BIOHYDROGEN PURIFICATION USING METHYLDIETHANOLAMINE AND CAUSTIC IN A TWO STAGE ABSORPTION SYSTEM

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ABSTRACT

As the research on biohydrogen production is growing, there is a need to explore the most suitable way to purify the biogas produced from the fermentation process so that pure biohydrogen can be obtained. The common biohydrogen gas composition produced from biological process is mainly hydrogen (H_2) and carbon dioxide (CO_2). The presence of CO_2 in biohydrogen will affect its application if biohydrogen is used in fuel cell application. In this work, solvent absorption was selected due to its simplicity and low cost. The CO_2 removal was performed by using two stage solvent absorption at which the activated methyldiethanolamine (MDEA) was used in the first stage and caustic (NaOH) in the second stage. The MDEA was activated by adding piperazine (PZ) into the MDEA solution. It was added to improve the reaction between CO_2 and MDEA. The operating pressure and temperature were 1 bar and 33°C respectively. The simulated untreated biohydrogen gas contained 50 mol% of H_2 and 50 mol% of CO_2. At first, 40 wt% MDEA was activated with different concentration of PZ and evaluated. It was found that 6 wt% of PZ was required to fully activate the 40 wt% MDEA. Next, the CO_2 removal was improved by implementing an improvised gas distributor at the first stage. Lastly, the CO_2 removal was further improved by utilizing a wire mesh packing at the first stage as to improve the contact area between the gas and the chemical solvent. At the same time caustic stage containing 20 wt% NaOH was added as the second stage. By doing so, the highest CO_2 removal achieved in this study at the first stage was 86% and 99.59% at the second stage, producing treated biohydrogen gas with purity of >99 mol%. Hence, this system has great potential to be used as a proper CO_2 removal system for biohydrogen gas produced by fermentation process.

ABSTRAK

Penyelidikan mengenai penghasilan biohidrogen kini kian berkembang, menyebabkan terdapatnya keperluan untuk meneroka cara yang paling sesuai bagi proses penulenan biogas yang dihasilkan dari proses penapaian, supaya biohidrogen tulen dapat diperolehi. Kebiasaannya, komposisi gas biohidrogen yang dihasilkan daripada proses biologi mengandungi terutamanya gas hidrogen (H_2) dan karbon dioksida (CO_2). Kehadiran CO_2 di dalam biohidrogen akan memberi kesan kepada penggunaannya terutama sekali jika ia digunakan dalam aplikasi sel bahan api. Di dalam kajian ini, penyerapan pelarut dipilih kerana ianya mudah dan berkos rendah. Penyingkiran CO_2 dilakukan dalam dua peringkat penyerapan pelarut di mana metildietanolamine (MDEA) teraktif digunakan pada peringkat pertama manakala kaustik (NaOH) digunakan pada peringkat kedua. MDEA diaktifkan dengan penambahan piperazine (PZ) ke dalam larutan MDEA. Larutan tersebut ditambah bagi meningkatkan tindakbalas di antara CO_2 dan MDEA. Tekanan dan suhu operasi masing-masing adalah 1 bar dan 33°C. Gas biohidrogen tidak dirawat yang digunakan mengandungi 50% mol H_2 dan 50% mol CO_2. Pada permulaannya, penilaian terhadap 40% berat MDEA diaktifkan dengan kepekatan PZ yang berbeza telah dilakukan. Didapati bahawa 6% berat PZ diperlukan untuk mengaktifkan sepenuhnya MDEA 40% berat. Seterusnya, penyingkiran CO_2 dipertingkatkan dengan menambahkan penyembur gas yang telah ditambahbaik pada peringkat pertama. Akhir sekali, penyingkiran CO_2 dipertingkatkan lagi dengan pengunaan kasa dawai pada peringkat pertama dengan tujuan untuk meningkatkan kawasan sentuhan antara gas dan pelarut kimia. Pada masa yang sama, kaustik yang mengandungi 20% berat NaOH telah ditambah sebagai peringkat kedua. Dengan berbuat demikian, penyingkiran CO_2 tertinggi yang dicapai dalam kajian ini adalah 86% di peringkat pertama dan 99.59% di peringkat kedua, menghasilkan gas biohidrogen terawat dengan ketulenan > 99% mol. Dengan itu, sistem ini sangat berpotensi untuk digunakan sebagai sistem penyingkiran CO_2 yang sesuai untuk gas biohidrogen yang dihasilkan oleh proses penapaian.

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INTRODUCTION

1.1 Background of Study

There has been rapid energy demand since 1970 which mainly satisfied by fossil fuels (World Energy Council, 2016). However, fossil fuels are non-renewable and will be depleted in near future. The use of fossil fuels caused various environmental problems since its utilization lead to the release of greenhouse gases. In response to this, many researches have been conducted to identify the alternatives to replace fossil fuels. One of the potential candidate identified to be an alternative energy is hydrogen. Hydrogen has the highest energy per unit mass of any known fuel. The specific energy of hydrogen is 141.9 MJ/kg which three times more than gasoline's (Debabrata et al., 2014). Moreover, hydrogen is considered as clean energy sources since its only produce water when it is being consumed as fuel in combustion chamber or as fuel cell.

According to Debabrata et al. (2014), current global hydrogen consumption is between 400 to 500 billion Nm^3 (Normal Cubic Meter) which is utilized for industrial purposes such as food, electronics, petrochemical and metallurgical. Only 3% is utilized as energy and it is expected to increase by 5 to 10% per year (Debabrata et al., 2014). World Energy Council (2013), in their report of 'World Energy Scenarios 2016: The Grand Transition' also stated that hydrogen utilization as fuel will increase by 29% by 2060.

Unlike fossil fuels, hydrogen is not readily available to be dig or harvested. It must be produced from other materials. Currently, around 96% of hydrogen is produced from fossil fuels using thermal processes (Debabrata et al., 2014). Among known issues in hydrogen production from fossil fuels are, they are not sustainable, requires high energy and high operating cost.

Hydrogen can be produced from water which is an abundance source. There are two methods at which hydrogen can be produced from water, either by electrolysis or photolysis. Electrolysis use electricity to split water into hydrogen and oxygen which lead to high operating and maintenance costs. Photolysis, on the other hand, uses bacteria in the presence of sunlight to breakdown water into hydrogen and oxygen. Though, the process is slow and hydrogen yield is small, by only 0.07 mmol H_2 L/minute of hydrogen can be produced (Rahman et al., 2016).

Hydrogen can also be produced from biomass by using thermochemical or biological processes. Thermochemical processes are much faster and offer higher stoichiometric yield of hydrogen. However, it requires high energy thus high operating cost. Whereas, biological processes are more environmental friendly and less energy intensive, as they operate under mild conditions (Nikolaidis & Poullikkas, 2017). Biological methods can be subdivided into three; biophotolysis, photofermentation and dark fermentation. Between the three methods, dark fermentation produces the highest biohydrogen yield (Debabrata et al., 2014). Hydrogen which is produced by microbes through biological activities such as biophotolysis and fermentation can be classified as biohydrogen. The various available processes to produce hydrogen is depicted in Figure 1.1.

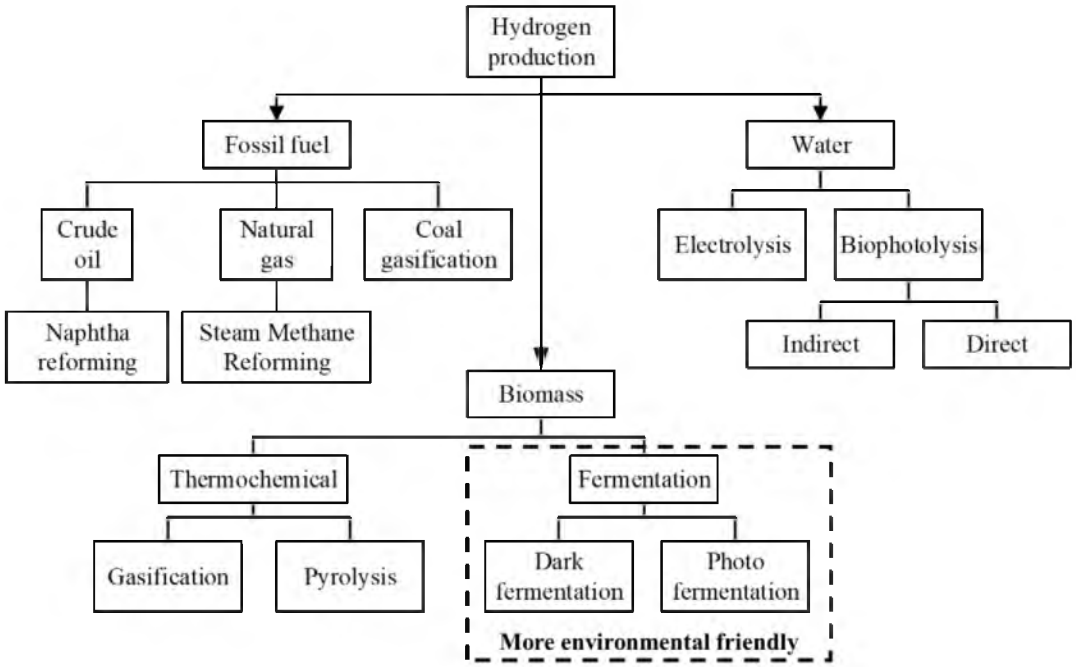

Figure 1.1 Various hydrogen production methods

Biohydrogen production development is moving towards maturity. Soon, downstream process such as biohydrogen purification should be ready. Biohydrogen purification process development should focus on developing a cheap and practical system. The most promising application of biohydrogen is fuel cell (Debabrata et al., 2014). However, fuel cell requires 99.9 % H_2 purity, 2 ppm CO and 0.004 ppm total sulfur (Murugan & Brown, 2015). On the other hand, most of the research on biohydrogen production reported their raw biohydrogen mainly contain H_2 and CO_2. Rahman et al. (2016) mentioned biohydrogen might also contain methane (CH_4), carbon monoxide (CO) and hydrogen sulfide (H_2S) in traces amount. The presence of CO_2 will reduce the fuel cell efficiency whereas CO and H_2S will poison the fuel cell stack as well as reducing the performance of the fuel cell (Rahman et al., 2016). The highest biohydrogen purity thus far was recorded by Morsy (2015a), which contain 56% H_2 and 44% CO_2. Prior to be used as fuel in fuel cell application, the raw biohydrogen must be purified. Thus, it is important to develop a system for biohydrogen separation and purification.

1.2 Problem Statement

In principle, there are four techniques to purify crude hydrogen, which are cryogenic separation, absorption, adsorption and membrane separation. These methods have been commercially used to purify conventional hydrogen. The issues are biohydrogen differ from conventional hydrogen in term of their gas composition and their physical state at the point of their production. For example, hydrogen produced from natural gas using steam methane reforming (SMR), at which the temperature and pressure of the hydrogen being produced is between 800 to 950 ^{0}C and 30 bar respectively. Whereas, biohydrogen is the gas yield of a bioreactor, hence its temperature is normally between 30 to 60 ^{0}C and the pressure is slightly above atmospheric pressure. Up to date, little research is being performed on biohydrogen purification especially in evaluating the most suitable technique to purify it.

Based on the literature review, four techniques of hydrogen purification have been studied in detail and screened. Theoretically, the absorption might be the most suitable technique to purify biohydrogen. The assumption has been made based on the possibility of operating at low pressure while producing high purity hydrogen. In absorption technique, chemical solvent such as amines is typically used. However, amines alone are insufficient to obtain 99.97 mol% hydrogen purity. Abdeen et al., (2016) in their paper on biogas upgrading using chemical absorption reported that various feed gas compositions containing methane (CH_4) between 51 to 79 % and carbon dioxide (CO_2) between 21 to 48 %, their CO_2 content were able to be reduced to between 1.3 to 10.0 %. Various types of amines were reported used in chemical solvent absorption technique. Among them is methyldiethanolamine (MDEA), a tertiary amine that has high CO_2 loading. So far, the absorption of CO_2 into MDEA is considered a slow process. This however can be overcome by adding an activator such as piperazine (PZ) into the MDEA solution.

Knowing that single stage chemical absorption using amines as solvent is not sufficient, a second polishing stage might be needed. In oil and gas refining

application, caustic wash is the most convenient solvent used for that purpose. Hence, this research will evaluate whether two stages absorption system is able to purify the raw biohydrogen which has higher CO_2 content, lower temperature and pressure when compare to conventional hydrogen.

1.3 Objective of Study

The main purpose of this work was to purify biohydrogen gas containing mainly CO_2 and H_2 to achieve purity of more than 99 mol% H_2. In achieving that, the following objectives were outlined:-

1) To predict the effect of operating at low pressure and temperature, and different piperazine (PZ) concentration as an activator in methyldiethanolamine (MDEA) stream towards CO_2 removal in a chemical absorption system by using ASPEN Hysys process simulator.
2) To verify experimentally the effect of piperazine (PZ) concentration as an activator in aqueous MDEA in a single stage chemical absorption towards CO_2 removal.
3) To evaluate the effect of gas distributor geometric surface area in a single stage absorption system containing activated MDEA towards CO_2 removal.
4) To evaluate the consequence of utilizing packed column in the first stage of absorption system containing activated MDEA and the addition of sodium hydroxide (NaOH) solution as the second stage towards the improvement of CO_2 removal

1.4 Scope of Study

Based on each objective, the scopes of the study are as follow:-

i) The simulation model was designed to treat 50 kmol/hour of 50 mol% H_2 and 50 mol% CO_2 using piperazine concentration between 0 to 10 wt% as an activator in 40 wt% MDEA in a chemical absorption system with a set pressure of 1 bar and set temperature of 30 °C. The MDEA concentration was fixed at 40 wt% so that only the effect of PZ towards CO_2 removal was studied and so that the total amine concentration did not exceed 50 wt% when 10 wt% PZ was studied.

ii) PZ concentration in 40 wt% MDEA solution was varied between 2, 4, 6, 8 and 10 wt%, in the experimental study of the effect of PZ concentration as an activator in aqueous MDEA in a single stage chemical absorption towards CO_2 removal. The inlet gas pressure was fixed at 1 bar and it was conducted at room temperature.

iii) In assessing the effect of gas distributor geographical surface area in amine solution containing PZ activated MDEA towards CO_2 removal, three different distributors were used. They were custom-made as follows:-
   a. 0.91 mm hole diameter with total of 4 holes
   b. 0.70 mm hole diameter with total of 5 holes
   c. 0.50 mm with total of 8 holes.

iv) In evaluating the effect of utilizing packing, stainless steel spiral ball was loaded into the first stage containing activated 40 wt% MDEA whilst 20 wt% NaOH was used as the second stage.

1.5 Significance of study

Regarding the high CO_2 content in crude biohydrogen, it is expected that this absorption technique will be the most suitable purification technique of biohydrogen. With this proposed method of two stages wet alkaline system (amines wash followed by sodium hydroxide wash), it is possible to produce high purity H_2 of >99% without even operating at high pressure such that in pressure swing adsorption (PSA) system which operates at 20 to 30 atm. This is mainly because bioreactor is normally operated at slightly above ambient pressure. Hence, only minor compression might be required to meet desired absorption pressure.

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