

**EFFECT OF CARBON DIOXIDE ON METHANE ADSORPTION ON
COCONUT SHELL ACTIVATED CARBON IN A PACKED BED COLUMN**

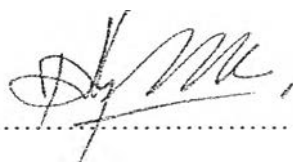
Chompunick Sitthirawiphong

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2013

I28372669

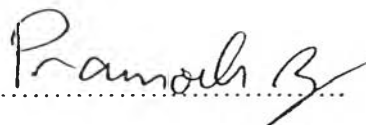
Thesis Title: Effect of Carbon Dioxide on Methane Adsorption on
Coconut Shell Activated Carbon in a Packed Bed Column
By: Chompunick Sitthirawiphong
Program: Petroleum Technology
Thesis Advisors: Assoc. Prof. Pramoch Rangsunvigit
Dr. Santi Kulprathipanja
Asst. Prof. Boonyarach Kitiyanan

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

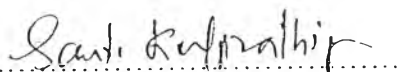


..... College Dean
(Asst. Prof. Pomthong Malakul)

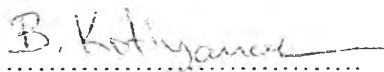
Thesis Committee:



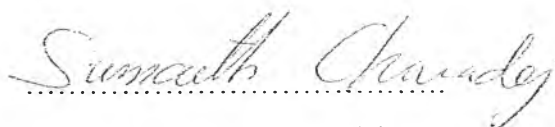
.....
(Assoc. Prof. Pramoch Rangsunvigit)



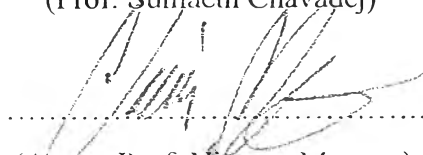
.....
(Dr. Santi Kulprathipanja)



.....
(Asst. Prof. Boonyarach Kitiyanan)



.....
(Prof. Sumaeth Chavadej)



.....
(Assoc. Prof. Vissanu Meeyoo)

561028

ABSTRACT

5473003063: Petroleum Technology Program

Chompunick Sitthirawiphong: Effect of Carbon Dioxide on Methane Adsorption on Coconut Shell Activated Carbon in a Packed Bed Column.

Thesis Advisors: Assoc. Prof. Pramoch Rangsunvigit, Dr. Santi Kulprathipanja, Asst. Prof. Boonyarach Kitiyanan 76 pp.

Keywords: Adsorption/ Activated carbon/ Carbon dioxide/ Methane

The investigation of methane adsorption with the presence of carbon dioxide on the coconut shell activated carbon (CSAC) was studied in a packed bed column. The adsorption kinetics of methane and carbon dioxide were examined at atmospheric pressure and room temperature. The dynamic adsorption of 75 to 85 vol% methane and 5 to 20 vol% carbon dioxide were first carried out in a packed bed column with approximately 5.0 g of the CSAC. The competitive adsorption of the two species on the CSAC was then studied at 10 vol% methane and 10 to 30 vol% carbon dioxide. After that, the comparison of competitive adsorption on different adsorbents including the untreated CSAC, the CSAC treated by sulfuric acid, the CSAC treated by potassium hydroxide, and the untreated palm shell activated carbon (PSAC) were studied at 10 vol% methane and carbon dioxide. Moreover, the 3-cycle adsorption-desorption was used to investigate the adsorbent stability. BET and SEM techniques were used to characterize the adsorbents. The composition of methane and carbon dioxide was determined by gas chromatography. Results show that carbon dioxide significantly affects the adsorption of methane. The breakthrough time of carbon dioxide is longer than that of methane, and the methane roll up increases with the increase in the concentration of carbon dioxide because carbon dioxide is more selectively adsorbed on all adsorbents than that of methane. For the adsorbent stability, results show that the increase in the adsorption-desorption cycle from 1 to 3 times slightly affects the adsorbent stability.

บทคัดย่อ

ชมพูนิกซ์ สิทธิวิพงษ์: ผลของคาร์บอนไดออกไซด์ต่อการดูดซับมีเทนบนถ่านกัมมันต์จากกะลามะพร้าวในคอลัมน์แบบเบดนิ่ง (Effect of Carbon Dioxide on Methane Adsorption on Coconut Shell Activated Carbon in a Packed Bed Column) อ. ที่ปรึกษา: รศ. ดร. ปราโมช รังสรรค์วิจิตร ดร. สันติ กุลประทีปปัญญา และ ผศ. ดร. บุนยรัชต์ กิตยานันท์ 76 หน้า

งานวิจัยนี้ศึกษาผลของคาร์บอนไดออกไซด์ต่อการดูดซับมีเทนบนถ่านกัมมันต์จากกะลามะพร้าว (Coconut Shell Activated Carbon, CSAC) ในคอลัมน์แบบเบดนิ่ง (Packed Bed Column) การศึกษาจลนศาสตร์ของการดูดซับมีเทนและคาร์บอนไดออกไซด์ภายใต้ความดันบรรยากาศและอุณหภูมิห้อง โดยครอบคลุมการศึกษาจลนศาสตร์ของการดูดซับมีเทนในช่วงความเข้มข้น 75 ถึง 85 vol% และคาร์บอนไดออกไซด์ในช่วงความเข้มข้น 5 ถึง 20 vol% ในคอลัมน์แบบเบดนิ่งโดยใช้ปริมาณของ CSAC ประมาณ 5.0 g และการศึกษาการแข่งขันการดูดซับของมีเทนที่ความเข้มข้น 10 vol% และคาร์บอนไดออกไซด์ในช่วงความเข้มข้น 10 ถึง 30 vol% จากนั้นศึกษาเปรียบเทียบการแข่งขันการดูดซับบนถ่านกัมมันต์ที่ต่างกันประกอบด้วย CSAC ที่ไม่ผ่านการบำบัด CSAC ที่บำบัดด้วยกรดซัลฟิวริก CSAC ที่บำบัดด้วยโพแทสเซียมไฮดรอกไซด์ และถ่านกัมมันต์จากเปลือกปาล์ม (Palm Shell Activated Carbon, PSAC) ที่ไม่ผ่านการบำบัด ที่ความเข้มข้น 10 vol% ของมีเทนและคาร์บอนไดออกไซด์ นอกจากนั้นศึกษาความคงตัวของตัวดูดซับโดยการหมุนเวียนการดูดซับและการปล่อยออกเป็นจำนวน 3 ครั้ง การพิสูจน์เอกลักษณ์ตัวดูดซับทำโดยใช้เทคนิคการทดสอบหาพื้นที่ผิวและรูพรุนด้วย BET และการทดสอบลักษณะทางสัณฐานวิทยาด้วย SEM ความเข้มข้นมีเทนและคาร์บอนไดออกไซด์ทำโดยใช้ GC ผลการทดลองแสดงให้เห็นได้ว่าคาร์บอนไดออกไซด์ส่งผลกระทบต่อประสิทธิภาพการดูดซับของมีเทน คาร์บอนไดออกไซด์ใช้เวลาหลุดออกจากตัวดูดซับมากกว่ามีเทน และการรวมตัวเพิ่มขึ้นของมีเทนจะเกิดขึ้นเมื่อความเข้มข้นของคาร์บอนไดออกไซด์เพิ่มมากขึ้น เนื่องจากตัวดูดซับทุกตัวเลือกดูดซับคาร์บอนไดออกไซด์มากกว่าดูดซับมีเทน สำหรับความคงตัวของตัวดูดซับ ผลการทดลองแสดงให้เห็นได้ว่าการเพิ่มจำนวนการหมุนเวียนการดูดซับและการปล่อยออกจาก 1 ถึง 3 ครั้งมีผลกระทบต่อความคงตัวของตัวดูดซับ

ACKNOWLEDGEMENTS

I would like to take this chance to sincerely thank my advisor, Assoc. Prof. Pramoch Rangsunvigit, for his helpful suggestions, discussions, supervision from the very early stage of this research. He also provided me unflinching encouragement, patience and support in various ways throughout my graduate thesis.

I would also like to thank my co-advisors, Dr. Santi Kulprathipanja and Asst. Prof. Boonyarach Kitiyanan for their advices, guidances, and willingness to share their bright thoughts with me, which were very helpful for shaping up my ideas and research.

I would like to thank Prof. Sumaeth Chavadej and Assoc. Prof. Vissanu Meeyoo for kindly serving on my thesis committee. Their suggestions are certainly important and helpful for completion of this thesis.

This thesis work is funded by the Petroleum and Petrochemical College; and the Center of Excellence on Petrochemical and Materials Technology, Thailand.

I would like to thank the entire faculty and staff at the Petroleum and Petrochemical College, Chulalongkorn University for their kind assistance and cooperation.

I would like to thank the Carbokarn Co., Ltd. for the kind support of activated carbon.

Finally, I would like to express my sincere gratitude to thank my whole family for showing me the joy of intellectual pursuit ever since I was a child, for standing by me and for understanding every single part of my mind.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Natural Gas	3
2.2 Natural Gas Storage Method	6
2.2.1 Liquefied Natural Gas (LNG)	6
2.2.2 Compressed Natural Gas (CNG)	7
2.2.3 Adsorbed Natural Gas (ANG)	8
2.3 Natural Gas Vehicles (NGVs)	12
2.4 Adsorption	14
2.5 Adsorption Isotherms	15
2.5.1 IUPAC Classification of Adsorption Isotherms	16
2.5.2 Measurement of Adsorption Isotherms	18
2.6 Adsorbents and Activated Carbon	18
2.7 Literature Review	21

CHAPTER	PAGE
III EXPERIMENTAL	27
3.1 Materials and Chemicals	27
3.2 Experimental Procedures	27
3.2.1 Adsorbent Preparation	27
3.2.2 Adsorbent Characterization	27
3.2.3 Adsorption Measurement	28
3.2.4 Adsorbent Stability	29
3.2.5 Adsorbent Surface Treatment	29
IV RESULTS AND DISCUSSION	30
4.1 Adsorbent Characterizations	30
4.1.1 Surface Area Analysis	30
4.1.2 Scanning Electron Microscopy	33
4.2 Adsorption Experiments	33
4.2.1 Single Component Adsorption	33
4.2.2 Competitive Adsorption	35
4.2.3 Adsorbent Stability	40
4.2.4 Comparison of Competitive Adsorption on Different Adsorbents	47
V CONCLUSIONS AND RECOMMENDATIONS	58
5.1 Conclusions	58
5.2 Recommendations	59
REFERENCES	60
APPENDICES	64
Appendix A Adsorbent Physical Characterization	64
Appendix B Adsorption and Desorption Curves in Different Scale	65

CHAPTER

PAGE

CURRICULUM VITAE

76

LIST OF TABLES

TABLE		PAGE
2.1	Typical composition of natural gas	3
2.2	Characteristics of natural gas components	4
2.3	Features of adsorption isotherms for all six types	16
4.1	BET surface area, micropore volume, and average pore diameter of investigated adsorbents	30

LIST OF FIGURES

FIGURE	PAGE
2.1 Adsorption of methane molecules on the activated carbon adsorbent in micropore, mesopore, and macropore structures.	9
2.2 A prototype of ANG tank with monolithic activated carbons inside.	9
2.3 Comparison between natural gas fuel systems and gasoline fuel system in terms of fuel, vehicle, and station costs.	13
2.4 Natural gas vehicles in the past; the first natural gas vehicle 1910 (USA) with balloon tank on trailer (left) and natural gas vehicle ~1930 (France) with balloon tank on roof (right).	13
2.5 Natural gas vehicles in the present and future; current natural gas vehicle with high-pressure in trunk (left) and future natural gas vehicle with low-pressure tank in unused space (right).	14
2.6 IUPAC classification of adsorption isotherms.	17
2.7 Commercial activated carbon from coconut shells-based precursor in powdered, granular, and pelletized forms.	19
2.8 Single-component adsorption isotherms for the n-alkanes C ₁ -C ₄ .	24
2.9 Single-component adsorption isotherms for CO ₂ and N ₂ .	25
2.10 Comparative of adsorption isotherms for the n-alkanes C ₁ -C ₄ at 25 °C.	26
2.11 Comparative of adsorption isotherms for CO ₂ and N ₂ at 37 °C.	26
3.1 Schematic diagram of the experimental set up.	28
4.1 Nitrogen adsorption-desorption isotherms of: untreated CSAC, CSAC treated by potassium hydroxide, CSAC treated by sulfuric acid, and untreated PSAC.	31
4.2 Pore size distribution (DA) of: untreated CSAC, CSAC treated by potassium hydroxide, CSAC treated by sulfuric acid, and untreated PSAC.	32
4.3 SEM micrographs of the CSAC with magnifications of (a) 250, (b) 1,000, (c) 1,500, and (d) 10,000.	33

FIGURE	PAGE
4.4 Breakthrough curves of methane from the adsorption on the CSAC with the initial concentration of methane at 75, 80, and 85 vol% at room temperature.	34
4.5 Breakthrough curves of carbon dioxide from the adsorption on the CSAC with the initial concentration of carbon dioxide at 5, 10, 15, and 20 vol% at room temperature.	34
4.6 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	35
4.7 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 15 vol% at room temperature.	36
4.8 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 20 vol% at room temperature.	37
4.9 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 25 vol% at room temperature.	38
4.10 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 30 vol% at room temperature.	38
4.11 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10, 15, 20, 25, and 30 vol% at room temperature.	39

FIGURE	PAGE
4.12 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	40
4.13 Three desorption cycles of methane and carbon dioxide from the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	41
4.14 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 15 vol% at room temperature.	42
4.15 Three desorption cycles of methane and carbon dioxide from the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 15 vol% at room temperature.	43
4.16 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 20 vol% at room temperature.	44
4.17 Three desorption cycles of methane and carbon dioxide from the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 20 vol% at room temperature.	44
4.18 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 25 vol% at room temperature.	45
4.19 Three desorption cycles of methane and carbon dioxide from the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 25 vol% at room temperature.	46

FIGURE	PAGE
4.20 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 30 vol% at room temperature.	46
4.21 Three desorption cycles of methane and carbon dioxide from the CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 30 vol% at room temperature.	47
4.22 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the untreated CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	48
4.23 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC treated by sulfuric acid with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	48
4.24 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC treated by potassium hydroxide with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	49
4.25 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the untreated PSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	49
4.26 Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the untreated CSAC, CSAC treated by sulfuric acid, CSAC treated by potassium hydroxide, and untreated PSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	50

FIGURE	PAGE
4.27 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	52
4.28 Three desorption cycles of methane and carbon dioxide from the untreated CSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	53
4.29 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by sulfuric acid with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	53
4.30 Three desorption cycles of methane and carbon dioxide from the CSAC treated by sulfuric acid with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	54
4.31 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by potassium hydroxide with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	54
4.32 Three desorption cycles of methane and carbon dioxide from the CSAC treated by potassium hydroxide with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	55
4.33 Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated PSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	55
4.34 Three desorption cycles of methane and carbon dioxide from the untreated PSAC with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol% at room temperature.	56