3 \times 10^{-5}$ cm$^2$s$^{-1}$) was extracted from a similar simulation study [32]. The results obtained clearly show that the diffusivity of CO$_2$ increases with increasing temperature that is typical for gases dissolved in liquids [33–35].

![Figure 2. Diffusion coefficients of CO$_2$ molecules across the microalgae lipid membrane. The solid lines represent the simulation set below the phase transition while the dashed lines represent above the phase transition.](image)

**Permeation Coefficient**

Table 1 shows the calculated $P$ of CO$_2$ molecules across the generated experimental space. The $P$ was calculated numerically by substituting the values obtained from the free energy profile and diffusion coefficient to equation 1. Simulation sets 1 to 10 represents the $P$ of CO$_2$ below the phase transition while 11 to 20 represents $P$ above the phase transition. Simulation set 2 (300 K and 0.426 M) showed the lowest permeation coefficient (1.2399 $\times 10^{-3}$ cms$^{-1}$) while simulation set 19 (330K and 0.550 M) demonstrate the highest (2.3994 $\times 10^{-3}$ cms$^{-1}$). Results suggest that CO$_2$ permeation increases linearly with temperature and salinity.

The study demonstrates the mobility of CO$_2$ molecules in the microalgae lipid bilayer with the presence of flue gas molecules. The results further support experimental studies involving utilization of microalgae to treat carbon dioxide from flue gas emissions. Future work should look into expanding the simulations to include other small molecules such as O$_2$, N$_2$, CO and H$_2$O that are all essential molecules for microalgae growth. The development of biofixation framework method to address carbon emissions is an imperative step to realize sustainable utilization of microalgae.
Table 1. Calculated permeation coefficient of CO₂ molecules

|     | Temp (K) | Salinity (M) | P (cm/s)       |
|-----|----------|--------------|----------------|
| 1   | 300      | -0.180       | 1.3694 x 10⁻³  |
| 2   | 300      | -0.426       | 1.2398 x 10⁻³  |
| 3   | 304      | 0.303        | 1.4541 x 10⁻³  |
| 4   | 304      | 0.550        | 1.4419 x 10⁻³  |
| 5   | 304      | 0.050        | 1.3285 x 10⁻³  |
| 6   | 309      | -0.180       | 1.3966 x 10⁻³  |
| 7   | 309      | 0.426        | 1.4429 x 10⁻³  |
| 8   | 313      | 0.050        | 1.5371 x 10⁻³  |
| 9   | 313      | 0.303        | 1.5882 x 10⁻³  |
| 10  | 313      | 0.550        | 1.4813 x 10⁻³  |
| 11  | 317      | 0.426        | 1.7425 x 10⁻³  |
| 12  | 317      | 0.180        | 1.9771 x 10⁻³  |
| 13  | 321      | 0.550        | 1.9269 x 10⁻³  |
| 14  | 321      | 0.303        | 2.1635 x 10⁻³  |
| 15  | 321      | 0.050        | 2.1424 x 10⁻³  |
| 16  | 326      | 0.426        | 2.2219 x 10⁻³  |
| 17  | 326      | -0.180       | 2.2065 x 10⁻³  |
| 18  | 330      | 0.303        | 2.2718 x 10⁻³  |
| 19  | 330      | 0.550        | 2.3994 x 10⁻³  |
| 20  | 330      | 0.050        | 2.2548 x 10⁻³  |

4. Conclusion
In this study, the effects of temperature and salinity on the carbon dioxide transport across the microalgal lipid membrane with the presence of flue gas molecules were investigated. The said parameters were crucial as it has a direct effect on the microalgal membrane structure, which is the primary pathway of small molecules such as carbon dioxide. The molecular structure of the microalgal lipid membrane was created, modified at different salinity, and equilibrated at various range of temperatures. The diffusion coefficient was calculated using the force auto correlation method while the permeation coefficient was numerically solved using the Inhomogeneous Solubility Diffusion model. The resulting diffusion coefficient shows an increasing pattern with increasing temperature and agrees well with the available experimental data. The highest calculated permeation coefficient was at 330K and 0.55 M with a value of 2.3994 x 10⁻³ cms⁻¹.

Acknowledgements
The authors would like to acknowledge the financial support of the Taiwan National Energy Program (NEP-II) with grant number MOST-107-3113-E-006-009. Part of the calculations were carried out using the computer facilities of High Performance Computing Laboratory (HPCL) under the Center for Natural Sciences and Environment Research (CENSER), De La Salle University Philippines.
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