

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

NOR AZIRA BIN ABDUL MUIN

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Master of Philosophy

School of Chemical and Energy Engineering  
Faculty of Engineering  
Universiti Teknologi Malaysia

AUGUST 2019

## **ACKNOWLEDGEMENT**

First and foremost, I wish to express my deepest gratitude to my supervisor Dr Umi Aisah Binti Asli for accepting me as her student and giving me the chance to explore the academic world. Thanks to her patience and time spent in guiding and shaping me into a research student. This research wouldn't be completed without continuous advices and motivation from her.

I am also indebted to Universiti Teknologi Malaysia (UTM) for funding my research and for providing adequate facilities to conduct the research. Not to forget, special thanks to my fellow postgraduate students at Hydrogen Lab, Block N29 for their encouragement, kind support and motivation.

Lastly, I would like to extend my sincere appreciation to my wife and children for their kind understanding and support during the tenure of my research study.

## 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  $33^\circ C$  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  $33^\circ C$ . 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 penggunaan 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.

## TABLE OF CONTENTS

	<b>TITLE</b>	<b>PAGE</b>
	<b>DECLARATION</b>	<b>ii</b>
	<b>ACKNOWLEDGEMENT</b>	<b>iii</b>
	<b>ABSTRACT</b>	<b>iv</b>
	<b>ABSTRAK</b>	<b>v</b>
	<b>TABLE OF CONTENT</b>	<b>vi</b>
	<b>LIST OF TABLES</b>	<b>ix</b>
	<b>LIST OF FIGURES</b>	<b>x</b>
<b>CHAPTER 1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Background of Study	1
	1.2 Problem Statement	4
	1.3 Objectives of Study	5
	1.4 Scopes of Study	6
	1.5 Significance of Study	7
<b>CHAPTER 2</b>	<b>LITERATURE REVIEW</b>	<b>9</b>
	2.1 Biohydrogen as an Alternative Fuel	9
	2.1.1 Biohydrogen Production Through Biophotolysis	10
	2.1.2 Biohydrogen Production Through Fermentation	12
	2.1.2.1 Photofermentation	12
	2.1.2.2 Dark Fermentation	14
	2.1.2.3 Integrated Fermentation of Dark Fermentation and Photofermentation	15
	2.2 Biohydrogen Versus Conventional Hydrogen	15
	2.2.1 Gas Composition of Raw Biohydrogen versus Raw Conventional Hydrogen	16
	2.2.1.1 Steam Methane Reforming (SMR)	16
	2.2.1.2 Partial Oxidation (POx)	18

2.2.1.3	Coal Gasification	19
2.2.1.4	Gas Composition of Biohydrogen	21
2.2.2	Difference in Temperature and Pressure	22
2.3	Hydrogen Purification Technologies	23
2.3.1	Cryogenic Separation	24
2.3.2	Gas Separation by Adsorption	26
2.3.3	Membrane Separation	28
2.3.4	Gas Separation by Absorption	31
2.3.4.1	Chemical Solvent and Physical Solvent	32
2.4	Chemical Absorption for Biohydrogen Purification	33
2.4.1	Amines as Chemical Solvent	33
2.4.1.1	Primary, Secondary and Tertiary Amines	34
2.4.1.2	Piperazine as MDEA Activator	36
2.4.1.3	Reaction mechanism of PZ activated MDEA with CO <sub>2</sub>	37
2.4.2	Caustic Wash as Polishing Stage	41
2.4.2.1	Caustic or NaOH wash usage in CO <sub>2</sub> removal	42
<b>CHAPTER 3</b>	<b>METHODOLOGY</b>	<b>45</b>
3.1	Introduction	45
3.2	Developing the Simulation Model for CO <sub>2</sub> Removal by Using PZ Activated MDEA	46
3.3	Constructing the Experimental Rig	49
3.3.1	Customized Gas Distributor	51
3.3.2	Material for Random Packing	52
3.4	Performing the Experimental Study	53
3.4.1	Preparation of Chemical Solution	53
3.4.1.1	Preparing Solutions of 40wt% Methyldiethanolamine (MDEA) with Different Concentration of Piperazine	54
3.4.1.2	Preparing 20wt% Caustic (NaOH) Solution	55
3.4.2	Experimental of semi-batch absorption process	55

3.4.2.1	Effect of PZ Concentration in MDEA Solution Towards CO <sub>2</sub> Removal	55
3.4.2.2	Effect of Geometrical Surface Area Towards CO <sub>2</sub> Removal	56
3.4.2.3	Effect of Utilizing Packing and Caustic as Second Stage Towards CO <sub>2</sub> Removal	56
3.4.3	Analyzing CO <sub>2</sub> Content in Hydrogen	57
3.4.4	Determination of CO <sub>2</sub> composition	58
<b>CHAPTER 4</b>	<b>RESULT AND DISCUSSION</b>	<b>59</b>
4.1	Simulation of the Effect of PZ Concentration in MDEA Solution and Operating at Low Pressure and Temperature Towards CO <sub>2</sub> Removal	60
4.2	Experimental Results From Semi-Batch Absorption Process	65
4.2.1	Effect of PZ Concentration in MDEA Solution Towards CO <sub>2</sub> Removal	66
4.2.2	Effect of Total Geometrical Surface Area Towards CO <sub>2</sub> Removal	68
4.2.3	Effect of Utilizing Packing and Caustic as Second Stage Towards CO <sub>2</sub> Removal	70
4.2.3.1	Caustic Wash as Second Stage	72
<b>CHAPTER 5</b>	<b>CONCLUSION AND RECOMMENDATIONS</b>	<b>77</b>
5.1	Conclusion	77
5.2	Recommendations	78
	<b>REFERENCES</b>	<b>79</b>
	<b>LIST OF APPENDICES</b>	<b>84</b>

## LIST OF TABLES

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
Table 2.1	Summary of biohydrogen gas composition from other research studies	21
Table 2.2	Operating temperature and pressure of SMR, POx and gasification	23
Table 2.3	Boiling points of typical components in crude hydrogen stream produced from fossil fuels	24
Table 2.4	Reaction rate constant of different amines towards CO <sub>2</sub> absorption	37
Table 2.5	Example of caustic wash in oil and gas industry	42
Table 2.6	Research work using NaOH to treat biogas	43
Table 3.1	Summary of gas distributor specification	51
Table 3.2	Volume used to produce amine solution with 40wt% MDEA and different PZ concentration	54
Table 4.1	CO <sub>2</sub> removal performance with and without PZ as an activator from simulation by Alvis et al. (2012) and this study	63
Table 4.2	Comparison of CO <sub>2</sub> removal between this study and research by others	75



## LIST OF FIGURES

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
Figure 1.1	Various hydrogen production methods	3
Figure 2.1	Methods of biohydrogen production	9
Figure 2.2	Process flow diagram of a typical SMR	17
Figure 2.3	Process flow diagram of natural gas partial oxidation	19
Figure 2.4	Process flow diagram of coal gasifier	20
Figure 2.5	Phase diagram of CO <sub>2</sub>	25
Figure 2.6	Typical process flow diagram of cryogenic separation	26
Figure 2.7	Typical adsorbents arrangement of PSA	27
Figure 2.8	Commercial hydrogen membrane PRISM by Air Products	29
Figure 2.9	Mechanism of membrane separation	30
Figure 2.10	Typical process flow diagram of a gas absorption system	31
Figure 2.11	General chemical structure of primary, secondary and tertiary amines	34
Figure 2.12	Shuttle mechanism proposed by Optimized Gas Treating	40
Figure 2.13	Proposed reaction path for PZ regeneration and CO <sub>2</sub> transport into MDEA phase	41
Figure 3.1	Overall workflow of this research study	46
Figure 3.2	Process flow diagram of CO <sub>2</sub> removal system developed using ASPEN HYSYS version 9.0	48
Figure 3.3	Process flow diagram of experimental setup for batch chemical absorption process	49
Figure 3.4	Experimental rig of semi-batch absorption process	50
Figure 3.5	Pictures of customized gas distributor	52

Figure 3.6	Spiral ball used as packing in this study	53
Figure 3.7	Tedlar bag used for sample collection	57
Figure 4.1	Process flow diagram of CO <sub>2</sub> removal system developed using Aspen HYSYS version 9.1	61
Figure 4.2	Effect of different PZ concentration in 40 wt% MDEA stream towards percentage of CO <sub>2</sub> removal in simulation study	62
Figure 4.3	Effect of PZ concentration in MDEA stream for 50 wt% total amine concentration on CO <sub>2</sub> concentration in treated syngas	65
Figure 4.4	Performance of CO <sub>2</sub> removal at different PZ concentration from single stage amine wash (Gas distributor size = 10.4 mm <sup>2</sup> )	66
Figure 4.5	Effect of different bubble size towards CO <sub>2</sub> removal treated with amine solution containing 6 wt% PZ and 40 wt% MDEA	69
Figure 4.6	Effect of packing towards CO <sub>2</sub> removal	71
Figure 4.7	Amine foaming during experiment with packing	72
Figure 4.8	The effect of using caustic as polishing stage towards CO <sub>2</sub> removal	74

# CHAPTER 1

## 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<sup>3</sup> (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 dug 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<sub>2</sub> 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.

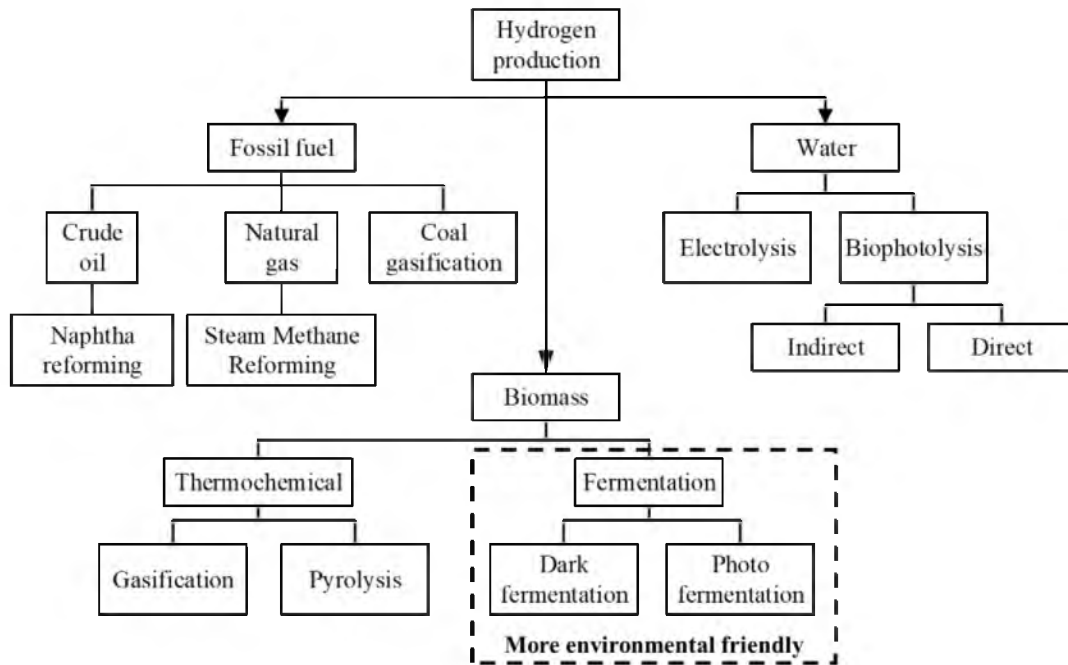


Figure 1.1 Various hydrogen production methods

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<sub>2</sub> 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<sub>2</sub> and CO<sub>2</sub>. Rahman et al. (2016) mentioned biohydrogen might also contain methane (CH<sub>4</sub>), carbon monoxide (CO) and hydrogen sulfide (H<sub>2</sub>S) in traces amount. The presence of CO<sub>2</sub> will reduce the fuel cell efficiency whereas CO and H<sub>2</sub>S 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<sub>2</sub> and 44% CO<sub>2</sub>. 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 °C and 30 bar respectively. Whereas, biohydrogen is the gas yield of a bioreactor, hence its temperature is normally between 30 to 60 °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<sub>4</sub>) between 51 to 79 % and carbon dioxide (CO<sub>2</sub>) between 21 to 48 %, their CO<sub>2</sub> 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<sub>2</sub> loading. So far, the absorption of CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> to achieve purity of more than 99 mol% H<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> removal.
- 3) To evaluate the effect of gas distributor geometric surface area in a single stage absorption system containing activated MDEA towards CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and 50 mol% CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 geometrical surface area in amine solution containing PZ activated MDEA towards CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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.

## LIST OF REFERENCES

- Abdeen, F. R. H., Mel, M., Jami, M. S., Ihsan, S. I., & Ismail, A. F. (2016). A review of chemical absorption of carbon dioxide for biogas upgrading. *Chinese Journal of Chemical Engineering*, 24(6), 693–702.
- Ahmad, N. A., Leo, C. P., Ahmad, A. L., & Mohammad, A. W. (2016). Separation of CO<sub>2</sub> from hydrogen using membrane gas absorption with PVDF/PBI membrane. *International Journal of Hydrogen Energy*, 41(8), 4855–4861.
- Akgün, F., Üresin, E., Saraç, H. İ., Sarioğlan, A., & Ay, Ş. (2014). An experimental study for H<sub>2</sub>S and CO<sub>2</sub> removal via Caustic scrubbing system. *Process Safety and Environmental Protection*, 94(June), 196–202.
- Akkerman, I., Janssen, M., Rocha, J., & Wijffels, R. H. (2002). Photobiological hydrogen production: Photochemical efficiency and bioreactor design. In *International Journal of Hydrogen Energy*.
- Alhseinat, E., Pal, P., Keewan, M., & Banat, F. (2014). Foaming study combined with physical characterization of aqueous MDEA gas sweetening solutions. *Journal of Natural Gas Science and Engineering*, 17, 49–57.
- Alvis, R. S., Hatcher, N. A., Weiland, R. H., & Rd, J. (2012). CO<sub>2</sub> Removal from Syngas Using Piperazine - Activated MDEA and Potassium Dimethyl Glycinate, (February), 20–23.
- Aslanzadeh, S., Ishola, M. M., Richards, T., & Taherzadeh, M. J. (2014). An Overview of Existing Individual Unit Operations. In *Biorefineries: Integrated Biochemical Processes for Liquid Biofuels* (pp. 3–36).
- Baghchehsaraee, B., Nakhla, G., Karamanev, D., & Margaritis, A. (2010). Fermentative hydrogen production by diverse microflora. *International Journal of Hydrogen Energy*, 35(10), 5021–5027.
- Bakonyi, P., Nemestóthy, N., & Bélafi-Bakó, K. (2013). Biohydrogen purification by membranes: An overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes. *International Journal of Hydrogen Energy*, 38(23), 9673–9687.

- Bakonyi, P., Nemestóthy, N., Lankó, J., Rivera, I., Buitrón, G., & Bélafi-Bakó, K. (2015). Simultaneous biohydrogen production and purification in a double-membrane bioreactor system. *International Journal of Hydrogen Energy*, *40*(4), 1690–1697.
- Barron, S. (1999). Cryogenic. In *CRC Handbook of Thermal Engineering* (pp. 4–407). CRC Press.
- Benemann, J. R. (2008). Biological production of H<sub>2</sub>: mechanisms and processes. In *Encyclopedia of Hydrocarbons* (Vol. III).
- Bharathiraja, B., Sudharsanaa, T., Bharghavi, A., Jayamuthunagai, J., & Praveenkumar, R. (2016). Biohydrogen and Biogas – An overview on feedstocks and enhancement process. *Fuel*, *185*, 810–828.
- Burr, B., & Lyddon, L. (2008). A comparison of physical solvents for acid gas removal. *GPA Annual Convention Proceedings*, *1*, 100–113.
- Camacho, F., Sánchez, S., Pacheco, R., La Rubia, M. D., & Sánchez, A. (2009). Kinetics of the reaction of pure CO<sub>2</sub> with N-methyldiethanolamine in aqueous solutions. *International Journal of Chemical Kinetics*, *41*(3), 204–214.
- Chew, L. W., Masdar, M. S., & Kamarudin, S. K. (2015). Purification of Bio-Hydrogen Using Absorption Techniques and the Effect of CO<sub>2</sub> Impurity on the PEMFC Performance, *5*, 24–34.
- Couchaux, G., Barth, D., Jacquin, M., Faraj, A., & Grandjean, J. (2013). Kinetics of Carbon Dioxide with Amines. I. Stopped-Flow Studies in Aqueous Solutions. A Review. *Oil & Gas Science and Technology – Revue d'IFP Energies Nouvelles*, *69*(5), 865–884.
- Damle, A. (2008). Hydrogen Separation and Purification. In *Hydrogen Fuel* (pp. 283–324). CRC Press.
- Debabrata, D., Namita, K., & Chitralkha Dasgupta, N. (2014). Biohydrogen Production Fundamentals and Technology Advances.
- Donaldson, T. L., & Nguyen, Y. N. (1980). Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes. *Industrial and Engineering Chemistry Fundamentals*, *19*(3), 260–266.
- Dunikov, D., Borzenko, V., Blinov, D., Kazakov, A., Lin, C. Y., Wu, S. Y., & Chu, C. Y. (2016). Biohydrogen purification using metal hydride technologies. *International Journal of Hydrogen Energy*, *41*(46), 21787–21794.

- Eroglu, E., & Melis, A. (2011). Bioresource Technology Photobiological hydrogen production : Recent advances and state of the art, *102*, 8403–8413.
- Felder, R., & Rousseau, R. (2005). *Elementary Principles of Chemical Processes. Chemical Engineering Journal* (Vol. 83).
- Ghalib, L., Ali, B. S., Ashri, W. M., Mazari, S., & Saeed, I. M. (2017). Modeling the effect of piperazine on CO<sub>2</sub> loading in MDEA/PZ mixture. *Fluid Phase Equilibria*, *434*, 233–243.
- Gilbert, J. J., Ray, S., & Das, D. (2011). Hydrogen production using Rhodospirillum rubrum (O.U. 001) in a flat panel rocking photobioreactor. *International Journal of Hydrogen Energy*.
- Gunardson, H. (1998). *Industrial gases in petrochemical processing. Chemical industries*. New York: Marcel Dekker.
- Gupta, R. B. (2009). *Hydrogen fuel: Production, Transport, and Storage. Solar Energy*.
- Hidayu, N., Rani, A., & Teknologi, U. (2015). Enhancement of Methylethanolamine (MDEA) absorption capacity for CO<sub>2</sub> capture using amine, (August).
- Ibrahim, A. Y., Ashour, F. H., Ghallab, A. O., & Ali, M. (2014). Effects of piperazine on carbon dioxide removal from natural gas using aqueous methyl diethanol amine. *Journal of Natural Gas Science and Engineering*, *21*, 894–899.
- Kamalaskar, L. B., Dhakephalkar, P. K., Meher, K. K., & Ranade, D. R. (2010). High biohydrogen yielding Clostridium sp. DMHC-10 isolated from sludge of distillery waste treatment plant. *International Journal of Hydrogen Energy*, *35*(19), 10639–10644.
- Keller, T., & Shahani, G. (2016). PSA technology: Beyond hydrogen purification. *Chemical Engineering*, *123*(1), 50–53.
- Khan, A. A., Halder, G. N., & Saha, A. K. (2017). Experimental investigation on efficient carbon dioxide capture using piperazine (PZ) activated aqueous methyldiethanolamine (MDEA) solution in a packed column. *International Journal of Greenhouse Gas Control*, *64*(February), 163–173.
- Kohl, A. L., & Nielsen, R. B. (1997). Chapter 15 - Membrane Permeation Processes. In *Gas Purification* (pp. 1238–1295).
- Kohl, A., & Nielsen, R. (1997). Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal. *Gas Purification*, 40–73.

- Li, P., Wang, Z., Qiao, Z., Liu, Y., Cao, X., Li, W., ... Wang, S. (2015). Recent developments in membranes for efficient hydrogen purification. *Journal of Membrane Science*, *495*, 130–168.
- Li, T., & Keener, T. C. (2016). A review: Desorption of CO<sub>2</sub> from rich solutions in chemical absorption processes. *International Journal of Greenhouse Gas Control*, *51*, 290–304.
- Mbodji, M., Commenge, J. M., Falk, L., Di Marco, D., Rossignol, F., Prost, L., ... Del-Gallo, P. (2012). Steam methane reforming reaction process intensification by using a millistructured reactor: Experimental setup and model validation for global kinetic reaction rate estimation. *Chemical Engineering Journal*, *207–208*, 871–884.
- Moon, D. K., Lee, D. G., & Lee, C. H. (2016). H<sub>2</sub> pressure swing adsorption for high pressure syngas from an integrated gasification combined cycle with a carbon capture process. *Applied Energy*, *183*, 760–774.
- Morsy, F. M. (2015). CO<sub>2</sub> free biohydrogen production by mixed dark and photofermentation bacteria from sorghum starch using a modified simple purification and collection system. *Energy*, *87*, 594–604.
- Nagarajan, D., Lee, D. J., Kondo, A., & Chang, J. S. (2017). Recent insights into biohydrogen production by microalgae – From biophotolysis to dark fermentation. *Bioresource Technology*, *227*(1), 373–387.
- Nikolaidis, P., & Poullikkas, A. (2017). A comparative overview of hydrogen production processes. *Renewable and Sustainable Energy Reviews*, *67*, 597–611.
- NirmalVGnanapragasam, BaleVReddy, & Rosen, M. (2014). Hydrogen Production Using Solid Fuels. *Handbook of Hydrogen Energy*, 61–112.
- Optimized Gas Treating. (2008). Piperazine - Why It's Used and How It Works. *The Contactor - Optimized Gas Treating, Inc*, *2*(4), 2. Retrieved from [http://www.ogtrt.com/files/contactors/vol\\_2\\_issue\\_4.pdf](http://www.ogtrt.com/files/contactors/vol_2_issue_4.pdf)
- Radebaugh, R. (2007). Historical Summary of Cryogenic Activity Prior to 1950. In K. D. Timmerhaus & R. P. Reed (Eds.), *Cryogenic Engineering* (pp. 3–27). New York, NY: Springer New York.
- Rahman, S. N. A., Masdar, M. S., Rosli, M. I., Majlan, E. H., Husaini, T., Kamarudin, S. K., & Daud, W. R. W. (2016). Overview biohydrogen technologies and application in fuel cell technology. *Renewable and Sustainable Energy Reviews*, *66*, 137–162.

- Ramírez-Morales, J. E., Tapia-Venegas, E., Nemestóthy, N., Bakonyi, P., Bélafi-Bakó, K., & Ruiz-Filippi, G. (2013). Evaluation of two gas membrane modules for fermentative hydrogen separation. *International Journal of Hydrogen Energy*, 38(32), 14042–14052.
- Sari, A. (2017). Chemical Engineering Research and Design A theoretical study on high pressure partial oxidation of methane in Rh-washcoated monoliths, *1*, 134–148.
- Schröder, C., Selig, M., & Schönheit, P. (1994). Glucose fermentation to acetate, CO<sub>2</sub> and H<sub>2</sub> in the anaerobic hyperthermophilic eubacterium *Thermotoga maritima*: involvement of the Embden-Meyerhof pathway. *Archives of Microbiology*, 161(6), 460–470.
- Shenoy, T. A. (1980). Cryogenic process for separating synthesis gas. Google Patents. Retrieved from <https://www.google.com/patents/US4217759>
- Smit, B., A.Reimer, J., Oldenburg, C. M., & Bourg, I. C. (2014). *Introduction to Carbon Capture and Sequestration*. Imperial College Press.
- Voldsund, M., Jordal, K., & Anantharaman, R. (2016). Hydrogen production with CO<sub>2</sub> capture. *International Journal of Hydrogen Energy*.
- World Energy Council. (2013). World Energy Resources 2016. *2013 Survey, 2007*.
- World Energy Council (WEC). (2016). World Energy Scenarios 2016 - The Grand Transition, 138.
- Yin, H., & Yip, A. C. K. (2017). A Review on the Production and Purification of Biomass-Derived Hydrogen Using Emerging Membrane Technologies. *Catalysts*, 7(10), 297.
- Ying, J., Raets, S., & Eimer, D. (2017). The Activator Mechanism of Piperazine in Aqueous Methyldiethanolamine Solutions. *Energy Procedia*, 114(November 2016), 2078–2087.
- Yu, J., & Takahashi, P. (2007). Biophotolysis-based Hydrogen Production by Cyanobacteria and Green Microalgae. *Communicating Current Research and Educational Topics and Trends in Applied Microbiology*, 1, 79–89.
- Zakkour, P., & Cook, G. (2010). CCS Roadmap for Industry: High-purity CO<sub>2</sub> sources, (September).
- Zhao, Q., Leonhardt, E., MacConnell, C., Frear, C., & Chen, S. (2010). Purification Technologies for Biogas Generated by Anaerobic Digestion. *Compressed Biomethane, CSANR, Ed*, 24.