UNIVERSITI PUTRA MALAYSIA

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By

MA'AN FAHMI R. ALKHATIB

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy

May 2007

DEDICATION

This work is especially dedicated to my beloved…

Mother Zainab Qattash
Father Fahmi Alkhatib
Wife Suhailah Marie
Sons Umar & Harith Alkhatib

who offered me unconditional love and support throughout the course of this thesis.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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May 2007

Chairman: Professor Fakhru'l Razi Ahmadun, PhD

Faculty: Engineering

Adsorbed natural gas (ANG) technique was used in this study to test the adsorption capacity of carbon materials fro methane gas storage. An adsorption system based on volumetric method was designed and fabricated for this purpose. The carbon materials used were Malaysian industrial activated carbon produced from palm kernel shell and coconut shells. These materials have not been thoroughly investigated for ANG applications. Also a new material which is a composite of CNTs and activated carbon (ACNT) produced in this work along with commercial CNTs were investigated as ANG storage media.

ACNT was produced using chemical vapour deposition (CVD) method using activated carbon as catalyst substrate. The presence of activated carbon, besides being substrate, served as auxiliary storage media. This method successfully produced CNTs with diameters ranged form 25 to 70 nm and lengths, mostly, of

more than 10 μm. These long tubes could be a result of the long reaction time (3 hours), thus if shorter CNTs are required, shorter reaction times should be applied.

The adsorption storage experiments were run at pressures up to 50 bar and temperatures of 30, 40 and 50 °C. The adsorption capacity on mass basis (at 35 bar and 30 °C) ranged from as low as 1.48 mmol/g for com-CNT to 6.20 mmol/g for CSAC3. ACNT showed a relatively high adsorption capacity of 4.51 mmol/g. The results indicate that there is a general trend of increasing in adsorption capacity with increasing micropore volume. However, micropore size distribution (MPSD) must be taken into account in evaluating the adsorbents.

The adsorption capacity on volume basis (V/V) ranged from 51.57 for com-CNT to 106.46 for CSAC2. These values are still below the targeted 150 V/V. While some adsorbents showed the highest adsorption capacity on mass basis compared to others (CSAC3 versus CSAC2), yet their capacity on volume basis was lower as a result of their lower bulk density. This showed the importance of this parameter in ANG applications.

The methane delivered values were 7-25% lower than the volumetric methane storage capacity. The high retention of methane gas at atmospheric pressure by some adsorbents could be explained by their narrow MPSD. Accordingly, the narrow MPSD helps in increasing the adsorption capacity, yet, the very narrow MPSD will increase the amount of gas retained.

Several single component isotherm models were used to fit the experimental adsorption isotherm data. All the adsorption isotherm models used showed a good fit to the experimental data. However, Langmuir isotherm model was chosen to be used in the dynamic model to restrict the already heavy computational load from being unrealistic.

The experimental data obtained from the storage and delivery tests were compared to those obtained from process simulation using a dynamic model. The simulation model was run using the measured equilibrium data as input parameters. A good agreement was observed between experimental and simulated results. Pressure and temperature histories were acceptably well predicted.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KEUPAYAAN PENJERAPAN GAS METANA BAGI BAHAN-BAHAN KARBON UNTUK KEGUNAAN GAS ASLI TERJERAP

Oleh

MA'AN FAHMI R. ALKHATIB

Mei 2007

Pengerusi: Profesor Fakhru'l Razi Ahmadun, PhD

Fakulti: Kejuruteraan

Teknik gas asli terjerap (GAT) telah digunakan di dalam kajian ini untuk mempelajari keupayaan penjerapan bahan karbon untuk penyimpanan gas metana. Sesuatu sistem penjerapan yang berdasarkan kaedah isi padu telah direka bentuk dan dibikin untuk tujuan ini. Bahan karbon yang digunakan adalah bahan industri karbon teraktif yang dihasilkan daripada tempurung buah sawit dan tempurung kelapa, dari Malaysia. Bahan-bahan ini belum pernah disiasat sepenuhnya untuk aplikasi GAT. Di dalam kerja ini, sebuah bahan baru iaitu komposit karbon teraktif dan tiub nano karbon (CNT), dan juga komersial tiub nano karbon telah disiasat sebagai media penyimpanan.

Tiub Nano Karbon Teraktif (ACNT) telah dihasilkan dengan kaedah penguraian wap kimia dengan menggunakan karbon teraktif sebagai susbtrat pemangkin. Kehadiran karbon teraktif, selain dari sebagai substrat, berfungsi sebagai bantuan media penyimpanan. Kaedah ini telah berjaya menghasilkan CNT dengan garis pusat julat

antara 25 hingga 70 nm and panjang, kebanyakannya melebihi 10 μm. Tiub-tiub yang panjang ini adalah hasil daripada masa tindak balas yang lama (3 jam). Oleh itu, jika lebih pendek CNTs dikehendaki, masa tindak balas yang lebih pendek patut dikenakan.

Ujikaji-ujikaji penyimpanan secara penjerapan dilakukan pada tekanan setinggi 50 bar dan suhu-suhu 30, 40 dan 50 darjah Celsius. Julat muatan penjerapan atas asas jisim (pada 35 bar dan 30^{o}C) ialah dari serendah 1.48 mmol/g untuk CNT komersil ke setinggi 6.12 mmol/g untuk CSAC3. ACNT menunjukkan muatan penjerapan yang agak tinggi, iaitu 4.51 mmol/g. Keputusan menunjukkan arah-tuju am di mana muatan penjerapan meningkat dengan isipadu liang mikro. Walau bagaimanapun, taburan saiz liang mikro (TSLM) mesti juga diambil-kira dalam penilaian calon-calon penjerap.

Muatan penjerapan berasaskan isipadu (V/V) menjangkau julat 51.57 untuk CNT komersil ke 106.46 untuk CSAC2. Nilai-nilai ini masih di bawah sasaran 150 V/V. Walaupun sesetengah zat penjerap menunjukkan muatan penjerapan tertinggi berasaskan jisim (CSAC3 lawan CSAC2), muatan penjerapan mereka berasaskan isipadu adalah lebih rendah disebabkan ketumpatan pukal mereka yang lebih rendah. Ini mencerminkan kepentingan ketumpatan pukal dalam penilaian penjerap.

Nilai metana-boleh-hasil ialah 7 ke 25% lebih rendah daripada muatan simpanan berasaskan isipadu. Nilai penahanan gas metana pada tekanan atmosfera oleh sesetengah zat penjerap boleh dijelaskan oleh TSLM-nya yang sempit. Sewajarnya, TSLM yang sempit membantu meningkatkan muatan penjerapan, tetapi TSLM yang tersangat sempit turut meningkatkan jumlah gas yang tertahan.

Beberapa komponen tunggal isterma telah digunakan untuk pemadanan eksperimen yang tersesuai bagi data penjerapan isoterma. Kesemua penjerapan isoterma model menunjukan pemadanan yang bagus terhadap data eksperimen. Bagaimanapun, isoterma model Langmuir telah dipilih untuk digunakan di dalam model dinamik untuk menghadkan beban pengiraan yang telah pun berat daripada menjadi tidak realistik.

Data eksperimen yang diperolehi daripada simpanan dan ujian serahan telah dibandingkan dengan data daripada proses simulasi menggunakan model dinamik. Model simulasi telah dijalankan dengan menggunakan data keseimbangan sebagai parameter input. Persetujuan yang baik telah diperhatikan di antara keputusan eksperimen dan simulasi. Sejarah tekanan dan suhu adalah seperti yang diramalkan.

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Last but not least, I feel speechless to express my feelings towards my beloved wife as she steadfast beside me regardless of the hardship days we went through. I carried her wordings of encouragements and support all times “Allah put you to it, He will put you through it”. I pray to Allah to enable me to compensate her and my two sons for the long times that I could not be with them while working on my research.

I certify that an examination committee met on 10th May, 2007 to conduct the final examination of Ma'an Fahmi Rashid AL Khatib on his Doctor of Philosophy thesis entitled "Methane Gas Adsorption Capacity of Carbon Materials for Adsorbed Natural Gas Applications" 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 submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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Date: 17 JULY 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

(signed)________________________

MA'AN FAHMI R. ALKHATIB

Date: 29 DECEMBER 2006

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ACNT	Activated carbon-nanotube composite
ANG	Adsorbed natural gas
BET	Brunauer, Emmet and Teller surface area
CNG	Compressed natural gas
CNT	Carbon nanotube
Com-CNT	Commercial carbon nanotube
CSAC	Coconut shell activated carbon
CVD	Chemical vapor deposition
DR	Dubinin-Radskuvich
LNG	Liquefied natural gas
MPSD	Micropore size distribution
NG	Natural gas
NGV	Natural gas vehicles
PSAC	Palm shell Activated carbon

A	parameter in isotherm equation	
A_c	total cross section of a packed vessel	m^2
b	the affinity constant	bar^{-1}
c	concentration	mol/m^3
Cpg	gas specific heat	J/kg K
Cps	solid specific heat	J/kg K
D_{bed}	bed diameter	m
D_k	Knudsen diffusion	cm^2/sec
D_m	molecular diffusion	cm^2/sec