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Feasibility of Biohydrogen Purification from Carbon Dioxide Mixture via Integrated Microalgae-Membrane Contactor Towards Zero Carbon Emission

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Abstract. Biohydrogen (H_2) mixed with carbon dioxide (CO_2) produced from the fermentation of Palm Oil Mill Effluent (POME) could be a potential renewable energy source. However, an effective technique to treat both gases towards zero carbon emission has become a major concern. In this study, a new approach was introduced to treat H_2/CO_2 mixture from POME fermentation by an integrated microalgae-membrane contactor system. Polyvinylidene fluoride (PVDF) hollow fibre membrane used in the integrated membrane contactor system able to give the highest purified $H_2\%$ from mixed H_2/CO_2 in the microalgae liquid absorbent (*Chlorella Vulgaris*) (69.4%) followed by Bold Basal Medium (BBM) (59.1%) and distilled water (55.9%). This initial result showed that the microalgae possessed better ability to absorb CO_2 into the liquid stream via the PVDF membrane contactor. Next, investigation on optimizing the system's operational parameters using BBM as liquid absorbent showed the highest CO_2 absorption flux and efficiency were obtained at initial solution pH of 10. Further investigation showed that the absorption efficiency was enhanced as the liquid flow rate increased up to 0.4 L/min and the gas flow rate was at 0.1 L/min. Upon utilizing 0.6 g/L microalgae, the purified $H_2\%$ found to remarkably increase up to 83.2%. In conclusion, the use of the developed integrated microalgae-membrane contactor system to purify the bio- H_2 from CO_2 mixture is a promising alternative method for zero carbon emission especially in palm oil industry.

1. Introduction

A high energy demand has led to massive research efforts towards improving different gas separation techniques for a more energy efficient and environmentally friendly methods. One of the potential renewable energy sources is considered from biogas produced from the fermentation of biomass such as Palm Oil Mill Effluent (POME). This biogas mainly consists of carbon dioxide (CO_2) and biohydrogen (H_2) gas mixtures [1, 2]. CO_2 is considered as the main anthropogenic greenhouse gas, which contributed towards the climate change phenomenon [3-5]. Since CO_2 is present in the biogas mixture, an effective technique to treat both gases towards zero carbon emission has become a major concern in the oil palm industry.

Membrane contactor is considered as a promising technique to attain the mentioning concern since it possesses the ability to solve the problem of CO_2 being released to the air and at the same time purifying the H_2 . There are several studies have been done on membrane contactor which mainly focused on (i) tailoring hydrophobic polymeric membranes to improve the membranes' performances in terms of its separation and wettability issues, (ii) selection of liquid absorbent that meets all the important



criteria such as high reactivity with CO₂, good compatibility with membrane material and regenerability, and (iii) operating conditions to influence the mass transfer resistance between the two phases. Of all factors, the separation using a membrane contactor is mostly dependent on the attraction of CO₂ to the liquid absorbent employed based on the physicochemical properties of the liquid and the membrane properties [6, 7]. Thus, more studies are essential on the development and enhancement of the liquid absorbent that can well performed as an absorber, compatible with the membrane and can be regenerated.

The most common liquid absorbent employed with the contactor system are alkaline solution, amine solution and other enhanced absorbent that can promote piperazine for the separation [5]. However, these liquid absorbents would require further treatment to eliminate the remaining CO₂ or any other chemical intermediates formed along the process in consideration to be known as a green process. On the other hand, there are suggestion to use CO₂ loaded solvent as a feedstock for microalgae production. However there is a mass transfer limitation if microalgae is contacted directly with the CO₂. Thus a new approach is introduced where two-stage process is involved; i) CO₂ is first loaded into the liquid absorbent and, ii) CO₂ rich solvent is then pumped into microalgae system. This approach may ease the solvent regeneration issue and further reduce the energy requirement by eliminating the use of reboiler in a common absorption system [8, 9].

In this attempt, instead of using a two-stage process as discussed above, purification of H₂ in a well-known CO₂ sequester system using microalgae [10, 11], integration of the microalgae system with a membrane contactor system could be used effectively to separate the H₂ and CO₂. Since microalgae could utilize the CO₂ for its cultivation, this microalgae will act as a green liquid absorbent, thus further treatment does not required to eliminate the remaining CO₂. Replacement of common chemical absorbents with microalgae in a membrane contactor could be a promising technique to treat both gases in a single step. Apart from being used as a CO₂ sequester in a wastewater treatment, microalgae is also used for production of valuable products. In this study, a novel technique was utilized to treat H₂ from CO₂ mixture simulated from POME fermentation by an integrated microalgae-membrane contactor system. A hollow fibre polyvinylidene fluoride (PVDF) membrane was used to permeate CO₂ through it and simultaneously purify the H₂. Critical parameters for the CO₂/H₂ gas separation namely pH, flow rate and concentration were investigated.

2. Materials and Method

2.1. Materials

PVDF hollow fibre membrane was purchased from the Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang (UMP). Commercial microalgae strain of *Chlorella Vulgaris* was obtained from the Algae Technology Malaysia. Medium that was used to culture the microalgae was Bold Basal Medium (BBM).

2.2. Membrane contactor gas permeation test

The strands of hollow fiber PVDF membranes were mounted into a hollow fiber membrane module where both ends of the module were sealed with cotton wool and epoxy resin. Next, the module was set up by connecting all tubes for gas and liquid stream. A counter-current flow mode was applied for the gas (lumen side) and liquid (shell side) phases. The schematic diagram of the module is shown in Figure 1 and the specifications of the used module in this experiment are presented in Table 1. The gas permeability test was performed by measuring the gas volume permeated through the membranes over the time for all gases (single and mixed gas). The pressure of the system was set to 1 bar, meanwhile the flow rate for gas and liquid phases were set at 0.1 and 0.2 L/min respectively.

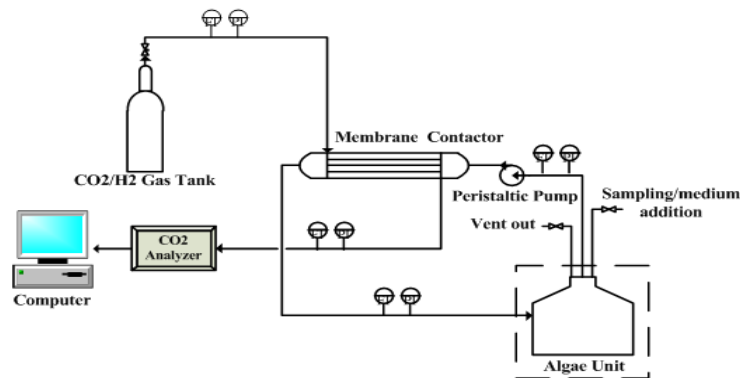


Figure 1. Design for the integrated microalgae-membrane contactor system

Table 1: Characteristics of gas-liquid membrane contactor system

Module inner diameter (mm)	9.5
Module length (mm)	275
Fiber inner diameter (mm)	0.109
Fiber outer diameter (mm)	0.312
Effective fiber length (mm)	220
Number of fibers	10

2.3. CO₂ Absorption test

Absorption test will be carried out by using pure CO₂ gas through the lumen side of the membrane. The studied operating parameters were initial pH of the BBM solution (pH 7 to 10) and the liquid/gas stream flow rate (0.1 to 0.4 L/min). The concentration of CO₂ in the liquid absorbent at the module outlet was measured by the titration method using phenolphthalein and methyl orange.

2.4. CO₂/H₂ separation membrane performance test

The composition of gas mixture applied was in accordance to the real composition of biogas mixture obtained from POME fermentation as reported in [1, 2]. The gas mixture consisted of 50% of H₂ and 50% CO₂ was flowed into the microalgae-membrane contactor system and the results were analysed by using CO₂ analyser (Quantek Instrument, Model 906).

3. Results and Discussion

3.1. PVDF membrane performance by using different absorptive liquids

The performance of the hollow fiber PVDF membrane used in this study was evaluated in terms of its permeability, selectivity and mixed H₂/CO₂ separation performances. The results were shown as in Figure 2, where three different liquid absorbents were used namely distilled water, Bold Basal Medium (BBM) and microalgae (*Chlorella Vulgaris* with biomass density of 0.4 g/L at pH 7.99). From the results (Figure 2(a)), the permeability of H₂ was higher than CO₂ for all liquid absorbent which is in the range of 61.5 - 68.6 GPU and 27.2 - 28.6 GPU respectively. This is because the CO₂ was absorbed to the liquid phase resulting a slow flow rate throughout the lumen of the membranes. Meanwhile, the separation capacity of the membrane for both gases was in the range of 2.26 to 2.53. Basically, the permeability and selectivity of the membranes on the gases were quite similar in all tests despite the use of different liquid absorbent. This can be explained by the use of the same gas and liquid flow rate which resulted to similar mass transfer. However, the separation performance by using H₂/CO₂ mixed gases through the membrane showed that the highest H₂ gas purity content was achieved by microalgae with 69.4% followed by BBM (59.1%) and distilled water (55.9%). These results showed that the microalgae possessed better ability to attract CO₂ into the liquid stream.

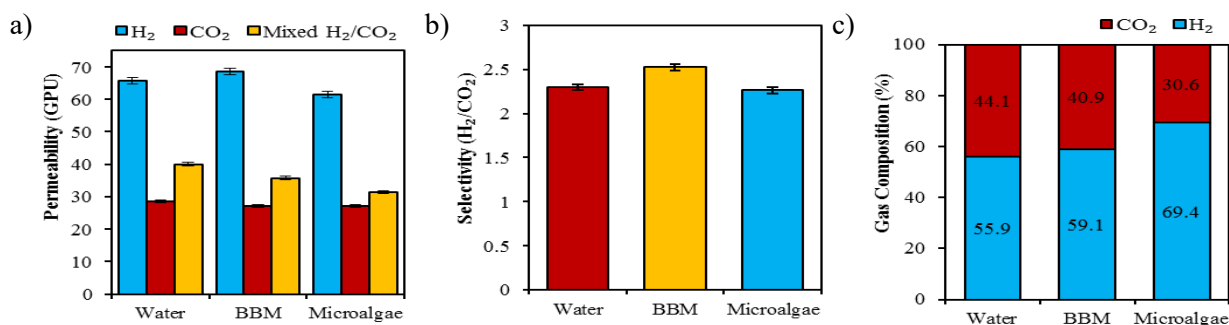


Figure 2. a) Permeability, b) Selectivity and c) separation performance of PVDF membrane by using different liquid absorbent

3.2. Influence of the operative variables to the absorption performances

The absorption ability of the microalgae acted as green liquid absorbent has been proved. However, it was believed that the absorption efficiency of the microalgae towards CO₂ can be enhanced by controlling its operating condition such as initial pH, liquid/gas flow rate and its concentration. Thus, detailed investigations on the operating parameters were done by using BBM as the absorptive liquid before the real solution containing microalgae was employed.

The initial operating parameter being evaluated was on the initial pH of the liquid absorbent. The ranges of the pH used for this study were 7 to 10 since these are suitable pH ranges for growing the microalgae. Meanwhile, distilled water was used as the control solution. From the results shown in Figure 3, the pH of the BBM solution was seen to decrease at the range of 5.5 to 6.0 after the pure CO₂ gas was flowed into the membrane contactor system for 90 min. It was believed that as the absorption proceeded, the pH of the solution continue to decrease as the CO₂ uptake in the solutions became more acidic and hence reduced the pH value. BBM solution at the initial pH of 10 was observed to have the highest reduction in pH value. This reduction signify the performance of the solution in absorbing the CO₂ during the process. As shown in Figure 2(b), the CO₂ absorption flux and absorption efficiency of the BBM solution increased as the initial pH of the solution increased. This increment was seen in line with the pH reduction rate and could be one of the good evidences in confirming that the CO₂ presence in the H₂ mixture have been absorbed in the solution during the absorption and further purify the H₂.

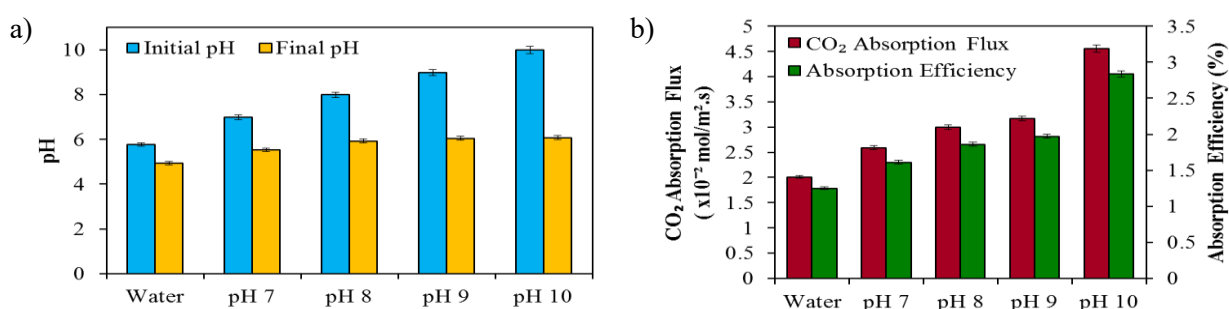


Figure 3. a) Final pH and b) CO₂ absorption flux and absorption efficiency at different initial pH of BBM solution as absorptive liquid

To further this study, CO₂ absorption flux and absorption efficiency with respect to the effect of liquid or gas flow rate were investigated. BBM solution at pH 10 was used since it showed the highest absorption efficiency with superior CO₂ absorption flux compared to the other pH range tested. As shown in Figure 4, an increased trend of CO₂ absorption flux was observed at increasing liquid flow rate. The enhancement of CO₂ absorption flux was due to the decrease in liquid boundary layer resistance which resulted to a higher mass transfer coefficient and thus increase the transfer rate of CO₂ into the liquid side [5]. However, increasing gas flow rate have an insignificant effect on the gas mass transfer

resistance as compared to the liquid mass transfer resistance because the contact time of the phases decreased at a higher gas flow rate [12]. Thus, a decreasing pattern of CO₂ absorption flux was seen when gas flow rate was increased as shown in Figure 3(b). These findings were in good agreement with previous report by [13] and [14]. At equal flow rate of liquid and gas stream, similar increasing trend in CO₂ absorption flux was observed when the flow rate is increased (Figure 4(c)). However, no enhancement in the absorption efficiency was observed though the flow rate was increased as observed in the case of liquid flow rate. Higher absorption efficiency can be achieved at a higher liquid flow rate but also depended on the gas flow rate. Thus, absorption efficiency at liquid and gas flow rate with ratio of 4:1 was much higher rather than at 1:1. From the results, the liquid mass transfer resistance was considered as the dominating factor for the overall mass transfer resistance in membrane contactor system and these can be achieved by increasing the liquid flow rate.

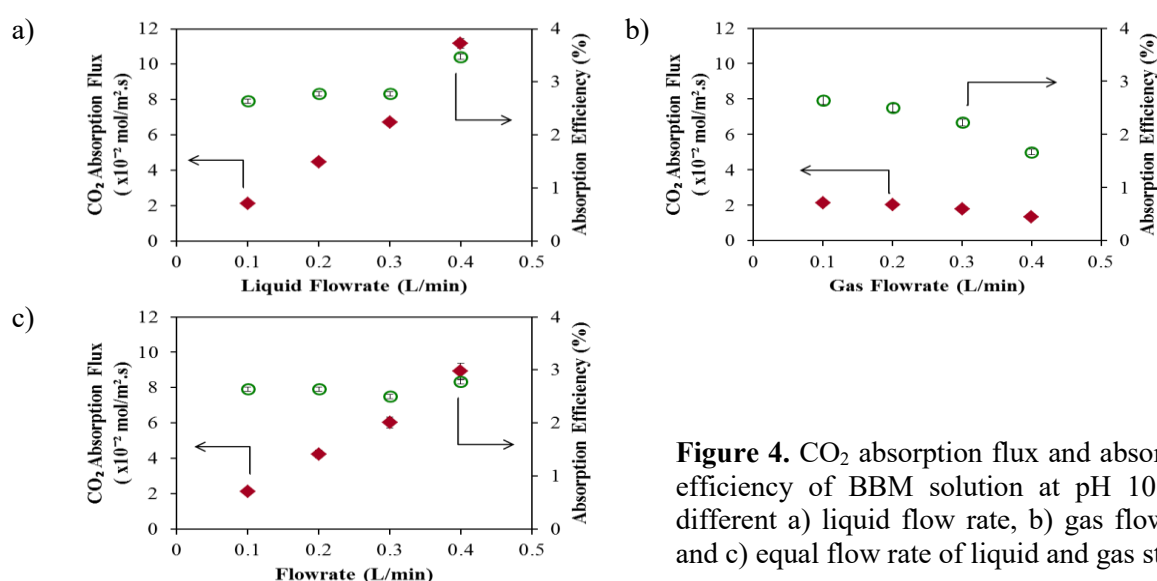


Figure 4. CO₂ absorption flux and absorption efficiency of BBM solution at pH 10 with different a) liquid flow rate, b) gas flow rate and c) equal flow rate of liquid and gas stream

3.3. Influence of the microalgae concentration to the separation performances

Detailed investigation on the operating parameters revealed that the optimum conditions to enhance the absorption efficiency of the membrane contactor system was at liquid and gas flow rate with ratio of 4:1 while the initial liquid pH was at pH 10. These conditions were further used in the integrated microalgae-membrane contactor system. An ideal concentration of the microalgae to be used in the integrated microalgae-membrane contactor system was investigated by using mixed gas consisted of 50% H₂ and 50% CO₂ as an imitation of the real composition of biogas mixture from POME fermentation. The microalgae concentration used in this study ranges between 0.2 to 2.0 g/L and the results of separation performances were shown in Figure 5.

At higher concentration of microalgae (ranges of 1.0 g/L and above), the H₂ purity was approximately 60%. As the concentration of the microalgae decreased to 0.8 g/L, the purity of the H₂ enhanced up to 70% and the H₂ percentage was found to remarkably increase up to 83.2% as the concentration of microalgae fed into the contactor decreased around 0.6 g/L. However, the H₂ percentage started to decrease again when lower microalgae concentration was fed in. Therefore, the ideal concentration of microalgae found in this preliminary study is at 0.6 g/L. In a real application, the use of different concentrations of microalgae can be a challenge as it will lead to different H₂/CO₂ separation performances. This is because microalgae utilizes the CO₂ from the biogas mixture to grow at certain growth rates and its concentration increases over time. The use of this integrated system is believed could sustainably separate the CO₂ from H₂ for a long period before the microalgae become saturated, either with CO₂ or cell content. Upon saturation, the microalgae will be harvested and new fresh medium or recycled cell-free medium will be loaded in the integrated system to continuously purify the H₂ by

absorbing the CO₂ for microalgae growth. Purified H₂ obtained from the process can be further used as fuel for proton exchange membrane fuel cell (PEMFC).

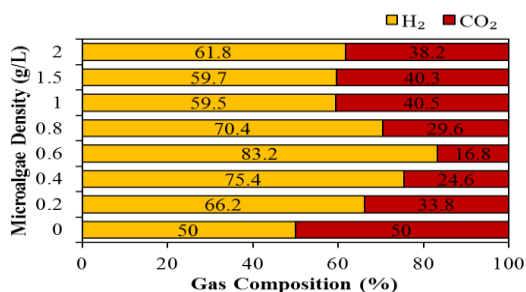


Figure 5. CO₂ and H₂ separation performances at different concentration of microalgae

4. Conclusions

In conclusion, the use of microalgae as a green liquid absorbent in the integrated microalgae-PVDF membrane contactor system is highly feasible. Microalgae showed a significant performance in absorbing the CO₂ into the liquid stream compared to distilled water and BBM. The optimum operating conditions to purify the H₂ was at both the highest set liquid flow rate (0.4 L/min) and the lowest set gas flow rate at 0.1 L/min. Under the controlled microalgae conditions (at pH 10 and microalgae concentration at 0.6 g/L), the purity of the H₂ increases up to 83.2 %. This work proved that the use of microalgae in the developed integrated membrane-contactor system is a promising alternative for H₂ purification and simultaneously would enhance the productivity of the microalgae, which will be focused next.

Acknowledgement

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