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# BIOHYDROGEN PURIFICATION FROM PALM OIL MILL EFFLUENT FERMENTATION FOR FUEL CELL APPLICATION

## (Penulenan Gas Biohidrogen yang Terhasil dari Fermentasi Efluen Kilang Minyak Kelapa Sawit Untuk Aplikasi Sel Bahan Api)

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### Abstract

Palm Oil Mill Effluent (POME) is one of the major pollutants generated from palm oil mills. In Malaysia, POME is recognised as a promising source for producing biogas through a controlled fermentation process, which can be used as a source of renewable energy. Therefore, this research was conducted to upgrade the biohydrogen produced from POME fermentation *via* (i) absorption and (ii) membrane techniques. In this study, the current and power capacity of the purified biohydrogen was verified by using fuel cell. From the results, POME fermentation was found to consist of mainly $H_2$ and $CO_2$ of equal amounts. Therefore, biohydrogen purification using the absorption technique was next performed using three different solvents: methyl ethanol amine (MEA), ammonia ($NH_3$) and potassium hydroxide (KOH) solutions and compared with the membrane permeation method using polysulfone (PSF) membrane. The highest $H_2$ purity for MEA solutions was found to be 99%, at 1 M concentration and 5.0 mL/s feed mixed gas flow rate at 60 minutes absorption time. The purified biohydrogen using PSF membrane possessed the highest $H_2$ purity at nearly 77% at the pressure of 3 bar. The purified biohydrogen obtained from the two separation techniques were next tested in a proton exchange membrane (PEM) fuel cell and directly compared with the original biohydrogen mixture obtained from POME fermentation (50% $H_2$), where the gas ratios were represented using simulated gas composition. The findings in this study identified that the current and power produced at 100% $H_2$ (similar $H_2$ purity from the absorption technique) was 1.66 A and 9.31 W while at 75% $H_2$ (similar $H_2$ purity from the membrane technique) the current was 0.69 A and 3.01 W. Therefore, the results prove that both purification techniques demonstrate the significant potential for $H_2$ purification efficiency.

**Keywords:** absorption, alkaline solvent, biohydrogen, carbon dioxide, palm oil mill effluent, treatment

### Abstrak

Efluen kilang minyak kelapa sawit (POME) merupakan salah satu daripada pencemar utama yang dihasilkan daripada kilang minyak sawit. Terkini, ianya telah dikenalpasti sebagai salah satu sumber yang berpotensi untuk menghasilkan biogas di Malaysia melalui kaedah fermentasi di dalam bioreaktor dalam keadaan terkawal, yang boleh dijadikan sebagai sumber tenaga diperbaharui. Oleh itu, kajian ini dijalankan bagi menambahbaik biohidrogen yang dihasilkan dari fermentasi POME menerusi (i) teknik penyerapan dan (ii) teknik membran. Kapasiti arus dan kuasa yang terhasil menerusi penulenan biohidrogen kemudiannya telah ditentukan menggunakan sel bahan api. Daripada keputusan yang diperoleh, fermentasi POME mengandungi gas $H_2$ dan $CO_2$ sahaja, dengan jumlah yang sama. Oleh itu, penulenan biohidrogen menggunakan teknik penyerapan telah dilakukan menggunakan tiga jenis pelarut iaitu larutan metil etanol amina (MEA), ammonia ($NH_3$) dan kalium hidroksida (KOH) dan kaedah ini kemudiannya dibandingkan dengan teknik pemisahan membran, iaitu dengan menggunakan membran polisulfon (PSF). Peratusan tertinggi bagi $H_2$ yang telah ditulenkan menggunakan pelarut MEA adalah 99% pada kepekatan 1 M, kelajuan gas 5.0 mL/s dan masa penyerapan 60 minit. Sementara itu, penulenan biohidrogen menggunakan membran PSF mempunyai peratusan tertinggi penulenan $H_2$ hampir 77% pada tekanan 3 bar. Biohidrogen yang telah ditulenkan melalui kedua-dua teknik pemisahan telah diuji dalam sel bahan api PEM dan ianya telah dibandingkan secara langsung dengan campuran biohidrogen asal dari fermentasi POME (50% $H_2$), yang mana kesemua nisbah gas telah diwakili oleh komposisi gas tersimulasi. Arus dan kuasa yang telah dihasilkan pada 100% $H_2$ (ketulenan $H_2$ menyerupai peratusan dari teknik penyerapan) adalah 1.66 A dan 9.31 W manakala pada 75% $H_2$ (ketulenan $H_2$ menyerupai peratusan dari teknik membran) adalah 0.69 A dan 3.01 W. Keputusan ini telah membuktikan bahawa kedua-dua teknik penulenan biogas berpotensi tinggi bagi meninggikan kecekapan penulenan gas $H_2$.

**Kata kunci:** penyerapan, pelarut alkali, biohidrogen, karbon dioksida, efluen minyak kelapa sawit, rawatan

## Introduction

The treatment of palm oil mill effluent (POME) has been an acceptable and widely used technique in the production of biogas as a potential source of renewable energy. The treatment process of POME is a method used to reduce its biochemical oxygen demand (BOD) and chemical oxygen demand (COD) before being discharged into the environment, releasing mixed gases comprising of CH4, $H_2$ and $CO_2$ [1]. The increasing concentrations of $CO_2$ into the atmosphere have raised concerns with respect to the environment. Notably, this prompted the need to consider new methods to control the emission of greenhouse gases (GHG). $CO_2$ is considered as the main anthropogenic contributor to the GHG effect, which is allegedly responsible for 60% of the increase in atmospheric temperature, commonly referred to as global warming [2]. Among the various sources of $CO_2$, fossil-fuel power plants are one of the major $CO_2$ contributors regarding this issue, generating approximately 30% of $CO_2$ from the production process into the earth's atmosphere [1]. Indeed, the POME treatment process under the anaerobic condition is believed to produce valuable biogases such as biohydrogen, which could be further upgraded to high value biohydrogen which could be utilised as alternative energy sources for the future sustainable development of energy [3]. The composition of biogas produced is highly dependent on the hydraulic retention time (HRT), in which HRT produced over 3 days would produce an equal amount of $H_2$ and $CO_2$ [4]. Thus, critical development of effective methods for the capture of $CO_2$ and biohydrogen purification has become a significant concern. The physical properties of $CO_2$ and $H_2$ (the major gases from POME treatment) are listed in Table 1.

Table 1. Physical properties of $CO_2$ and $H_2$ [5]

| Gas | Molecular Weight ($g\ mol^{-1}$) | Kinetic Diameter (Å) | Critical Pressure (kPa) | Critical Temperature (K) |
|---|---|---|---|---|
| $CO_2$ | 44.0 | 3.30 | 7386 | 304.2 |
| $H_2$ | 2.0 | 2.89 | 1296 | 33.14 |

To date, numerous gas upgrading methods have been developed globally, including absorption, adsorption and membrane technology [6]. Gas absorption using alkanolamine has been used for $CO_2$ scrubbing on an industrial scale for decades. However, several drawbacks such as high energy consumption and severe corrosion problems are inherent in this process. Hence, the exploration of improved gas separation technology by researchers in this area is of great significant. Currently, the novel technology associated with membrane separation has emerged as one of the most feasible technologies for biohydrogen separation and purification processes [7]. Membrane technology in the development of biological systems can play multiple roles, including in fermentative biohydrogen technology. For example, a membrane bioreactor which employed submerged or externally connected porous-water filtration (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)) membranes could retain active biomass efficiently within the fermenter. Furthermore, it has been discovered that membrane technology could also assist in overcoming the issue of low reaction yields by allowing *in situ* and continuous removal of biohydrogen using membranes from the membrane bioreactor [7]. Gas upgrading for $H_2$ and $CO_2$ capture via absorption, membrane permeation and membrane contactor were reported as shown in Table 2.

Table 2. Summary of gas upgrading via absorption and membrane techniques

| **Technique** | **Gas Composition** | **Condition** | **Recovery** | **Reference** |
|---|---|---|---|---|
| Absorption | 10- 14 v/v% $CO_2$ | Ammonia, sieve plate, 25 -55 $^oC$ | 95-99% $CO_2$ capture | Diao et al. [8] |
| Absorption | 8- 16 v/v% $CO_2$ | MEA, 10-40 $^oC$ | >97% $CO_2$ capture | Ma et al. [9] |
| Membrane | Pure gases of $H_2$ and $CO_2$ were tested in sequence | Polybenzimidazole based asymmetric hollow fiber membrane, 400$^o$C | $H_2$ permeance 2.6 GPU<br>$CO_2$ permeance 0.096 GPU Selectivity ($H_2$/ $CO_2$) 27.28 | Kumbharkar et al. [10] |
| Membrane | 79% $CO_2$, 21% $H_2$ | Membrane Contactor, MEA as liquid carriers | 92% $H_2$ purity | Modigell et al. [11] |

## Materials and Methods

The initial work on POME anaerobic fermentation to produce biogas was carried out by the Biohydrogen Research Group in Universiti Kebangsaan Malaysia (UKM) [4, 13]. The composition of the biogas mixture produced during the process mainly consisted of 39% $H_2$ and 49% $CO_2$ as reported by the literature and in previous work with no presence of $H_2S$ [13, 14]. Since the capacity of biogas produced from fermentation in one day (24 hours) is limited to only 15 - 20 L/d and considered insufficient for continuous upgrading mode, a simulated model gas of $H_2$ and $CO_2$ was used with similar composition found in the literature. A mixed gas of $H_2$ and $CO_2$ at 50v%/50v% and single gases of $H_2$ gas (99.5%) and $CO_2$ gas (99.8%) were used and supplied by NIG Gas Sdn. Bhd. A mixed gas of $H_2$ and $CO_2$ (ratio 50:50) was also used in both absorption and membrane separation for $H_2$ purification evaluation.

### Absorption

The absorption process was conducted using three types of alkaline solution, i.e. potassium hydroxide (KOH), mono-ethanolamine (MEA) and ammonia ($NH_3$). The absorption began by allowing the fixed feed mixture flow rate of gas comprising fixed gas of $H_2/CO_2$ with 50%/50% to enter the bubble glass reactor filled with an alkaline solution of different molarity (refer Figure 1). Next, the purified $H_2$ permeated at the outlet point was collected in a gas syringe to determine its final composition. For each experiment, data were averaged from two replicates for reproducibility. The parameters involved in the absorption process are listed in Table 3. The range of each parameter used was adapted from the study by Maceiras et al. where the solvent concentration, solvent temperature, gas mixture flow rate, and absorption time was in the range of 0 to 1 M, 25 to 70 $^oC$, 2 to 7 mL/s and 0 to 100 min, respectively [15]. For the experiment, the solvent volume was kept constant at 1 L.

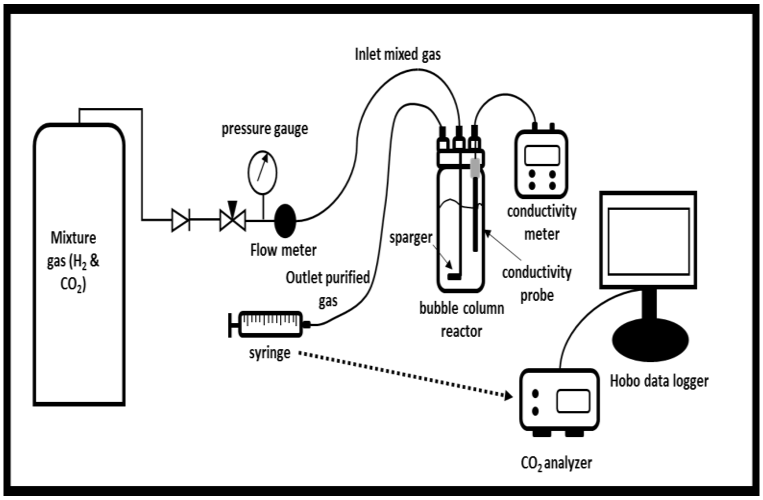

Figure 1. Schematic diagram of $CO_2$ absorption technique

Table 3. List of parameters for absorption technique

| Parameter | Range of Parameter |
|---|---|
| Feed mixture gas flow rate (mL/s) | 5.0 |
| Feed mixture gas composition ($H_2/CO_2$) | 50%/50% |
| Type of alkaline solution | KOH, $NH_3$, MEA |
| Concentration of solution (M) | 1.0 |
| Temperature of solution ($^oC$) | 28 |
| Time data recorded (min) | 2,5,15,30 and 60 |
| Diameter and height of reactor (cm) | 8 and 22 |
| Volume of solution (ml) | 500 |

**Membrane separation**

Polysulfone (PSF) membranes were used in this study to determine the permeability and selectivity of $H_2$ and $CO_2$ during the gas separation and purification process (refer Figure 2). The PSF asymmetric membranes were supplied by the Advanced Membrane Research Centre (AMTEC), The University of Technology Malaysia (UTM), which was synthesised from PSF granules (Udel-P1700) in a solvent mixture of N,N dimethylacetamide, tetrahydrofuran and ethanol at an appropriate composition.

Gas permeation rate can be calculated by using pressure normalized flux in Eq. (1):

$$\frac{P}{l}i = \frac{Q_i}{(\Delta P)(A)} \tag{1}$$

where ($P/l$) is defined as pressure-normalized flux or permeability for gas $i$ in GPU unit; $Q_i$ is volumetric flow rate of gas $i$, $\Delta P$ is the pressure difference across membrane, $A$ is the membrane effective surface area and $l$ the membrane skin thickness.

Membrane selectivity (α) can be determined by dividing the permeability, $p$ of $H_2$ over $CO_2$ as stated in Eq. (2):

$$\alpha = \frac{pH_2}{pCO_2} \tag{2}$$

The gas composition was determined by using Gas Chromatography (GC, model SRI 8600C, USA) to measure the composition of the mixed gases of $H_2$ and $CO_2$.

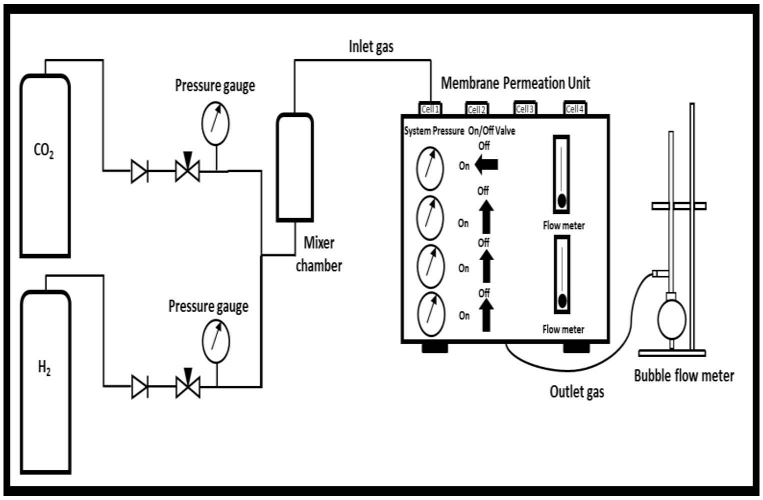

Figure 2. Schematic diagram of Membrane Permeation Unit

### Fuel cell application

Finally, the purified $H_2$ mixture from the simulated model gas (using a similar composition obtained from the absorption and membrane separation technique) was tested in a fuel cell system supplied by the PEMFC stack from the Horizon Fuel Cell, model FCS-B20 with a maximum power capacity of 10 W. The effect of $CO_2$ the concentration on the PEMFC performance (voltage, current and power) was monitored to determine the optimum composition of $H_2$ with $CO_2$ existence for the fuel cell application. For each experiment, the power, current and voltage data were obtained from the average value of duplicate experiments. The data were presented in the plotted graph of power versus current, voltage versus time and power versus percentage of $CO_2$. The summary of the parameters involved in the $H_2$ PEMFC testing is listed in Table 4.

Table 4. List of parameters for PEMFC application

| **Parameters** | **Range of parameters** |
|---|---|
| Composition mixture of $H_2$ and $CO_2$ (v%/v%) | 50/50, 75/25, 90/10 and 100/0 of $H_2$ & $CO_2$ |
| Feed mixture gas flow rate (cc/min) | 55 |
| Time of application (min) | 30 |

## Results and Discussion

The absorption and membrane separation techniques were employed to compare the $H_2/CO_2$ separation and purification efficiency in this work. The purified $H_2$ (simulated gas composition with the purity obtained *via* these methods) was then utilised in the fuel cell application for performance evaluation.

### Absorption

In this study, the absorbents effects (KOH, $NH_3$, MEA) at 1 M concentration towards $H_2$ purification was performed at the highest feed gas flow rate (5.0 mL/s) (refer Figure 3). The findings indicated a significant effect of 1 M solution concentration to the purification of $H_2$. The $H_2$ purity had reduced significantly at 1 M of KOH and MEA after 30 minutes of absorption, in which the reduction from 99% to 64% and 75% was observed for KOH and MEA solutions. While the purity for ammonia absorption was found relatively higher at 79% after 60 min of absorption. Also, the higher absorbent concentration could release more free ionic species which contributed to a greater $CO_2$ reaction in the absorption process. However, the decrement trend of gas purity indicated the presence of a $CO_2$ saturation stage during absorption [15]. Moreover, a higher feed flow rate was used to create turbulence effects for a rapid reaction between the gas and free ionic species contained in the solution [16].

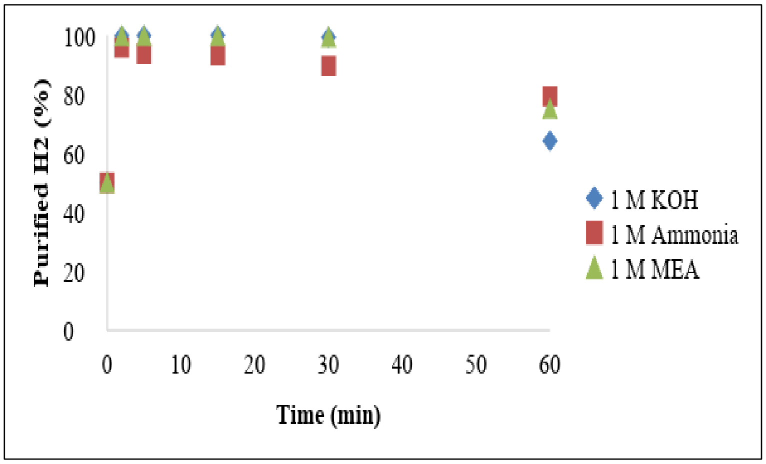

Figure 3. Purified $H_2$ composition *via* absorption technique with different alkaline solutions (KOH, $NH_3$, MEA) at 1 M concentration

Among these three solvents, MEA was preferred due to its excellent absorption performance in comparison to $NH_3$ and KOH solutions regarding its $H_2$ purification percentage. Although MEA exhibited similar absorption performance as KOH, MEA was more reliable and preferable in the market. Possibly due to its low cost and its ability to handle low $CO_2$ partial pressure gas stream during the absorption [2, 17]. Hence, MEA was concluded as a potential absorbent candidate for better absorption efficiency and to be further utilised instead of KOH.

**Membrane separation**

The separation performance of PSF membranes regarding $CO_2$ and $H_2$ permeance rate and selectivity at the pressure range of 1 to 8 bar was successfully measured. According to Figure 4, the highest permeance rate for $H_2$ for PSF membrane was indicated at 13.08 GPU (at 2 bar) while the highest permeability for $CO_2$ was recorded at 7.24 GPU (at 1 bar). Additionally, the selectivity for $H_2/CO_2$ was increasing proportionately concerning the pressure increment, in which the best selectivity was observed at 4.07 (tested at 4 bar). The PSF membrane was known as a glassy polymer and the permeant diffusion coefficient was more dominant than the solubility coefficient. Therefore, the smaller and non-condensable $H_2$ gas with a molecular diameter of 2.9 Å, was preferentially permeated through PSF polymer instead of $CO_2$ with a larger molecular diameter (3.3 Å) [18]. Hence, the permeance rate for $H_2$ was always higher than $CO_2$. In addition to the decrement trend of $H_2$ and $CO_2$ permeance against pressure, this could be explained based on the competitive solubility effects between the gas and polymer structures and the saturation of the polymer sorption site with gas molecules which resulted in membrane compaction [19, 20]. The plasticisation effect was not detected in this study due to the absence of $CO_2$ permeance increment with pressure.

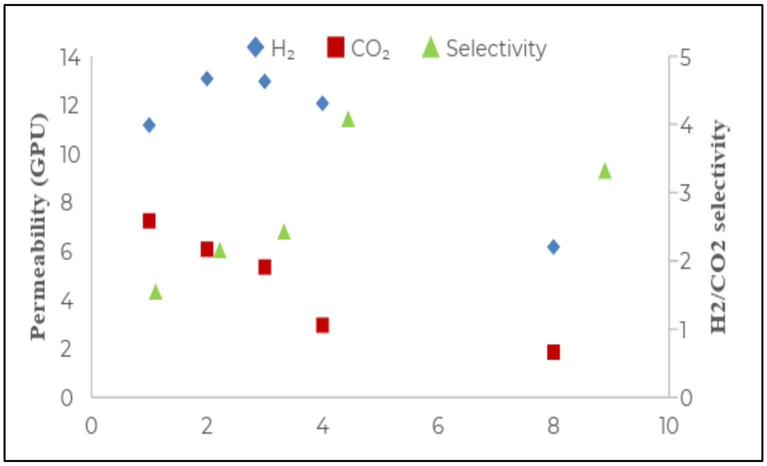

Figure 4. Gas permeation rate and selectivity for PSF Membrane

On the other hand, Figure 5 depicts the pressure effect on the $H_2$ and $CO_2$ gas composition in the permeate stream with different pressure using a fixed composition of 50%/ 50% of $H_2/CO_2$ feed gas mixture. The findings indicated that the $H_2$ purity increased significantly from 68 % to 77 % from the pressure of 1 to 3 bar. However, when the applied pressure increased from 4 to 8 bars, the $H_2$ purity began to gradually reduce with the lowest recorded at 52% (8 bar). This scenario was possibly due to the flux increment which enhanced the solubility and diffusion rates of $H_2$ [21]. Also, the optimum pressure for the satisfactory $H_2$ permeance rate was within the range of 1 to 3 bar. Thus, the integration between the membrane and bioreactor system was observed as being a practical approach since the internal pressure range was similar for both systems [22]. Therefore, this work has proven the separation efficiency of PSF membrane in the biohydrogen purification process with high permeability, the selectivity of $H_2/CO_2$ and high $H_2$ purity (77%).

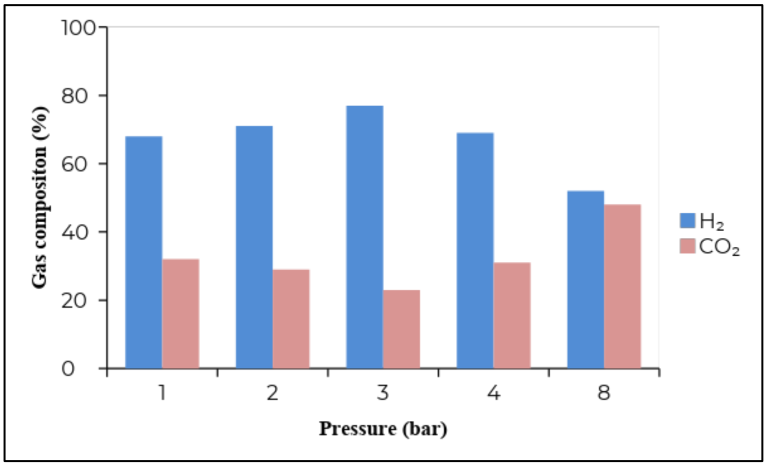

Figure 5. Gas composition in permeate stream after gas permeation test for PSF membrane

## Fuel cell application

The purified biohydrogen from the two separation techniques was tested in the PEM fuel cell and compared with the original biohydrogen mixture from POME fermentation. Indeed, this composition was important to observe the fuel cell performance profile, when the fermented gas was used without further purification. Based on the results as shown in Figure 6, the profiles of stack power with current were found to be similar. At the beginning of the cell operation, the power increased steadily with the current, until a maximum power peak was achieved before the power decreased with the current. The highest current recorded was in parallel with the $H_2$ composition, where the highest $H_2$ purity gave the highest current value and vice versa. The highest current recorded was 1.66 A for 100% $H_2$ purity while the lowest current was 0.32 A for 50% $H_2$ purity. Accordingly, this has proven that higher $H_2$ % supplied into PEMFC could generate a higher amount of current, which resulted in the higher amount of power. Hence, in a real fuel cell operation, the supply of high purity $H_2$ into the fuel cell is essential to ensure higher power generation.

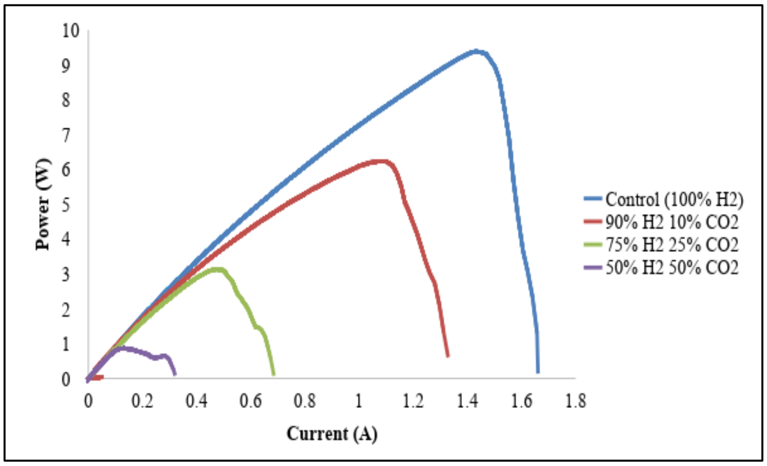

Figure 6. Power profile with current at different $H_2$ concentration

Meanwhile, Figure 6 also shows the average power produced by different $CO_2$ compositions. The power produced reached the highest value which was close to 9 W and conversely, the power recorded was less than 1 W for the lowest $H_2$ composition. The graph plotted showed a linear pattern of power produced with $CO_2$ composition present in the PEMFC. Therefore, it proved that the existence of $CO_2$ in the PEMFC gave a significant effect on PEMFC performance. Further, the $CO_2$ had obviously decreased the amount of power produced by PEMFC. The $CO_2$ presence in the PEMFC would affect the electrochemical catalytic rates, which interfere with proton transport across the polymer electrolyte or prevent the flow of reactants to or the reaction of products away from the anode or cathode charge transfer interfaces. Also, the presence of impurities may also decrease the operational lifetime of the fuel cell by increasing the component failure rate. Ahluwalia et al. suggested that any $CO_2$ impurity in the fuel adsorbs weakly on the platinum (Pt) catalyst [23]. According to Chew et al., at low $CO_2$ concentrations, the observed degradation in cell power can be explained based on CO produced from $CO_2$ on the active Pt surface and the subsequent adsorption of CO on the active Pt sites via the reverse water gas shift reaction (RWGSR) between $CO_2$ and the adsorbed $H_2$ [24]. Furthermore, at higher $CO_2$ concentrations, the decrease in cell potential due to the dilution of the $H_2$ also contributed to performance degradation. Therefore, it was essential to minimise the amount of $CO_2$ in the $H_2$ mixture to gain more power produced from the PEMFC.

Hence, this study has revealed that different $H_2$ concentrations supplied into the PEMFC would present different performances on the current and power produced. It was also proven that biohydrogen separation using the absorption technique could provide the best purification (close to 100% $H_2$ purity) and in turn, demonstrated the higher capacity of current and power (1.66 A and 9.31 W) in comparison to the membrane technique.

## Conclusion

The absorption and membrane separation techniques were successfully investigated in $H_2/CO_2$ separation and the purification process where the highly-purified $H_2$ was further utilised in the fuel cell application. The observations and separation performance between the two separation techniques were satisfactory. Therefore, it could be concluded that MEA is the best alkaline solvent for absorption due to the high percentage of purified $H_2$ produced (99% for 1 M MEA). The PSF membranes possessed high $H_2$ permeance rate and $H_2/CO_2$ selectivity, which was obtained at 13.08 GPU (at 2 bar) and 4.07 (tested at 4 bar), respectively. The absorption technique possessed better $H_2$ purity as the percentage of purified $H_2$ was close to 100% purity, while for membrane technique it was close to 80%. The highest current and power generated were 1.66 A and 9.31 W respectively from the feed mixture gas with 100%/0% of $H_2/CO_2$.

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