

Purification of biohydrogen from fermentation gas mixture using two-stage chemical absorption

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Abstract. Research on biohydrogen production via fermentation process has shown a tremendous progress for the past few years. As biohydrogen production is being established, the purification of biohydrogen should consider the process flow for future application. This paper presents an experimental study of biohydrogen purification using two-stage chemical absorption. The research work focuses on carbon dioxide (CO₂) removal, which is a major unwanted fermentation gas product *via* activated methyldiethanolamine (MDEA) and caustic (NaOH) in two-stage chemical absorption. The experiment was conducted at low pressure of 1 bar and normal room temperature of 29 °C using a ratio of 1:1 of CO₂:H₂ standard gas mixture as the feed. In the first stage, 40 wt. % MDEA was activated by using piperazine (PZ) with the concentration between 2 and 10 wt. %, whereas 20 wt. % NaOH was used in the second stage. It was found that 6 wt. % of PZ was required to fully activate 40 wt. % MDEA, which resulted in 79% CO₂ removal. To improve CO₂ removal, a gas distributor and wire mesh packed were used to create gas bubbles at higher geometrical surface. The experimental study successfully removed 99.59% of the total CO₂, producing >99 mol% hydrogen gas purity from the second stage that used 20 wt. % NaOH.

1 Introduction

Hydrogen (H₂) has been identified as a potential secondary source of energy, which is also termed as an energy carrier. The use of H₂ can reduce the dependency on fossil fuels. H₂ has the highest energy per unit mass of any known fuel. The energy per unit mass of H₂ is 141.9 J kg⁻¹, which is three times higher than gasoline that contains 47.4 J kg⁻¹ of energy [1]. H₂ produces only water, which makes it clean energy. There are many methods to produce H₂. For example, steam methane reforming, coal gasification, pyrolysis, biophotolysis, and fermentation. H₂ produced through fermentation has been the focus of many researchers as this process can utilise renewable resources such as biomass as the raw material, as well as it is environmentally friendly and has low energy consumption. From the literature, the

optimum biohydrogen production can be obtained *via* combination of dark and photofermentation processes. Morsy [2] produced a maximum of 56% H₂ and 44% CO₂ by integrating dark and photofermentation from sorghum starch. However, for biohydrogen to be used as a fuel for vehicle, it has to meet the ISO 14687-2 Hydrogen Fuel Specification that requires the minimum H₂ purity of 99.97 mol% [3]. Four techniques for purifying crude H₂ are cryogenic separation, absorption, adsorption, and membrane separation. These methods have been commercially used to purify conventional H₂. Biohydrogen is normally produced at the temperature between 30 and 60 °C and atmospheric pressure. Thus, chemical absorption is the most suitable technique for biohydrogen purification because it can be operated at low temperature and pressure.

Amine is one of the common solvents used in chemical absorption. Chemically, amine is a compound that contains nitrogen atom attached to hydrocarbon chain and/or hydrogen atom. From the industrial perspective, Kohl [4] expressed amine as a molecule that contains amino (-NH) group with at least one hydroxyl (-OH) group attached to it. The general functions of a hydroxyl group are to reduce the vapour pressure of a solvent so that it will not be easily vapourised and to increase the solvent solubility in water. Meanwhile, an amino group will create an alkaline environment in a solvent for the extraction of acid gases. In general, amines can be divided into primary, secondary, and tertiary amines. Primary amines are those with a nitrogen atom that is directly attached with two hydrogen atoms. For secondary amines, only one hydrogen atom is directly attached to nitrogen. In tertiary amines, no hydrogen atom is directly attached to nitrogen.

In CO₂ removal, tertiary amines such as methyldiethanolamine (MDEA) is normally used due its superiority compared to primary and secondary amines in terms of CO₂ loading capacity, less energy requirement for regeneration, thermal and oxidative stability (i.e., less degrade), and minimum amine loss due to low vapour pressure. The drawback of tertiary amines is slower absorption rate than primary and secondary amines. This is because it cannot react directly with CO₂. It must be hydrolysed before it can react with MDEA. The addition of an activator in the form of primary or secondary amine could overcome the drawback. The most commonly used activator is activated MDEA or piperazine (PZ)-MDEA mixture [5]. Hidayu [6] reported CO₂ loading of PZ-MDEA mixture of 1.32 mole CO₂ per mole amine, whereas the CO₂ loading of MDEA alone was 0.83 mole CO₂ per mole amine.

In this work, two-stage chemical absorption was adopted for the purification of biohydrogen. The biohydrogen was modelled by mixing pure H₂ and CO₂. The main objective was to absorb CO₂ for H₂ purification and achieve 99.9% purity. In the first stage, MDEA was used with the activation of PZ whereas in the second stage, the modelled biohydrogen gas was further purified with a caustic wash (NaOH).

2 Methodology

In this experiment, 50 mol% H₂ and 50 mol% CO₂ gas mixture was used. The ratio of mixture was chosen based on the common highest production obtained from the literature review. As for chemical solvents, 40 wt. % MDEA activated with different concentrations of PZ and 20 wt. % NaOH were utilised. The experimental setup is shown in Figure 1.

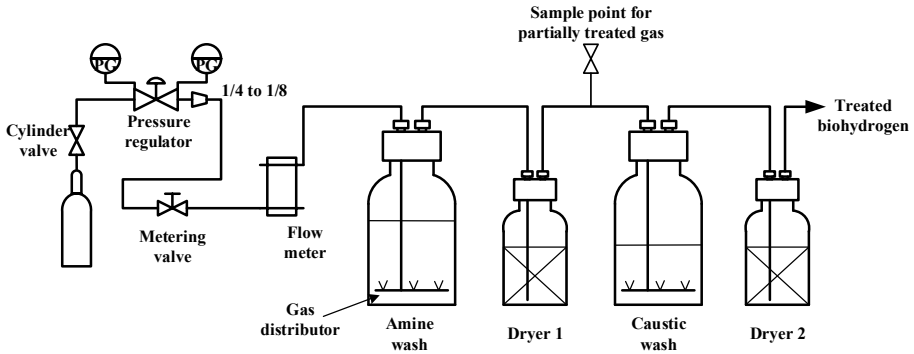


Fig. 1. Schematic diagram of experimental setup.

The experimental study was conducted in three parts as follows:

- Part 1: In assessing the effect of PZ concentration in MDEA solution towards CO_2 removal, only amine wash and dryer 1 were used. In this part, 40 wt. % MDEA activated with different PZ concentrations (2, 4, 6, 8, and 10 wt. %) were studied. In this part only, a gas distributor of 10.4 mm^2 was used.
- Part 2: Once the right amount of PZ required to activate 40 wt. % MDEA had been determined in Part 1, the effect of total surface contact area towards CO_2 removal was studied by using three different gas distributors that produced geometrical gas bubble area of 10.4, 7.7, and 6.3 mm^2 , respectively. In this part, only amine wash and dryer 1 were used.
- Part 3: In this final part of the experiment, the aim was to further improve CO_2 removal of the latter part by utilising packing in amine wash and the use of caustic wash as the second stage. The study was conducted for gas distributors of 10.4 and 6.3 mm^2 only. The packing specifications are shown in Table 1.

Table 1. Packing specifications.

| | |
|---|--|
| Packing Type | Commercial stainless steel spiral ball |
| Packed Diameter (m) | 0.095 |
| Packed Height (m) | 0.1058 |
| Surface Area (m^2) | 0.3948 |
| Volume (m^3) | 0.00075 |
| Ratio of Surface Area to Volume ($\text{m}^2 \text{ m}^{-3}$) | 526 |

3 Results and discussion

Figure 2 presents the results from Part 1 of the experimental study. There are two key points to be highlighted. First, in the absence of PZ as an activator, the process did not achieve any CO_2 removal. However, as 2 wt. % PZ was used to activate 40 wt. % MDEA, it significantly improved CO_2 removal by 40%. This is because CO_2 does not react directly with a tertiary amine such as MDEA. On the other hand, PZ is a secondary amine that reacts with CO_2 to form carbamate, which later takes part in base-catalysed hydration reaction between CO_2 and MDEA, producing bicarbonate and protonated MDEA.

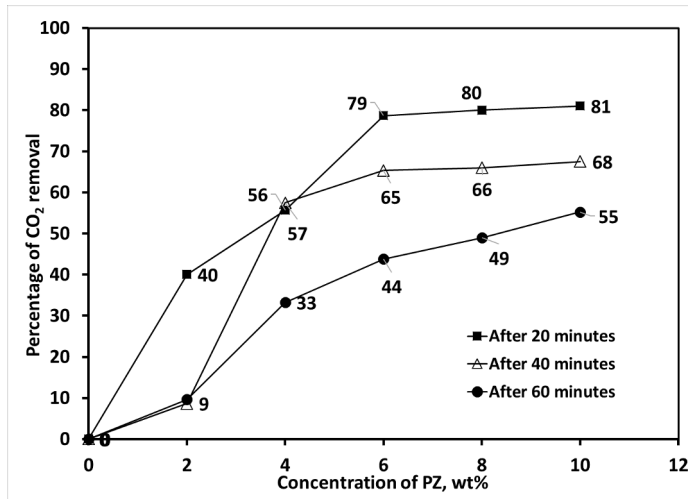


Fig. 2. The effect of 40 wt. % MDEA activated with different PZ concentrations (2, 4, 6, 8, and 10 wt. %) towards CO₂ removal.

Secondly, CO₂ removal improved significantly as the amount of PZ in MDEA was increased to 4 and 6 wt. %, where the removal was 56% and 79%, respectively. However, increasing PZ concentration beyond 6 wt. % had a minimal effect on CO₂ removal. For example, by increasing PZ concentration from 6 to 10 wt. %, only 2% improvement of CO₂ removal was observed. This is because at 6 wt. % PZ, there is a sufficient amount of PZ to transport CO₂ from the gas phase into the MDEA phase. As commented by Ibrahim *et al.* [7], once there is enough PZ molecules to transport CO₂, any increase in PZ concentration will not improve CO₂ removal significantly. Alvis *et al.* [8] in their simulation study on the effect of PZ concentration in MDEA stream towards CO₂ removal also raised the same indication. In their study, at 4 wt. % PZ concentration, 99.68% of CO₂ removal was achieved *via* a multi-stage absorption process. The concentration was lower by 2 wt. % compared to this study.

Based on Figure 3, at 20 min of experimental time, CO₂ removal with the gas distributor of 6.3 mm² was 67%. However, as the surface area was increased to 7.7 mm², which was an increase of 22%, the percentage of CO₂ removal increased to 72%. Increasing the surface area by 65% from 6.3 to 10.4 mm² improved CO₂ removal from 67% to 79%. This indicates that CO₂ removal can be improved by increasing the surface area.

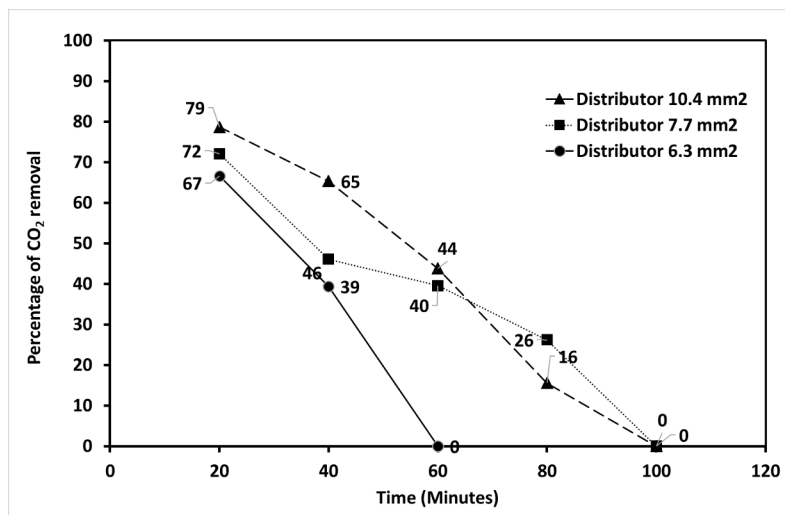


Fig. 3. Effect of total geometric surface area towards CO₂ removal (amine used = 40 wt. % MDEA activated with 6 wt. % PZ).

As the experiment was further continued, the gas distributor of 6.3 mm² was no longer able to reduce CO₂ at 60 min of running time. For the gas distributors of 7.7 and 10.4 mm², CO₂ removal achieved the maximum level at 100 min of running time. Based on the running time, it seemed a larger surface area prolonged CO₂ removal. Note that the same concentration of amine mixture was used for all three gas distributors and it was not replenished during the experiment. It could be anticipated that a lower surface area gas distributor should have longer running experimental time compared to higher surface area since it absorbs less CO₂. However, the opposite behaviour was observed in this experiment. The possible explanation for this behaviour relies on how gas bubbles are created by gas distributors. The gas distributor with surface area of 10.4 mm² consists of four holes with the diameter of 0.91 mm each, whereas the gas distributor with surface area of 7.7 mm² is made of five holes with 0.70 mm diameter each, and the gas distributor with surface area of 6.3 mm² has eight holes with 0.50 mm diameter each. In short, a gas distributor with a smaller surface area creates smaller gas bubbles than a gas distributor with a larger surface area. Due to this, it is suspected that smaller bubbles have higher velocity than bigger bubbles. This will reduce the residence time of the gas phase, hence reducing CO₂ removal. A detailed study might be required to prove this claim.

Figure 4 shows CO₂ removal with two different sizes of distributor at the amine wash stage with packing as carried out in Part 3 of the experiment. There are two key points to be highlighted. First, the utilisation of packing improved CO₂ removal as compared to Figure 3, which only utilised a gas distributor. For the gas distributors with surface area of 10.4 and 6.3 mm², the packing improved CO₂ removal by 6% and 14%, respectively. Second, as shown in Figure 4, despite different gases were used, the trend of CO₂ removal was almost similar, unlike Figure 3 that clearly shows different performance for different gas distributors. This indicates that the utilisation of packing has more significant effect towards CO₂ removal as compared to manipulating geometrical surface area.

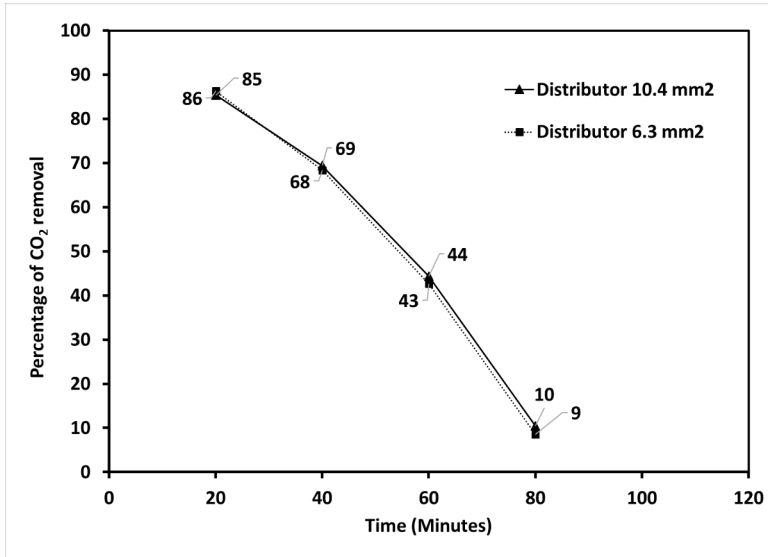


Fig. 4. CO₂ removal by utilising packing at amine wash.

Figure 5 presents CO₂ removal obtained from the continuation of experimental study, with 6 wt. % PZ in 40 wt. % MDEA was used in the first stage and 20 wt. % NaOH was used in the second stage. The addition of NaOH in the second stage significantly improved CO₂ removal and also prolonged high CO₂ removal as compared to the amine stage.

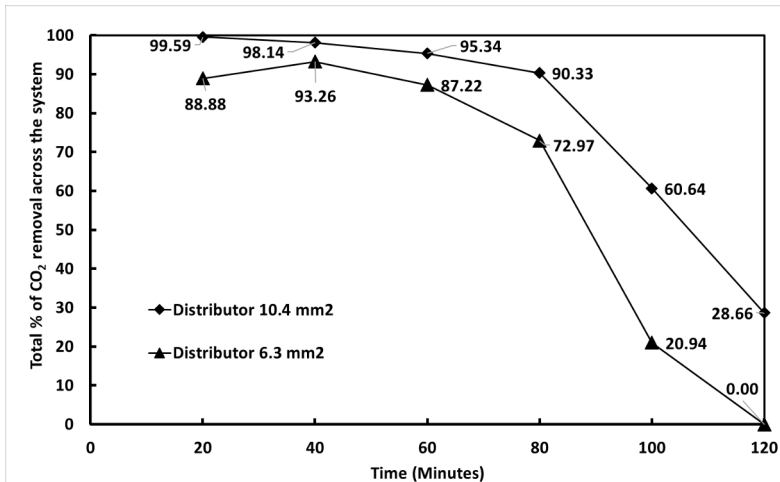


Fig. 5. Total CO₂ removal by utilising packing at amine wash towards CO₂ removal and the addition of second stage containing 20 wt. % NaOH.

4 Conclusion

In general, this work shows that a two-stage chemical absorption system using MDEA activated with PZ and NaOH has successfully purified the fermentation product of CO₂ and H₂ mixture up to 99 mol% hydrogen purity. Furthermore, the process is feasible to be carried out at ambient pressure and temperature.

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