FINAL REPORT
ON
EXONMOBIL EDUCATION GRANT

(Award 2006/2007)

EXPERIMENTAL AND MODELING STUDIES FOR A COMPOSITE MEMBRANE/ADSORBER SYSTEM BASED ON HYDROTALCITE FOR REMOVAL OF CO_2 FROM NATURAL GAS

Associate Professor Dr.W.J.N.Fernando
Dr. Mohd. Roslee Othman
School of Chemical Engineering,
Engineering Campus,
Universiti Sains Malaysia
14300, Nibong Tebal
Pulau Penang
October 2008

UNIVERSITI SAINS MALAYSIA

October 2008

EXXONMOBIL SUPPORT TO HIGHER EDUCATION: GRANT FOR RESEARCH- 2006. FINAL REPORT OF RESEARCH PROJECT

By
PROF. MADYA DR.W.J.N.FERNANDO
School of Chemical Engineering,
Universiti Sains Malaysia.

1. BACKGROUND

An award of RM30,000 was made in 2006 by Messrs. ExxonMobil Exploration and Production Malaysia to the Universiti Sains Malaysia for carrying out research on "Experimental and modeling studies for a composite membrane/adsorber system based on hydrotalcite for removal of CO_2 from natural gas", subsequent to an application made by the grantees. The ExxonMobil Exploration and Production Malaysia Inc., Menara ExxonMobil, Kuala Lumpur City Center, 50088, Kuala Lumpur made the award for research on the scheme "ExxonMobil Support to Higher Education".

Confirmation of the award was received by the grantees on 17th October, 2006 by an award letter of Exxon Mobil. Subsequently the financial allocation of RM 30,000 was received by the USM on the 20th December 2006. The project officially commenced thereafter and was scheduled to complete on 31st December 2007. However, due to an unforeseen delay in recruiting a graduate research assistant (detailed below), the project was extended by Messrs. ExxonMobil Exploration and Production Malaysia by a few months up to 31st August 2008. In-spite of the shortcomings the project progressed well with activities as outlined below.

Unforeseen delays experienced:
Due to ample opportunities which were available for young graduates of Chemical Engineering in Malaysia, a shortage of research staff was experienced in nearly all the Universities in Malaysia early 2007. However, with the passing out of new graduates in April 2007 the situation was eased. This difficulty was faced by the ExxonMobil research project as well. Only after the USM convocation in September 2007, a graduate research assistant could be recruited. We were fortunate to recruit a graduate research assistant (Ms. Nadia Isa) for the project with a GPA above 3 and the research assistant is registered for a Masters under the research.

In spite of this, the abovementioned delay was partly compensated with the involvement of short term student research assistants from time to time as outlined in later sections.

2. ACTIVITIES:

Phase I. Dec 2006-February 2007

In spite of the above delays, a literature survey was carried out by the grantees as planned.

Phase II February 07- May 07

Initially, it was anticipated that during this period the task of development and design of the membrane and Adsorption unit be carried out. However due to un-availability of a research assistant, the work was a little delayed as outlined earlier. This situation was partially overcome in May 2007 as described earlier. In spite of this drawback the grantees were able to carry out preliminary studies on Hydrotalcite-Al sol precursor to prepare inorganic membrane for carbon dioxide separation.

Based on the literature survey and the above work carried out by the grantees together with a co-opted research assistant Ms. N.M.Rashid, a paper was submitted for the 11th Colloquium on membrane. The paper was accepted in poster form and presented on the 28th and 29th March 2007 at the 11th Colloquium on membrane held at - Institut für Verfahrenstechnik, RWTH- Aachen at IVT. The paper (Full paper given in Appendix 1) was titled "Studies on the properties of HT-Al sol precursor to prepare inorganic membrane for carbon dioxide separation". Appropriate acknowledgement has been made to the Messrs. ExxonMobil Exploration and Production Malaysia.

Phase III May 07- July 07

Two student research assistants were employed under the project as follows.
Mr. Chew Kean Khoon 2 May – 6 July 07
Mr. Wong Kai Seng 30 Apr 07- 6 July 07

During this period it was possible to Develop and design the adsorption and membrane unit. Details of the unit are shown in Appendix 2. Setting Up of the experimental rig was thereafter carried out with an existing furnace as an auxiliary to the set-up.

Mathematical Modeling of the adsorption/desorption process was carried out based on monomolecular and multimolecular adsorption theories.

Further, a final year student's project was initiated under the current project. A student Ms. Elma Masrini Binti Halim was assigned the project and she commenced work on the project in July 2007

Phase IV. August 07- December 07

A graduate research assistant Ms. Nadia Isa (graduate in Chemical Engineering) was employed under the project on 21st August 2007 – 30th November 2007. In September 2007, a request for extension of the project was submitted to ExxonMobil Exploration and Production Malaysia on the basis of the delay mentioned earlier. Ms Nadia was awarded a Scholarship (NSF/FRGS) in December 2007 and she continued work under the current thereafter.

Two members of the academic staff of the School of Chemical Engineering of the USM (namely: Professor A.L. Ahmad, (Dean) and Dr. S.R.Abd. Shukor, (Deputy Dean) were co-opted for the project in 2007 due to the absence of Dr. Roslee Othman who was on overseas leave.

A research assistant Mr. Keng Poh Wee was employed for the project on 18th November 07 to 16th December2008. The theoretical model compiled under phase III was validated. Based on this work a paper was presented (Appendix 3) at the 21st Symposium of Malaysian Chemical Engineers (Challenges and Opportunities in Chemical Engineering for Sustainable Future) on 11th – 13th of December 2007. The paper was titled "A study on the temperature and pressure swing adsorption of carbon dioxide on hydrotalcite with a view to remove carbon dioxide from natural gas". The authors of the paper have been Fernando, W.J.N., Ahmad, A.L., Othman, M.R., Abd. Shukor, S.R. and Keng Poh Wee. Appropriate acknowledgement has been made to the Messrs. ExxonMobil Exploration and Production Malaysia in this paper.

The research assistant Ms. Nadia commenced experimental work in relation to hydrotalcite membrane for removal of CO_2. Ms. Nadia was registered for Masters at the USM.

Ms. Elma Masrini Binti Halim (Student involved with the Final Year project) continued her studies on Carbon dioxide adsorption /chemi-sorption on hydrotalcites.

Phase V January 2008 to August 2008

Ms Masrini continued her studies on adsorption of carbon dioxide on hydrotalcites. In April 2008, Ms. Masrini completed her Final Year project thesis on "Development of adsorption/ chemi-sorption model for carbon dioxide adsorption on Hydrotalcite" and made a presentation at the School as a Final year coursework requirement.

The graduate research assistant Ms. Nadia continued experimental work in relation to adsorption and desorption of carbon dioxide using hydrotalcite. Based on the above work a paper has been accepted for presentation at the International Conference on Environment 2008, Penang, Malaysia, 15-17 December 2008.The paper is titled "Studies on adsorption/ desorption of carbon dioxide with respect to thermal regeneration of hydrotalcites"

Further work has been carried out for the combined adsorber and membrane effects of removal of carbon dioxide using the adsorber/membrane unit.. The pressure drops and adsorption capacities of the combined system evaluated. It is anticipated that a Masters thesis will be submitted to the USM on the work carried out by Ms. Nadia in the near future.

The project was officially completed on the 31st August 2008

3. PERSONNEL INVOLVED

Fernando, W.J.N. (Main recipient/main researcher)
Othman, M.R. (co-recipient/co-rsearcher)

Following staff were involved with the project as further co-researchers during the overseas leave period of Dr. Othman (2007)
Ahmad, A.L., (Dean of the School of Chemical Engineering)
Abd. Shukor, S.R. (Deputy Dean of the School of Engineering)

Undergraduate Students in Chemical Engineering-

Keng Poh Wee.	December 2007
Mr. Chew Kean Khoon.	May –July 2007
Mr. Wong Kai Seng.	April-July 2007

Undergraduate Student carrying out Final Year Project.
Ms.Elma Nasrini (2007)

Postgraduate Student Carrying out Masters Research
Ms. Nadia Isa (2007-2008)

4. FINANCIAL
(A COPY OF THE FINAL PRINT OUT OF STATEMENT OF EXPEDITURE OF THE USM IS ATTACHED IN APPENDIX 5)

Grant received in December 2006 from Messrs. ExxonMobil Exploration and Production Malaysia =

RM 30,000

Major items of expenditure:
(a)Salaries (Under Vote 11000)
RM10957.84
Employment of Undergraduate Research assistants during University Vacations
Undergraduate Students in Chemical Engineering:

Mr. Chew Kean Khoon	May – July 07
Mr. Wong Kai Seng	April 07- July 07
Mr. Keng Poh Wee	November -December 2007

Employment of Graduate Research Assistant:

Ms. Nadia Isa	August 07 – November 07

(b) Equipment items (costing more than RM 1000) Total RM14055.00
(Inventorized under USM: School of Chemical Engineering)

Details:

Carbon dioxide analyzer (QDS Technologies)	RM 6600
Composite membrane/adsorber unit -stainless steel (SHXP Trading)	RM 3055
Vacuum pump-oil free type (Ever Win Engineering &Supply Sdn.Bhd)	RM 4400

(c) Other expenditure	**RM4897.65**

Details:
Gases
Chemicals
Services: Analysis of samples. SEM, Autosorb, XRD etc.
And USM overhead handling charges (RM750)

(d) Closing Balance	**RM 89.51**
	TOTAL RM 30,000

5. SCIENTIFIC STUDIES CARRIED OUT

Details of scientific studies carried out are elaborated in papers presented in Appendix 1, 3 and 4 and hence will not be elaborated herein in order to avoid duplication of the same.

However, details of achievement of intended tasks are outlined below.

Task	*Status*
Task I: Literature survey	Achieved
Task II. Development and design of the membrane and Adsorption unit	Achieved. Appendix 2
Task III. Setting Up of the Experimental Rig	Achieved Appendix 2
Task IV Experiments.	Achieved Outlined in Papers Appendix 3 and 4
Task V Mathematical Modeling	Achieved Presented in Paper in Appendix 3 and To be presented soon in Masters Thesis of Ms. Nadia.
Task VI. Validation of the model	
Task VII Final Report	Submitted herein

6. OUTCOMES

6(a) Technical Outcomes:

Technical outcomes and results of research were disseminated as presentations as follows.

Presentations.

Othman, M.R; Fernando, W.J.N; Rasid, N.M. "Studies on the properties of HT-Al sol precursor to prepare inorganic membrane for carbon dioxide separation", 11th Colloquium on membrane held at - Institut für Verfahrenstechnik, RWTH- Aachen at IVT, 28th and 29th March 2007

Fernando, W.J.N., Ahmad, A.L., Othman, M.R., Abd. Shukor, S.R. and Keng Poh Wee. "A study on the temperature and pressure swing adsorption of carbon dioxide on hydrotalcite with a view to remove carbon dioxide from natural gas", 21st Symposium of Malaysian Chemical Engineers (Challenges and Opportunities in Chemical Engineering for Sustainable Future) on 11th – 13th of December 2007

6. APPENDICES

APPENDIX . 1

supported by

IVT- Institut für Verfahrenstechnik, RWTH- Aachen

Studies on the properties of HT-Al sol precursor to prepare inorganic membrane for carbon dioxide separation

Othman, M.R; Fernando, W.J.N; Rasid, N.M
School of Chemical Engineering, Universiti Sains Malaysia,
14300 Nibong Tebal, Penang
Malaysia
chroslee@eng.usm.my

Keywords: carbon dioxide, sol ge

1. Introduction

The main contributor to increasing atmospheric carbon dioxide concentration in Malaysia is fossil fuel combustion for power generation, transport, industry and domestic use. Malaysia energy consumption by fuel type could be presented as; natural gas (45%), oil (44%) and coal (8%). Almost every year, carbon dioxide emission increased in the air and the drastic change was in the year of 1995 due to rapid economic growth in Malaysia [CDIAC, (2005)]. Increasing concentrations of greenhouse gases are likely to accelerate the rate of climate change (Tagaya et al., 1992; Horiuchi et al., 1998). Several options exist to abate carbon dioxide emissions from fossil fuel utilization, including increasing the efficiency of fossil fuel combustion systems (Horiuchi et al., 1998), or replacing fossil fuels with renewable energy sources (Yong et al., 2002). These alternatives are very attractive in controlling carbon dioxide emissions in the environment, but each has its own limitation. Another option to manage carbon dioxide emission is carbon sequestration that is, capturing and securely storing the carbon dioxide emitted from large point sources, such as fossil-fuel-fired power plants (Yong et al., 2001). Others include pressure swing adsorption (PSA), amine absorption and polymeric membrane. PSA is well suited for the removal and recovery of carbon dioxide and it can be operated at elevated temperatures. It can remove most of the carbon dioxide and overcome the need to cool the fuel gas to ambient temperature (Yong et al., 2002).

However, PSA has the disadvantage of being energy intensive, it is not continuous and the use of high pressure technology renders it expensive. Membrane provides an attractive alternative to PSA, since it does not require any phase transformation and the necessary process equipment is very simple with relatively ease of operation and control, compact and convenient to scale up. These advantages make the membrane process ideal for separation of carbon dioxide if a membrane with good chemical and thermal stability and high carbon dioxide permselectivities /permeance can be developed. In industry, ranging from food and beverage processing, desalination of seawater, and gas separations, to medical devices, the use of polymeric membranes is on the rise (Funk and Li, 1989), but these membranes could not withstand in an environment requiring chemical and thermal endurance. An alternative and more promising candidate for carbon dioxide separation is to use inorganic (ceramic) membrane. Recently, research directed at the development and application of inorganic membrane is gaining momentum because of their high demand in the new application fields such as fuel cells, membrane reactors and other high temperature separation processes. In many cases, it is highly desirable to separate carbon dioxide from flue gas at a high temperature (around 400°C) without cooling the flue gas to room or even lower temperature. The high temperature carbon dioxide separation process would produce concentrated, warm carbon dioxide which can be subsequently used directly as a feedstock for chemical synthesis of fuels (e.g., methanol or chemicals). This application requires a membrane or adsorbent selectively permeable to or adsorptive for carbon dioxide at high temperature. Therefore, materials like hydrotalcite or hydrotalcite modified with basic metal oxides could be considered excellent candidate membrane materials because of their higher carbon dioxide adsorption capacity at elevated temperature, while maintaining thermal stability. In this work, synthesis of hydrotalcite (HT) membrane from sol-gel route was attempted and the effects of such parameters as hydrotalcite loading, acid concentration, type of acid and aging on the sol properties were investigated.

2. Procedures

2.1 Effect of hydrotalcite loading

The effect of hydrotalcite loading in hydrotalcite-alumina sol was studied to study the volume fraction of hydrotalcite required to form clear sol (peptized). The sol with hydrotalcite loading of 2 wt%, 5 wt% and 10 wt% from the total sol volume were used in this work, during which, 0.07 mole ratio of HCl (12M) was added.

2.2 Effect of acid concentration

Different concentrations of acid were used to investigate their effect on the behaviour of hydrotalcite–alumina sol. The concentrations of HCl were varied with 1M, 5M and 12M, respectively.

2.3 Effect of type of acid

In this study, two type of acid were used; one was hydrochloric acid (HCl, 12M) and another was nitric acid (HNO3, 15 M) in order to investigate the role of acid type in sol peptization.

3.4 Effect of aging on sol viscosity

The effect of aging on sol viscosity was studied, to obtain the information on how long the sol could be stored before it became unsuitable for dip coating to form membrane. The viscosity of sol was determined using Brookfield rheometer accompanied with Rheocalc V2.1 software. The speed was set between 10 to 100 rpm to run in auto mode. The analysis was done at 30°C and temperature was maintained using temperature bath.

3. Discussion

3.1 Effect of hydrotalcite loading

Table 1 and Figure 1 demonstrate that the addition of 5% and 10% hydrotalcite from the total sol volume resulted in white precipitation. Precipitation in 10% hydrotalcite with alumina was higher than that of 5% hydrotalcite while 2% hydrotalcite dissolved completely in the precursor solution. These suggest that higher volume fraction of hydrotalcite into alumina sol have a tendency for agglomeration and aggregation of the particles.

Table 1: Effect of hydrotalcite loading on sol peptization

Sample	Appearance of sol after 1 day heat treatment at 90°C.
HTsg-3 HTs 2%	clear sol
HTsg-3 HTs 5%	white precipitate
HTsg-3 HTs 10%	white precipitate

*HTs = hydrotalcite loading

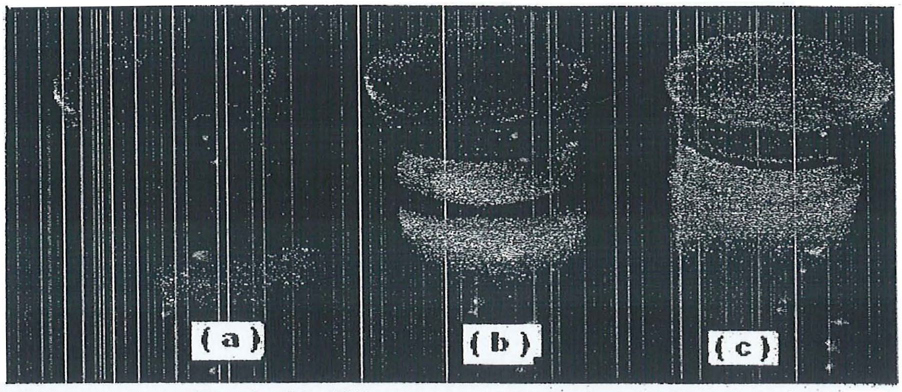

Figure 1: HTsg-3 with different hydrotalcite loading a) 2% b) 5% c) 10%

3.2 Effect of acid concentration.

In the hindsight of the loading effect, 2% of hydrotalcite loading was selected for this study. Table 2 and Figure 2 show that HTsg-3 for 1M and 5M of HCl did not peptize, but white precipitate was formed instead. While HTsg-3 peptized with 12M of HCl to form clear sol. At relatively low concentration of acid, the suspended boehmite particles seemed to exhibit low electric charges, allowing gelatinous precipitate to form. At higher acid concentration, higher electric charges compelled the particles to organize each other, maintaining stable sol dispersion that formed clear sol.

Table 2: Effect of acid concentration on the sol appearances.

Sample	Apperance of sol after 1 day heat treatment at 90oC.
HTsg-3 HCl 1M	White precipitate
HTsg-3 HCl 5M	White precipitate
HTsg-3 HCl 12M	clear sol

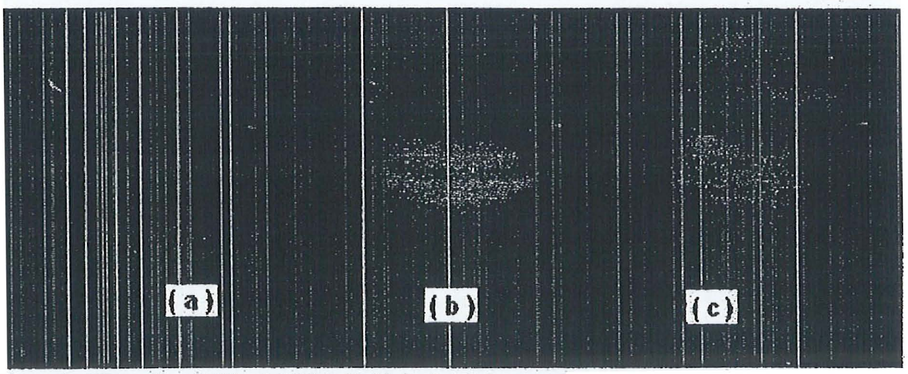

Figure2: HTsg-3 at HCl a) 12 M, b) 5M, c) 1 M.

3.3 Type of acid

We attempted to study two types of acid; hydrochloric acid (HCl, 12M) and nitric acid (HNO3, 15 M) because HCl carries Cl ions, which would modify the acid base properties of the layered double hydroxide (Prinetto et al., 2000). Therefore, HNO3 was proposed to evaluate its effectiveness in the peptization. Table 3 and Figure 3 show that HNO3 was not able to perform peptization as intended, suggesting that HNO3 was not sufficiently strong to produce the necessary charge effect in the sol, despite it was applied at higher molar concentration than HCl.

Table 3: Peptizing effect of selective acids.

Sample	Appearance of sol after 1 day heat treatment at 90°C.
HTsg-3 HNO3	Cloudy sol
HTsg-3 HCl	Clear sol

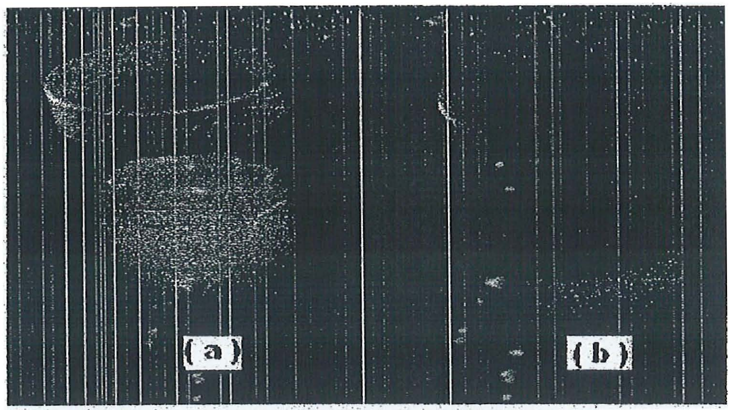

Figure 3:HTsg-3 with a) HNO3 15 M, b) HCl 12M.

3.4 Effect of aging on sol viscosity

Figure 4 shows that viscosity increased with increase in aging time. All of the samples exhibited rheopectic flow behaviour since the viscosity increased with time. HTsg-3 (containing 3:1 mole ratio of Mg:Al) demonstrated nearly constant values of viscosity after 168 hours. HTsg-0.5 (containing 0.5:1 mole ratio of Mg:Al) and HTsg-4 (containing 4:1 mole ratio of Mg:Al) showed continuous increase of viscosity with time. HTsg-3 was found to be favourable for dip coating since its viscosity value was constant with time and it could be stored for as long as 672 hours (1 month). Whereas, HTsg-0.5 and HTsg-4 sol could not be used for coating to form the membrane, since its viscosity continued to increase as it aged. Increasing viscosity of the sol resulted thick layers, leading to greater risk of cracks formation and lower adhesion of coating to the support (Haas-Santo et al., 2001).

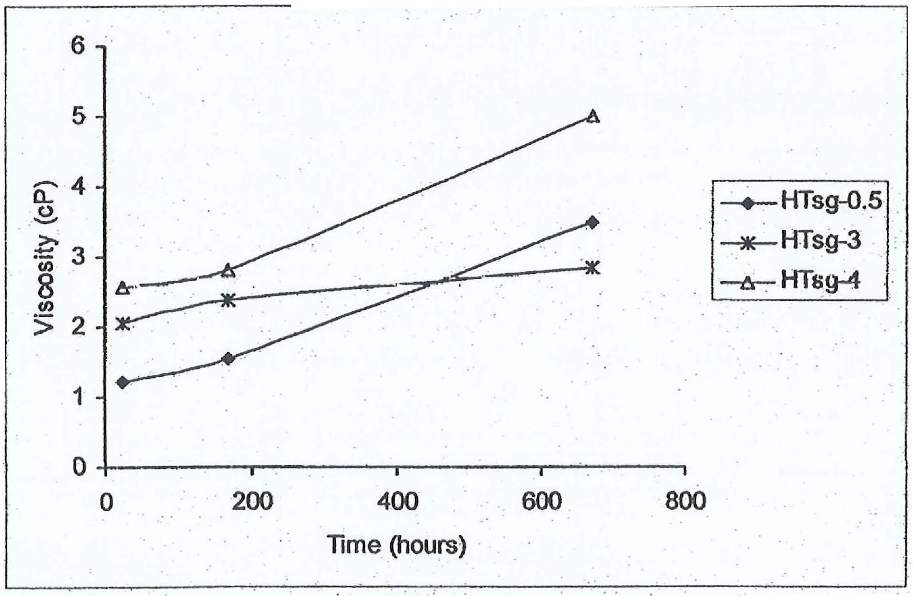

Figure 4: Viscosity versus time for different Mg:Al molar ratio.

4. Conclusions

The application of sol-gel technique to prepare sol precursor for forming hydrotalcite membrane was explored for the first time in this work. From the sol characteristics, it was shown that hydrotalcite - alumina sol (HTsg-3) containing 2wt% of hydrotalcite loading with 12M of HCl concentration would form a stable sol. HTsg-3 behaved as rheopectic fluid and it could be stored for 672 hours.

Acknowledgement

Financial support from USM/MOSTI/ EXXONMOBIL Exploration and Production Malaysia is gratefully acknowledged.

References

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APPENDIX 2 DETAILS OF EXPERIMENTAL RIG AND ASSOCIATED UNITS

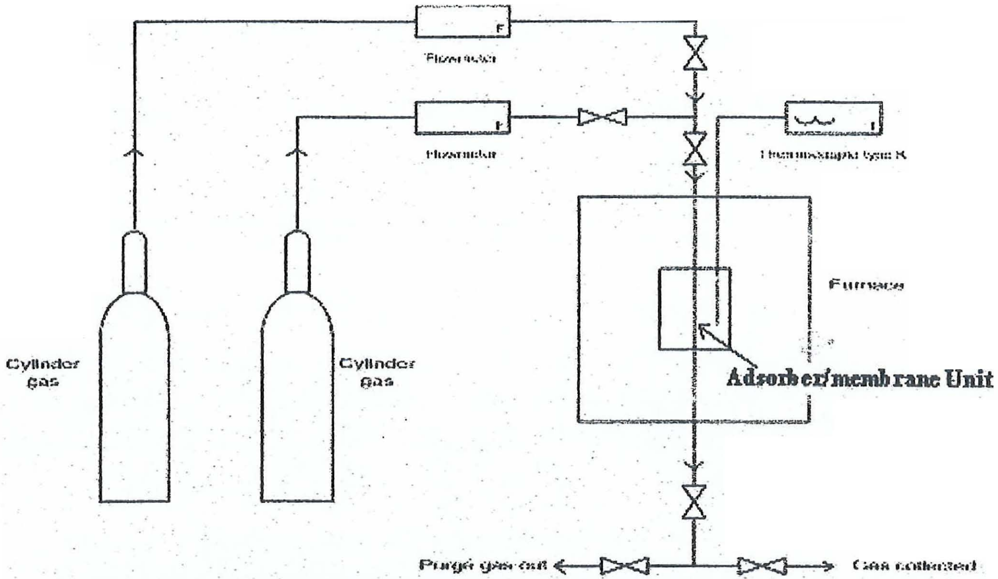

Figure 1 The experimental rig layout diagram

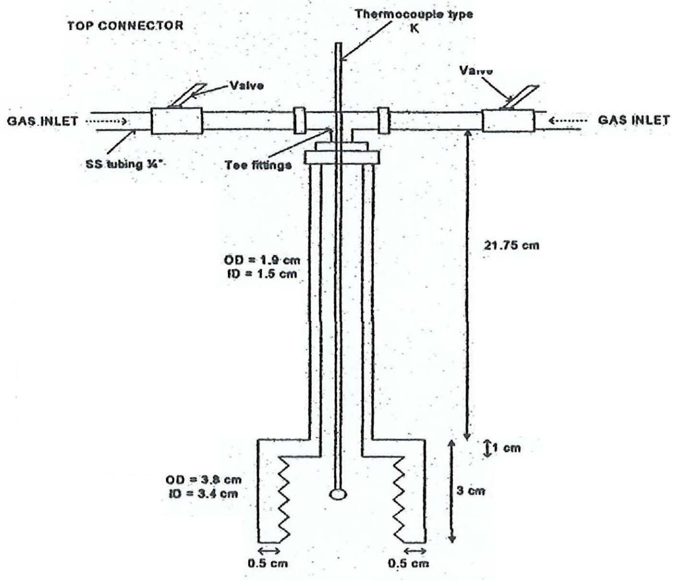

Figure 2 : Top connector of the adsorber/membrane unit

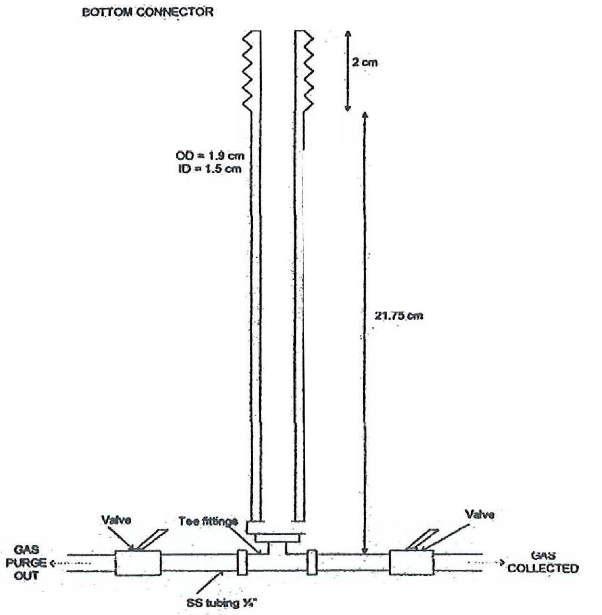

Figure 4 : Bottom connector of the adsorber/membrane unit

APPENDIX 3

(SOMCHE 2007)

21st Symposium of Malaysian Chemical Engineers
Challenges and Opportunities in Chemical Engineering for Sustainable Future
11 – 13th of December 2007

A STUDY ON THE TEMPERATURE AND PRESSURE SWING ADSORPTION OF CARBON DIOXIDE ON HYDROTALCITE WITH A VIEW TO REMOVE CARBON DIOXIDE FROM NATURAL GAS.

by

Fernando, W.J.N., Ahmad, A.L., Roslee,M.R., Abd. Shukor, S.R. and Keng Poh Wee
(School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300,Nibong Tebal, Pulau Pinang, Malaysia)

ABSTRACT

Natural gas generally constitutes of hydrocarbons such as methane, ethane, propane, butane, and non-hydrocarbon component such as carbon dioxide, nitrogen and hydrogen sulfide. Presence of carbon dioxide in natural gas is known for its dilution leading to a gas of lean calorific value. The hydrotalcite is known as an effective absorbent for carbon dioxide, because of its preferential adsorptivity for carbon dioxide. Hence, hydrotalcite is used as a potential adsorbent for carbon dioxide, which could be used for enriching natural gas. Adsorption isotherms for carbon dioxide on hydrotalcite under different temperature and pressure are studied. The isotherms are tested for conformity with different adsorption models such as Langmuir, Freundlich and BET. The isotherms are further analysed in order to obtain carbon dioxide removal potentials for rages of pressure swing and temperature swing adsorption processes.

Key words: Adsorption, carbon dioxide, hydrotalcite

1.INTRODUCTION

Malaysia processes the twelfth largest gas reserves in the world with a stock of 97.6 trillion cubic feet (tcf) in January 2001. This figure is equivalent to about 66.8 years of natural gas availability. Some offshore wells producing a natural gas having a high (over 10 vol %) carbon dioxide content [Hays, and Cook, 1980]. The processed natural gas can contain about 0.7 to 1.83 mole % of carbon dioxide [Gas Malaysia, online 2007, Union Gas online 2007]. Removal of carbon dioxide from the natural gas becomes important in the enrichment of natural gas.

Pressure swing adsorption (PSA), amine absorption and polymeric membrane are well suited for the removal and recovery of carbon dioxide and it can be operated at elevated temperatures. (Yong et al., 2002). PSA is reported to have the disadvantage of being energy intensive. It is also a non continuous process making the application of high pressure technology expensive. However, use of hydrotalcite ha been found to be highly selective to carbon dioxide and has stable capacity to adsorb carbon dioxide making its use attractive. Hydrotalcites are well known because of their unique properties obtained after calcination, such as high surface area, very strong basicity, formation of thermally stable homogeneous mixtures of oxides with very small crystal sizes and ability for reconstruction of the original structure under mild conditions [Horiuchi et al. 1998. Ivan and Lapkin, 2005]. They are also well known for fast adsorption of carbon dioxide [Paul and Liu , 2003, Ivan and Lapkin, 2005]. The hydrotalcite also has stable mechanical strength during cyclic exposure under high temperature and pressure. The amount of carbon dioxide adsorbed in hydrotalcite varies with its partial pressure and temperature. The study herein is to evaluate the behaviour of the adsorption characteristics of hydrotalcite for different temperatures and partial pressures and to evaluate the efficiencies of hydrotalcite in adsorption and subsequent regeneration for re-use in pressure and temperature swing effects thereof.

2.METHODOLOGY

In order to analyse the effect of pressure and temperature swings in adsorption/desorption of carbon dioxide in hydrotalcite, adsorption data for carbon dioxide on hydrotalcite under isothermal conditions were assimilated from the survey as well as from experiments described below. Several published works [Hays and Cook,1980, Ding and Alpay, 2000, Yong and Rodrigues,2002,Othman et al.,2006a,] were accessed for data in this respect. The data were investigated for their conformity with the Langmuir, Freundlich and BET theories. The hydrotalcite was prepared via the co-precipitation method [Othman et al.,2006b]where the magnesium sources were from magnesium nitrate hexahydrate whereas aluminium sources were from aluminium nitrate nanohydrate and carbonate from potassium carbonate. The process was maintained at pH10. The hydrotalcite yield by means of co-precipitation method was calcined under 600°C for 15 hours. Experiments were conducted to study the adsorption of carbon dioxide by the hydrotalcite. Based on the data, a theoretical analysis was made to investigate the effects of pressure and temperature swings in the effectiveness of adsorption of carbon dioxide on hydrotalcite.

3. ANALYSIS

3.1 Analysis of the isotherms

The data obtained for the adsorption of carbon dioxide by the hydrotalcite for temperatures 481K,575K,673K and 753K are presented in Tables 1 to 3.

Table 1 : Adsorption data (Q vs. P) for Carbon dioxide in hydrotalcite for 451 and 575K
[Hays and Cook,1980, Ding and Alpay, 2000, Yong and Rodrigues,2002,Othman et al. ,2006a]

TEMPERATURE (K)		PRESS (kPa)						
		5	9	15	21	30	51	101
451	Q_{451}(moles/kg)	0.51	0.661	0.71	0.722	0.842	0.88	0.94
575	Q_{575}(moles/kg)	0.4	0.495	0.57	0.661	0.695	0.771	0.83

Table 2 : Adsorption data for Carbon dioxide in hydrotalcite at 673K

	PRESSURE(kPa)			
	5	12	27.5	45
Q (mol/kg)	0.318	0.4	0.528	0.57

Table 3 : Adsorption data for Carbon dioxide in hydrotalcite at 753K
[Hays and Cook,1980, Ding and Alpay, 2000, Ong and Rodrigues,2002,Othman et al. ,2006a]

	PRESSURE(kPa)		
	24	57.5	58.5
Q (mol/kg)	0.41	0.46	0.48

The data were investigated for their conformity with the Langmuir theory. This has been made through plots of Q vs. Q/P for the different temperatures. Fig 1 to 4 show the plots so obtained for temperatures 481K,575K, 673K and 753K respectively.

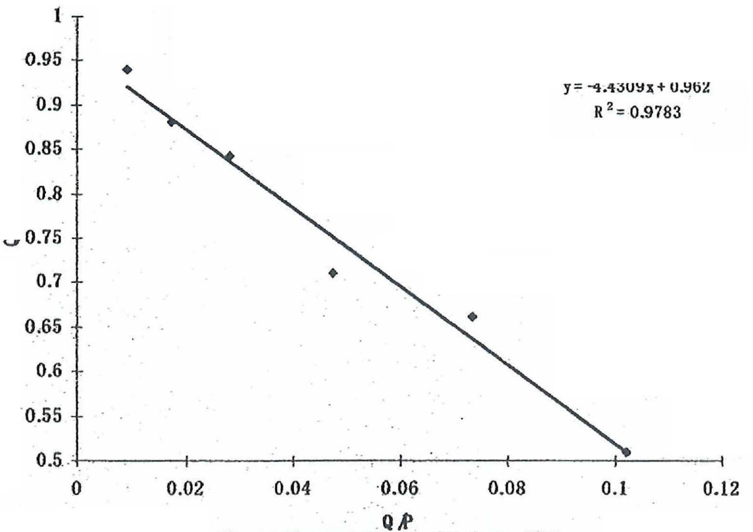

Figure 1. The graph Q versus Q/p for T = 481K

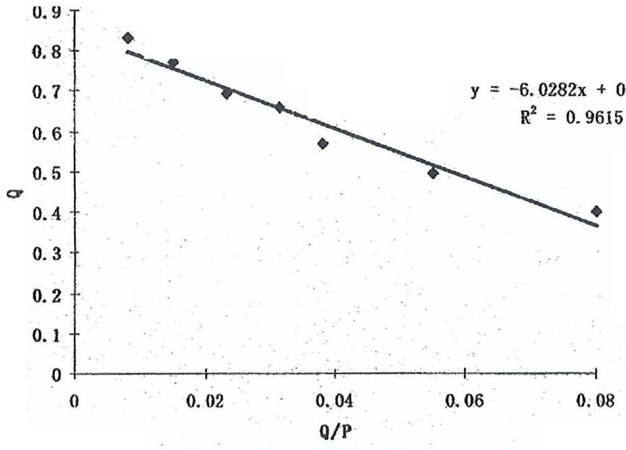

Figure 2. The graph Q versus Q/p for T = 575K

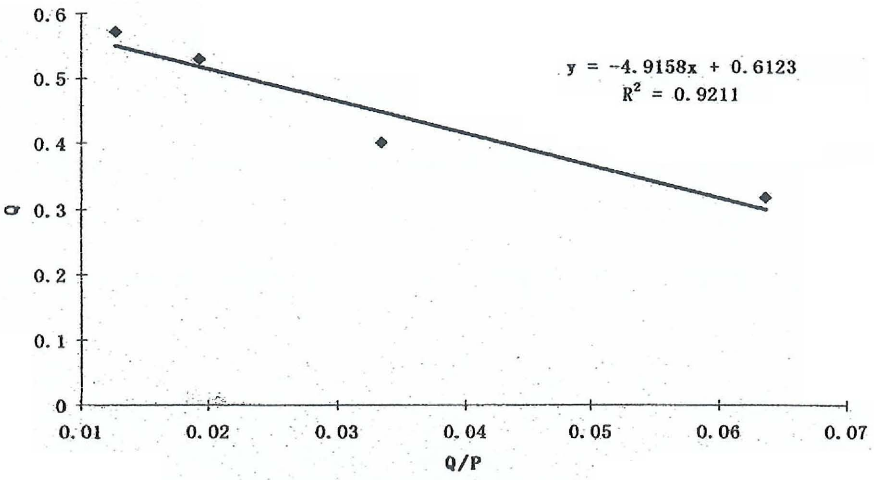

Figure 3. The graph Q versus Q/p for T = 673K

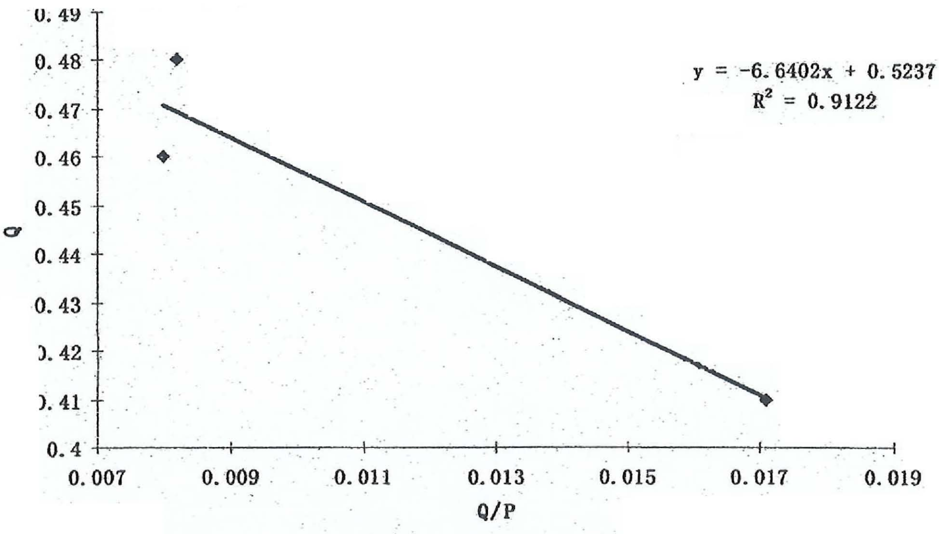

Figure 4. The graph Q versus Q/p for T = 753K

The compatibility of data with the Freundlich theory was also tested here for conformity with linearity of the plots of ln(Q) vs. ln(p). The figures 5 to 8 show the plots of In (Q) versus ln(p).

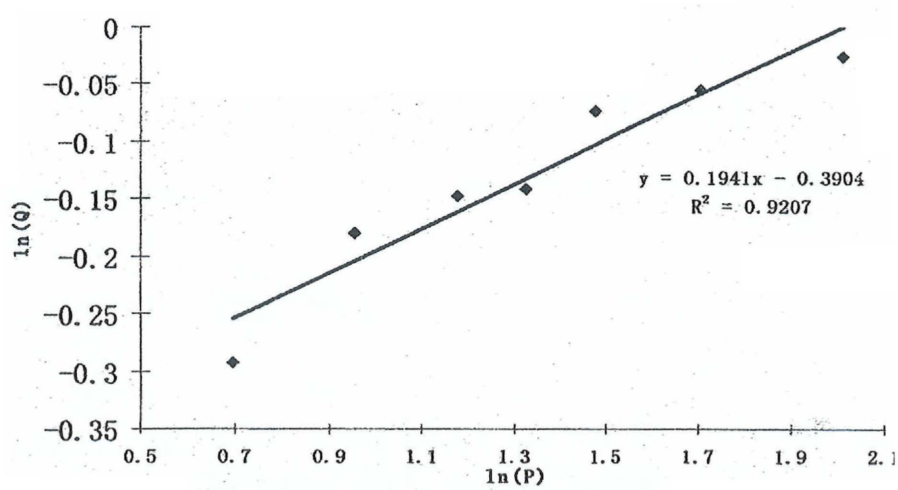

Figure 5. The graph ln(Q) versus ln(p) for T =481 K

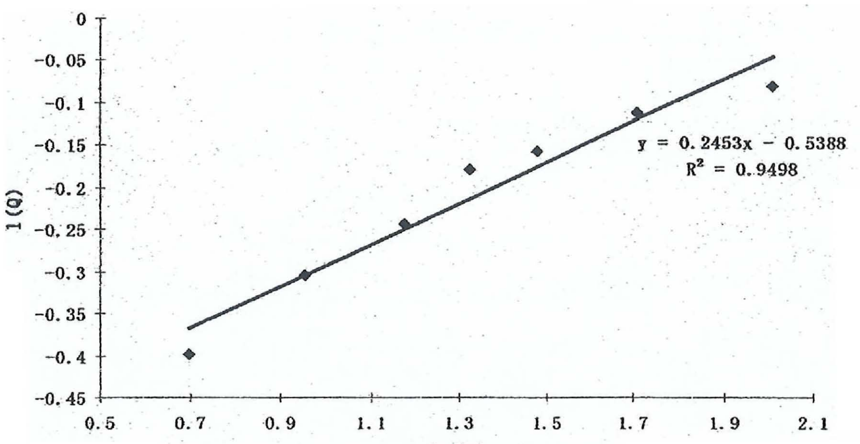

Figure 6. The graph ln(Q) versus ln(p) for T =575 K

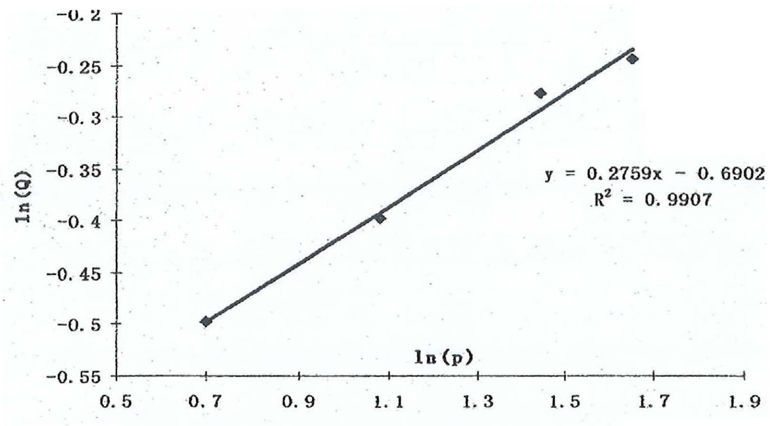

Figure 7. The graph ln(Q) versus ln(p) for T =673 K

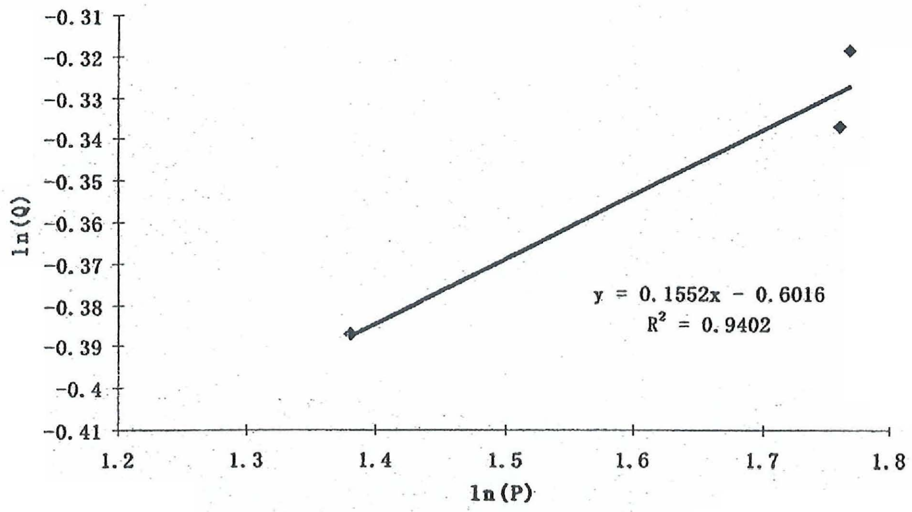

Figure 8. The graph ln(Q) versus ln(p) for T =753 K

Data for their applicability with the BET theory was also investigated . The BET equation was re-arranged in the form

$$\frac{x}{Q(1-x)} = \frac{1}{kQ_T} + \frac{(k-1)}{kQ_T}x \qquad (1)$$

and plots of *x/{Q(1-x)* vs. *x* were examined. Figures 9 to 11 show the plots so obtained.

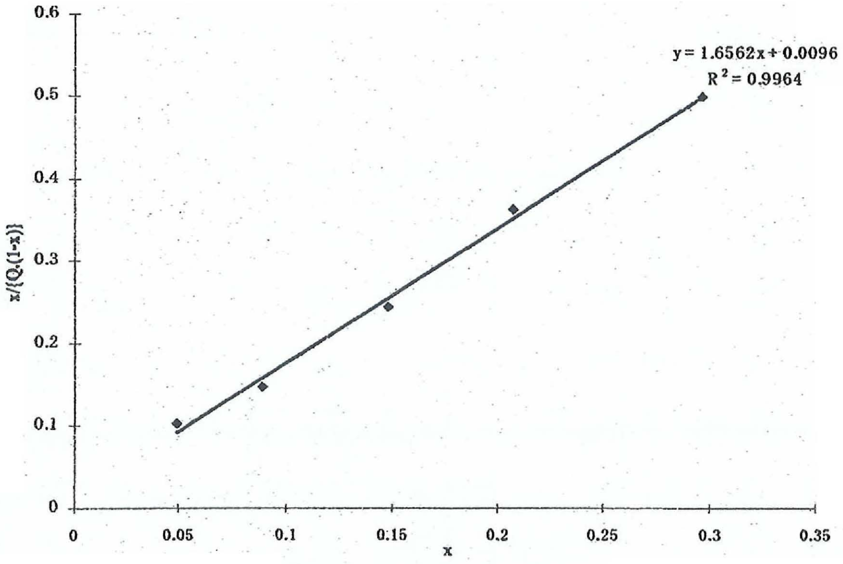

Figure 9. the graph versus x for T = 481K

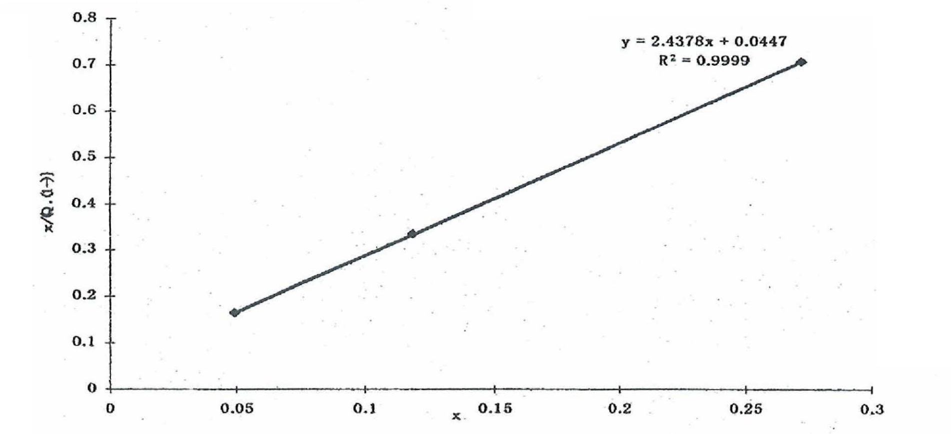

Figure 10. the graph versus x for T = 575K

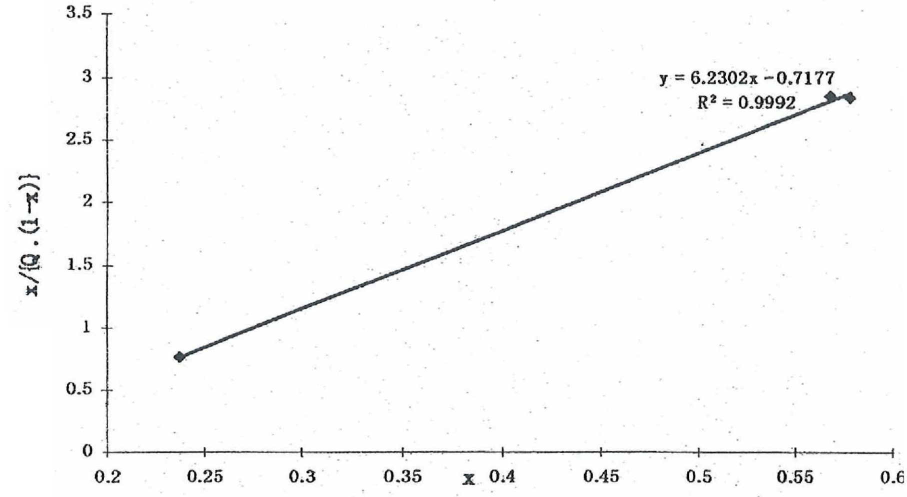

Figure 11 the graph versus x for T = 673K

Table 4 below summarizes the results of the above investigation with the respective isotherm data..

Table 4 Summary of Isotherm analysis

	Temperature	b	Q_T	R^2	Range of partial pressure of carbon dioxide
Langmuir	481K	0.22569	0.962	0.9783	0-1
	575K	0.156589	0.8478	0.9615	0-1
	673K	0.23865	0.5693	0.9211	0-0.5
	753K	0.1506	0.5237	0.9122	0-0.594
		k	n	R^2	
Freundlich	481K	0.407	5.152	0.9207	0-1
	575K	0.2892	4.0766	0.9498	0-1
	673K	0.2041	3.6245	0.9907	0-0.5
	753K	0.25092	6.4433	0.9402	0-0.594
		k	Q_T	R^2	
BET	481K	173.521	0.6003	0.9964	Only 0-0.3
	575K	71.5242	0.5198	0.993	Only 0-0.3
	673K	55.5369	0.4028	0.9999	Only 0-0.3
	753K	NA	NA	NA	NA

3,2 Analysis of Pressure/Temperature swing

Based on the previous analysis, it was observed that the BET isotherms fit satisfactorily with the experimental data. The BET theory was applied to the case where adsorption at a temperature T′ of a carbon dioxide gas stream of mole fraction x′ was carried out initially. The respective equilibrium adsorption per unit weight of the adsorbent is denoted by Q′. Subsequently, regeneration of the hydrotalcite is considered at a lower pressure and lower mole fraction x and a higher temperature T. The fraction of x/x′ is denoted by α Here it is assumed that the effect of adsorption desorption hysteresis is negligible. The experiments conducted in this study have shown that this is accurate for the case of adsorption of nitrogen on hydrotalcite. Even though some hysteretic effect is observed for adsorption of carbon dioxide on hydrotalcite, the hysteretic effect is observed not to be particularly significant after a few adsorption-regeneration cycles. (Yong et al, 2002).

Then by means of the BET isotherm, it can be shown that,

$$\frac{Q}{Q'} = a.\frac{K.Q_T}{K'.Q'_T}.\frac{\left[1+(K'-1).x'\right]}{\left[1+(K-1).\alpha.x'\right]}\frac{\left[1-x'\right]}{\left[1-\alpha.x'\right]} \tag{2}$$

Here K ,K’,Q_T and Q_T’ are dependant on respective temperatures
Using the above equation it is possible to estimate the amount of carbon dioxide when pressures and temperatures were changed. Here, the pressure swing is denoted by a factor α which represents the ratio of the pressure on adsorption and desorption. The value of α is changed from 0.1 to 1.0 where the latter represents pressure swing. The temperature swing is investigated by evaluating the Q values for three different temperature swings from 481 K through 575 K to 673 K.

Plots of Q/Q’ vs. α for different temperature swings with adsorption temperature of 481 K and desorption temperatures of 481K, 575K and 673 K are shown in figure 12.

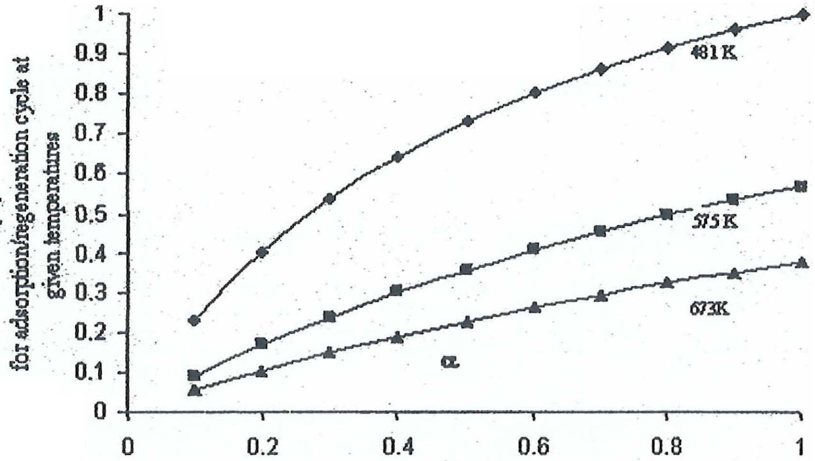

Figure 12. Plots of Q/Q' vs α for given temperatures

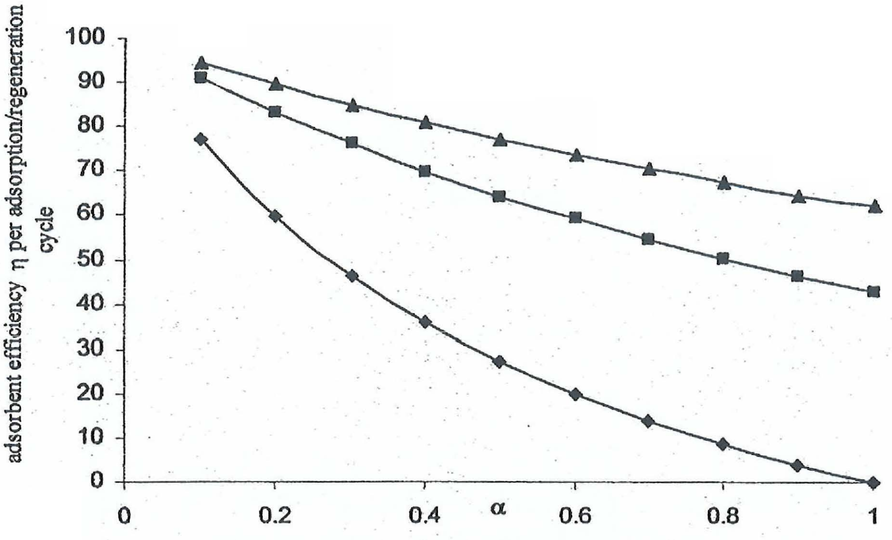

Figure13. plots of η vs. α for different Temperatures

Figure 13 shows the efficiency of the adsorbent during the pressure and temperature swings. Here the plot η {=Q-Q')/Q} vs. α is shown for three different temperatures.

4. DISCUSSION AND CONCLUSION

From the above analysis it can be seen that the BET model suits most the data obtained for temperatures 481K, 575K and 673K. The BET fitting method gives the almost perfect fitting for the partial pressure range from 0 to 0.3 which is within the concentration rages of carbon dioxide in natural gas. Figure 12 shows that for a given temperature. the retention of carbon dioxide within hydrotalcite increases with the factor a. This result is expected as the higher the ratio of adsorption to desorption pressure generally reduces the effectiveness of the pressure swing effect of adsorption. Figure 12 also shows that for a given value of α, a temperature rise decreases the retention of carbon dioxide within hydrotalcite leading to a better utilization of the adsorbent. e.g. if the temperature is increased from 481K to 673K and α is made 0.1 , a value of Q/Q' of 0.055 is obtained showing the effectiveness in trapping CO2 in the adsorption/regeneration process. Figure 13 shows the variation of the capture efficiency {(Q'-Q)/Q'} of the adsorption/regeneration system with α for different temperatures. Here too higher the temperature and lower the value of α are seen to produce efficiencies closer to 90%. Pressure swing efficiencies of 75 to 85 % are reported in real practice

NOMENCLATURE

P	pressure of adsorption stream (kPa)
P'	pressure of desorption stream (kPa)
Q	Amount of CO_2adsorbed at a temperature T°K per unit weight of adsorbent (mol/kg)
Q'	Amount of CO_2adsorbed at a temperature T'°K per unit weight of adsorbent (mol/kg)
Q_T	Total amount of CO_2adsorbed at a temperature T°K per unit weight of adsorbent (mol/kg)
Q_T'	total amount of CO_2adsorbed at a temperature T'°K per unit weight of adsorbent (mol/kg)
x	mole fraction of CO_2 of adsorption stream (kPa)
x'	mole fraction of CO_2 of desorption stream (kPa)

α x/x'

η Efficiency of desorption in pressure/temperature swing

ACKNOWLEDGEMENTS

The authors wish to acknowledge with thanks Messers ExxonMobil Exploration and Production Malaysia Inc. for their financial support in the form of grant "ExxonMobil support to Higher Education" awarded in 2006.

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APPENDIX 4

(ICENV paper)

STUDIES ON ADSORPTION/DESORPTION OF CARBON DIOXIDE WITH RESPECT TO THERMAL REGENERATION OF HYDROTALCITES

N. ISA, *W.J.N. FERNANDO, M.R. OTHMAN AND A.L. AHMAD
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,
Seri Ampangan, 14300 Nibong Tebal,
Pulau Pinang, Malaysia.
*Corresponding author, Tel.: +60-4-599-6248, Fax: +60-4-594-1013
E-mail : chnoel@eng.usm.my

ABSTRACT

This research is focused on evaluation of conditions for thermal regeneration of hydrotalcite. In this study synthesized hydrotalcite prepared under reported optimum conditions namely calcination temperature (600°C) and Mg/Al mol ratio (3.0), and commercial hydrotalcite are used as the test materials The optimum synthesized sample and also commercial hydrotalcite samples were saturated with carbon dioxide. The saturated samples were tested for BET surface area and pore sizes. The saturated samples were thermally regenerated (heat treated) at 200°C, 450°C and 700°C and surface morphology and pore distributions were re-evaluated. TGA studies on these samples were carried out. It was observed that two regions of desorption exist, namely the first region around 316.5°C and 180°C for the synthetic and commercial hydrotalcites respectively and the second region at 600°C on the average for both types of hydrotalcite with percentage CO_2 reduction of 15% and 24.7% respectively based on the original sample. This could be attributed to different modes of association of CO_2 in the hydrotalcite. The structural changes attributing to the behaviour of carbon dioxide on hydrotalcite under adsorption and re-generation are discussed. A temperature beyond 600°C is found to be best suited for regeneration.

Keywords : Hydrotalcite; Adsorption; Regeneration; Carbon dioxide

INTRODUCTION

Natural gas is a gaseous fossil fuel consisting primarily of methane (70% - 90%) but including significant quantities of ethane (5% - 15%), butane (<5%), propane (<5%), carbon dioxide (0.7 - 50%) and small amounts of nitrogen, helium and hydrogen sulfide [1,[2]. Because of the existence of carbon dioxide in the natural gas, its calorific value is lowered leading to requirements of handling higher volumes of natural gas in applications. As a result it has been felt that removal of carbon dioxide from the natural gas is important.

Hydrotalcite. Hydrotalcite possesses capabilities to separate carbon dioxide by means of adsorption because of high abrasion resistance, high thermal stability and small micropore diameter which results in higher exposed surface area and hence high capacity of adsorption and stable interdispersion of the active species with high reproducibility [3,4]. The high affinity of hydrotalcite materials to carbonate species has mostly led to the use of carbonate containing compounds as precursors of catalysts [3]. Hydrotalcite is a natural layered mineral or anionic clay, constitute a class of lamellar ionic compound where as Layered Double Hydroxides, LDH or Hydrotalcite like compounds is synthetically prepared. It contains a positively charged (cations) hydroxide layer or brucite sheet and charge-balancing anions which is carbonate in the interlamellar space besides water molecules (Figure 1). Hydrotalcite like compounds are represented by the general formula $\left[M_{1-x}^{2+}M_x^{3+}(OH)_2\right]^{x-}\left[A_{x/n}^{n-}\right]mH_2O$ where M^{2+} and M^{3+} are bi and tri-valent metal cations, respectively and A is an interlamellar anion with charge n- [5].

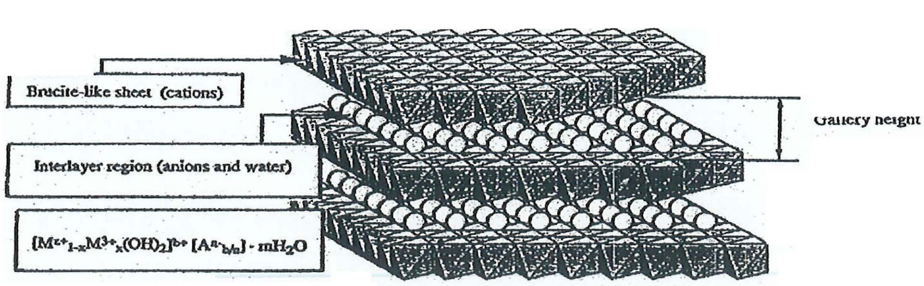

Figure 1: Hydrotalcite type structure [6]

These materials have been used as catalyst or adsorbents for several applications and their use in the carbon dioxide adsorption at temperature range between 400°C to 480°C was reported recently [7], [8]. This application is very important for the purification of natural gas, the possibility of CO_2 emissions controlled in the combustion of fossil fuels and for a new steam reforming process [9].

Co-precipitation method is the most commonly used method to prepare hydrotalcite like compounds. It is applied because other methods like decomposition-recrystallization, urea method and microwave irradiation are time consuming and require high amounts of water [10].

MATERIALS AND METHODS

Preparation of Hydrotalcite. The method used in the preparation of hydrotalcite samples were in conformity with previous studies [9]. Here, magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$), Aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) and 32ml deionized water were mixed together to form a solution. Mg/Al ratio used is 3.0. Then, the mixture is added with 95ml potassium carbonate, K_2CO_3 (1M) dropwise under vigorous stirring over hot plate magnetic stirrer at 60°C for 15 minutes to. An amount of sodium hydroxide, NaOH is added to the solution and the pH is maintained at 10. After that, the precipitation solution was maintained in stirring mode at 60°C for 3 hours. The precipitate was filtered and washed several times with deionized water to remove nitrate, NO_3 and excess sodium ion, Na^+. The solution was washed until the filtrate achieved pH 7 (neutral) [11]. The precipitate is dried in oven for 1 day at 100°C. Finally, the dried precipitate is calcined in furnace at 600°C for 15 hours [9].

Experimental setup. Figure 2 shows the schematic diagram of the experimental setup. A continuous flow reactor contained samples connected to a cylinder gas (purified carbon dioxide), pressure gauge and flowmeter are needed. A small amount of sample in powder form is placed inside the reactor to saturate the hydrotalcite samples with CO_2. The reactor was sealed tightly in order to prevent gas leakages. The gas is fixed at 5 ml/min at ambient temperature. The process is left to run for more than 24 hours when samples could be assumed to be completely saturated with carbon dioxide gas. The saturated samples later tested for BET surface area and pore sizes. Then, the saturated samples were thermally regenerated by heating in the carbolite furnace at 200°C, 450°C and 700°C for 4 hours.

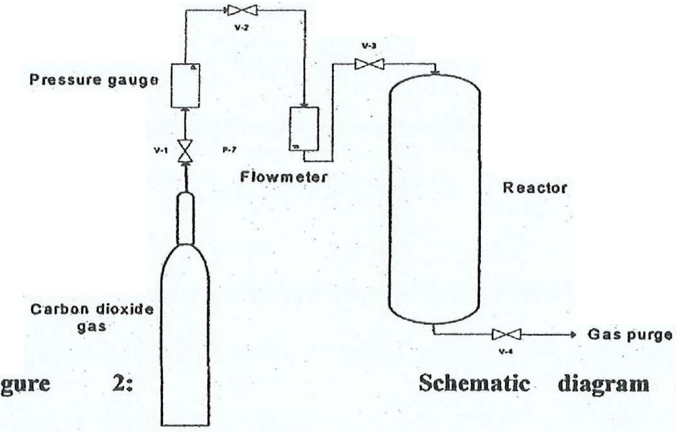

Figure 2: Schematic diagram of experimental setup

Characterization of Sample. The saturated sample with carbon dioxide gas and thermally regenerated sample were characterized to determine the desorption effects towards hydrotalcite. X-ray Diffraction, XRD (Diffraktometer D5000, Siemens) was tested to determine the significant chemical composition inside the samples. Thermogravimetric Analyzer, TGA (Perkin Elmer) was used to measure the weight loss at increasing temperature and time. Quantachrome Autosorb analyzer was used to measure the surface area and pore size inside the sample. Finally, Scanning Electron Microscopy, SEM was tested to monitor the structures of synthesized and commercial Hdrotalcite.

RESULTS AND DISCUSSION

Thermogravimetric analyses at 20°C/min of synthesized hydrotalcite, commercial hydrotalcite and regenerated samples where regeneration was conducted at 200°C, 450°C and 700°C. For the synthesized sample, the sample prepared under optimum reported condition (i.e. sample preparation at calcined temperature of 600°C) was taken. A typical TGA curves for commercial TGA are shown in Figures 3 to 6. The TGA results for the synthetic hydrotalcites were of similar behaviour. Analysis of TGA curves showed that significant reductions of CO_2 occurred at temperatures indicated in table below.

Table 1: Analysis of TGA curves for fresh and regenerated samples of commercial and synthesized hydrotalcite.

Sample	1st Reduction		2nd Reduction	
	Temperature (°C)	Percentage Reduction (%)	Temperature (°C)	Percentage Reduction (%)
Fresh Commercial Hydrotalcite	160	15	560	27.5
Regenerated Commercial Hydrotalcite at 200°C	160	15	580	27.5
Regenerated Commercial Hydrotalcite at 450°C	180	11.5	620	24.5
Regenerated Commercial Hydrotalcite at 700°C	200	14	600	23
Average	180.0	13.5	593.3	25.0
Fresh Synthesized Hydrotalcite	360	22.5	450	27.5
Regenerated Synthesized Hydrotalcite at 200°C	300	24	570	23.5
Regenerated Synthesized Hydrotalcite at 450°C	360	10	600	20
Regenerated Synthesized Hydrotalcite at 700°C	230	12.5	750	26.5
Average	316.7	15.0	600.0	24.7

The highest desorption temperature has been reported to be at 457°C [7] which is in conformity with the present findings. The results are also compatible with other previous studies [12], [13], [14]. The findings for synthesized hydrotalcite are slightly different from commercial hydrotalcite as seen from Table 1. In order to investigate the above behaviour around 200°C, 450°C and 700°C, a series of investigations based on BET surface area, SEM and XRD were carried out.

Tables 2 and 3 show the BET surface areas, micropore areas and the average pore diameters of the fresh hydrotalcite, CO_2 adsorbed hydrotalcite and heat treated hydrotalcite at various regeneration temperatures of synthesized and commercial hydrotalcite as obtained from the Quantachrome Autosorb. Commercial hydrotalcite is seen to have significant micropore areas compared with the synthesized hydrotalcite. Furthermore it can be seen that the available BET area decreased to about 97% and 89% after CO_2 adsorption for synthesized and commercial hydrotalcites respectively showing significant adsorption of CO_2 in adsorption process. Figures 3 to 6 show the TGA studies made for commercial hydrotaclite samples regenerated at 200°C, 450°C and 700°C repectively. Respective reductions of BET and micropore areas seem to be nearly 99.9% for 200°C, nearly 100% for 400°C and it is negligible for 700°C respectively (Table 2). It can be seen that the micropore areas are quite insignificant after regeneration showing either the micropores are destructed beyond 200°C or the CO_2 is still intact with the hydrotacites beyond 200°C. In order to ascertain the reason for this phenomenon, SEM studies are carried out for the samples. Figures 6, Figure 7, Figure 8(a),(b),(c),(d),(e) and (f) compare the SEM images obtained for fresh, CO_2 saturated and regenerated at 450°C and 700°C of synthesized and commercial hydrotalcite respectively. The figure shows similarities between structures of fresh and CO_2 adsorbed samples. However after heat treatments the structures differed drastically from fine to agglomerate type for both types of hydrotalcites. For regenerated samples of both types of hydrotalcite subsequent to adsorption with CO_2, the BET surface area showed a minimum peak around 450°C whereas the micropore area still remained negligible. This effect was investigated using XRD analysis of the respective samples. The XRD patterns showed a reduction of hydrotalcite content to periclase content at 450°C and regaining of the hydrotalcite content at 700°C for both synthetic and commercial hydrotalcites. This shift to could have lead to increase in adsorption BET surface areas at 700°C. Also both synthetic and commercial hydrotalcite showed dominance of periclase content at 450°C and a shift of the dominance from periclase content to magnesia content at 700°C. The structural changes observed between SEM images of samples regenerated at 450°C and 700°C could be attributed to this phenomenon.

Table 2: Autosorb properties for fresh synthesized hydrotalcite, CO_2 adsorbed synthesized hydrotalcite and heat treated synthesized hydrotalcite at various temperatures.

Autosorb	**Fresh**	**After CO_2 adsorbed**	**After heat treatment (°C)**		
			200	**450**	**700**
BET surface area (m^2/g)	110.98	2.90	19.24	1.08	6.97
Micropore area (m^2/g)	1.69	-	0.0018	-	negligible
Average pore diameter (nm)	12.14	25.58	23.97	1.92	1.8

Table 3: Autosorb properties for fresh commercial hydrotalcite, CO_2 adsorbed commercial hydrotalcite and heat treated commercial hydrotalcite at various temperatures.

Autosorb	**Fresh**	**After CO_2 adsorbed**	**After heat treatment (°C)**		
			200	**450**	**700**
BET surface area (m^2/g)	552.07	60.63	53.92	33.57	60.45
Micropore area (m^2/g)	292.91	3.50	negligible	negligible	negligible
Average pore diameter (nm)	2.35	19.22	1.8	1.94	1.92

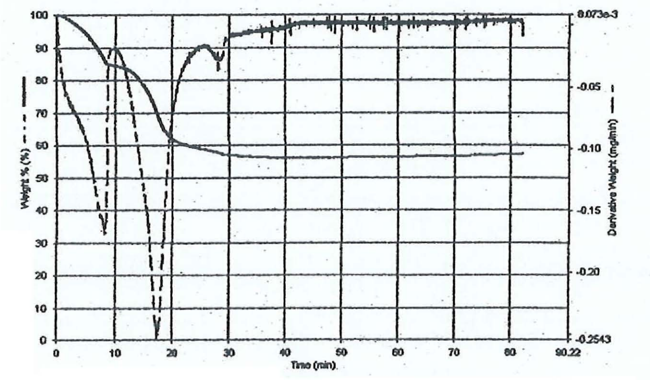

Figure 3: Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite

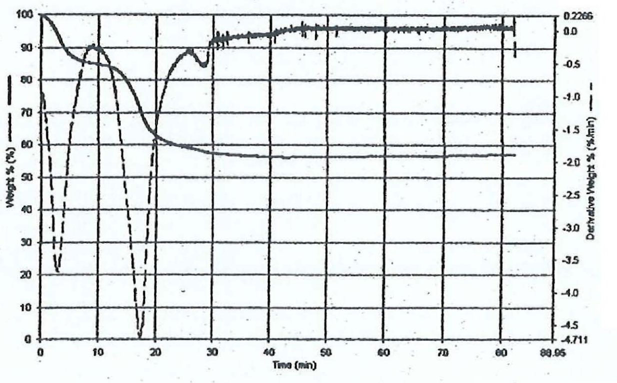

Figure 4: Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 200°C.

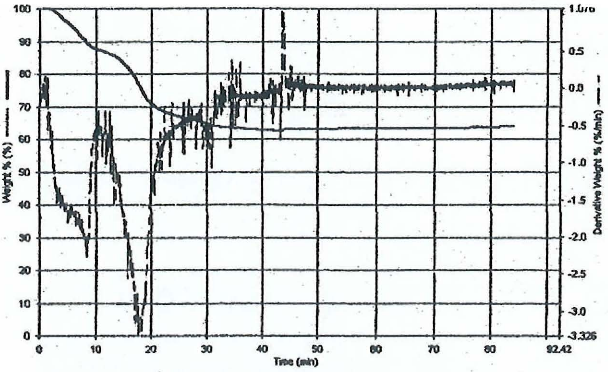

Figure 5(a): Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 450°C.

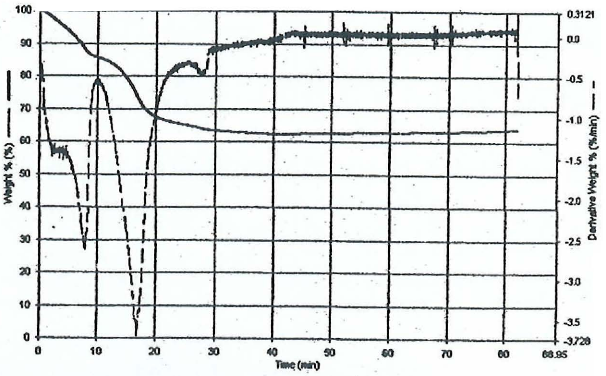

Figure5(b): Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 700°C.

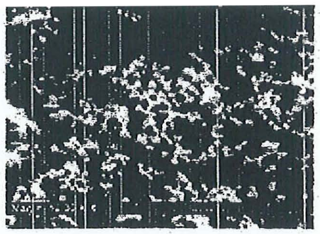

Figure 6: SEM image of fresh synthesized hydrotalcite calcined at 600°C

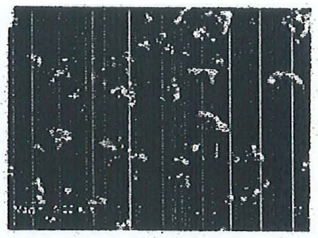

Figure 7: SEM images of fresh commercial hydrotalcite

CONCLUSIONS

Thermal gravimetric analysis was studied to investigate the thermal desorption properties of CO_2 in synthesized hydrotalcite and commercial hydrotalcite carried out at regeneration temperatures of 200°C, 450°C and 700°C. It was found that there are two regions of CO_2 adsorption/desorption in the hydrotalcite structures. From the above analysis, it could be concluded that:

1. Desorption of CO_2 from adsorbed samples of hydrotalcite reached an optimum at approximately 600°C.
2. The percentage reduction is found to be around 25% of the original weight.
3. At around 180°C the commercial hydrotalcite showed an initial desorption of about 13.5% and at around 316.7°C an initial desorption of approximately 15 % for the synthetic hydrotalcite at 180°C.
4. At around 600°C, both hydrotalcites showed a minimum BET surface area which could be attributed to the formation of periclase.
5. However, increase of temperature further showed a re-formation of hydrotalcite which was confirmed by XRD analysis for samples regenerated at 700°C.
6. After 600°C, desorption rate did not show any significant change.
7. However, further heating of both synthetic and commercial hydrotalcite beyond 600°C seems to be required in order to increase its BET area and re-conversion of periclase to hydrotalcite for re-use

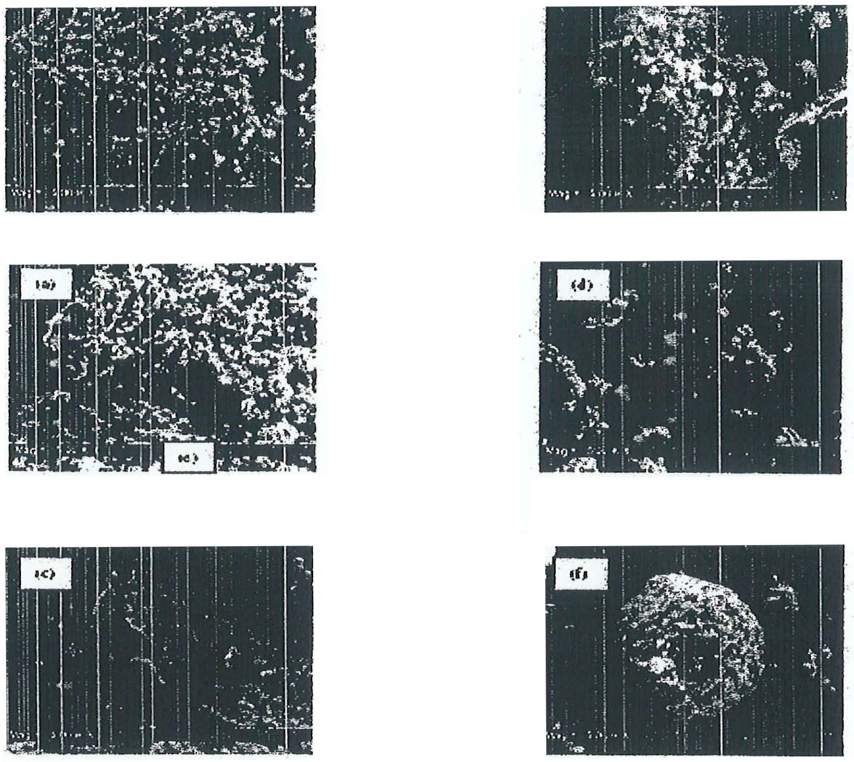

Figure 8: SEM images of (a) CO_2 adsorbed synthesized hydrotalcite, (b) heat treated synthesized hydrotalcite at 450°C, (c) heat treated synthesized hydrotalcite at 700°C, (d) CO_2 adsorbed commercial hydrotalcite, (e) heat treated commercial hydrotalcite at 450°C and (f) heat treated commercial hydrotalcite at 700°C.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support extended in terms of ExxonMobil Education Grant (2006) awarded for Research to the USM by Messers ExxonMobil Bhd. of Malaysia and the FRGS grant (2007) awarded by the Ministy of Higher Education of Malaysia.

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APPENDIX 5
Details of expenditure

JABATAN BENDAHARI
UNIT KUMPULAN WANG AMANAH
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN
PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 30/09/2008

Tempoh Projek: - 31/08/2008

PROF MADYA DR. W.J.N FERNANDO

304.PJKIMIA.6050112

JUMLAH GERAN :- 30,000.00

NO PROJEK :-

PANEL :

PENAJA :- EXXON MOBIL(E113)

EXPERIMENTAL AND MODELING STUDIES FOR THE COMPOSITE MEMBRANE/ADSORBER

Vot	Peruntukan (a)	Perbelanjaan sehingga 31/12/2007 (b)	Tanggungan semasa 2008 (c)	Perbelanjaan Semasa 2008 (d)	Jumlah Perbelanjaan 2008 (c + d)	Jumlah Perbelanjaan Terkumpul (b+c+d)	Baki Peruntukan Semasa 2008 (a-(b+c+d))
77000 SUMBANGAN BADAN LUAR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78000 YURAN DAN PENDAPATAN	0.00	(30,000.00)	0.00	0.00	0.00	(30,000.00)	30,000.00
	0.00	(30,000.00)	0.00	0.00	0.00	(30,000.00)	30,000.00
11000 GAJI KAKITANGAN AWAM	0.00	8,761.83	0.00	2,196.01	2,196.01	10,957.84	(10,957.84)
14000 ELAUN LEBIH MASA KAKITANGAN AWAM	0.00	212.76	0.00	0.00	0.00	212.76	(212.76)
21000 PERBELANJAAN PERJALANAN DAN SARAHID	0.00	0.00	0.00	269.70	269.70	269.70	(269.70)
23000 PERHUBUNGAN DAN UTILITI	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27000 BEKALAN DAN ALAT PAKAI HABIS	0.00	5,757.00	0.00	(635.81)	(635.81)	5,121.19	(5,121.19)
29000 PERKHIDMATAN IKTISAS & HOSPITALITI	0.00	1,225.00	0.00	6,974.00	6,974.00	8,199.00	(8,199.00)
35000 HARTA-HARTA MODAL LAIN	0.00	0.00	0.00	4,400.00	4,400.00	4,400.00	(4,400.00)
42000 PEMBERIAN	0.00	750.00	0.00	0.00	0.00	750.00	(750.00)
	0.00	16,706.59	0.00	13,203.90	13,203.90	29,910.49	(29,910.49)
Jumlah Besar	0.00	(13,293.41)	0.00	13,203.90	13,203.90	(89.51)	89.51

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Re: ExxonMobil Support to Higher Education: Final Report of Grant for Research

Wednesday, 29 October, 2008 13:36

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Profesor Madya Dr.W.J.N.Fernando,

Thank you for sending the Final Report of the Research Proposal to us. EMEPMI wish you all the Best and hope USM will continue to benefit from our yearly Education Funds given out to Higher Learnings.

Regards,
Serena Yong
Technical Development Unit
Menara ExxonMobil, ME26:17
Tel: (603) 2380-2603

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Ms Serena Yong
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Dear Ms. Serena Yong

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Further to my e-mail of August 2008 and to your subsequent reply, I am pleased to forward the Final Report of the above project in .pdf format (attachment herewith please). A hard copy of the report will be posted today.