

Purification of Biohydrogen Produced From Palm Oil Mill Effluent Fermentation for Fuel Cell Application

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Abstract – Fermentation of palm oil mill effluent (POME) produces biohydrogen in a mixture at a specific set condition. This research was conducted to purify the produced mixed biohydrogen via absorption and membrane techniques. Three different solvents, methyl ethanolamine (MEA), ammonia (NH₃) and potassium hydroxide (KOH) solutions, were used in absorption technique. The highest H₂ purity was found using 1M MEA solution with 5.0 ml/s feed mixed gas flow rate at 60 minutes absorption time. Meanwhile, the purified biohydrogen using a polysulfone membrane had the highest H₂ purity at 2–3 bar operating pressure. Upon testing with proton exchange membrane fuel cell (PEMFC), the highest current and power produced at 100% H₂ were 1.66 A and 8.1 W, while the lowest were produced at 50/50 vol% H₂/CO₂ (0.32 A and 0.49 W). These results proved that both purification techniques have significant potential for H₂ purification efficiency.

Key words: Absorption, Alkaline solvent, Biohydrogen, Carbon dioxide, Palm oil mill effluent

1. Introduction

Palm oil mill effluent (POME) treatment has been a favorable technique in the production of biogas as a potential source of renewable energy. The treatment process of POME as a way to reduce its biochemical oxygen demand (BOD) and chemical oxygen demand (COD) before being discharged into the environment releases mixed gases, comprising CH₄, H₂ and CO₂ [1]. The vastly increasing concentration of CO₂ in the atmosphere has raised environmental concerns, which makes it imperative to consider ways of controlling the emission of this greenhouse gas (GHG) into the atmosphere. To date, CO₂ 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 CO₂, fossil-fuel power plants are considered as one of the major CO₂ contributors, which generate approximately 30% of CO₂ from the production process [1]. Besides, the POME treatment process under anaerobic condition could produce valuable biogas such as bioH₂, which could be further upgraded to a high value bioH₂ and utilized as alternative energy source for future sustainable development [3]. Thus, a critical development of effective methods for CO₂ capture and bioH₂ purification has become a major concern.

Recently, numerous gas upgrading methods have been developed worldwide, including absorption, adsorption and membrane technology [5]. Gas absorption using alkanolamine has been used for CO₂ scrubbing on an industrial scale for decades, but it brings several drawbacks such as high energy consumption and severe corrosion problems [1]. Hence, the exploration of better gas separation technology is of great interest. Currently, the novel technology with membrane separation has appeared as one of the most feasible technologies for bioH₂ separation and purification processes [6]. Membrane technology can play multiple roles in the development of biological systems as well as in fermentative bio H₂ technology. For example, membrane bioreactors which employ submerged or externally connected porous-water filtration (MF, UF, NF, and RO) membranes could retain active biomass efficiently within the fermenter. Thus, it has been discovered that membrane technology could assist in overcoming the issue of low reaction yields by allowing *in situ* and continuous removal of bioH₂ using membranes from the membrane bioreactor [6]. Gas upgrading for H₂ and CO₂ capture by absorption, membrane permeation and membrane contactor were also reported in open literature as summarized in Table 1. Based on the studies, high purity of CO₂ was captured by absorption (above 95%), while high purity of H₂ (up to 92%) and H₂/CO₂ selectivity of around 27.3 were achieved upon using different absorbents and membranes, respectively.

Since the current production of bioH₂ from biomass is found on a relatively smaller scale (lab or pilot scale) while larger scale of gas upgrading technology is commonly used in industry, the adaptation is very much needed on the current gas upgrading technology such as absorption, adsorption and membrane. Among the aforementioned

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Table 1. Summary of gas upgrading by absorption and membrane techniques

Technique	Gas composition	Condition	Recovery	Reference
Absorption	10-14 v/v% CO ₂	Ammonia, sieve plate, 25-55 °C	95-99% CO ₂ capture	Diao et al. 2004 [7]
Absorption	8-16 v/v% CO ₂	MEA, 10-40 °C	>97% CO ₂ capture	Ma et al. 2013 [8]
Membrane	Pure gases of H ₂ and CO ₂ were tested in sequence	Polybenzimidazole based asymmetric hollow fiber membrane, 400 °C	H ₂ permeance 2.6 GPU CO ₂ permeance 0.096 GPU Selectivity (H ₂ /CO ₂) 27.28	Kumbharkar et al. 2011 [9]
Membrane	79% CO ₂ , 21% H ₂	Membrane Contactor, MEA as liquid carriers	92% H ₂ purity	Modigell et al. 2008 [10]

technologies, membrane technology has gained tremendous attention while absorption and adsorption are conventional and well-established technologies for gas purification. Hence, it is important to evaluate the workability and separation efficiency of these technologies for bioH₂ gas upgrading from biomass fermentation, especially for fuel cell application. Therefore, the main goal of this work was to determine the optimum operating conditions for bioH₂ purification by employing two methods: bioH₂ separation by absorption and membrane separation technique. Finally, the highly-purified bioH₂ was utilized in proton exchange membrane fuel cell (PEMFC) to identify the maximum current and power generated for further application.

2. Materials and Methods

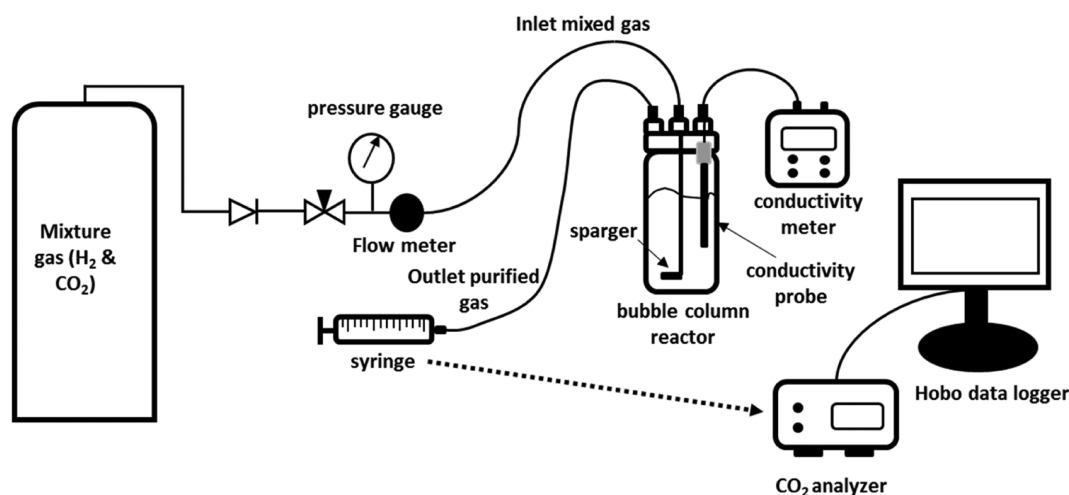
The initial work on POME anaerobic fermentation to produce biogas was carried out by the Biohydrogen Research Group in UKM [11,12]. The composition of the biogas mixture produced during the process mainly consisted of 39% H₂ and 49% CO₂ as reported by literature and our previous work with no presence of H₂S [12,13]. Since the capacity of biogas produced from fermentation in one day (24 h) is limited to only 15~20 L/d and considered insufficient for continuous upgrading mode, a simulated model gas of H₂ and CO₂ was used with similar composition found in literature. Mixed gas of H₂ and CO₂ at 50%/50% and single gases of H₂ gas (99.5%) and CO₂ gas (99.8%) were used and supplied by NIG Gas Sdn. Bhd. Mixed gas of H₂ and CO₂ (ratio 50:50) was also used in both absorption and membrane separation for H₂ purification evaluation.

2-1. Absorption

The absorption process was conducted using three types of alkaline solution: potassium hydroxide (KOH), mono-ethanolamine (MEA) and ammonia (NH₃). These three absorbents were chosen due to their chemical component presence that consists of mainly N and K, which are main compounds in common fertilizer. It is targeted that the precipitate formed from the absorption process in the end will be applied as fertilizer in the oil palm plantation. The absorption was started by allowing the fixed feed mixture flow rate of gas comprising fixed gas of H₂/CO₂ with 50%/50% to enter the bubble glass reactor filled with alkaline solution of different molarity. The purified H₂ 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 2. The range of each parameters used was referred from the study by Maceiras et al. (2008) where the solvent concentration, solvent temperature, gas

Table 2. 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 (°C)	28
Time data recorded (min)	2,5,15,30 and 60
Diameter and height of reactor (cm)	8 and 22 respectively
Volume of solution (ml)	500

**Fig. 1. Schematic diagram of CO₂ absorption technique.**

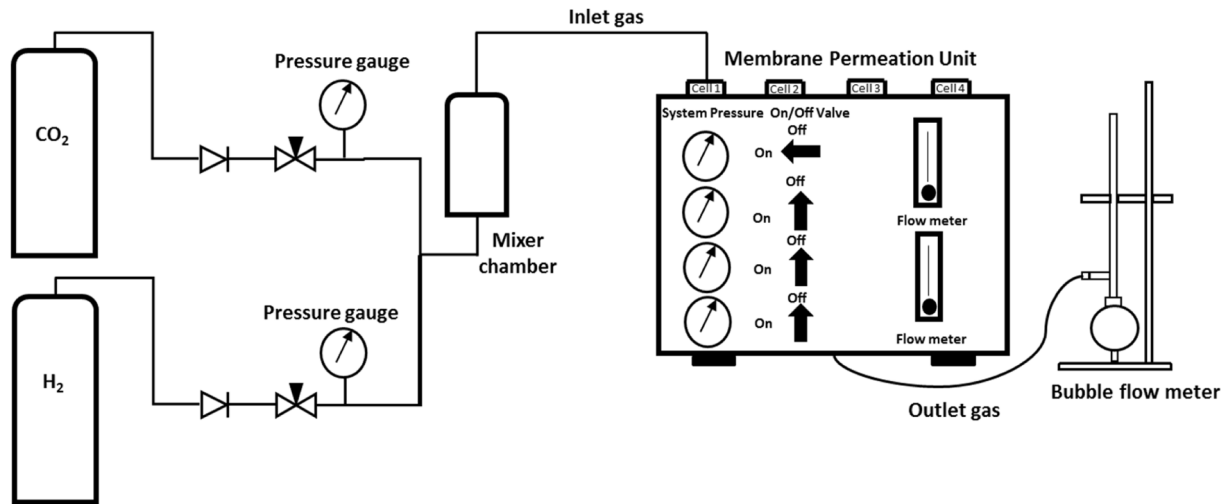


Fig. 2. Schematic diagram of Membrane Permeation Unit.

mixture flow rate, absorption time were in the range of 0 to 1 M, 25 to 70 °C, 2 to 7 ml/s and 0 to 100 min, respectively [14]. The solvent volume was kept constant at 1 L for the experiment.

2-2. Membrane Separation

Polysulfone (PSF) membranes were used in this study to determine the permeability and selectivity for H₂ and CO₂ during the gas separation and purification process. These PSF asymmetric membranes, which were supplied by the Advanced Membrane Research Centre (AMTEC), the University of Technology Malaysia (UTM), were synthesized 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):

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{(\Delta P)(A)} \quad (1)$$

where $(P/l)_i$ is defined as pressure-normalized flux or permeability for gas i in GPU unit; Q_i is volumetric flow rate of gas i , ΔP 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 H₂ over CO₂ as stated in Eq. (2):

$$\alpha = \frac{p_{H_2}}{p_{CO_2}} \quad (2)$$

The gas composition was determined by using gas chromatography (GC, model SRI 8600C, USA) to measure the composition of the mixed gases of H₂ and CO₂.

2-3. Fuel Cell Application

Finally, the purified H₂ mixture from simulated model gas (by using similar composition obtained from absorption and membrane separation technique) was tested in a fuel cell system which was supplied by PEMFC stack from Horizon Fuel Cell, model FCS-B20

Table 3. List of parameter for PEMFC application

Parameters	Range of parameters
Composition mixture of mixed gas in % (H ₂ /CO ₂)	50/50, 75/25, 90/10 and 100/0
Feed mixture gas flow rate (cc/min)	55
Time of application (min)	30

with a maximum power capacity of 10 W. The effect of CO₂ concentration on the PEMFC performance (voltage, current and power) was monitored to determine the optimum composition of H₂ with CO₂ existence for fuel cell application. For each experiment, the power, current and voltage data were obtained from an average value of duplicate experiments. The data was presented in plotted graph of power versus current, voltage versus time and power versus percentage of CO₂. A summary of the parameters involved in the H₂ PEMFC testing is listed in Table 3.

3. Results and Discussion

The absorption and membrane separation techniques were employed in this work to compare the H₂/CO₂ separation and purification efficiency. The purified H₂ obtained via these methods was then utilized in fuel cell application for performance evaluation.

3-1. Absorption

In this study, the absorbents effects (KOH, NH₃, MEA) at 1 M concentration towards H₂ purification were performed at the highest feed gas flow rate (5.0 ml/s). The findings indicated a significant effect of 1 M solution concentration on the purification of H₂. The H₂ purity was reduced significantly at 1 M of KOH and MEA after 30 minutes of absorption, in which the reduction was observed from 99% to 64% and 75% for KOH and MEA solutions, while the purity for ammonia absorption was found relatively higher at 79% after 60 minutes of absorption. Higher absorbent concentration could release more free ionic species, which contributed to more CO₂ reaction in absorption process. However, the decrement trend of gas purity

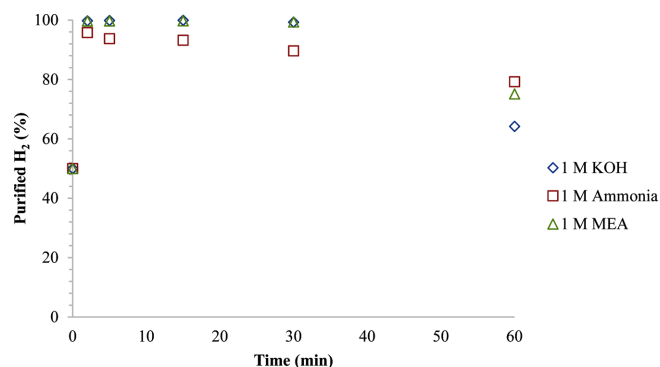


Fig. 3. Composition of purified H₂ obtained via absorption technique with different alkaline solutions (KOH, NH₃, MEA) at 1 M concentration.

indicated the presence of CO₂ saturation stage during absorption [14]. Besides, 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 [15].

From the results, MEA has better absorption performance in comparison to NH₃ solution in term of H₂ purification percentage. Although MEA exhibited similar absorption performance as KOH, MEA is much more reliable and preferable in the market, possibly due to its low cost and its ability to handle low CO₂ partial pressure gas stream during the absorption [16,17]. Hence, MEA was concluded as the most potential absorbent candidate for better absorption efficiency to be further utilized instead of KOH.

3-2. Membrane Separation

The separation performance of PSF membranes in terms of CO₂ and H₂ permeance and selectivity at the pressure range of 1 to 8 bar was successfully measured. According to Fig. 4, the highest permeance for H₂ for PSF membrane was at 13.08 GPU (at 2 bar), while the highest permeability for CO₂ was recorded at 7.24 GPU (at 1 bar). Additionally, the selectivity for H₂/CO₂ was increasing proportionately with respect to pressure increment, in which the best selectivity was observed at 3.32 (at 8 bar). High permeability of H₂ with low permeability of CO₂ is desired in order to consider the membrane as selective for the specific mixed gas separation. PSF membrane is

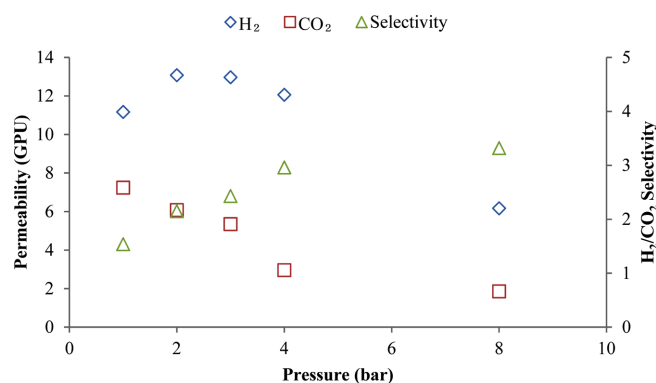


Fig. 4. Gas permeation and selectivity for PSF Membrane.

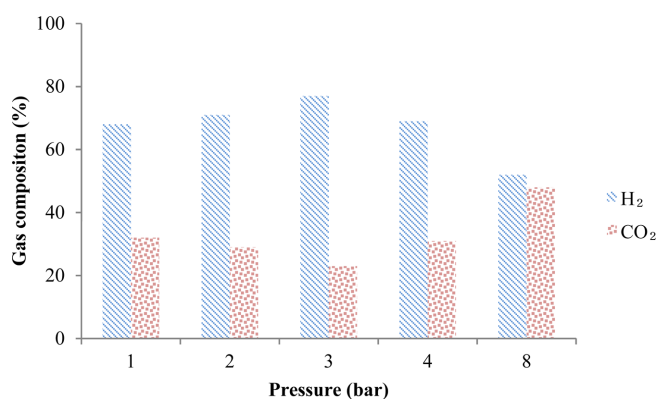


Fig. 5. Gas composition in permeate stream after gas permeation test for PSF membrane.

known as a glassy polymer and the permeant diffusion coefficient is more dominant than solubility coefficient. Therefore, the smaller and non-condensable H₂ gas with molecular diameter of 2.9 Å, was preferentially permeated through PSF polymer instead of CO₂ with larger molecular diameter (3.3 Å) [18]. Hence, the permeance rate for H₂ was always higher than CO₂. Besides, the decrement trend of H₂ and CO₂ permeance against pressure could be explained based on the competitive solubility effects between gas and polymer structures and the saturation of polymer sorption site with gas molecules, which resulted in membrane compaction [19, 20]. The plasticization effect was not detected in this study due to the absence of CO₂ permeance increment with pressure.

On the other hand, Fig. 5 demonstrates the pressure effect on the H₂ and CO₂ gas composition in the permeate stream with different pressure by using a fixed composition of 50%/ 50% of H₂/CO₂ feed gas mixture. The findings indicated that the H₂ permeance increased significantly from 68% to 77% from pressure of 1 to 3 bar. However, when the applied pressure increased from 4 to 8 bar, the H₂ permeance started to reduce gradually, 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 H₂ [21]. The optimum pressure for satisfactory H₂ permeance rate was within the range of 1 to 3 bar. Thus, the integration between membrane and bioreactor system was a practicable approach since the internal pressure range was similar for both systems [22]. Hence, this work has proven the separation efficiency of PSF membrane in bioH₂ purification process with high permeability, selectivity of H₂/CO₂ and high H₂ purity (77%).

3-3. Fuel Cell Application

The purified biohydrogen from the two separation techniques was tested in PEM fuel cell and compared with the original biohydrogen mixture from POME fermentation. This composition is important in order to see the fuel cell performance profile, if and when the fermented gas is used without further purification. Based on the results in Fig. 6, the profiles of stack power with current were found to be similar to each other. At the beginning of the cell operation, the power had increased steadily with the current, until a maximum power peak was

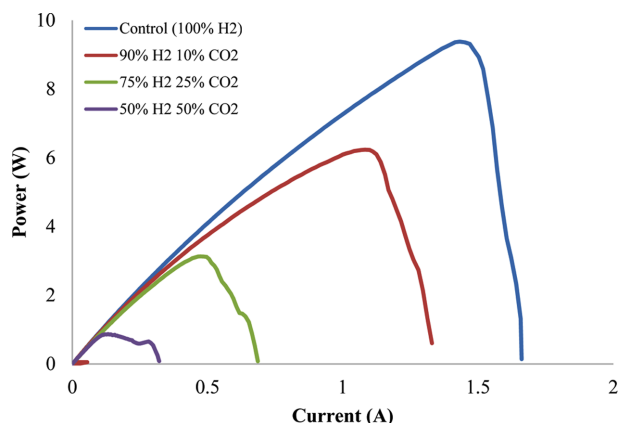


Fig. 6. Power profile with current at different H₂ concentration.

achieved before the power decreased with the current. The highest current recorded was in parallel with the H₂ composition, where the highest H₂ purity gave the highest current value and vice versa. The highest current recorded was 1.66 A for 100% H₂ purity, while the lowest was 0.32 A for 50% H₂ purity. This has proven that higher H₂% supplied into PEMFC could generate higher amount of current, which resulted in higher amount of power. Hence, in a real fuel cell operation, the supply of high purity H₂ into the fuel cell is essential to ensure higher power generation.

Meanwhile, Fig. 7 shows the average power produced by different CO₂ compositions. The power produced reached the highest value which was close to 8 W and, conversely, the power recorded was less than 1 W for the lowest H₂ composition. The graph plotted showed a linear pattern of power produced with CO₂ composition present in the PEMFC. It proved that CO₂ existence in the PEMFC had a significant effect on PEMFC performance. CO₂ had obviously decreased the amount of power produced by PEMFC. The CO₂ 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 reaction products away from anode or cathode charge transfer interfaces. 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 CO₂ impurity in the fuel adsorbs weakly on the Pt catalyst [23]. At low CO₂ concentrations,

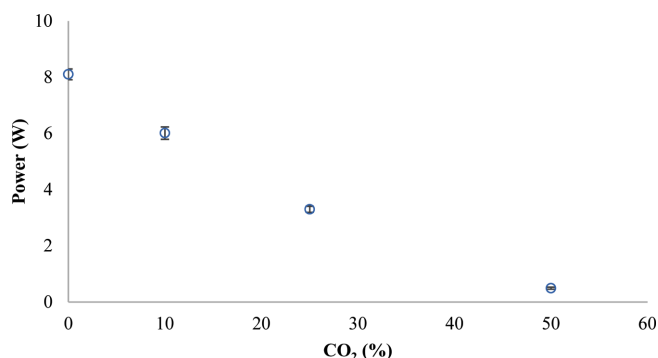


Fig. 7. Average maximum power of PEMFC with different CO₂ concentration.

the observed degradation in cell power can be explained on the basis of CO produced by the reverse water gas shift reaction (RWGSR) between CO₂ and the adsorbed H₂. At higher CO₂ concentrations, the decrease in cell potential due to the dilution of the H₂ also contributed to performance degradation. Therefore, it was essential to minimize the amount of CO₂ in the H₂ mixture in order to gain more power produced from PEMFC.

Hence, this study has revealed that different H₂ concentrations supplied into the PEMFC would present different performance on the current and power produced. It was also proven that bioH₂ separation using the absorption technique could give the best purification (close to 100% H₂ purity) and in turn, demonstrated higher capacity of current and power (1.66 A and 8 W) in comparison to membrane technique.

5. Conclusion

The absorption and membrane separation techniques were successfully investigated in H₂/CO₂ separation and purification process and the highly-purified H₂ was further utilized in fuel cell application. The observations and separation performance between two separation techniques were satisfactory. It could be concluded that MEA is the best alkaline solvent for absorption due to the high percentage of purified H₂ produced (99% for 1 M MEA). Meanwhile, PSF membranes had high H₂ permeance and H₂/CO₂ selectivity, which was obtained to be 13.08 GPU (at 2 bar) and 3.32 (at 8 bar), respectively. Absorption technique had better H₂ purity as the percentage of the purified H₂ was close to 100% purity, while for membrane technique, it was close to 80%. The highest current and power generated was 1.66 A and 8.1 W, respectively, from the feed mixture gas with 100%/0% of H₂/CO₂.

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