HYDROGEN RECOVERY FROM THE REFORMING GAS USING COMMERCIAL ACTIVATED CARBON

MEHDI RAHMANIAN

A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

MAY 2014

Specially dedicated to my parents, sister and wife, for their love and support

ACKNOWLEDGEMENT

In preparing this dissertation, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my supervisor, Dr. Tuan Amran Tuan Abdullah, for encouragement, guidance, critics and friendship. I am also very thankful to my friend Abdoullatif Gharibi for his guidance, advices and motivation.

My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them. I am deeply grateful to all my family members.
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ABSTRACT

Hydrogen recovery from reforming gas products was investigated using commercial activated carbon in an adsorption column. The commercial activated carbon obtained from market that used for drinking water treatment was applied in this work. In the first part of this study, the effect of treated process of activated carbon by acetic acid, ammonia and steam on hydrogen recovery was studied. In the adsorption study, pressure was increased from atmospheric pressure 1 to 6 bar to investigate the amount of gas adsorbed on fresh activated carbon. In the desorption study, the effects of decreasing pressure was investigated as well. The effect of particle size on the efficiency of hydrogen recovery was emphasis in this study. The results from the experiments indicated that commercial activated carbon was a good candidate for hydrogen recovery because no hydrogen that was adsorbed by activated carbon during our experiments. The recovery of hydrogen was improved to 30.64% and CO_2 was the highest adsorbed compared other gases. The results proved that, a small particle size (171μm) has better performance in comparison to other particle sizes. The activated carbon treated with steam showed the best performance on the hydrogen recovery

ABSTRAK

Pemulihan hidrogen daripada pembaharuan produk gas telah kaji menggunaka karbon teraktif komersial dalam kolum penjerapan. Karbon teraktif komersil diperolehi dari pasaran yang digunakan untuk minum rawatan air telah digunakan dalam kajian ini. Dalam bahagian pertama kajian ini, kesan daripada proses penjanaan semula karbon diaktifkan oleh asid asetik, ammonia dan air pemulihan hidrogen telah dikaji. Dalam kajian penjerapan, tekanan ditingkatkan daripada tekanan atmosfera 1 kepada 6 bar untuk menyiasat jumlah gas yang terserap ke karbon diaktifkan segar. Dalam kajian nyahpenyerapan, kesan mengurangkan tekanan juga disiasat. Kesan saiz zarah terhadap kecekapan pemulihan hidrogen adalah perkara yang ditekankan dalam kajian ini. Keputusan daripada eksperimen kami menunjukkan bahawa karbon teraktif komersial adalah penjerap yang baik untuk pemulihan hidrogen kerana tiada hidrogen yang terserap oleh karbon diaktifkan semasa ujikaji. Pemulihan hidrogen telah meningkat kepada 30.64% dan CO_2 adalah terjerap tertinggi gas lain dibandingkan. Keputusan juga menunjukkan bahawa, saiz zarah kecil (171µm) mempunyai prestasi yang lebih baik berbanding dengan saiz zarah lain. Karbon diaktifkan rawatan yang diterima wap menunjukkan prestasi yang terbaik kepada pemulihan hidrogen.

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LIST OF SYMBOLS

AC	-	Activated Carbon
BET	-	Brunaue, Emmett, Teller
CAC	-	Commercial Activated Carbon
CH_4	-	Methane
C_2H_4	-	Ethylene
C_2H_6	-	Ethane
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
Eq.	-	Equation
H_2	-	Hydrogen
IEA	-	International Energy Agency
N_2	-	Nitrogen
PSA	-	Pressure swing adsorption
RSM	-	Response Surface Methodology
RT	-	Room Temperature
SMR	-	Steam Methane Reformation
TCD	-	Thermal Conductivity Detector
TPD	-	Temperature Programmed Desorption
TPD-MS	-	Temperature Programmed Desorption-Mass Spectrometer

LIST OF ABBREVIATION

%	-	Percent
ΔH	-	Enthalpy
KJ	-	Kilojoule
mol	-	Mole
k°	-	Kelvin
C°	-	Centigrade
g	-	Gram
m^2	-	Square meter
ml	-	Milliliter
bar	-	Bar
min	-	Minute
Sccm	-	Standard Cubic Centimeters Per Minute
μl		microlitter
μm		micromilimeter

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Global energy demand is rising and increasing in the future. The International Energy Agency (IEA) estimate that the growth of 40% in energy consumption by 2030 based on the current trends and about 20% in a scenario where emissions are sharply constrained (Carley, 2009).

IEA anticipates that fossil fuels will still be dominant until years of 2030 even with the limitation of carbon emissions over the next two decades. New technologies in the future will continue to open up previously unreachable supplies of natural gas, crude oil and other fossil fuels. However, the sources of fossil fuel are decreasing and BP's analysis implies that "plentiful energy resources exist to meet growing global demand. Proved reserves offer enough oil to last around 40 years and enough gas for around 60 years at today's consumption rates" (Carley, 2009). From this, it can be obviously seen that the fossil fuel will be finished up by human being in the future (Carley, 2009).

Hydrogen is a promising candidate for the energy carrier. The lower cost to product hydrogen is through steam reforming. Instead of hydrogen, carbon dioxide, methane, and small amount of carbon monoxide, ethylene and ethane are found from the reforming of any liquid hydrocarbon. A pressure swing adsorption is the common technology for purifying the hydrogen product from the reforming gas. Molecular sieve 5A, zeolite and activated carbon are main absorber materials for the process.

Activated carbon is known to have a capability to absorb the hydrocarbon such as methane, ethylene and ethane. The amount of the adsorption is depend on the pore size, surface area and its activation size.

1.2 Problem statement

Hydrogen is a component of many important compounds also hydrogen is a promising energy to replace fossil energy and plays an important role in future energy systems. Since hydrogen is the lightest components and highly dangerous gas, transportation of the gas to fueling station is difficult. In future, if is possible to produce a small scale or in-situ production rather than big production at a petrochemical plant. A purification of hydrogen from reformate gas is critical for certain application such as polymer membrane fuel cell. In order to make a purification of hydrogen possible, low cost process and material are needed.

Commercial activated carbon for drinking water is sold widely even can be found in the grocery store. From the knowledge, until date, no study or limited on this commercial activated carbon for hydrogen separation specifically in the literature. Therefore, this activated carbon is a good candidate to study for this process.

1.3 Objective of study

The objectives of this study are:

i. To characterize the physical properties of activated carbon (total surface area and pore size) using BET surface analyzer.

ii. To evaluate the performance of the activated carbon adsorption hydrocarbon from the artificial reforming gases on different pressure range 1 to 6 bar and the particle size (1000 µm, 510 µm and 171µm) .

iii. Treatment the activated carbon with steam acetic acid and ammonia were studied on adsorption and desorption as well.

1.4 Scope of study

The scopes of study in this study are:

i. The commercial activated carbon that used for drinking water in the market will be obtained in this study and will be characterized physically using the BET-nitrogen surface area.

ii. Adsorption pressure was varied from 1 to 6 bar, and desorption pressure reverse from 6 to 1 bar

iii. The activated carbon were treated using steam, ammonia and acetic acid.

1.5 The significant of the study

Small scale hydrogen production requires low cost process and material. Low pressurize gas is reasonable for a small scale hydrogen production. To meet this requirement, this study is important to evaluate the capability of the commercial activated carbon. The commercial hydrogen is consider cheap and easy to obtain from the market. This research also contributes some knowledge on the commercial activated carbon for the hydrogen recovery.

REFRENCES

Adhikari, S., and Fernando, S. (2006). Hydrogen membrane separation techniques. *Industrial & Engineering Chemistry Research*, *45*(3), 875-881.

Atkinson, D., McLeod, A. I., and Sing, K. S. W. (1984). Adsorptive Properties of Microporous Carbons-Primary and Secondary Micropore Filling. *Journal De Chimie Physique Et De Physico-Chimie Biologique*, *81*(11-1), 791-794..

Bansal, R.C. and Goyal, M. (2005).*Activated Carbon Adsorption*.CRC Press – Taylor & Francis Group, Boca Raton.

Bockris, J.O.M., and Khan, S.U. (1993). *Surface Electrochemistry*. New York: Plenum Press;. p. 280–3

Brunauer, S., Emmett, P. H., and Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*(2), 309-319.

Carley, S. (2009). State renewable energy electricity policies: An empirical evaluation of effectiveness. *Energy Policy*, *37*(8), 3071-3081

Dormant, L. M., and Adamson, A. W. (1968). Physical adsorption behavior of molecular solids. *Journal of Colloid and Interface Science, 28*(3), 459-465.

Geankoplis, C. (2003). *Transport processes and separation process principles (includes unit operations)*. Prentice Hall Press.

Gregg S. J. and Sing, K. S. W. (1982). Adsorption, Surface Area, and Porosity , 2nd ed., Aca-demic Press, London, , 303 pp. An indispensable text on the interpretation and significance of adsorption data

Hassler J. W.(1963). Activated Carbon. Chemical Publishing Co., Inc., New York, 1963, 1– 14. A comprehensive account of the development and use of activated carbon pro-ducts to about 1960

Jorge H. Foglietta, Paul Milios, FereidounYamin (2005). *Cryogenic process for increased recovery of hydrogen*, US: AbbLummus Global, Inc.

Kisliuk, P. (1957). The sticking probabilities of gases chemisorbed on the surfaces of solids. *Journal of Physics and Chemistry of Solids*, *3*(1), 95-101.

Langmuir, I. (1916). The Mechanism of The Reaction. *Journal of the American Chemical Society 38* (11): 2221–2295.

Lee, J. J., Kim, M. K., Lee, D. G., Ahn, H., Kim, M. J., and Lee, C. H. (2008). Heat-exchange pressure swing adsorption process for hydrogen separation.*AIChE journal*, *54*(8), 2054-2064.

Lopes, F. V., Grande, C. A., Ribeiro, A. M., Oliveira, E. L., Loureiro, J. M., and Rodrigues, A. E. (2009). Enhancing capacity of activated carbons for hydrogen purification. *Industrial & Engineering Chemistry Research*, *48*(8), 3978-3990

Lu, Q., and Sorial, G. A. (2004). The role of adsorbent pore size distribution in multicomponent adsorption on activated carbon. *Carbon*, *42*(15), 3133-3142

Martin, R. J., and Ng, W. J. (1987). The repeated exhaustion and chemical regeneration of activated carbon. *Water research*, *21*(8), 961-965.

Marsh H. and Butler,J., Unger, J.,Rouquerol, K.K., Sing,K. S. W. and H. Kral,eds. (1988). Characterization of Porous Solids. Proceedings of the IUPAC Symposium(COPS I), Bad Sodena.Ts., FRG, Apr. 26–29, 1987, Elsevier, Amsterdam, The Neth-erlands, 139–149.

Marsh, H., Crawford, D., O'Grady, T. M., and Wennerberg, A. (1982). Carbons of high surface area. A study by adsorption and high resolution electron microscopy. *Carbon*, *20*(5), 419-426.

McEnaneyB.,Mays,T. J. and Marsh,H. (1989).Intro*duction to Carbon Science*. Butterworth’s, London, 153–196.

Miguel, G. S., Lambert, S. D., & Graham, N. J. D. (2001). The regeneration of field-spent granular-activated carbons. *Water research*, *35*(11), 2740-2748.

Miller, GQ. and Stocker, J. (1989).*Selection of a Hydrogen Separation Process*. No. CONF-8903125--. Washington, DC; National Petroleum Refiners Association, 1989.

Rodriguez-Reinoso, F. (1997). Activated carbon: structure, characterization, preparation and applications. *Introduction to carbon technologies*, 60

Peramanu, S., Cox, B. G., & Pruden, B. B. (1999). Economics of hydrogen recovery processes for the purification of hydroprocessor purge and off-gases.*International Journal of Hydrogen Energy*, *24*(5), 405-424.

Rabiei, Z.(2012). Hydrogen Management In Refineries. *Petroleum & Coal 2012; 54*(4) .

Sing K. S. W. and Co-workers. (1985).*Reporting Physisorption Data For Gas/Solid Systems With Special Reference to The Determination of Surface Area and Porosity*. Pure Appl. Chem. 57, 603–619

Sircar, S., & Golden, T. C. (2000). Purification of hydrogen by pressure swing adsorption. *Separation Science and Technology*, *35*(5), 667-687.

Slejko, F.L. (1985). *Adsorption Technology*. Marcel Dekker, New York, pp. 1–36.

Whysall, M., and Picioccio, K. W. (1999). *Selection and revamp of hydrogen purification processes*. American Institute of Chemical Engineers.

Yang, J., Han, S., Cho, C., Lee, C. H., and Lee, H. (1995). Bulk separation of hydrogen mixtures by a one-column PSA process. *Separations Technology*,*5*(4), 239-249.