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H2S ADSORPTION FROM BIOGAS USING NATURAL CLINOPTILOLITE

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By

HAMED POURZOLFAGHAR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2012

Dedicated to

My dearest parents

For *their endless love, support and encouragement*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

H_2S ADSORPTION FROM BIOGAS USING NATURAL CLINOPTILOLITE

By

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October 2012

Chairman: Associate Professor Mohd. Halim Shah Ismail, PhD

Faculty: Engineering

Adsorption of H_2S by solids fixed in a bed column is the most efficient, environmental friendly, and economical process compared to other technologies. It can be studied through three different approaches; (1) Modeling (2) Laboratory scale experiments and (3) Pilot scale experiments. Many laboratorial scale experiments proved that the Clinoptilolite is a promising medium to be used as an adsorbent of H_2S from gas streams at low temperatures whereby few of them are focused to inspect usage of this material in its natural form. Using natural Clinoptilolite may results into a dramatic decrease of the adsorption process costs if its efficiency and performance during the process could be satisfied. In this study, H_2S removal efficiency of Clinoptilolite is surveyed at ambient temperature and atmospheric pressure during experiments on a biogas produced directly from an anaerobic digester. An adsorption column unit designed and fabricated for this study by

ASEPTIC Sdn Bhd contains three fixed bed columns, flow rate and pressure control, and gas sampling systems. The experiments can be categorized into two main subjects; (1) Key experiments (2) Supplementary experiments. The key experiments results show that according to the developed optimized conditions of the process, adsorption efficiency is 43.44%. This adsorption efficiency rate could be increased up to 94% at supplementary experiments by applying the time duration between the experiments. Other process characteristics like intrinsic regeneration and CH_4/CO_2 upgrading ratio were interpreted using analytical equipment results like FTIR, EDX, SEM, BET and XRD. Besides, in order to catch a relationship between different parameters and measured experimental data, a data fitting was performed using Microsoft Excel software.

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Abstrak tesis yan dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Master Sains

H_2S PENJERAPAN DARIPADA BIOGAS MENGGUNAKAN CLINOPTILOLITE ASLI

Oleh

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Oktober 2012

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Penjerapan H_2S oleh pepejal tetap dalam turus adalah proses yang paling cekap, mesra alam, dan murah berbanding teknologi-teknologi lain. Ia dapat dikaji melalui tiga pendekatan berbeza; (1) Permodelan (2) Eksperimen berskala makmal dan (3) Eksperimen berskala loji pandu. Banyak eksperimen berskala makmal membuktikan yang Clinoptilolite ialah satu medium yang sesuai untuk digunakan sebagai bahan penjerap H_2S daripada aliran gas pada suhu rendah di mana beberapa Clinoptilolite ditumpukan untuk mengkaji kegunaan bahan ini dalam bentuk semula jadinya. Penggunaan Clinoptilolite semula jadi boleh menyebabkan penurunan yang dramatik terhadap kos proses penjerapan jika kecekapan dan prestasi semasa proses penjerapan adalah memuaskan. Dalam kajian ini, kecekapan penyingkiran H_2S menggunakan Clinoptilolite dikaji pada suhu ambien dan tekanan

atmosfera semasa eksperimen terhadap penghasilan biogas secara langsung daripada pencernaan anaerobik. Unit turus penjerapan untuk kajian ini, difabrikasi oleh ASEPTIC Sdn Bhd mengandungi tiga turus tetap, kadar aliran dan pengawal tekanan , dan system pensampelan gas. Eksperimen tersebut dapat dikategorikan kepada dua subjek penting; (1) Eksperimen utama (2) Eksperimen tambahan. Eksperimen utama menunjukkan bahawa, kecekapan penjerapan adalah 43.44% berdasarkan keadaan optimum proses tersebut. Kadar kecekapan penjerapan ini boleh ditingkatkan kepada 94% semasa eksperimen tambahan dengan menggunakan tempoh masa antara kedua-dua eksperimen. Selain itu, data yang diperolehi daripada eksperimen tambahan adalah sangat berguna dan boleh di applikasikan untuk meningkatkan proses penjerapan ini. Ciri-ciri proses lain seperti penjanaan semula intrinsik dan menaiktaraf nisbah CH_4/CO_2 ditafsir dengan menggunakan peralatan analisis seperti FTIR, EDX, SEM, BET and XRD. Selain itu, dalam usaha untuk memahami satu hubungan antara parameter yang berbeza dan data eksperimen yang diukur, kajian data pemasangan telah dijalankan menggunakan perisian Microsoft Excel.

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I certify that an Examination Committee has met on 11 October 2012 to conduct the final examination of Hamed Pourzolfaghar on his Master of Science thesis entitled "H_2S adsorption from biogas using natural Clinoptilolite" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

HAMED POURZOLFAGHAR

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Notations / symbols

Å	Angstrom/Unit of length	10^{-10} m
A	Adsorbent surface area	m^2g^{-1}
A	Differential molar work or the change of Gibbs free energy (ΔG) or the adsorption potential [A= -RT (P/P^o)]	kJ mol^{-1}
a	Constant of trendline equation achieved from experimental results of C_{out}/C_{in} vs. $time^{-1}$ for different material sizes of adsorbent	
a_0	Correlated value of a	
a_1	Correlated value of a	
σ_{N2}	The projected area covered by a nitrogen molecule (0.162 nm^2)	
β	Affinity coefficient	
θ	Portion of the bed saturated	
b	Affinity constant or Langmuir constant being a function of temperature	
b	Constant of trendline equation achieved from experimental results of C_{out}/C_{in} vs. $time^{-1}$ for different material sizes of adsorbent	
B_0	Correlated value of b	
b_1	Correlated value of b	
C	Constant	
C_e	Equilibrium concentration of the adsorbate after the adsorption	mg/L
c	Constant of trendline equation achieved from experimental results of C_{out}/C_{in} vs. $time^{-1}$ for different flow rates of the biogas	
c_0	Correlated value of c	

c_1	Correlated value of c	
D	Adsorbent diameter	cm
d	The distance between different planes of atoms in the crystal lattice	nm
d	Constant of trendline equation achieved from experimental results of C_{out}/C_{in} vs. time^{-1} for different flow rates of the biogas	
d_0	Correlated value of d	
d_1	Correlated value of d	
E_0	Characteristic adsorption energies	kJ mol^{-1}
K_f	Freundlich constants	
l	The wavelength of the X-Rays	nm
l	The actual length of the bed	cm
l'	Length of the unused bed	
n	An integer	
n	Freundlich constants	
N_{AV}	The Avogadro number (6.02×10^{23} mol^{-1})	
P	The equilibrium pressure of the adsorption	ppm
P^o	The Vapor pressure of the adsorbate	ppm
Q	The volumetric flow rate	
q	The angle of diffraction	degrees
R^2	R-squared	
t_B	Time at breakthrough	min
t_E	The adsorbent saturation time	min
V	The Volume of the adsorbed gas at equilibrium	mg/L

V_m	The Volume of the adsorbed gas required to cover the surface of the adsorbent with a single layer of molecules (a monolayer)	$molg^{-1}$
V_m	The amount of monolayer coverage	
W	The volume of the gas adsorbed	$molg^{-1}$
W_0	Total volume of the micropore	cm^3g^{-1}
X	Relative pressure (P/P^o)	
y	The outlet gas concentration	ppm
y_0	The inlet gas concentration	ppm

AC	Activated carbon
AZ	Adsorption zone
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BOD	Biochemical oxygen demand
DOE	Department of environment
EDX	Energy-dispersive X-ray spectroscopy
EPA	Environmental protection agency
FTIR	Fourier transform infrared spectroscopy
IAC	Impregnated activated carbons
L.O.I.	Loss on ignition
MPOC	Malaysian palm oil council
MTZ	Mass transfer zone
OSHA	Occupational safety and health administration

POME	Palm oil mill effluent
ppb	Part per billion
PPE	Personal protective equipment
ppm	Part per million
PSA	Pressure swing adsorption
SEM	Scanning electron microscope
TDBE	Time duration between experiments
VOC	Volatile organic components
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Importance of the Study

Palm oil is healthy edible oil produced from oil palm (Lam, 2009). According to the MPOC (Malaysian Palm Oil Council), palm oil dominates 25% of entire worldwide oil and fat manufactured in 2007 and has been supposed as the most talented feedstock for biodiesel production (MPOC, 2011).

Malaysia alone accounted for more than 39% of the entire world palm oil production and 44% of world exports. Malaysia's oil palm plantation area and crude palm oil production also have been increasing gradually since the past five decades. From a mere 54,000 hectares in the early 1960s, it increased gradually to reach 4.85 million hectares in 2010. Concurrently, Malaysia's crude palm oil production increased from 2.6 million tons in 1960 to 16.99 million tons in 2010. The aforementioned growth in palm farm area and palm oil production, leads to the creation of annual gigantic amounts of effluents (POME) by this industry.

The biochemical oxygen demand (BOD) of raw POME is high, about one hundred times more than the sewage and could pose as a high organic contaminant if not treated properly (Poh & Chong, 2009). Anaerobic process provides outstanding pollutant destruction efficiency of above 95% whereas extended aeration guarantees that the final pollutant levels in the effluent are within the essential limits set by the Department of Environment (DOE).

In the anaerobic digestion process, the raw POME is first converted into volatile fatty acids by acid forming bacteria. The volatile acids are then converted into methane and carbon dioxide. This gas Produced by anaerobic digester is called biogas. Biogas is typically a gas produced by the biological breakdown of organic matter. It originates from biogenic material and is a type of biofuel (Fang, 2010). This kind of biogas comprises primarily of methane (CH_4) and carbon dioxide (CO_2), with smaller amounts of water vapor, trace amounts of hydrogen sulfide (H_2S), and other impurities. The gases carbon monoxide methane and hydrogen can be combusted or oxidized with oxygen. This energy release lets biogas to be used as a fuel. Biogas can be used as a low-cost fuel in any country for any heating purpose, such as cooking. It can also be used in modern waste management facilities where it can be used to run any type of heat engine, to generate either mechanical or electrical power. Biogas can be compressed, like natural gas, and used for power motor vehicles.

As it mentioned before, the biogas has trace amount of H_2S, around 3000 ppm. Hydrogen sulfide is corrosion and toxic contaminant and considers as the most problematic impurity to the most equipment. Furthermore, burning of H_2S results to sulfur dioxide releases, which have detrimental ecological effects (EPA, 1991). Eliminating H_2S as soon as possible is indorsed to protect downstream equipment, increase safety, and enable possible utilization of more efficient technologies such as microturbines and fuel cells.

Many processes can be used to remove the H_2S from POME biogas. Adsorption of H_2S by solids into a fixed bed column is the most efficient, environment friendly, and economical process comparing to other technologies. Cheah *et al*. (2009) reviewed researches have been done on the biogas desulfurization to identify the most proper adsorbent material, and operational conditions.

Tennamaran palm oil factory which is located in west Malaysia, served as the site for the experimental testing. Even though elimination of carbon dioxide, water vapor, VOCs and other pollutants is also desirable, considering all of the technologies required for removal of these compounds is beyond the scope of this project. It is hoped that this project can be used in industries to save the energy and increase the factory efficiency considering the ecology effects.

1.2 Background of the Study

Many researchers have studied the adsorption of H_2S from biogas at ambient temperatures (Baird *et al.*, 1995; Garces *et al.*, 2010; Xu, Novochinskii, & Song, 2005). They have used different adsorbents and operational conditions. One of the most proper adsorbents with regard to the criteria for the adsorption process is Clinoptilolite which is a kind of zeolite.

Alonso-Vicario *et al.* (2010) studied the application of Clinoptilolite in the adsorption of H_2S from a synthetic biogas using pressure-swing adsorption (PSA) in ambient temperature. They expressed the influence of different operational conditions on the adsorption efficiency, e.g. activation of the adsorbent, flow-rate, and temperature. They concluded that Clinoptilolite is the best choice as a medium for adsorption of H_2S in an ambient temperature since it is instantaneously proper both for the cleaning and upgrading of biogas. Moreover, Clinoptilolite is stable through a number of cycles of adsorption-desorption and also can be regenerated fully which, together with its abundance and low price, make this process extremely attractive from an economical view.

Yasyerli *et al.* (2002) investigated the removing of the H_2S from biogas by Clinoptilolite at temperatures between 100-600℃. They reported that by decreasing the temperature from 600 to 100℃, the adsorption capacity of the material increases from 0.03 g sulfur/g adsorbent to 0.087 g sulfur/g adsorbent. The authors also point out to the easy regeneration process of the Clinoptilolite.

The mentioned studies prove that the Clinoptilolite is a promising material in adsorption process. Nevertheless, there is lack of sufficient study on this adsorbent, like few applicable data about the adsorption capacity of Clinoptilolite in ambient temperature and pressure. Furthermore, the mechanism of the adsorbing the H_2S molecules on the material surface is not very well understood. Moreover, regeneration process of this material is not described very well by previous studies (Alonso-Vicario *et al*., 2010; Yasyerli *et al*., 2002). The proposed information like adsorption capacity in a certain conditions, regeneration of material, mechanism, and using natural biogas as an applied gas are of importance matter because they are necessary for application of Clinoptilolite in an industrial scale. For instance, evaluation of the process costs is achieved by exploiting the results from adsorption capacity, regeneration, and mechanism of the medium.

1.3 Statement of the Problem

Regarding to the importance of Hydrogen Sulfide removal from biogas streams, different materials that have been used as adsorbent at low temperature, were compared and a zeolite has been chosen for this investigation.

Zeolites are extensively used in a variety of chemical processes as adsorbents for eliminating or removing different compounds, as ion exchangers in detergent formulations, supports for active metals in petrochemical industry or as shape-selective catalysts (Yilmaz & Muller, 2009). There is a growing concern over using natural zeolites, such as Clinoptilolite, for gas separation, though most zeolites commercially available are produced synthetically (Ackley *et al*., 2003). Natural zeolites typically need previous activation and packaging steps which not always makes their use cost-effective. Because of this purpose, natural zeolites must demonstrate distinctive or better properties to substitute synthetic ones in commercial separations.

Most of the studies of adsorption with natural zeolites are theoretical comparisons of binary pure mixtures based on isotherms or Henry's law constants alone. So, the results and information about using Clinoptilolite are not useful to apply in an industrial scale.

In this research, the behaviors of a natural zeolite (Clinoptilolite) as adsorbent in a fixed bed column is studied at process conditions using natural biogas produced directly from anaerobic digester to simultaneously clean and upgrade the biogas stream. When the optimal activation conditions had been recognized, biogas adsorption studies were conducted by a fixed bed column unit at ambient temperature and pressure using adsorption capacity, selectivity and regenerability as response factors. The selection criteria for the optimal zeolite size and operational conditions for biogas cleaning and upgrading has been based on a compromise between response factors and economical aspects. Adsorptive properties of the Clinoptilolite have been clarified by taking into account their physical and chemical properties as determined by SEM, X-ray diffraction (XRD), FTIR, and BET surface analysis.

1.4 Research Questions

The main research question for this study is stated below:

Main RQ: How efficient is using Clinoptilolite as an adsorption medium?

To answer the main research question there are two sub-research questions:

Sub-RQ1: What is the efficiency of the Clinoptilolite as an adsorbent of hydrogen sulfide from biogas streams in an ambient temperature?

Sub-RQ2: How many times can it be used in the adsorption process of removing hydrogen sulfide from biogas? How can it be regenerated?

1.5 Research Objectives

This research aims to two objectives,

- To determine the biogas H_2S removal efficiency of fresh Clinoptilolite in ambient temperature and pressure onto a fixed bed column
- To determine the fresh Clinoptilolite lifetime in a continuous adsorption process and study its regeneration ability
- To find a relationship among different material sizes and flow-rates with experimental data.

1.6 Research Methodology

The experimental method has been used in this study to fulfill the research questions. To do this, a unit containing three fixed bed columns has been designed and fabricated. The efficiency of the process is determined by measuring the amount of H_2S in inlet and outlet biogas flow from columns. Measuring of H_2S is done on-site with a portable gas analyzer. Also, the experimental data from H_2S adsorption of biogas streams used to model an exponential equation in order to catch a relationship between different parameters.

1.7 Organization of Thesis

This study is organized in five chapters. Details of which are explained below:

Chapter1: Firstly, there is a journey through the background of the study. Then the problem, research question and research objectives are expressed. Finally, methodology to solve the stated problem and also other criteria and requirement for validating the data and results are explained.

Chapter 2: This chapter explains the structure of studied literature toward gathering sufficient information; existing knowledge associated with the subject of this research and performed researches in relation with the adsorption process.

Chapter 3: In this chapter selected research methodology and its relevant components are explained in detail.

Chapter 4: In this chapter, the procedure of data collection and the results are demonstrated. The data then, interpreted through different ways e.g. graphs, tables, and mechanism. At the end of this chapter the first two objectives of this study and therefore the first two sub research questions are answered.

Chapter 5: This chapter concludes the results obtained through this study and illustrates the benefits of using this medium as an adsorbent.

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