

การแยกโดยการดูดซับของแก๊ส H_2 , CO_2 , CH_4 , CO และ N_2 ด้วยซีโอไลต์



นางสาวแสงโสม จงโสทธิจักร

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ADSORPTION SEPARATION OF H₂, CO₂, CH₄, CO AND N₂ BY ZEOLITES



Miss Sangsom Chongsotichat

ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย

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แสงโสม จงโสตติฉัตร : การแยกโดยการดูดซับของแก๊ส H_2 , CO_2 , CH_4 , CO และ N_2 ด้วยซีโอไลต์ (ADSORPTION SEPARATION OF CO_2 , CH_4 , N_2 , CO AND H_2 BY ZEOLITES) อ. ที่ปริกษาวิทยานิพนธ์หลัก อ.ดร.ดวงกมล นันทศรี, 109 หน้า.

ในงานวิจัยนี้ศึกษาตัวดูดซับและภาวะที่เหมาะสมในการทำ แก๊สไฮโดรเจนให้บริสุทธิ์ โดยการดูดซับ ปัจจัยที่ศึกษาได้แก่ ชนิดของซีโอไลต์ที่ใช้ในการดูดซับ อุณหภูมิ ความดัน ป้อนเข้า ขนาดของซีโอไลต์ และอัตราส่วนระหว่าง ซีโอไลต์และอลูมินา และได้ทำการศึกษาอายุการใช้งานของตัวดูดซับด้วย โครงสร้างของซีโอไลต์ ได้ถูกวิเคราะห์โดย เอกซ์ อาร์ ดี ซี โอไลต์ที่ใช้ในการศึกษาครั้งนี้ ได้แก่ ซีโอไลต์ 3 เอ 4 เอ 5 เอ 13 เอกซ์ และ บีดี โดยทำการทดลองที่อุณหภูมิ -196 องศาเซลเซียส 0 องศาเซลเซียส และ อุณหภูมิห้อง ($25^{\circ}C$) ความดันป้อนเข้าอยู่ที่ 5 10 15 และ 20 บาร์เกจ ขนาดของเม็ดซีโอไลต์ที่ใช้ในการทดลอง ได้แก่ 1-2 และ 2.5-5 มม. อัตราส่วนของ อลูมินา:ซีโอไลต์ได้แก่ 9:3 และ 5:7 โดยน้ำหนักและทำการศึกษาอายุการใช้งานของตัวดูดซับโดยทำการทดลองซ้ำเป็นจำนวน 4 ครั้ง ให้ความร้อนที่อุณหภูมิ 300 องศาเซลเซียส เป็น เวลา 3 ชั่วโมงสำหรับซีโอไลต์ และ 180 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง สำหรับ อลูมินา แล้วเปรียบเทียบ ความบริสุทธิ์ของ ไฮโดรเจน ที่ได้หลังจากการดูดซับในแต่ละรอบ แก๊สป้อนเข้าที่ใช้ได้แก่ แก๊สผสมมาตรฐาน ที่มีองค์ประกอบของ แก๊สคาร์บอนมอนออกไซด์ 10.1% คาร์บอนไดออกไซด์ 9.9% มีเทน 10.1% ไนโตรเจน 10.0% และ ไฮโดรเจน 59.8% นอกจากนั้นยังใช้ ไฮโดรเจนเกรดอุตสาหกรรม เป็นแก๊สป้อนเข้าอีกด้วย จากผลการทดลองพบว่า เม็ดซีโอไลต์ สามารถดูดซับ แก๊สคาร์บอนไดออกไซด์ มีเทน คาร์บอนมอนออกไซด์ และไนโตรเจนได้ดีตามลำดับ ความดันป้อนเข้าที่เหมาะสมคือที่ 10 บาร์เกจ อุณหภูมิที่คอลัมน์เป็น -196 องศาเซลเซียส ขนาดของตัวดูดซับที่ 2.5-5 มม. และอัตราส่วนของ อลูมินา : ซีโอไลต์ที่เหมาะสมคือที่ 9:3 เมื่อนำภาวะนี้ไปประยุกต์ใช้กับแก๊สไฮโดรเจนเกรดอุตสาหกรรม เป็นสารป้อนเข้าทำให้ได้ แก๊สไฮโดรเจนที่มีความบริสุทธิ์สูงถึง 99.9999% ตัวดูดซับดังกล่าวถูกนำกลับมาใช้ใหม่ หลังการทดลอง 4 ครั้ง พบว่าไม่มีผลต่อการเปลี่ยนแปลงความบริสุทธิ์ของแก๊สไฮโดรเจนอย่างมีนัยสำคัญ

สาขาวิชา: ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา: 2551.....

ลายมือชื่อนิสิตแสงโสม จงโสตติฉัตร
ลายมือชื่อ อ.ที่ปริกษาวิทยานิพนธ์หลักดวงกมล นันทศรี

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SANGSOM CHONGSOTICHAT : ADSORPTION SEPARATION OF
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This experiment studies hydrogen purification by cryogenic adsorption. Effect of zeolite molecular sieves, temperature, bead size, inlet pressure and ratio of zeolite/alumina were studied. Life time of adsorbents was also investigated. The characterization of each zeolite was determined by XRD. Zeolite were studied are 3A, 4A, 5A, 13X and beta at the temperature of -196°C, 0°C and ambient (25°C). The inlet pressure are 5, 10, 15, 20 bar g. Bead size are 1-2 and 2.5-5 mm. The ratio of alumina:zeolite are 9:3 and 5:7 by weight. Life time of adsorbents were studied by repeating 4 times of calcination at 300°C, 3 hours for zeolite and 180°C, 3 hours for alumina. Then compare purity of hydrogen after each adsorption cycle. Feed gases are standard mixed gas composed of 10.1% CO, 9.9% CO₂, 10.1% CH₄, 10.0% N₂, 59.8% H₂ and hydrogen industrial grade. According to the results, beta zeolite has a good adsorption ability for CO₂, CH₄, CO and N₂ respectively. The suitable inlet pressure is 10 barg and the temperature at purify tank -196°C. The pellet size is 2.5-5 mm. and the ratio of alumina:zeolite is 9:3. When this condition was applied to, hydrogen industrial grade as a feed gas, hydrogen purity would be increased up to 99.9999%. This adsorbent was test to reuse. After four times of adsorption cycles, this adsorbent can be reused without a significant changing in H₂ purity.

Field of Study : Petrochemistry and Polymer Science

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Student's Signature Sangsom

Advisor's Signature D. Nuntasri

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT (THAI).....	iv
ABSTRACT (ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
LIST OF ABBREVIATIONS.....	xiv
CHAPTER I INTRODUCTION.....	1
1.1 Introduction.....	1
1.1.1 Technical data of hydrogen.....	3
1.1.2 Sources of hydrogen.....	3
1.1.3 Uses of hydrogen.....	4
1.1.4 Hydrogen purities and forms.....	7
1.1.5 Hydrogen purification technology.....	8
1.2 Objective and scope of the research.....	12
1.2.1 Objectives.....	12
1.2.2 Scope of the research.....	12
CHAPTER II THEORY AND LITERATURE REVIEWS.....	13
2.1 Gas separation by adsorption process.....	13
2.2 Industrial sorbent.....	16
2.2.1 Activated carbon.....	17
2.2.2 Zeolites.....	22
2.2.3 Silica gel.....	31
2.2.4 Activated alumina.....	34
2.3 Selection of sorbent.....	35

2.4 Effect of molecular sieve on adsorption	36
2.5 Literature reviews.....	42
CHARPTER III EXPERIMENTAL.....	44
3.1 Materials and equipments.....	44
3.1.1 Chemicals.....	44
3.1.2 Equipments.....	50
3.2 Experiment.....	55
3.2.1 Hydrogen purification.....	55
3.2.2 Outlet gas analysis.....	56
3.2.3 Study factor that affect hydrogen purification process.....	57
3.2.4 Study life time of zeolite.....	57
3.2.5 Compare the best and present condition.....	57
CHARPTER IV RESULTS AND DISCUSSIONS.....	59
4.1 Characterization of adsorbents.....	59
4.2 Effect of molecular sieve (zeolite).....	61
4.3 Effect of temperature.....	64
4.4 Effect of inlet pressure.....	67
4.5 Effect of pellet size.....	68
4.6 Effect of ration of alumina and zeolite.....	70
4.7 Life time of adsorbent.....	73
4.8 Comparison of the best and present condition.....	75
CHARPTER V CONCLUSIONS AND DISCUSSIONS.....	78
5.1 Conclusions.....	78
5.2 Suggestions.....	78
REFERENCES.....	79
APPENDICES.....	81
APPENDIX A	82
APPENDIX B.....	100
VITA.....	109

LIST OF TABLES

Table		Page
1.1	Cost comparison.....	4
1.2	Uses and purities of hydrogen.....	7
1.3	Commercial grade hydrogen purities (maximum impurity level in v.p.m).....	8
2.1	Application and Annual Productions of Major Industrial Sorbents.....	17
2.2	Characteristic of Major Synthetic Zeolite Sorbents.....	30
2.3	Molecules Admitted to Zeolites According to Molecular Dimensions and zeolite Aperture Sizes.....	32
2.4	Table of Dimensions for Various Molecules.....	39
3.1	Composition of standard mixed gas.....	46
3.2	Properties of zeolite 3A.....	46
3.3	Properties of zeolite 4A.....	47
3.4	Properties of zeolite 5A.....	48
3.5	Properties of zeolite 13X.....	48
3.6	Properties of beta zeolite.....	49
4.1	Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta / - 196°C / 10 barg).....	61
4.2	%Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C / 10 barg.).....	62
4.3	Table of Dimensions for H ₂ , N ₂ , CO, CO ₂ , CH ₄	63
4.4	Concentration of output gas (beta zeolite / -196°C, 0°C, ambient / 10 barg).....	64
4.5	boiling and melting point of CO, CO ₂ , CH ₄ , N ₂ and H ₂	66
4.6	Concentration of output gas (beta zeolite / -196°C / 5, 10, 15, 20 bar g).....	67
4.7	Concentration of output gas (2.5 mm., 1-2 mm. of zeolite 3A / -196°C / 10 barg).....	69

Table		Page
4.8	Concentration of output gas by vary ratio of alumina and zeolite	70
4.9	Concentration of output gas after each calcination (beta zeolite / -196°C / 10 barg).....	74
4.10	Compare concentration of output gas by present factory condition and best condition.....	76
4.11	Product specification of hydrogen (industrial and ultra high purity grade).....	77



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figure		Page
1.1	U.S. Hydrogen Market.....	1
1.2	European Hydrogen Market.....	2
1.3	Hydrogen Recovery vs Product Purity Membrane Systems.....	10
2.1	Equilibrium sorption of methane at 25°C on silica gel, zeolite 5A, and activated carbon.....	19
2.2	Equilibrium sorption of water vapor from atmospheric air at 25°C on (A) alumina (granular); (B) alumina (spherical); (C) silica gel; (D) 5A zeolite; (E) activated carbon. The vapor pressure at 100% R.H. is 23.6 Torr.....	20
2.3	Pore-size distribution for activated carbon, silica gel, activated alumina, two molecular-sieve carbons, and zeolite 5A.....	21
2.4	Line representation of zeolite structure.....	23
2.5	Line representation of beta zeolite structure.....	23
2.6	Relationship between equilibrium diameter, γ_{min} and kinetic diameter, σ_{min} . $r_{min} = 2^{1/6} \sigma$	37
2.7	Chart showing a correlation between effective pore size of various zeolites in equilibrium adsorption over temperature of 77 to 420°K (indicated by - - -), with the kinetic diameters of various molecules as determined from the L-J potential relation.	41
3.1	Zeolite A molecular structure.....	49
3.2	Zeolite X molecular structure.....	49
3.3	Zeolite beta molecular structure.....	50
3.4	Diagram of experiment process.....	51
3.5	Tube apparatus.....	51
3.6	Gas Chromatography (Agilent 6890 N).....	53
3.7	Gas Chromatograph (Shimatsu model GC 14B).....	53
3.8	Schematic diagram of a gas chromatograph.....	53
4.1	XRD patterns of zeolite 3A, 4A, 4A (Factory), 5A and 13X.....	59

Figure		Page
4.2	XRD patterns of zeolite beta.....	60
4.3	N ₂ adsorption-desorption isotherms of 13X and beta zeolite	60
4.4	Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta / -196°C /10 bar g).....	62
4.5	%Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C/10 bar g.).....	62
4.6	Concentration of output gas (beta zeolite / -196°C, 0°C, ambient / 10 bar g).....	65
4.7	Molecules in the gas phase, upon contact with a cryo-cooled surface, condense on that surface. The residence time for molecules is dependent upon the specie of gas, the temperature of the cryo-surface and the heat of adsorption.....	66
4.8	Concentration of output gas (beta zeolite / -196°C / 5, 10, 15, 20 bar g).....	68
4.9	Concentration of output gas (2.5 mm., 1-2 mm. of zeolite 3A / -196°C/10 bar g).....	69
4.10	Concentration of output gas (zeolite 3A, beta, alumina (100%wt)/ -196°C/10 bar g.).....	71
4.11	Concentration of output gas (zeolite 3A, beta / alumina : zeolite : 9 : 3 , 5 : 7 / -196°C/ 10 bar g).....	72
4.12	Concentration of output gas after each calcination (beta zeolite / -196°C / 10 bar g).....	74

LIST OF ABBREVIATIONS

Å	=	Angstrom
approx	=	Approximate
barg	=	Bar guage
°C	=	Degree Celsius
CH ₄	=	Methane
CO	=	Carbon monoxide
CO ₂	=	Carbon dioxide
g.	=	Gram
GC	=	Gas chromatography
H ₂	=	Hydrogen
mm.	=	Millimetre
% (mol)	=	Percent by mole
N ₂	=	Nitrogen
ppm (mol)	=	Part per million by mole
wt	=	By weight
vpm	=	Part per million by volume

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CHAPTER I

INTRODUCTION

1.1 Introduction

Hydrogen has great potential as an energy carrier. The data from multimedia research group indicates that the overall US hydrogen market is estimated at \$798.1 million in 2005 and is expected to rise to \$1,605.3 million in 2010.

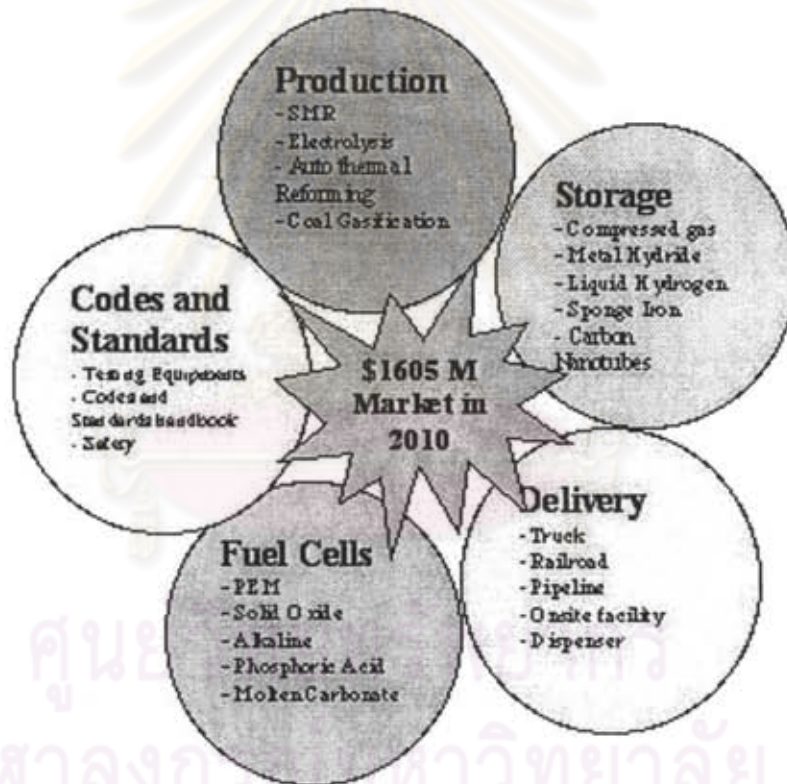


Figure 1.1 U.S. Hydrogen market.

Source: FKU (Fuji-Keizai USA)

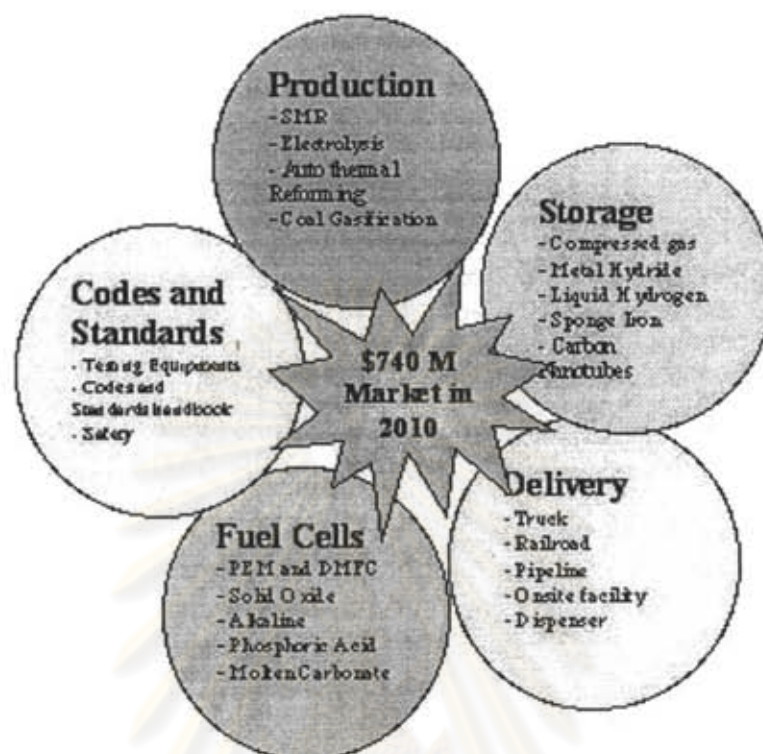


Figure 1.2 European Hydrogen Market.

Source: FKU (Fuji-Keizai USA)

The overall European hydrogen market is estimated to be about \$368 million in 2005 and is expected to grow at an average annual growth rate of 15 percent to \$740 million in 2010. European community is funding various projects on hydrogen production, storage and hydrogen refueling stations.

Increased demand for lighter fuels and products, a desire for higher-performance products, and an insistence on more environmentally acceptable products require refiners to alter processing conditions and technologies so that they can successfully meet the demands of today's society. These demands relate to product slate or quality, they also have a significant impact on a valuable but often overlooked refinery by-product: hydrogen, which is important as both a commodity and a reactant in the total refinery. The hydrogen balance in a typical refinery is straightforward: hydrogen supplied by the feedstock leaves in the products, by-products, and wastes. In the 1950s, catalytic

reforming provided refiners with a relatively pure hydrogen stream as a by-product of normal refining practice. Refiners had a ready-made source of hydrogen, which could be used as a reagent in the chemistry of their refining schemes. In the 1990s, increasingly demanding product specifications require more hydrogen content in the products as well as removal of contaminants [1].

To avoid investing in a new hydrogen-producing plant, a refiner with a light hydrogen balance needs to consider three main issues:

- Maximizing the hydrogen yield from the refinery with particular attention to the primary source: the catalytic reformer.
- Determining the hydrogen required to produce increasing amounts of high-performance products.
- Considering the hydrogen management technologies required to convey hydrogen from the source to the user under the most-appropriate conditions [2].

Because of large market value and application of hydrogen make it is interesting to develop hydrogen technology to meet the today's demand and quality.

1.1.1 Technical data of hydrogen

Molecular weight	2.02 g./mol
Boiling point	-252.77°C at 101.3 KPa
Specific volume	11.967 m ³ kg ⁻¹ at 20°C, 101.3 KPa
Critical temperature	-239.77°C
Critical pressure	1298 KPa
Heat capacity	1432 J kg ⁻¹ K ⁻¹ at 25°C, 101.3 KPa
Flammable limits in air	4-74.5 percent
TLV (Threshold Limit Values)	not established (considered non toxic)

1.1.2 Sources of hydrogen

Gaseous hydrogen can be made using several commercially feasible processes. These include:

- Electrolysis of water
- Thermal-catalytic dissociation of ammonia
- Thermal-catalytic dissociation of methanol
- Steam-iron conversion of reducing gas
- Partial oxidation of hydrocarbon
- Catalytic steam-reforming of hydrocarbons
- Catalytic steam-reforming of hydrocarbons
- The water-gas process

Table 1.1 compare production costs for various methods for a typical capacity of 2,865 kg of hydrogen per day (basis = 2005)

Table 1.1 Cost comparison [3]

Process	Hydrogen production cost (per kg)
Gas Reformation	\$1.15
Wind Electrolysis	\$3.10
Nuclear Electrolysis	\$1.48
PV Plate Electrolysis	\$7.40
CPV Electrolysis	\$3.18

1.1.3 Uses of hydrogen

A significant amount of gaseous hydrogen is produced by steam reforming of natural gas or naphtha and consumed in a downstream process. One notable example is in the fertilizer industry, where NH_3 synthesis gas is produced by steam reforming of hydrocarbon followed by air addition and secondary reforming to produce a mixture which contains H_2 and N_2 in a ratio approximately 3:1. A second important area of the process industry which produces and uses hydrogen is oil refining. Many refineries have reformers which produce relatively pure hydrogen for use on site by hydrogen-consuming processes. These processes include hydrotreating, hydrodealkylation, hydrodesulphurization, hydrogenation, and hydrocracking of heavy residues.

These processes require hydrogen of 90-99 percent purity by volume and all take place at ambient and higher temperatures, and so do not often use cryogenic technology.

Typical operations involved may be reforming, CO₂ removal by absorption and final upgrading by methanation, and sometimes adsorption.

The bulk of the hydrogen is made at moderate purities but in vast quantities and is consumed in situ or in downstream processing units. The hydrogen balance is one of the fundamental parts of the make-up of a sophisticated refinery and many cryogenic processes have been effectively utilized to remove medium purity hydrogen to improve the hydrogen balance when refineries turn to more severe processing of their crudes.

The remaining users of hydrogen are highly varies, but have two things in common: first, they consume much smaller amounts of hydrogen; secondly they require much higher purities.

Also many of the small consumers require liquid hydrogen and hence require cryogenic technology for its production. These areas include:

- liquid hydrogen engines
- liquid hydrogen rockets
- metallurgical applications

Liquid hydrogen engines were researched extensively in the 1950s in the USA with encouraging results. The test program began with military intentions but the results were also applied by the NASA space program. The program began with conversions of aircraft jet engines to be fired on hydrogen and resulted in rocket engines of the 1970s and 1980s which ultimately carried the famous Shuttles into space. Hydrogen was advantageous as a fuel due to its high performance with minimum weight for fuel storage in the booster rockets. The use of hydrogen and oxygen propellants is not without its hazards, as highlighted in the ill-fated Challenger flight in January 1986 which resulted in the deaths of seven astronauts.

Although hydrogen/oxygen combustion is a common means of propulsion in rocketry, another more effective method has also been seriously investigated. Liquid hydrogen can also be used as a coolant and propellant in a nuclear reactor and this energy provides the thrust for a rocket. An extensive test programme to investigate this was undertaken in the USA in the late 1950s. Liquid hydrogen is also used in a variety of test programmes in atomic physics areas, but the quantities involved are much smaller than

the military and space programmes, In all cases, liquid hydrogen is of a very high purity, as necessary in order to allow liquefaction without freezing problems.

High purity gaseous hydrogen is also use in some chemical and metal industries, e.g. hydrogenation of fats and edible oils and in nickel refining [4].

There are lots of applications for hydrogen as energy-source, if people really want to use it. The most important application for hydrogen as energy-source is the car. Cars are very important for this new technique, because a lot of the carbon dioxide (CO₂) pollution is coming from the emission of cars. If cars in the future are driving on hydrogen-gas instead of petrol, the emission will be vapor instead of pollution with CO₂.

The hydrogen Fuel initiative provides funding to accelerate R&D of hydrogen fuel and infrastructure technology. The goal is to enable industry to make commercialization decisions by 2015, so that hydrogen fuel cell vehicles can be available for purchase in showrooms by 2020. Success will require hydrogen production and distribution at a price that is competitive with gasoline, as well as hydrogen fuel cell vehicles that are competitive with gasoline and electric-hybrid vehicles.

The hydrogen-rich gas mixture produced via reforming or gasification contains 40-70% hydrogen and a variety of contaminants including carbon monoxide, carbon dioxide, nitrogen, methane, water, sulfur, and possibly tar and ash. The necessary purity of hydrogen in a polymer electrolyte membrane (PEM) fuel cell is not clearly elucidated by the percentage; while some chemicals do not affect membrane performance even in large amounts, others can cause detrimental effects in small quantities. Common safe chemicals (such as nitrogen) are considered diluting agents and must be removed simply to reduce compression and storage volumes. Dangerous agents (such as carbon monoxide, sulfur, and ammonia) are considered impurities and must be almost entirely removed. PEMs are poisoned by CO at more than 10 parts per million and by sulfur at the parts-per-billion level. Based on current available PEM fuel cell information, the tentative contaminant targets are; <10ppb sulfur, <1 ppm carbon monoxide, <100 ppm carbon dioxide, < 1 ppm ammonia, < 100 ppm non-methane hydrocarbon on a C-1 basis, oxygen, nitrogen and argon can not exceed 2% in total, particulate levels must meet ISO standard 14787. Future information on contaminant limits for on-board storage may add additional constraints. By contrast, solid-oxide fuel cells (SOFCs) for stationary

applications can accept a less pure hydrogen feed, since they are not poisoned by carbon monoxide (CO) and can tolerate some sulfur [5].

1.1.4 Hydrogen purities and forms

Hydrogen is available in purities which broadly fall into two groups, the first having purities up to 99.9 percent and the second greater than 99.9 per cent by volume. The majority of hydrogen is produced at purities up to 99 percent and is usually consumed as soon as it is produced in a down stream process, e.g. ammonia synthesis. This hydrogen is invariably made only in gaseous form. Typical uses and purities are given in table 1.2.

The second category of hydrogen product is generally for special uses such as welding, hydrogenation of edible oils and fats, reduction of metal oxides, research, and as a rocket fuel. BOC limited produces four typical grades of high-purity gases and these are listed in Table 1.3. These grades are usually supplied in gas bottles, although research and space exploration establishments use liquid hydrogen. In order to liquefy this hydrogen, a comparable purity must be generated [4].

Table 1.2 Uses and purities of hydrogen.

Hydrogen user	Typical purity (%)	Typical impurities (%)
Ammonia synthesis	74-75*	24% nitrogen – used in ammonia synthesis Approx. 1-1.5% argon + methane
Hydrocracking	97-99	Methane
Hydrodealkylation	90-98	Methane Traces of ethane
Hydrotreating	90-98	Methane and other light hydrocarbons
Methanol synthesis	65-75	Carbon oxides used in reaction to form methanol

*85-90 percent for hydrogen recycled from ammonia purge gas recovery.

Table 1.3 Commercial grade hydrogen purities (maximum impurity level in v.p.m.).

Impurity	Grade			
	N4.0	N5.0	N5.5	N6.0
Oxygen	2	1	1	0.1
Nitrogen	30	5	1	0.4
Hydrocarbons	32	1	1	0.05
Carbon dioxide	3	0.05	0.05	0.05
Carbon monoxide	1	1	1	0.05
Water	2	2	1	0.5
Minimum hydrogen content (mol.%)	99.99	99.999	99.9995	99.9999

* v.p.m. = ppm by volume

1.1.5 Hydrogen purification technology

The purity of the hydrogen available to consumers can have a significant effect on the design and operation of the consuming units which is generally a hydro-processing unit. The three main hydrogen purification technologies used in refineries are 1. adsorption process, 2. selective permeation using polymer membranes, and 3. cryogenic separation. Each of these processes is based on a different separation principle, and consequently, the process characteristics differ significantly. Selecting the appropriate H₂ purification technology depends not only on the economics, but also on such project considerations as process flexibility, reliability, and ease of future expansion. This part reviews the purification process characteristics and equipment as well as other project considerations for these technologies. General selection guidelines are presented along with process integration that takes advantage of the complementary characteristics of the three processes.

- Adsorption Process

Adsorption, as applied to gas purification, is the selective concentration of one or more components of a gas at the surface of a microporous solid. The mixture of adsorbed components is called the adsorbate, and the microporous solid is the adsorbent. The

attractive forces holding the adsorbate on the adsorbent are weaker than those of chemical bonds, and the adsorbate can generally be released (desorbed) by raising the temperature or reducing the partial pressure of the component in the gas phase in a manner analogous to the stripping of an adsorbed component from solution. When an adsorbed component reacts chemically with the solid, the operation is called chemisorption and desorption is generally not possible [9].

- Membrane Process

POLYSEP™ membrane systems are based on the difference in permeation rates between hydrogen and impurities across a gas-permeable polymer membrane. Permeation involves two sequential mechanisms: the gas-phase component must first dissolve into the membrane and then diffuse through it to the permeate side. Different components have different solubility and permeation rates. Solubility depends primarily on the chemical composition of the membrane and diffusion on the structure of the membrane. Gases can have high permeation rates as a result of high solubility, high diffusivity, or both. The driving force for both solution and diffusion is the partial pressure difference across the membrane between the feed and permeate sides. Gases with higher permeability, such as H₂, enrich on the permeate side of the membrane, and gases with lower permeability enrich on the non-permeate side of the membrane because of the depletion of components with high permeability. The first fraction of the gas to permeate through the membrane consists primarily of the components with the highest permeability. As a larger fraction of the feed gas is allowed to permeate, the relative amount of the components with lower permeability increases in the permeate stream. In hydrogen separations, higher purity hydrogen is associated with lower recovery, and lower purity hydrogen is associated with higher recovery. The effect of hydrogen purity on recovery is much more dramatic with membrane systems than with PSA or cryogenics units. A fairly small change in hydrogen purity can change the recovery significantly as shown in Figure 1.3.

Hydrogen Recovery vs Product Purity Membrane Systems

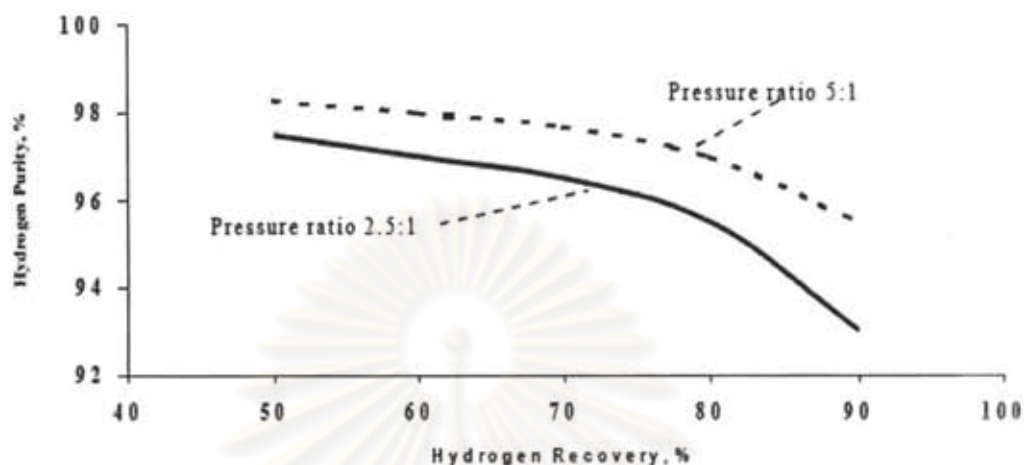


Figure 1.3 Hydrogen recovery vs product purity membrane systems.

Higher hydrogen recovery also requires that more membrane area be provided. The membrane area required when feed composition and system pressure levels are fixed increases exponentially at high hydrogen recovery. The performance of a specific membrane system, that is, the recovery versus the product purity for a given feedstock, is primarily dependent on the ratio of feed to permeate pressure and is largely independent of the absolute pressure level. However, the area requirement is inversely proportional to the feed pressure. Hence, compressing the feed gas rather than the permeate, even though the permeate flow is smaller, is often preferable when the objective is to achieve the required pressure ratio.

- Cryogenic Process

Cryogenic units are based on the difference in boiling temperatures (relative volatility) of the feed components. Hydrogen has a high relative volatility compared with hydrocarbons. The process condenses the required amount of feed impurities by cooling the feed stream against the warming product and tail-gas streams in brazed aluminum multi-pass heat exchangers. The refrigeration required for the process is obtained by Joule-Thomson refrigeration, which is derived from throttling the condensed liquid

hydrocarbons. Additional refrigeration, if required, can be obtained by external refrigeration packages or by turbo expansion of the hydrogen product. The partial condensation process is normally applied to hydrogen-hydrocarbon separations. The feed needs to be pretreated to remove water and other components that could freeze in the system. The pretreated feed at high pressure, 300 to 1,200 psig, is cooled against a stream leaving the cryogenic unit to a temperature at which the majority of the C₂+ hydrocarbons condense. The two-phase stream is sent to a separator where the H₂-CH₄ vapor stream is taken overhead and further cooled to a temperature low enough to give the desired hydrogen purity. The cooled stream is fed to another separator, and the hydrogen product is taken overhead. Before leaving the cryogenic unit, the hydrogen is heated by heat exchange against the hydrogen methane from the first separator and the feed. The liquid CH₄ from the second separator is expanded to a suitable pressure so that it will vaporize against the hydrogen-methane stream from the first separator. Additional cooling is provided by expanding part of the C₂+ hydrocarbons product, if necessary. Thus, the cryogenic unit typically splits the feed into three products: a high purity hydrogen stream, a methane rich stream at fuel gas pressure, and C₂+ hydrocarbons product, which may be two phase. By using additional separators, additional products, such as ethane-propane and LPG streams, can also be produced. If the feed stream does not contain sufficient hydrocarbons to achieve the necessary cooling by the Joule-Thomson effect alone, then additional refrigeration can be provided by expansion of the hydrogen product or a package refrigeration system, normally at 5 to -40°F [2].

This research studies the suitable condition for hydrogen purification by adsorption process which is economic when impurities are present in quantities significantly greater than a few v.p.m. (ppm by volume) to obtain the higher purity of hydrogen. The gas adsorption properties of alumina, zeolite 3A, 4A, 5A, 13X and beta are also studied.

1.2 Objective and scope of the research

1.2.1 Objective

- a) To find out the best condition and suitable adsorbent for hydrogen purification by adsorption process.
- b) To study gas adsorption properties of zeolite 3A, 4A, 5A, 13X and beta.

1.2.2 Scope of the research

This research studies the suitable condition for hydrogen purification by adsorption system. The various parameters such as type of adsorbents, temperature, size of adsorbents, an inlet pressure, ratio between alumina and zeolite and the life time of adsorbents were studied.



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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Gas separation by adsorption process

Separation may be defined as a process that transforms a mixture of substances into two or more products that differ from each other in composition. The process is difficult to achieve because it is the opposite of mixing, a process favored by the second law of thermodynamics. Consequently, the separation steps often account for the major production costs in chemical and petrochemical industries. Separation also plays a key role in chemistry and related scientific disciplines. Through the endeavor of human ingenuity, there exist a multitude of industrial separation processes and laboratory separation techniques [6].

The surface of a solid represents a discontinuity of its structure. The forces acting at the surface are unsaturated. Hence, when the solid is exposed to a gas, the gas molecules will form bonds with it and become attached. This phenomenon is termed adsorption.

Adsorptive gas separation processes can be divided into two types: bulk separation and purification. The former involves adsorption of a significant fraction, 10% by weight or more according to Keller's definition, from a gas stream, whereas in purification less than 10% by weight of a gas stream to be adsorbed. Such a differentiation is useful because, in general, different process cycles are used for different types of separation.

Purification includes: drying (or dehydration) of air, natural gas, olefin-containing cracked gas, synthesis gas and other industrial gases; hydrogen purification; sweetening (removal of acid gases) of natural gas and plant-separation processes are the production of oxygen and nitrogen from air, separation processes are the production of oxygen and nitrogen from air, separation of n-paraffins from iso-paraffins and aromatics, and hydrogen from industrial gases. Molecular-sieve zeolites and activated carbon are the major sorbents used. However, the molecular-sieving property is not used in most of the commercial processes where zeolites are used. The separation is based on differences in equilibrium isotherms, and the slow intracrystalline diffusion is actually detrimental to

separation. The molecular-sieving property is used in only three known commercial processes:

- a) n- and iso-paraffin separation using 5A zeolite
- b) Drying of various gas streams using zeolites
- c) Nitrogen production from air using molecular-sieve carbon

The two former separations are accomplished based on selective molecular exclusion, whereas the latter is the only process using differences in pore diffusivity.

Fixed-bed adsorbers are used in almost all known commercial processes with the exception of the Purasiv HR process. For continuous feed and products, dual-bed or multibed systems are used in which each bed goes through adsorption regeneration cycles. Although the operation of each bed is batchwise, the system as whole is a continuous one that is operated in a cyclic steady state. Based on the method of sorbent regeneration and the mechanical arrangement, a number of process cycles and combinations of cycles have been developed. They are:

- a) Thermal-swing adsorption: In this process cycle, the bed is regenerated by raising the temperature. The most convenient way of raising the temperature is by purging the bed with a preheated gas. This is the oldest and most completely developed adsorption cycle. Because heating is a slow and often rate-limiting step, the length of each cycle usually ranges from several hours to over a day. In order to make the time length of the adsorption step comparable to that of regeneration, the cycle is used only for purification purposes.
- b) Pressure-swing adsorption: In this cycle the bed regeneration is accomplished by reducing the total pressure. The cycle time is short, usually in minutes or even seconds, due to the possibility of rapid pressure reduction. Though ideally suited for bulk separations, this cycle can be used for purifications as well. An increasing number of purification processes are being switched from temperature swing to this cycle, and an increasing number of bulk separation processes are being developed using this cycle. This is the youngest basic cycle and also the

most flexible one in terms of process modification. Unlike the temperature-swing and other cycles, many new applications are possible with the pressure-swing cycle. This cycle is also the most difficult and complex to model.

- c) Inert purge: This cycle is similar to the temperature-swing cycle except that preheating of the purge gas is not required. Usually a fraction of the light product (raffinate) is used as the inert purge gas.
- d) Gas chromatography: The laboratory analytical chromatography has been an appealing tool for large-scale separation for many years. Only recently have commercial attempts appeared successful
- e) Parametric pumping and cycling-zone adsorption: These two processes have yet to find a commercial application. Nevertheless, there are still ongoing research activities, and future applications are not out of the question.
- f) Moving-bed and simulated moving-bed processes: In these processes the gas mixture and solid sorbent are contacted in a countercurrent movement. Thus, unlike the temperature- and pressure-swing processes, the process is truly steady state in that the flow rates and compositions of all streams entering and leaving the adsorbent bed are constant. Besides the process simplicity, a further advantage of the moving-bed process is in minimizing the required inventory of adsorbent.

This research studies the condition and adsorbent that are suitable for hydrogen purification by adsorption process which purifies hydrogen by adsorbing impurities molecules on a very porous material like molecular sieve which is cooled by a cryogen, typically liquid nitrogen. The main advantages are simple process, low pressure drop for light product.

Construction and Operation

This process employs compressors to control the feed gas (hydrogen, HP industrial grade 99.99%) to an acceptable pressure. The feed gas was pre-treated by silica gel before passing the 2 columns made from stainless steel filled with alumina and zeolite dipped in liquid nitrogen bath. Gases will now either condense or be adsorbed by the large surface of the molecular sieve. Then the purified gas will pass the water bath to adjust the temperature before filling into the cylinders as ultra high purity hydrogen (99.999%).

In the regeneration, the molecular sieves are heated to 300 °C for zeolite and 180°C for alumina to drive off guest molecules accumulate in the molecular sieve. It takes typically 3 hours to fully regenerate.

2.2 Industrial sorbents

In principle, all microporous materials can be used as sorbents for gas purification and separation. For example, bone chars, coal chars, calcined clays, iron oxide, calcined bauxite, and the like have all found commercial uses. The four sorbents to be discussed here, however, are those with well-controlled and high microporosity, and are produced in large quantities. Table 2.1 provides a perspective of the relative amounts used and the major gas separations performed in industry. In addition to developed since about the mid-1970s, will also be discussed because of its unique ability to perform kinetic separation based on the different pore diffusion rates of different gas molecules.

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Table 2.1 Application and annual productions of major industrial sorbents.

Sorbent	Annual U.S. production ^a	Major uses for gas sorption
2.1.1 Activated carbon	90,000 (major)	Removal of nonpolar gases and organic vapors (e.g., solvents, gasoline vapor, odors, toxic and radioactive gases); H ₂ purification; etc.
2.2.2 Zeolites:		
Synthetic	30,000 ^b (major)	Drying; H ₂ purification; air purification; air separation; separations based on molecular size and shape (e.g., n- and iso-paraffins, aromatics, etc.); gas chromatography
Natural	250,000 ^b (minor)	
2.2.3 Silica gel	150,000 (minor)	Drying; gas chromatography
2.2.4 Activated alumina	25,000 (major)	Drying; gas chromatography

a Late 1970s figure in metric tons. The fraction used as sorbent is indicated in parentheses.

b Worldwide total figure.

2.2.1 Activated Carbon

Manufacturing Processes

The manufacture and use of activated carbon date back to the nineteenth century. The modern manufacturing processes basically involve the following steps: raw material preparation, palletizing, low-temperature carbonization, and activation. The conditions are carefully controlled to achieve the desired pore structure and mechanical strength.

The raw materials for activated carbon are carbonaceous matters such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts. Anthracite and bituminous coals have been the major sources. Starting with the initial pores present in the raw material, more pores, with desired size distributions, are created by the so-called activation process. After initial treatment and palletizing, one activation process involves carbonization at 400-500°C to eliminate the bulk of the volatile matter, and then partial

gasification at 800-1,000°C to develop the porosity and surface area. A mild oxidizing gas such as CO₂, steam, or flue gas is used in the gasification step because the intrinsic surface reaction rate is much slower than the pore diffusion rate, thereby assuring the uniform development of pores throughout the pellet. The activation process is usually carried out in fixed beds, but in recent years fluidized beds have also been used. The activated carbon created by this activation process is used primarily for gas and vapor adsorption processes. The other activation process that is used commercially depends on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. Lignin, usually the raw material that is blended with activators such as phosphoric acid, zinc chloride, potassium sulfide, or potassium thiocyanate, is carbonized at temperatures up to 900°C. The product, usually in powder form, is used for aqueous or gas purposes. The inorganic material contained in activated carbon is measured as ash content, generally in the range between 2 and 10%.

Surface Properties for Adsorption

The unique surface property of activated carbon, in contrast to the other major sorbents, is that its surface is nonpolar or only slightly polar as a result of the surface oxide groups and inorganic impurities. This unique property gives activated carbon the following advantages:

- a) It is the only commercial sorbent used to perform separation and purification processes without requiring prior stringent moisture removal, such as is needed in air purification. (It is also useful in aqueous processes.)
- b) Because of its large accessible internal surface, it adsorbs more nonpolar and weakly polar organic molecules than other sorbents do. For example, the amount of methane adsorbed by activated carbon at 1 atmosphere (atm) and room temperature is approximately twice that adsorbed by an equal weight of molecular sieve 5A (Figure 2.1)

- c) The heat of adsorption, or bond strength, is generally lower on activated carbon than on other sorbents. Consequently, stripping of the adsorbed molecules is easier and results in lower energy requirements for regeneration of the sorbent.

It is not correct, however, to regard activated carbon as hydrophobic. The equilibrium sorption of water vapor on an anthracite-derived activated carbon is compared with that of other sorbents in Figure 2.2. The sorption of water vapor on activated carbon follows a Type V isotherm (according to the BDDT classification) due to pore filling or capillary condensation in the micropores. Activated carbon is used, nonetheless, in processes dealing with humid gas mixtures and water solution because the organic and nonpolar or weakly polar compounds adsorb more strongly, and hence preferentially, on its surface than water does.

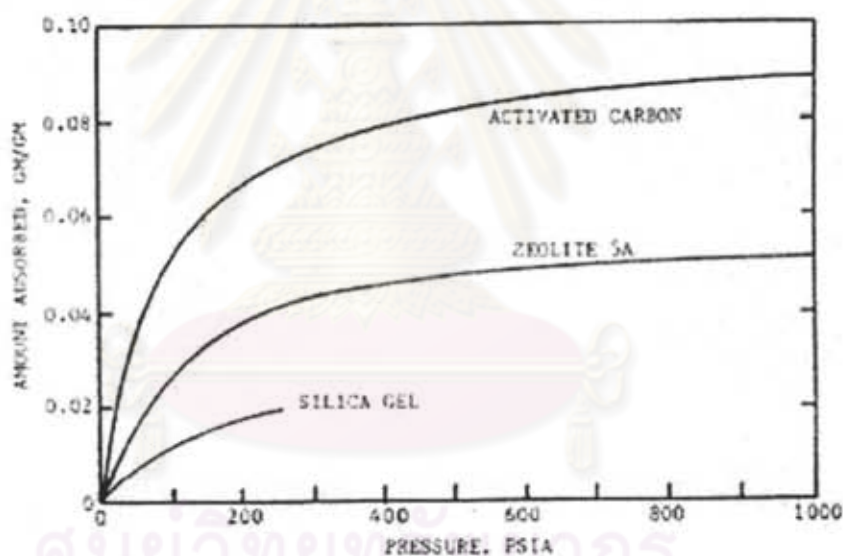


Figure 2.1 Equilibrium sorption of methane at 25°C on silica gel, zeolite 5A, and activated carbon.

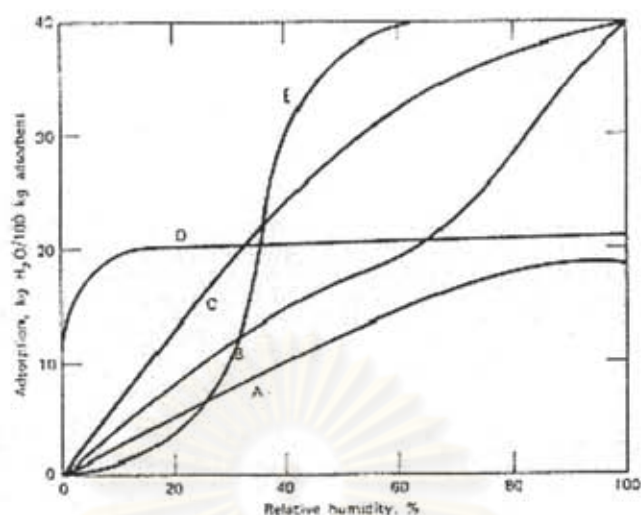


Figure 2.2 Equilibrium sorption of water vapor from atmospheric air at 25°C on (A) alumina (granular); (B) alumina (spherical); (C) silica gel; (D) 5A zeolite; (E) activated carbon. The vapor pressure at 100% R.H. is 23.6 Torr.

Attempts have been made to modify the surface of activated carbon chemically for special applications. However, successful commercial operations have been limited to liquid-phase applications. In gas-phase applications, it has been shown that by increasing the polarity of the surface, the amount of water vapor adsorbed at low relative pressures (below 4 Torr at 25°C; see Figure 2.2) can be drastically increased. For example, Walker and co-workers showed a hundred fold increase in water vapor adsorption by activated carbon after surface oxidation by HNO_3 . Exchange of the surface H-ions by cations (Li, Na, K, Ca) on the oxidized carbon further increased the moisture capacity at low vapor pressures to amounts comparable to that on zeolites. The ion-exchanged carbon was fully regenerated at 140°C, in contrast to temperatures over 350°C required for zeolite regeneration.

Pore Structure of Activated Carbon

Activated carbons are characterized by a large surface area between 300 and 2,500 m^2/g , as measured by the BET method, which is the largest among all sorbents. Commercial grades of activated carbon are designated for either gas phase or liquid phase of adsorbates, depending on its application. A majority of the pore volume is near or

larger than 30 Å in diameter in carbons for liquid phase adsorbate, whereas the pores of carbons for gas-phase adsorbate are mostly in the range from 10 Å to 25 Å in diameter. Carbons for liquid phase adsorbate need large pores because of the large size of many dissolved adsorbates, and the slower diffusion in liquid than in gas for the same size molecules.

A polymodal pore-size distribution is generally found in activated carbon. The pore structure may be pictured as having many small pores branching off from large ones, which are open through the entire particle. The large pores are called feeder or transport pores; the smaller ones, which may be dead-end, are called adsorption pores. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the pores are subdivided by diameter (d) into macropores ($d > 500$ Å), mesopores (20 Å $< d < 500$ Å), and micropores ($d < 20$ Å). The cumulative pore-volume distribution of the fine pores for a typical gas-phase activated carbon is shown, along with four other sorbents, in Figure 2.3. The larger pores are mostly submicron in size, and their total volume amounts to a fraction of that found in the fine pores.

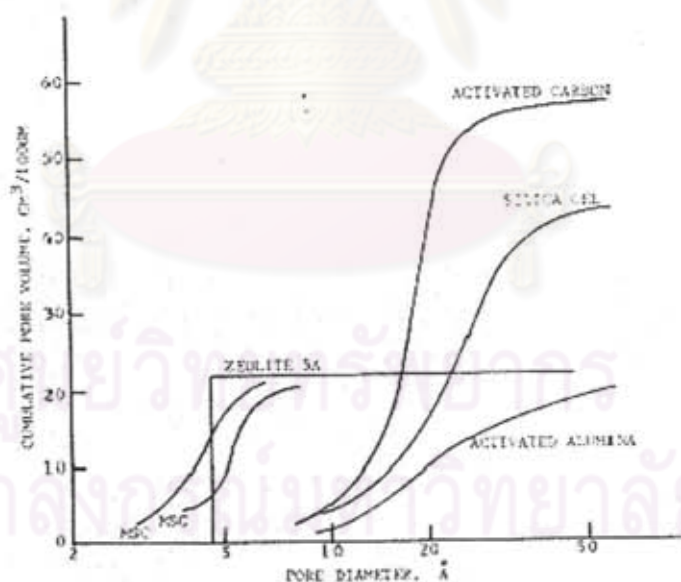


Figure 2.3 Pore-size distribution for activated carbon, silica gel, activated alumina, two molecular-sieve carbons, and zeolite 5A.

2.2.2 Zeolites

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium, represented by the stoichiometry:



Where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M , and Z is the number of water molecules in each unit cell. Unit cells are shown in Figure 2.6(b) and (c). The cations are necessary to balance the electrical charge of the aluminum atoms, each having a net charge of -1 . The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are usually interconnected by six windows in each cage. The cages can imbibe or occlude large amounts of guest molecules in place of water. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 Å to 10 Å. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent because of the surface property in the cages) – hence the name *molecule sieve*.

At least forty species of naturally occurring zeolites have been found. The principal ones are chabazite, $(Ca,Na_2)Al_2Si_4O_{12}(6H_2O)$; gmelinite, $(Na_2,Ca)Al_2Si_4O_{12}(6H_2O)$; modenite, $(Ca,K_2,Na_2), Al_2Si_{10}O_{24}(6.66H_2O)$; levynite, $CaAl_2Si_3O_{10}(5H_2O)$; and faujasite, $(Na_2,Ca,Mg,K_2)OAl_2Si_{4.5}O_{12}(7H_2O)$. More than 150 types of zeolites have been synthesized; they are designated by a letter or group of letters – Type A, Type X, Type Y, Type ZSM, and so on. The commercial production of synthetic zeolites started with the successful development of low-temperature (25-100°C) synthesis methods using very reactive materials such as freshly coprecipitated gels or amorphous solids. Two comprehensive monographs, by Barrer and Breck, deal with all aspects of zeolites.

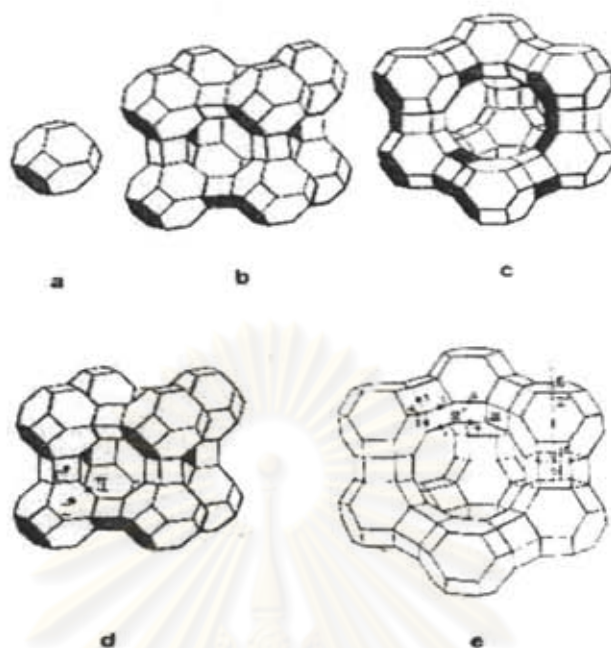


Figure 2.4 Line representation of zeolite structure: (a) sodalite cage, or truncated octahedron; (b) type A zeolite “unit cell”; (c) “unit cell” of types X and Y, or faujasite; (d) cation sites in type A (there are eight I, three II, and twelve II sites per unit cell); (e) cation sites in types X and Y (16 I, 32 I', 32 II', 48 III, and 32 III' sites per unit cell).

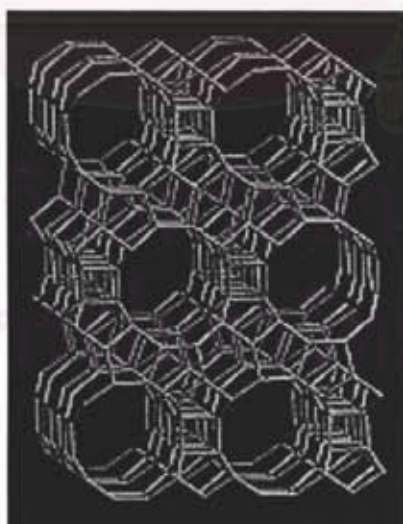


Figure 2.5 Structure of beta zeolite

Structures and Cation Sites

The primary structural units of zeolites are the tetrahedral of silicon and aluminum, SiO_4 and AlO_4 . These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedral, and truncated octahedral. The silicon and aluminum atoms, located at the corners of the polyhedral, are joined by a shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The ratio Si/Al is commonly one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations; and the cations can also be exchanged. The inner atoms in the windows are oxygen. The size of the windows depends, then, on the number of oxygen atoms in the ring – four, five, six, eight, ten, or twelve. The aperture size, as well as the adsorptive properties, can be further modified by the number and type of exchanged cations. A description of the structures will be given only for the zeolites important in gas separation, Type A and Types X and Y.

Zeolite A The structural unit in Type A zeolite, as well as in Types X and Y, is the truncated octahedron, shown in Figure 2.4(a). This unit is also called sodalite cage, as sodalite is formed by directly fusing the four-member rings of the units. The four-member rings of the sodalite units can also be linked through four-member rings of the units. The four-member rings of the sodalite units can also be linked through four-member rings of the units. The four-member rings of the sodalite units can also be linked through four-member prisms, as shown in Figure 2.4(b), which is Type A zeolite. The unit cell of Type A zeolite, as shown in this figure, contains 24 tetrahedral, 12 AlO_4 and 12 SiO_4 . When fully hydrated, 27 water molecules are contained in the central cage or cavity of the unit cell, and in the eight smaller sodalite cages. The free diameter in the central cavity is 11.4 Å, which is entered through six eight-member oxygen-ring apertures with a minimum diameter of 4.4 Å. There are twelve negative charges to be balanced by cations in each unit cell. The most probable locations for the cations are indicated in Figure 2.4(d). Type I is at the center of the six-member ring, thus at one of the eight corners of the cavity. Type II is at the eight-member aperture, directly obstructing the entrance. Type III is near the four-member ring inside the cavity. Type A zeolites are synthesized in the sodium form, with 12 sodium cations occupying all eight

sites in I and three sites in II, plus one site in III. This is the commercial Type 4A zeolite, with an effective aperture size of 3.8 Å. The sodium form can be replaced by various other cations or by a hydrogen ion. The commercial Type 3A zeolite is formed by exchanging Na⁺ with K⁺, resulting in a smaller effective aperture size due to the large K⁺. The aperture size of the sodium form can also be increased by exchanging Na⁺ with Ca⁺² or Mg⁺², since 2 Na⁺ are replaced by one bivalent cation. The form of the exchanged Ca⁺² or Mg⁺² is Type 5A with rather unobstructed and larger apertures.

Framework

Space Group:	Pm-3m		
Cell Parameters:			
$a = 11.919 \text{ \AA}$	$b = 11.919 \text{ \AA}$	$c = 11.919 \text{ \AA}$	
$\alpha = 90.000^\circ$	$\beta = 90.000^\circ$	$\gamma = 90.000^\circ$	
Volume =	1693.24 Å ³		
R _{DLS} =	0.0026		
Framework density (FD_{Si}):	14.2 T/1000 Å ³		
Topological density:	TD ₁₀ = 641	TD = 0.533333	
Ring sizes (# T-atoms)	8	6	4
Channel system:	3-dimensional		
Secondary Building Units:	8 or 4-4 or 6-2 or 6 or 1-4-1 or 4		

Source : International Zeolite Association (IZA)

Zeolite X and Y The skeletal structure of Types X and Y zeolites is the same as that of the naturally occurring faujasite. The sodalite units are linked through six-member prisms, as shown in the unit cell in Figure 2.4(c). Each unit cell contains 192 (Si,Al)O₄ tetrahedral. The number of aluminum ions per unit cell varies from 96 to 77 for Type X zeolite, and from 76 to 48 for Type Y zeolite. This framework has the largest central cavity volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. A unit cell, when fully hydrated, contains approximately 235 water

molecules, mostly in the supercage, The aperture is formed by the twelve-member oxygen rings with a free diameter of approximately 7.4 Å. Three major locations for the cations are indicated in Figure 2.6(e). The locations are: center of the six-member prism (I) and opposite to I in the sodalite cage (I'); similar to I and I' but further from the central cavity (II and II'); and at the twelve-member aperture (III and III'). The commercial 10X zeolite contains Ca^{+2} as the major cation, and Na^+ is the major cation for 13X zeolite. The distribution of Na^+ , K^+ , Ca^{+2} , other cations and H_2O in X and Y zeolites among the sites have been discussed in detail by Barrer. The BET surface area measured with N_2 for zeolites falls in the range between 500 and 800 m^2/g [6].

Framework

Space Group: Fd-3m (origin choice 2)

Cell Parameters:

$$a = 24.345 \text{ \AA} \quad b = 24.345 \text{ \AA} \quad c = 24.345 \text{ \AA}$$

$$\alpha = 90.000^\circ \quad \beta = 90.000^\circ \quad \gamma = 90.000^\circ$$

$$\text{Volume} = 14428.77 \text{ \AA}^3$$

$$R_{\text{DLS}} = 0.0009$$

Framework density
(FD_{Si}): 13.3 T/1000 \AA^3

Topological density: $\text{TD}_{10} = 579$ $\text{TD} = 0.476190$

Ring sizes (# T-atoms) 12 6 4

Channel system: 3-dimensional

Secondary Building Units: 6-6 or 6-2 or 6 or 4-2 or 1-4-1 or 4

Source : International Zeolite Association (IZA).

Beta zeolite Crystallographic faulting in zeolite structures affects both the catalytic and sorption properties, and can greatly complicate attempts at structural characterization. A near extreme example of stacking disorder is provided by zeolite beta, a large pore, high-silica zeolite that was first reported in 1967. Zeolite beta can be regarded as a highly intergrown hybrid of two distinct, but closely related structures that

both have fully three-dimensional pore systems with 12-rings as the minimum constricting apertures. One end member, polymorph A, forms an enantiomorphic pair, space group symmetries $P4_122$ and $P4_322$, with $a = 1.25$ nm, $c = 2.66$ nm. Polymorph B is achiral, space group $C2/c$ with $a = 1.76$ nm, $b = 1.78$ nm, $c = 1.44$ nm, $\beta = 114.5$ circ. Both structures are constructed from the same centrosymmetric tertiary building unit (TBU), arranged in layers that, successively, interconnect in either a left- (L) or a right- (R) handed fashion. Polymorph A represents an uninterrupted sequence of RRRR... (or LLLL...) stacking. Polymorph B has an alternating RLRL... stacking sequence. The TBU has no intrinsic preference for either mode of connection, enabling both to occur with almost equal probability in zeolite beta, giving rise to a near random extent of interplanar stacking faults and, to a lesser extent, intraplanar defects terminated by hydroxyl groups. The faulting does not significantly affect the accessible pore volume, but influences the tortuosity of the pore connectivity along the c direction. The high stacking fault densities give rise to complex powder X-ray diffraction (PXD) patterns for zeolite beta materials that comprise both sharp and broad features. By exploiting recursive relations between possible stacking sequences, PXD patterns have been calculated as a function of faulting probability. Reasonable agreement with observed PXD profiles is observed for a 60% faulting probability in the chiral stacking sequence, suggesting a slight preference for polymorph B. The framework building units observed in zeolite beta can also be used to construct other frameworks [7].

Framework

Space Group: $P4_122$

Cell Parameters:

$$a = 12.632 \text{ \AA} \quad b = 12.632 \text{ \AA} \quad c = 26.186 \text{ \AA}$$

$$\alpha = 90.000^\circ \quad \beta = 90.000^\circ \quad \gamma = 90.000^\circ$$

$$\text{Volume} = 4178.43 \text{ \AA}^3$$

$$R_{\text{DLS}} = 0.0022$$

Framework density

$$(\text{FD}_{\text{Si}}): 15.3 \text{ T}/1000 \text{ \AA}^3$$

Topological density: $TD_{10} = 805$ $TD = 0.704545$

Ring sizes (# T-atoms) 12 6 5 4

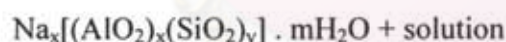
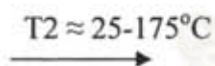
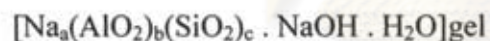
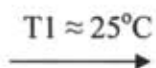
Channel system: 3-dimensional

Secondary Building Units: combinations only

Source : International Zeolite Association (IZA)

Manufacture Procedure and Applications for Gas Separation

Commercial zeolite pellets are made in the following sequence: synthesis, palletizing, and calcination. Many alkali metal hydroxides and raw materials containing silica and alumina can be used in low-temperature synthesis. The steps involving the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, which is used in synthesizing zeolites of types A, X and Y, are as follows;



The first step involves gel formation between sodium hydroxide, sodium silicate, and sodium aluminate in aqueous solution at room temperature. The gel is probably formed by the copolymerization of the silicate and aluminate species by a condensation-polymerization mechanism. Expressed in mole per mole of Al_2O_3 for $\text{Na}_2\text{O}/\text{SiO}_2/\text{H}_2\text{O}$, the compositions of the reactants are:

1. Type 4A zeolite, 2/2/35
2. Type X zeolite, 3.6/3/144
3. Type Y zeolite, 8/20/320

The gels are crystallized in a closed hydrothermal system at temperatures between 25°C and 175°C. Higher temperatures upto 300°C are used in some cases. The time for crystallization ranges from a few hours to several days.

The crystals formed are cubic single crystals with sizes ranging from 1 to 10 microns. For example, the commercial 5A zeolite contains cubic crystals with a mean size slightly greater than 2 microns. (The largest crystal synthesized is near 100 microns.) Types 3A and 5A zeolites are formed by ion exchange in the crystallization step by adding aqueous solutions of potassium and calcium salts, respectively. The crystals, after calcination at about 600°C, are further agglomerated and palletized with or without a binder amounting to less than 20% of the pellets. The binder has a negligibly small capacity for the adsorption of gases. The characteristics of the major commercial zeolite sorbents in the palletized forms are given in Table 2.2.



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Table 2.2 Characteristic of major synthetic zeolite sorbents.

Zeolite type	Major cation	Nominal aperture size, Å	Bulk density ^a , lb/ft ³	Water ^b capacity, wt%
3A (Linde)	K	3	40	20.0
3A (Davidson)	K	3	46	21.0
4A (Linde)	Na	4	41	22.0
4A (Davidson)	Na	4	44	23.0
5A (Linde)	Ca	5	45	21.5
5A (Davidson)	Ca	5	44	21.7
10X (Linde)	Ca	8	40	31.6
13X (Linde)	Na	10	38	28.5
13X (Davidson)	Na	10	43	29.5
Beta (Zeochem)	Na	7.6x6.4 / 5.5x5.5	-	-

^aBased on 1/16 inch pellets or beads.

^bThe dried sorbent contains < 1.5 weight-percent water in Linde products and 1.5 weight-percent in Davidson products.

In Table 2.3, important industrial gases are grouped according to their molecular sizes, which are smaller than the apertures of the zeolite types, and hence can be adsorbed. In principle, any mixture containing gases from different groups can be separated by molecular sieving. Many of the important zeolite-based gas separation processes currently practiced in industry, however, are not based on molecular-sieving action. They are based on the different equilibrium amounts adsorbed, of the constituents in the mixture. The important gas separation processes using zeolite sorbents are: air

n-paraffins from branched-chain and cyclic hydrocarbons, aromatic hydrocarbon separation, and drying. Except for the n-paraffin and aromatics separations, these processes employ the preferential adsorption of certain components. For example, nitrogen is preferentially adsorbed over oxygen (by approximately threefold in 5A zeolite) as a result of its quadruple moment, which forms a strong bond with the polar surface.

2.2.3 Silica Gel

Silica gel is one of the synthetic amorphous silica. It is a rigid, continuous network of spherical particles of colloidal silica. There are a number of preparation methods, which result in different pore structures.

Manufacturing Procedure

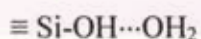
Commercially, silica gel is prepared by mixing a sodium silicate solution with a mineral acid such as sulfuric or hydrochloric acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated SiO_2 , known as silica hydrosol or silicic acid:



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The hydrosol, on standing, polymerizes into a white jellylike precipitate, which is silica gel. The resulting gel is washed, dried and activated. Various silica gels with a wide range of properties such as surface area, pore volume and strength can be made by varying the silica concentration, temperature, pH and activation temperature. Two typical types of silica gel are known as regular-density and low-density silica gels, although they have the same densities (true and bulk). The regular-density gel has a surface area of 750-850 m²/g and an average pore diameter of 22-26 Å, whereas the respective values for the low-density gel are 300-350m²/g and 100-150 Å. The micropore volume of the regular-density gel is shown in Figure 2.3.

Silica gel, along with activated alumina, is a desirable sorbent for drying because of its high surface areas and unique surface properties. Silica gel contains 4-6% "water" by weight, which is the measured "loss on ignition." This so-called water is essentially a monolayer of hydroxyl groups bound to the silicon atoms on the surface, forming the silanol, Si-O-H, groups. The surface chemistry of silica gel has been extensively studied by infrared and near-infrared spectroscopic techniques, as it is a good infrared window and hence suitable for these techniques. Some of these studies on the interaction of water on silicas were reviewed by Klier and Zettlemoyer. At a low surface coverage, evidence shows that the water molecule is bound to the silanol group "oxygen down"



At higher coverages, hydrogen bonding within clusters of water becomes predominant, with a bond strength or heat of adsorption approaching of water vapor on silica gel is approximately 11 kcal/mole --- essentially the same as that on activated alumina. The relatively low heat of adsorption and consequently, weakly held water are desirable for sorbent regeneration. Regeneration of silica gel is achieved by heating to approximately 150°C, as compared to 350°C for zeolites, where the heats of adsorption of water vapor are considerable higher. A lower heat of adsorption is also desirable in separation processes because the temperature rise resulting from adsorption lowers the adsorption capacity, and a detrimental temperature drop occurs during desorption or regeneration. (Zeolites, however, the advantage of higher water capacities at low relative pressures; hence they are used at high temperatures.)

The equilibrium water sorption capacity at 25°C for the regular-density gel is shown in Figure 2.2. The water capacity for the low-density gel is substantially lower.

2.2.4 Activated Alumina

Activated alumina is one of the solids having the greatest affinity for water. An important industrial application for activated alumina continues to be the drying of gases and liquids, because of its hydrophilic property and large surface area. The term activated alumina refers to dehydrated or partially dehydrated alumina hydrates, both crystalline and amorphous, with high surface areas. It has been prepared by a variety of procedures.

Manufacturing Procedures and Surface Areas

Commercial production is exclusively by thermal dehydration or activation of aluminum trihydrate, $\text{Al}(\text{OH})_3$ or gibbsite. The oldest form, which is still widely used, is made from Bayer α -trihydrate, which is a by-product of the Bayer process for aqueous caustic extraction of alumina from bauxite. The trihydrate, in the form of gibbsite, is heated or activated in air to about 400°C to form crystalline γ/η -alumina with a minor amount of boehmite, and has a surface area of approximately 250 m²/g. Alternatively, the trihydrate is heated very rapidly at 400-800°C to form an amorphous alumina with a higher surface area, 300-350 m²/g. The major impurity in these products, besides water (typically 6%), is Na_2O at nearly 1%. The micropore volume is shown in Figure 2.3, but there is a considerable number of pores with sizes greater than 50 Å. A highly impure form of activated alumina is made by the thermal activation of bauxite, which contains alumina in the form of gibbsite.

Adsorption Applications

The major use of activated alumina as a sorbent is in drying. It also finds application in chromatography. A partial list of industrial gases that can be dried by activated alumina includes: Ar, He, H_2 , low alkanes (mainly C1-C3) and hydrocarbons, Cl_2 , HCl, SO_2 , NH_3 , and Freon fluorochloralkanes. It has been especially important in the drying of hydrocarbons produced by the thermal cracking of petroleum fractions. It, however, suffers a loss of adsorption capacity with prolonged use as a result of coking

and contamination. This is a common problem for all sorbents. The moisture content can be reduced to below 1 ppm using activated alumina in suitable designed adsorbers.

2.3 Selection of Sorbent

The selection of a proper sorbent for a given separation is a complex problem. The predominant scientific basis for sorbent selection is the equilibrium isotherm. The equilibrium isotherms of all constituents in the gas mixture, in the pressure and temperature range of operation, must be considered. As a first and possibly oversimplified approximation, the pure-gas isotherms may be considered additive to yield the adsorption from a mixture. Based on the isotherms, the following factors that are important to the design of the separation process can be estimated:

1. Capacity of the sorbent, in the operating temperature and pressure range.
2. The method of sorbent regeneration – for example, thermal or pressure swing and the magnitude of the required swing.
3. The length of the unusable (or unused) bed (LUB).
4. The product purities.

The LUB is approximately one-half of the span of the concentration wavefront, or the mass transfer zone. The LUB is primarily determined by the equilibrium isotherm. A sharp concentration front, or a short LUB, is desired because it results in a high sorbent productivity as well as a high product purity.

Consideration should also be given to other factors. As mentioned, activated carbon is the only commercial sorbent used for wet gas stream processing. (A predryer is required for other sorbents.) Sorbent deactivation, primarily by coke deposition, is an important consideration in the processing of hydrocarbon containing gases. Coke is formed catalytically, and zeolites are excellent catalysts for these reactions. Pore-size distribution can play a role in the LUB, but not as importance role as that of the equilibrium isotherm, since the commercial sorbent pellets are designed to minimize the pore-diffusion resistance. Kinetic separation that is, separation based on the difference between pore diffusivities of two gases has found only one application: the production of

nitrogen from air by molecular sieve carbon. Dehydration of cracked gases with 3A zeolite and the separation of normal and iso-paraffins with 5A zeolite are based on selective molecular exclusion. All other commercial processes are based on the equilibrium isotherms. Temperature for activation and regeneration of the sorbent should also be considered. A high temperature of nearly 300°C is required for zeolites, whereas activated carbon usually requires the lowest temperature for regeneration.

The total void space in the bed, which varies with the sorbents, is also an important factor. A low void space is desired for high product recoveries since the gas mixture remaining the void space in the saturated bed is usually not recovered as a useful product. Silica gel and activated alumina have the lowest void fraction, usually slightly below 70%; activated carbon has the highest void fraction, at nearly 80%.

2.4 Effect of molecular sieve on adsorption

Molecular sieving by dehydrated zeolite crystals is caused by the size and/or shape differences between the crystal aperture and the adsorbate molecule [14].

In order to correlate the crystallographic aperture or pore size of a zeolite with the dimensional parameters of various adsorbate molecules, a scale of molecular dimensions was established. In early experiments, the molecular size was based upon the equilibrium diameter of the adsorbate molecule. This was arrived at by calculation using the known molecular shape, bond distances, bond angles, and van der Waals radii. It was observed that certain molecules were freely adsorbed but were larger than the known aperture size of the zeolite crystal. In an improved treatment of this problem, Kington and MacLeod have utilized the collision or kinetic diameter.

The effective pore size of a zeolite molecular sieve can be determined from the sizes of molecules which are or are not adsorbed under a given set of conditions. For example, at temperatures of -183 to -196°C, zeolite A adsorbs oxygen freely while nitrogen is not adsorbed over long periods of time. At these temperatures, nitrogen diffusion is so slow that true equilibrium cannot be attained.

The Kinetic Diameter

For spherical and nonpolar molecules the potential energy of interaction, $\phi(r)$ is well described by the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

The parameters, σ and ϵ , are constants which are characteristic of the molecular species and are determined from second virial coefficients. At large separations the attractive component, $(\sigma/r)^6$, is dominant and describes the induced dipole-induced dipole interaction. At small separations the repulsive component is dominant (Fig. 2.5). When the potential equals 0 the diameter, r , is equal to σ . The *kinetic* or collision diameter is the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy. The maximum energy of attraction, ϵ , occurs at r_{\min} , where $r_{\min} = 2^{1/6} \sigma$.

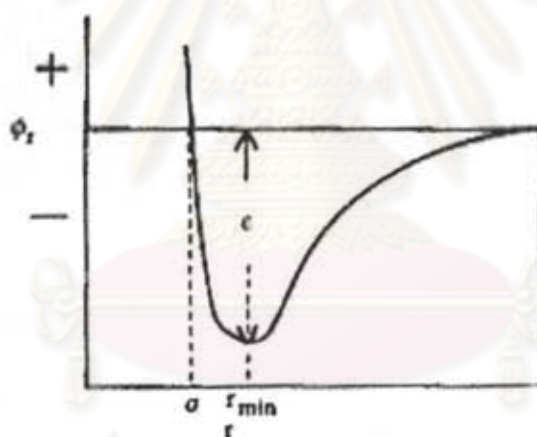


Figure 2.6 Relationship between equilibrium diameter, r_{\min} and kinetic diameter, σ .
 $r_{\min} = 2^{1/6} \sigma$.

In assessing the apparent pore size of molecular sieve zeolites, the critical dimensions for spherical molecules are given by the value of r_{\min} . For diatomic molecules, r_{\min} is based upon the van der Waals length, and represents the molecule in all orientations. For long molecules, such as hydrocarbons, the dimension is the minimum cross-sectional diameter. It is preferred to use σ values obtained from minimum cross-sectional diameters for more complex molecules, such as n-paraffins.

For polar molecules, the Stockmayer potential function is widely used for describing the interaction between molecules for which dipole-quadrupole interactions are not important. Values of the parameter σ determined for certain polar molecules have been used. Kihara's data were used for spherocylindrical and ellipsoidal molecules (H_2 and N_2).

Table 2.4 lists molecular dimensions calculated from Pauling along with r_{min} and σ , the minimum kinetic diameter. For complex molecules, the minimum equilibrium diameter of Pauling was used to compute σ . Adsorption phenomena indicate that the minimum equilibrium diameter should be used as r_{min} in computing σ . For example, the Lennard-Jones approach gives a value of $\sigma = 4.05$ for CO_2 and 3.64 for N_2 . Under equivalent conditions, KA adsorbs CO_2 but not N_2 . Therefore, the minimum equilibrium dimension of 3.7 Å was used to compute a σ value of 3.3 Å. The σ values for H_2O and NH_3 were obtained from data given by the Stockmayer potential.

Figure 2.6 compares σ , the minimum kinetic diameter, with the apparent pore diameter of various zeolites. Calcium A has a pore diameter of 4.2 Å as determined by structural analysis. This compares well with the σ value of 4.3 for n-paraffins and 4.4 Å for CF_2Cl_2 which is adsorbed at about 150°C. Thus, the apparent pore size of CaA varies from 4.2-4.4 Å. NaA adsorbs C_2H_4 (slowly) and CH_4 , $\sigma = 3.9$ and 3.8 Å, respectively. At low temperatures, it does not adsorb N_2 . The apparent pore diameter is 3.6 to 4.0 Å, depending on temperature. The explanation for this variation has been based upon a process of activated diffusion. It has also been postulated that thermal vibration of the oxygen ions, and cations, in the zeolite lattice surrounding the apertures is responsible [14].

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Table 2.4 Dimensions for various molecules.

	Pauling		Lennard-Jones	
	length (Å)	Width (Å)	r_{min} (Å)	σ (Å) ^a
He		~3	3.0	2.6
H ₂	3.1	2.4	3.24	2.89
Ne		3.2	3.08	2.75
Ar		3.84	3.84	3.4
O ₂	3.9	2.8	4.02	3.46
N ₂	4.1	3	4.09	3.64
Kr		3.96	3.96	3.6
Xe		4.36	4.45	3.96
NO	4.05	3	3.58	3.17
N ₂ O	4.2	3.7		3.3
CO	4.2	3.7	4.25	3.76
CO ₂	5.1	3.7		3.3
Cl ₂	5.6	3.6		3.2
Br ₂	6.2	3.9		3.5
H ₂ O	3.9	3.15		2.65
NH ₃	4.1	3.8		2.6
SO ₂	5.28	4		3.6
CH ₄		4.2	4.25	3.8
C ₂ H ₂	5.7	3.7	3.7	3.3
C ₂ H ₄	5	4.4		3.9
C ₃ H ₈	6.5	4.9		4.3
n-C ₄ H ₁₀		4.9		4.3
HCl	4.29	3.6		3.2
HBr	4.6	3.9		3.5
H ₂ S	4.36	4		3.6
CS ₂		4		3.6
CF ₂ Cl ₂		5		4.4
CCl ₄			6.65	5.9

	Pauling	Lennard-Jones		
	length (Å)	Width (Å)	r_{min} (Å)	σ (Å) ^a
iso-C ₄ H ₁₀		5.6		5
Butene-1			5.1	4.5
CF ₄		4.9	5.28	4.7
SF ₆		5.8	6.18	5.5
Neopentane		7		6.2
(C ₄ H ₉) ₃ N			9.1	8.1
(C ₂ F ₅) ₂ NC ₃ F ₇		8.7		7.7
(C ₄ F ₉) ₃ N		11.5		10.2
Benzene		6.6		5.85
(C ₂ H ₅) ₃ N			8.8	7.8
Cyclohexane		6.7		6

^a Kinetic diameter, σ calculated from the minimum equilibrium cross-sectional diameter.

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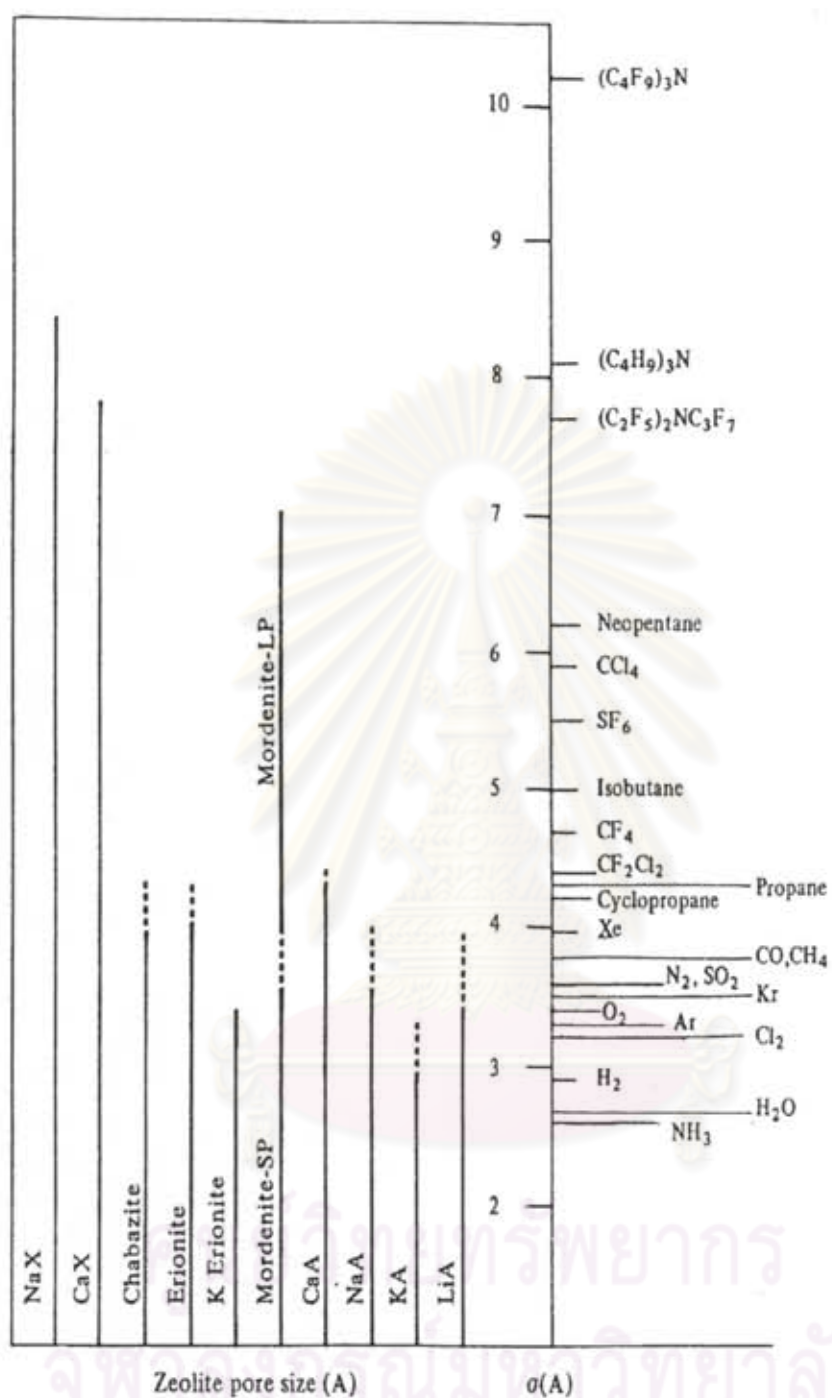


Figure 2.7 Chart showing a correlation between effective pore size of various zeolites in equilibrium adsorption over temperatures of 77° to 420°K (indicated by - - -), with the kinetic diameters of various molecules as determined from the L-J potential relation.

2.5 Literature Review

In 2008, Thiti L. and Tharapong V. studied suitable condition for separation of moisture from ethanol in gas phase by zeolite 3A and 4A at atmosphere. The ratio of zeolite 3A and 4A was investigated. The feed gas is 95%wt EtOH in moisture. They found that 100% of 3A provides the best result. The suitable condition is 90°C, flowrates 1 ml/min [11].

In 2006, Peiyuan Li and F. Handan Tezel studied adsorption equilibrium and kinetic separation potential of β -zeolite for N_2 , O_2 , CO_2 and CH_4 gases by using concentration pulse chromatography. With β -zeolite, CO_2 has the highest adsorption, followed by CH_4 , N_2 and O_2 . CO_2 separation from O_2 , N_2 and CH_4 has good equilibrium separation factors. This factor is not very high for CH_4/N_2 and CH_4/O_2 systems and is the lowest for N_2/O_2 system. With β -zeolite, the kinetic separation factors are very small at high temperatures for all the systems studied. N_2/CO_2 and O_2/CO_2 can be separated in kinetic processes with reasonable separation factors at temperatures lower than 31.9°C. Both equilibrium and kinetic separation factors decrease as column temperature increases [8].

In 2006, Simone Cavenati and colleagues studied adsorption-based process for removal of carbon dioxide and nitrogen from low and medium natural gas flowrates. The layered pressure swing adsorption (LPSA) process studied is composed of a zeolite 13X followed by a layer of carbon molecular sieve 3K. Experiments were performed in a single-column LPSA unit. The effect of temperature and ratios of adsorbent layer were studied. The feed gas is 60% CH_4 /20% CO_2 /20% N_2 . CH_4 purity of 86.0% with 52.6% recovery was obtained at ambient temperature while 88.8% purity with 66.2% recovery was obtained at 323 K. At both temperatures there was a ratio of adsorbent layers where purity reaches a maximum, while product recovery always decreases for larger zeolite 13X layers [13].

In 2005, José A. Delgado and colleagues studied the adsorption equilibrium isotherms of CO_2 , CH_4 and N_2 on Na- and H-mordenite at three temperatures (279, 293 and 308 K) for pressures up to 2 MPa. For Na-mordenite, the selectivity order is: carbon

dioxide \gg methane > nitrogen. The selectivity order is the same for H-mordenite. The selectivity ratio CO_2/CH_4 is smaller than CH_4/N_2 . The adsorption capacity for CH_4 and N_2 is recovered with vacuum in both adsorbents, whereas this does not apply to CO_2 for Na-mordenite [16].

In 1999, S. E. Iyuke and colleagues studied Sn-activated carbon (Sn-AC) in pressure swing adsorption (PSA) system in the purification of hydrogen for PEM fuel cell application. Activated carbon was impregnated with 34.57% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ salt and then dried to produce AC- SnO_2 to improve its adsorptive interaction with CO. The concentration of CO, which was 1000 ppm, was reduced to 40.2 and 10.4 ppm by the pure and the impregnated activated carbons, respectively. The use of AC- SnO_2 in adsorbing CO proved superior to that when pure carbon was used for H_2 purification in a PSA system [10].

In 1991, Shang-Bin Liu and colleagues studied the thermal stability of zeolite beta by ^{129}Xe NMR and adsorption isotherm of adsorbed xenon in correlation with data from X-ray diffraction and ^{27}Al magic-angle-spinning NMR experiments. Samples subject to different calcination and dehydration conditions were examined. Minor destruction of the crystalline framework resulting from dealumination processes has been found for samples treated at a temperature 400°C [12].

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CHAPTER III

EXPERIMENTAL

This research studies hydrogen purification by adsorption process. The factors that would be studied are type of zeolite, temperature, bead size, inlet pressure and the ratio of adsorbent (zeolite and alumina). The life time of the zeolite is also studied. The detail of experimental apparatus and chemicals are shown below.

3.1 Material and equipments

3.1.1 Chemicals

1. Hydrogen UHP
2. Hydrogen (industrial grade, 99.8%)
3. Standard mixed gas

Standard mixed gas composed of 10% CO, 10% CO₂, 10% CH₄, 10% N₂ and 60% H₂. They were mixed by gravimetric method and were analyzed the concentration by gas chromatography.

Preparation of standard mixed gas (raw material gas)

- Cylinder preparation

Valve CGA 350 Brass was put on the aluminum cylinder 29.5 L. Then the cylinder was purged with nitrogen at 5 barg and vent, vacuum respectively. This cycle was done 3 times together with heated at 70°C. The total period is 1.5 hours. After that moisture in the cylinder was checked to be less than 5 ppm.

- Gas filling

Carbon dioxide 250.846 g. , carbon monoxide 159.652 g., methane 91.439g., nitrogen 159.671 g., hydrogen 68.941 g., were filled into the cylinder respectively by gravimetric method. Then the cylinder was rolled 15 minutes.

- Gas analysis

Analyze the concentration of hydrogen, nitrogen, methane, carbon monoxide by gas chromatography

GC condition

Instrument	:	Gas Chromatography (Shimatsu model GC14A)
Detector	:	TCD @ 70 mA
Carrier	:	Ar
Flowrates	:	300 kPa
Column	:	Molecular Sieve 5A, 80/100, 3 m x 1/8" SS
Column temperature	:	80°C
Injection temperature	:	Ambient
Detector temperature	:	110°C
Sample volume	:	0.1 cc.

Analyze the concentration of carbon dioxide by gas chromatography.

GC condition

Instrument	:	Gas Chromatography (Shimatsu model GC 14B)
Detector	:	TCD @ 140 mA
Carrier	:	He
Flowrates	:	150 kPa
Column	:	Porapak Q, 80/100, 3 m x 1/8" SS
Column temperature	:	50°C
Injection temperature	:	Ambient
Detector temperature	:	110°C
Sample volume	:	0.1 cc.

The reference standard gases are from Thai industrial gases (Public) Co.,Ltd.

- a) 10.09+/-0.01% N₂ in He
- b) 49.70+/-0.05% H₂ in N₂
- c) 10.03+/-0.06% CO in N₂
- d) 10.10+/-0.01% CH₄ in Ar
- e) 9.955+/-0.01% CO₂ in N₂

The concentration of raw material gas is shown in the table 3.1.

Table 3.1 Composition of standard mixed gas.

component	concentration (%)
hydrogen	59.8%
nitrogen	10.0%
Carbon monoxide	10.1%
methane	10.1%
Carbon dioxide	9.9%

4. Adsorbent

The adsorbents are zeolite 3A, 4A, 5A, 13X and Beta from Zeochem Co.,Ltd. Bead sizes are 1 – 2 mm. and 2.5 - 5mm. In addition, silica gel (SiO₂) and alumina (Al₂O₃) were used in this experiment. Some of the relevant properties of molecular sieves are listed in Table 3.2 - 3.6. Figure 3.1 – 3.3 show structure of zeolites.

Table 3.2 Properties of Zeolite 3A

source: Zeochem Co.,Ltd.

Subject	Unit	Value	
Chemical name	N	0.4K ₂ O·0.6Na ₂ O·Al ₂ O ₃ ·2.0SiO ₂ ·4.5H ₂ O	
Structure Type	N	A	
Major Cation	N	K	
Pore Size	A	3	
Tapped bulk density, EN ISO 787-11	Kg/m ³	710	
Bead size nominal	mm	1-2	2.5-5
Crush strength	N	20	70
Equilibrium water adsorption capacity, @20°C/50%rh/24h	%	20.5	
Residual water content, 550°C as shipped	%	1.5	

Subject	Unit	Value
Heat of adsorption	kJ/kg water	4200
Specific heat (approx)	kJ/kg °C	1.07
Regeneration temperature recommended	°C	200-300

Table 3.3 Properties of Zeolite 4A

source: Zeochem Co.,Ltd.

Subject	Unit	Value	
Chemical name	N	Al ₂ O ₃ ·2.0SiO ₂ ·4.5H ₂ O	
Structure Type	N	A	
Major Cation	N	Na ⁺	
Pore Size	A	4	
Tapped bulk density, EN ISO 787-11	Kg/m ³	720	
Bead size nominal	mm	1-2	2.5-5
Crush strength	N	20	70
Equilibrium water adsorption capacity, @20°C/50%rh/24h	%	22 min	
Residual water content, 550°C as shipped	%	1.5 max	
Heat of adsorption	kJ/kg water	4200	
Specific heat (approx)	kJ/kg °C	1.07	
Regeneration temperature recommended	°C	250-300	

Table 3.4 Properties of Zeolite 5A

source: Zeochem Co.,Ltd.

Subject	Unit	Value	
Chemical name	N	0.7CaO·0.30Na ₂ O·Al ₂ O ₃ ·2.0SiO ₂ ·4.5H ₂ O	
Structure Type	N	A	
Major Cation	N	Ca ⁺⁺	
Pore Size	A	5	
Tapped bulk density, EN ISO 787-11	Kg/m ³	720	
Bead size nominal	mm	1-2	2.5-5
Crush strength	N	20	70
Equilibrium water adsorption capacity, @20°C/50%rh/24h	%	22 min	
Residual water content, 550°C as shipped	%	1.5 max	
Heat of adsorption	kJ/kg water	4200	
Specific heat (approx)	kJ/kg °C	1.07	
Regeneration temperature recommended	°C	250-300	

Table 3.5 Properties of Zeolite 13X

source: Zeochem Co.,Ltd.

Subject	Unit	Value	
Chemical name	N	Na ₂ O·Al ₂ O ₃ ·2.45SiO ₂ ·6.0H ₂ O	
Structure Type	N	X	
Major Cation	N	Na	
Pore Size	A	10	
Tapped bulk density, EN ISO 787-11	Kg/m ³	650	
Bead size nominal	mm	1-2	2.5-5

Subject	Unit	Value	
Crush strength	N	20	70
Equilibrium water adsorption capacity, @20°C/50%rh/24h	wt%	26	
Residual water content, 550°C as shipped	%	1.5	
Heat of adsorption	kJ/kg water	4200	
Specific heat (approx)	kJ/kg °C	1.07	
Regeneration temperature recommended	°C	280-300	

Table 3.6 Properties of beta zeolite

source: Zeochem Co.,Ltd.

Subject	Unit	Value
Chemical name	N	$(0-0.3)\text{Na}_2\text{O} \cdot (0.5-10)\text{Al}_2\text{O}_3 \cdot (1.3-10)\text{P}_2\text{O}_5 \cdot (0.7-15)\text{MxO}_y \cdot (70-97)\text{SiO}_2$
Structure Type	N	BEA
Major Cation	N	Na^+
Pore Size	A	7.6 x 6.4 / 5.5 x 5.5
SiO ₂ /Al ₂ O ₃ , mol ratio		20±5
Crystal size, SEM	µm	< 0.5



Figure 3.1 Zeolite A molecular structure

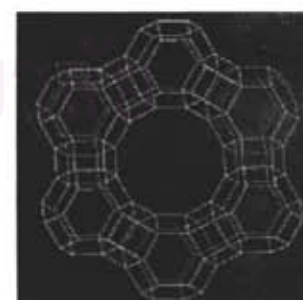


Figure 3.2 Zeolite X molecular structure

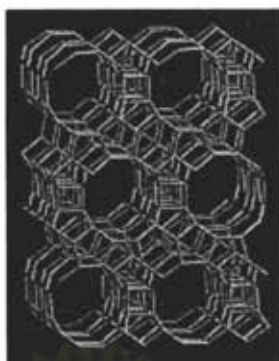


Figure 3.3 Zeolite beta molecular structure

Zeolite Characterization

The structure of zeolites were verified by XRD Rigaku D/MAX-2200 Ultima⁺ X-ray diffractometer equipped with Cu target X-ray tube (40 kV, 30mA) at 2-theta ranged from 5.0 to 50.0 degree with a scan speed of 1.00 degree/min and sampling width of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.05 degree, 0.5 degree, and 0.15 mm, respectively. The measured diffractograms were analyzed using MDI software (Jade6.5).

N₂ adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the adsorbents were performed using a BEL Japan, BELSORP- mini instrument. The samples were pre-treatment at 300°C for 3 hours before each quantification.

3.1.2 Equipments

1 Purification Unit

Set of hydrogen purification process consisted of

- Vacuum pump
- Regulator
- Steel tube containing the adsorbent
- Liquid nitrogen tank
- Pressure gauge
- Bomb

In lab scale, set of hydrogen purification process was decreased around 10 times from industrial process. It consisted of purifier unit (to control temperature of adsorption process), water bath (to adjust the temperature of output gas). A cylinder of raw material gas and a vacuum pumping system connected to the molecular sieve tube. The Figure 3.4 displays the connections between the zeolite tube, the vacuum pump, the raw material gas, and the open air. The most relevant aspects are labeled. Figure 3.5 shows the zeolite tube apparatus.

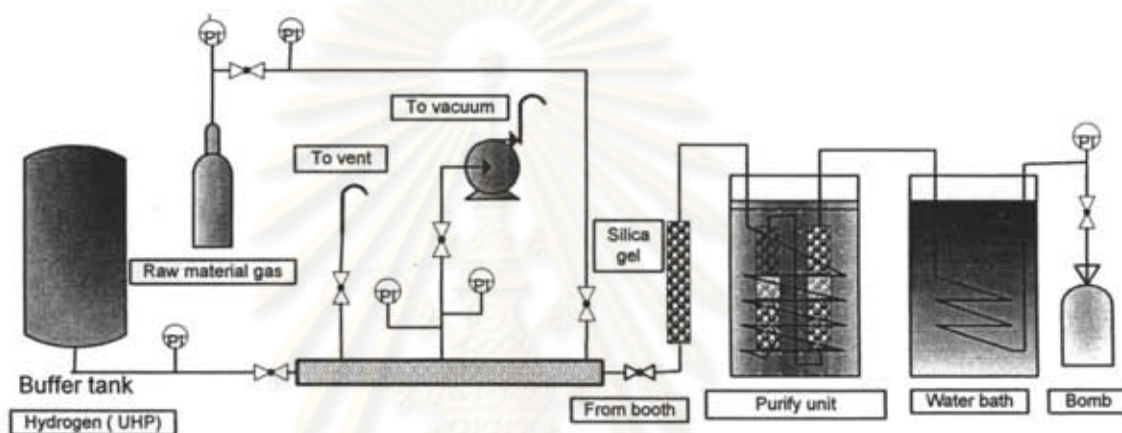


Figure 3.4 Diagram of experiment process

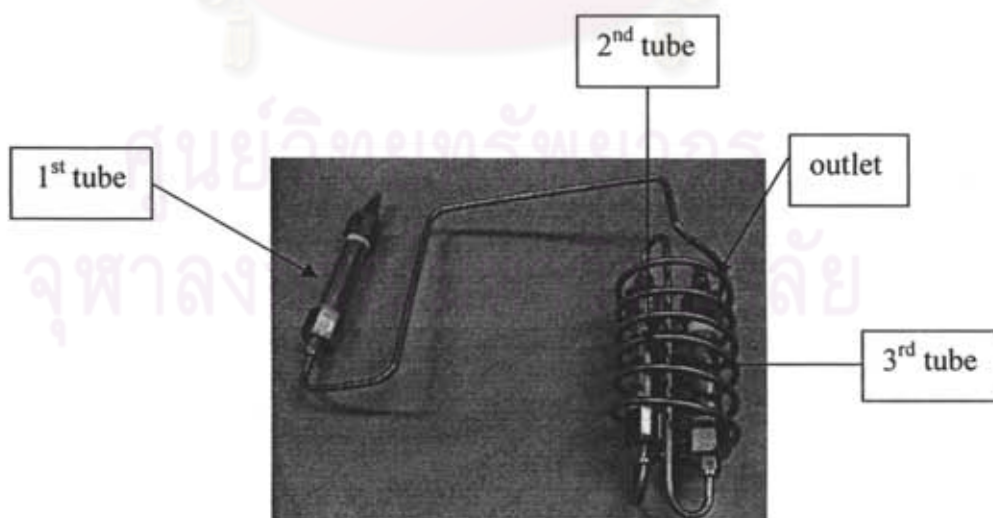


Figure 3.5 Tube apparatus

As the experiment progress, all molecular sieves are put sequentially inside the tube shown in Figure 3.5 and covered each layer with a thin steel sieve to prevent mixing of each. The dimension of tube is 1.3 cm. x 12 cm. Volume is 15.9 cm³. The first tube was packed with silica gel. The second and the third were packed with zeolite and alumina with the controlled ratio. Both second and third tubes were dipped in liquid nitrogen tank or ice bath or ambient depending on selected temperature. The inlet pressure was controlled by regulator. Before doing the test, it was tested the system for leak, and vacuumed the tube out completely (-30 barg).

After vacuum process, the raw material gas was released pass all 3 columns and water bath before collecting into bomb. The water was heated at 55°C to warm gas which came from refrigerator tank. Bomb 1,000 CC. was used to fill up the outlet gas (gas product). The pressure gauge was connected at the front of bomb.

2 Gas chromatography

Gas chromatography involves a sample being vapourised and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a stationary phase which is a microscopic layer of liquid or polymer on an inert solid support. The instrument used to perform gas chromatographic separation is called a gas chromatograph (also: aerograph, gas separator) In this experiment, the below gas chromatograph instruments were used for analysis.

1. Shimatsu model GC-14A
2. Shimatsu model GC-14B
3. Agilent 6890N (G 1530N)
4. Agilent 6890N (G 1540N)

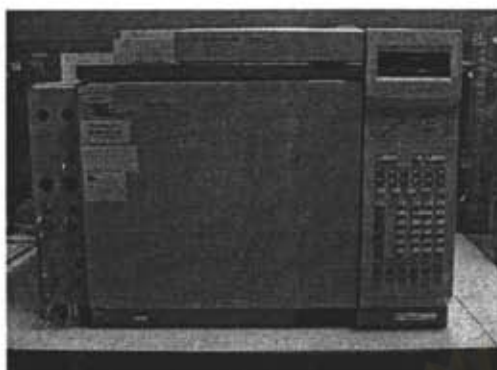


Figure 3.6 Gas Chromatography
(Agilent 6890 N)

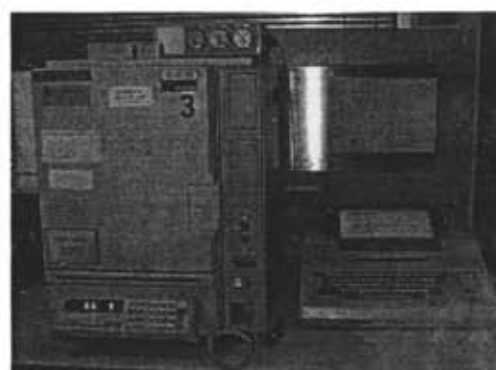


Figure 3.7 Gas Chromatograph
(Shimadzu model GC 14B)

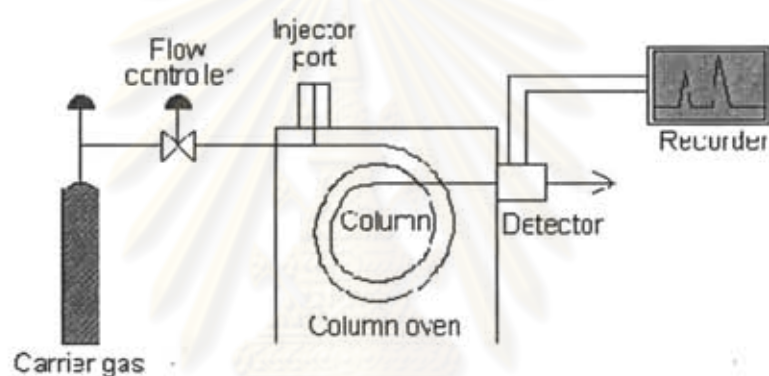


Figure 3.8 Schematic diagram of a gas chromatograph

Instrumental components

- a) Carrier Gas
- b) Flow Controller
- c) Injector Port
- d) Column
- e) Detector
- f) Recorder

The details of main components are below.

a) Carrier gas

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. In this experiment argon, nitrogen and helium were used as carrier gases.

b) Columns

There are two general types of column, packed and capillary (also known as open tubular). In this experiment, both packed and capillary columns were used as below.

- 1) Molecular Sieve 5A, 80/100, 3 m x 1/8" SS was used to separate hydrogen, carbon monoxide, nitrogen, methane at %level.
- 2) Porapak Q, 80/100, 3 m x 1/8" SS was used to separate carbon dioxide at %level.
- 3) 5' x 1/8" Hyayesep Q was used to separate carbon monoxide and methane at ppm level.
- 4) Porapak S was used to separate carbon dioxide at ppm level.
- 5) 25 m x 0.53 mm Porabond Q was use to separate carbon dioxide at ppm level.
- 6) 39 m x 0.53 mm molsieve 5A was use to separate carbon monoxide, methane, nitrogen, oxygen at ppm level.

C) Detectors

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. In this experiment, the following detectors were used.

a) Thermal conductivity detector (TCD)

In this experiment, a thermal conductivity detector (TCD) was use to detect hydrogen, carbon monoxide, methane, carbon dioxide, nitrogen at %level. This detector senses changes in the thermal conductivity of the column effluent and compares it to a reference flow of carrier gas. Since most

compounds have a thermal conductivity much less than that of the common carrier gases of helium or hydrogen (Argon was used in this experiment), when an analyte elutes from the column, the effluent thermal conductivity is reduced and produces a detectable signal.

b) Flame ionization detector (FID)

A flame ionization detector (FID) was used for trace analysis of carbon monoxide, carbon dioxide, methane. The gas sample is separated on the column and passed over the hot catalyst in the presence of hydrogen, which converts the carbon monoxide and carbon dioxide to methane

c) Helium ionization detector (HID)

A helium ionization detector (HID) was used to analyze impurities in hydrogen UHP and industrial grade (oxygen, nitrogen, carbon monoxide, carbon dioxide, methane at ppm level). An HID is an ion detector which uses a radioactive source to produce ions. The radioactive source ionizes helium atoms by bombarding them with emissions. As components elute from the GC's column they are mixed with the helium ions, which then ionize the components. The ions produce an electric current, which is the signal output of the detector. The greater the concentration of the component, the more ions are produced, and the greater the current.

3.2 Experiment

3.2.1 Hydrogen purification

a) Column packing

- Heat the alumina and silica gel at 170°C, 3 hours and keep in the desiccators.
- Heat the zeolites at 300°C for 3 hours and cool down at 100°C for 1 hour. Keep in the desiccators.
- Heat the steel pipe at 170°C, 10 minutes before packing the adsorbents.
- Weight the silica gel 12 g. and fill in the first tube.
- Weight the alumina, the zeolite at the selected ratio. Then fill sequentially in the second and the third tube.

b) Hydrogen purification

- Vacuum the bomb 1000 CC. until the pressure inside the bomb is -20 bar g.
- Connect the set of the apparatus as the figure 3.4. The valve of the bomb still in closed.
- Purge the H₂ UHP pass the system except the bomb. Check the leak point by the snoop, seal them when found. Then vent the purged gas and vacuum the system until the pressure is -30 bar g. Repeat 3 times.
- Keep warm water at 55°C in the water bath.
- Put liquid nitrogen or ice or nothing in purify tank. Wait for 10 minutes.
- Open valve of the bomb.
- Release the raw material gas passes the system.
- The inlet pressure was controlled by the regulator at 5, 10, 15, 20 barg.
- The raw material gas will flow pass all of 3 columns which were packed with the selected type of molecular sieve at the selected ratio.
- The outlet gas flowed pass the water bath to adjust the temperature and was collected in the bomb.
- Close valve of the bomb when the pressure gauge indicated at 10 barg.

3.2.2 Outlet gas analysis

- The %level of hydrogen, nitrogen, carbon monoxide and carbon dioxide were analyzed by gas chromatography and the conditions which mention on item 3.1.1 (raw material analysis)
- ppm level of carbon dioxide and methane were analyzed by gas chromatography. The condition is shown below.

GC condition

Instrument	:	Gas Chromatography (Agilent 6890 G1540N)
Detector	:	FID
Carrier	:	He
Column	:	5' x 1/8" Silcosteel HyeSep Q (80/100) Porapak S

- The standard gases are from Thai Industrial Gases (Public) Co.Ltd.

1. H₂ UHP (99.9995%)
2. 1.992+/-0.003% N₂ in Ar
3. 1.04+/-0.002% CO in N₂
4. 1.6+/-0.1ppm CO₂ in N₂
5. 200+/-1ppm CH₄ in N₂

3.2.3 Study factors that affect hydrogen purification process.

- The type of zeolite. The zeolites were used in this study are 3A, 4A, 5A, 13X and beta.
- The temperature at purify tank is varied at ambient (25°C) , 0°C and -196°C.
- The bead size of zeolites are 1-2mm. and 2.5-5mm.
- The ratio of the alumina:zeolite:alumina is varied at 4.5:3:4.5 g. and 2.5:7:2.5 g.
- The inlet pressure is varied at 5, 10, 15, 20 barg.

3.2.4 Study life time of zeolite

- Calcine zeolite at 300°C, 3 hours. Calcine alumina and silica gel at 180°C 3 hours.
- Feed raw material gas passes the system continuously.
- Analyze the outlet gas.
- Repeat again 3 times.
- Compare the concentration of outlet gas.

3.2.5 Compare our best condition to present company condition

1. Use the mixed gas as a feed gas.
2. Use the H₂ industrial grade as a feed gas.

The present company condition	lab scale	industrial scale
Zeolite	4A	4A
Inlet pressure	15 barg	140 bar g
Temperature	-196°C	-196°C
Pellet size	2.5-5 mm.	2.5-5 mm.
Alumina:Zeolite:Alumina (wt)	4.5:3:4.5 g.	4.5:3:4.5 kg.

- Analyze outlet gas (ppm level of N_2 , O_2 , CO, CO_2 , CH_4) by gas chromatography.

GC condition

Instrument : Gas Chromatography (Agilent 6890 N)
Detector : HID
Carrier : He
Flowrates : -
Column : 25 m x 0.53 mm Porabond Q and 30 m x 0.53 mm Molsieve 5A



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CHAPTER IV

RESULTS AND DISCUSSION

This experiment studies hydrogen purification by adsorption. The factors that were studied are type of zeolite, temperature, bead size, initial pressure and the ratio of zeolite and alumina. The life time of the zeolite is also studied.

4.1 Characterization of adsorbents

The commercial adsorbents were used in this experiment are silica gel, activated alumina and 5 different type of zeolite (3A, 4A, 5A, 13X and beta). In order to verify types of zeolite, the XRD spectrum of each sample was compared with the reference patterns collected by International Zeolite Association Structure Commission (IZA-SC). XRD spectrum of zeolite samples were obtained using x-ray diffractometer (Rigaku D/MAX-2200 Ultima[†]). The XRD spectrum zeolite 3A, 4A, 4A (factory) 5A, beta and 13X exist in the respective sample (Figure 4.1 and 4.2) which correspondent to their structural units.

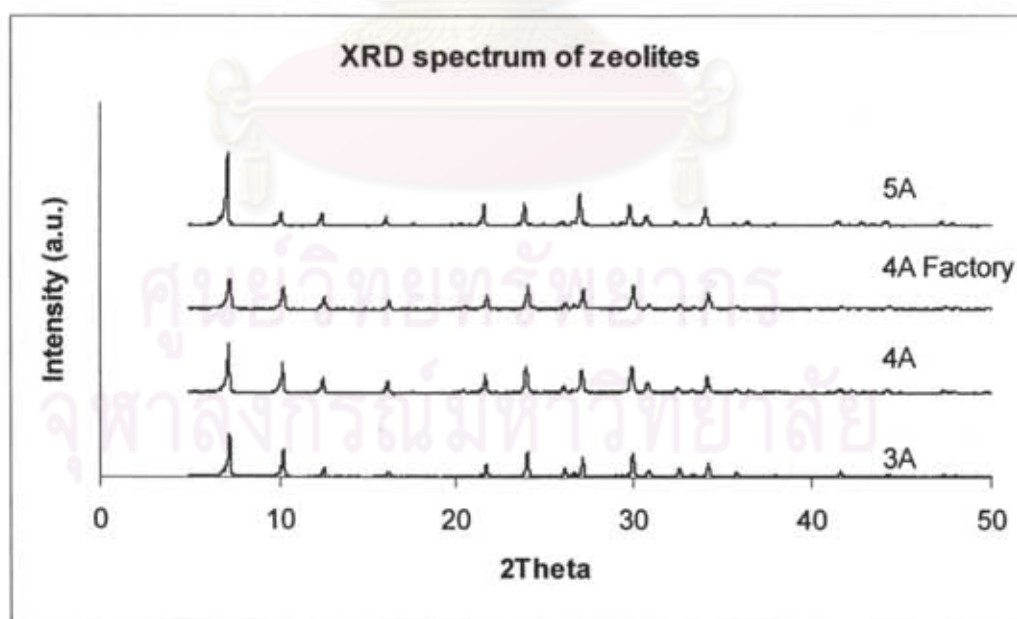


Figure 4.1 XRD spectrum of zeolite 3A, 4A, 4A factory, 5A.

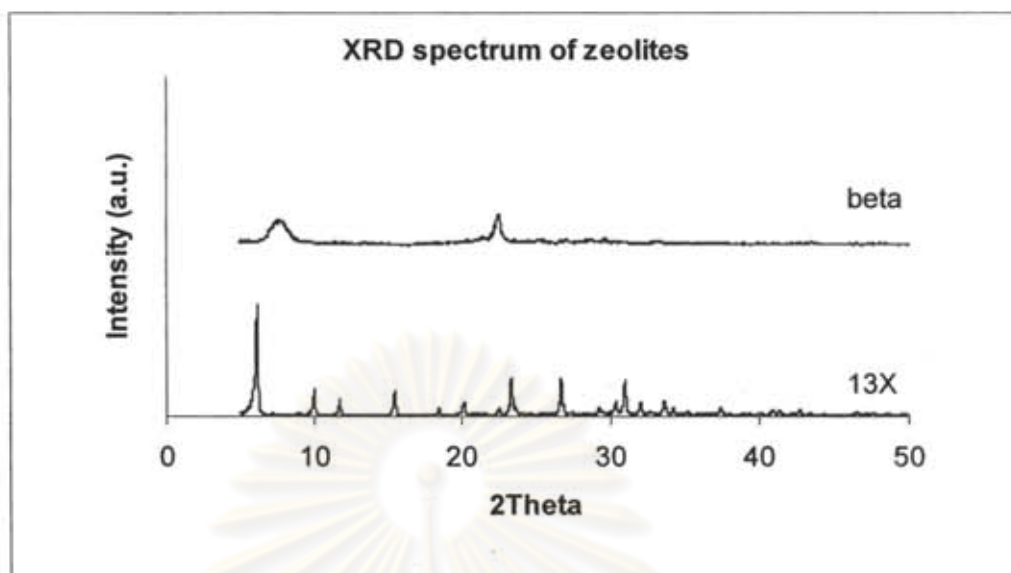


Figure 4.2 XRD spectrum of zeolite beta and 13X.

Surface area of zeolite 13X and beta was analyzed by BEL Japan, BELSORP-mini instrument. The samples were pre-treatment at 300°C for 3 hours. It is unable to analyze surface of zeolite 3A and 4A by this method because the pore size of these zeolites are too small to adsorb N_2 . Surface area of zeolite 13X and beta are 531 and 681 (m^2g^{-1}) respectively. N_2 adsorption-desorption isotherms of 13X and beta zeolite are showed in Figure 4.3.

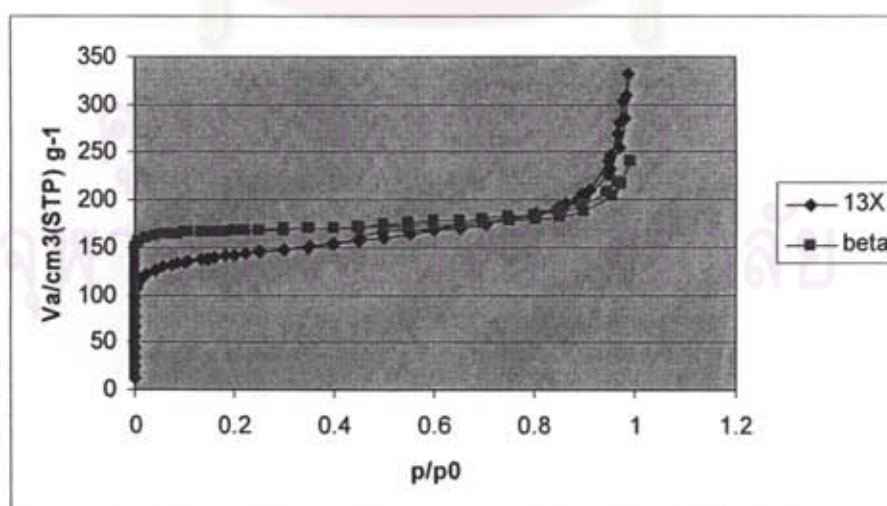


Figure 4.3 N_2 adsorption-desorption isotherms of 13X and beta zeolite.

4.2 Effect of molecular sieve (zeolite)

Effect of molecular sieve (zeolite) was determined by using the standard mixed gas (10.1% CO, 9.9% CO₂, 10.1% CH₄, 10.0% N₂, 59.8% H₂) flows through hydrogen purification system. The condition is shown as below. The obtained results are shown in the table 4.1.

Feed gas	:	standard mixed gas
Zeolite	:	3A, 4A, 5A, 13X and beta
Inlet pressure	:	10 bar g
Temperature	:	-196°C
Pellet size	:	2.5-5 mm.
Alumina : Zeolite : Alumina (g.)	:	4.5 : 3 : 4.5

Table 4.1 Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta/-196°C/10 barg)

Molecular sieve	Number run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
3A	1 st	91.3	6.0	2.7	434	0	100
	2 nd	91.3	5.9	2.8	461	1.1	100
	avg	91.3	6.0	2.8	448	0.6	100
4A	1 st	92.1	5.6	2.3	240	0	100
	2 nd	91.2	5.9	2.9	460	0	100
	avg	91.7	5.8	2.6	350	0	100
5A	1 st	91.0	6.0	2.9	517	1.3	100
	2 nd	91.1	6.0	2.9	533	0.3	100
	avg	91.1	6.0	2.9	525	0.8	100
13X	1 st	91.0	6.0	3.0	513	1.2	100
	2 nd	90.9	6.1	3.0	509	1.0	100
	avg	91.0	6.1	3.0	511	1.1	100
beta	1 st	93.5	4.6	1.7	278	0	100
	2 nd	93.7	4.6	1.7	277	0	100
	avg	93.6	4.6	1.7	278	0	100

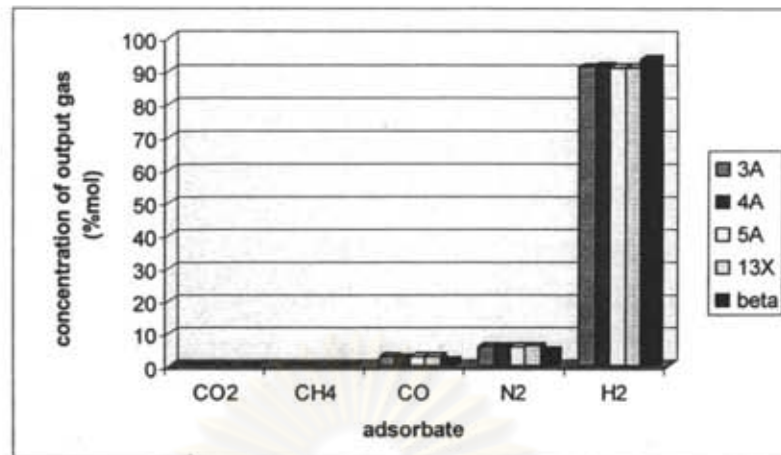


Figure 4.4 Concentration of output gas (zeolite 3A, 4A, 5A, 13X, beta/-196°C/10 barg).

Table 4.2 %Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C/10 barg)

Molecular sieve	% Adsorption			
	N ₂	CO	CH ₄	CO ₂
3A	40.0	72.0	99.6%	99.9%
4A	42.0	74.0	99.7%	100%
5A	40.0	71.0	99.5%	99.9%
13X	39.0	70.0	99.5%	99.9%
beta	54.0	83.0	99.7%	100.0%

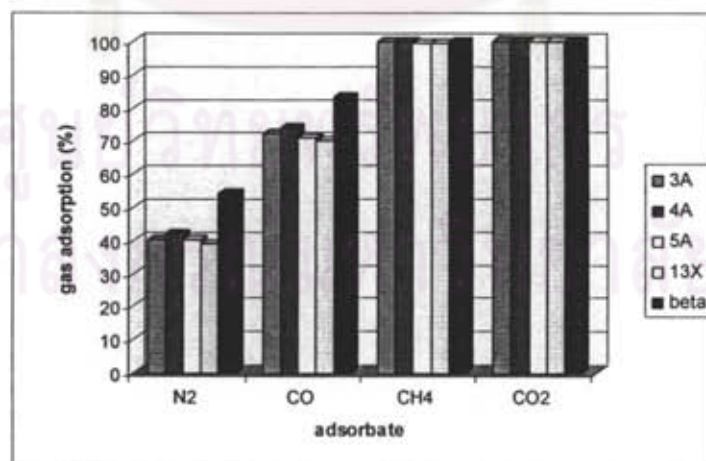


Figure 4.5 %Adsorption by zeolite 3A, 4A, 5A, 13X and beta (-196°C/10 barg).

Purity of hydrogen when using zeolite 3A, 4A, 5A, 13X and beta as adsorbent are 91.3, 91.7, 91.1, 91.0, 93.6% respectively, comparing to 59.8% of inlet standard mixed gas. CO₂ were adsorbed more than CH₄ > CO > N₂ in all type of zeolites. This result corresponds to Peiyuan Li which reported beta zeolite can adsorb CO₂ > CH₄ > N₂ > O₂ [8]. Gas adsorption ability of each zeolite from this experiment is shown below.

N₂ beta > 4A > 3A = 5A > 13X

CO beta > 4A > 3A > 5A > 13X

CH₄ beta > 4A > 3A > 13X > 5A

CO₂ beta > 4A > 3A > 5A > 13X

Beta is a good adsorbent for all of gases. Refer to kinetic diameter theory CO, CO₂, CH₄, N₂ which has a kinetic diameter, σ of 3.76, 3.30, 3.80 and 3.64 Å respectively (Table 4.3). It seems appropriate to zeolite 4A which has a pore diameter of 4 Å. This is compared well to this experiment that adsorption ability of 4A for CO, CO₂, CH₄, N₂ is better than 3A, 5A and 13X. However, from this experiment beta zeolite which has pore diameter of 7.6×6.4 and 5.5×5.5 Å provides the best result for adsorption of CO, CO₂, CH₄, N₂. The result shows that not only pore diameter that affects the adsorption ability. The other factors are zeolite structure and adsorption area. The nitrogen adsorption analysis was done for zeolite beta and 13X. The results are 681 (m²g⁻¹) and 531 (m²g⁻¹) respectively which correspond to this experiment. The adsorption ability for N₂ of beta zeolite is better than zeolite 13X.

According to these results, Beta zeolite was chosen to be a representative for the next experiments.

Table 4.3 Dimensions of H₂, N₂, CO, CO₂, CH₄

	Pauling	Lennard-Jones		
	length (Å)	Width (Å)	γ min (Å)	σ (Å) ^a
H ₂	3.1	2.4	3.24	2.89
N ₂	4.1	3	4.09	3.64
CO	4.2	3.7	4.25	3.76
CO ₂	5.1	3.7		3.30
CH ₄		4.2	4.25	3.80

^a Kinetic diameter, σ calculated from the minimum equilibrium cross-sectional diameter.

4.3 Effect of the temperature

Effect of temperature was determined by using the following conditions. The results are shown in the table 4.4.

Feed gas	:	standard mixed gas
Zeolite	:	Beta
Initial pressure	:	10 barg
Temperature	:	-196°C, 0°C, ambient (25°C)
Pellet size	:	2.5-5 mm.
Alumina : Zeolite : Alumina (g.)	:	4.5 : 3 : 4.5

Table 4.4 Concentration of output gas (beta zeolite/-196°C, 0°C, ambient/10 barg)

Molecular sieve	Number run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (%)	CO ₂ (%)	Total
Beta -196°C	1 st	93.5	4.6	1.7	277 ppm	0	100
	2 nd	93.7	4.6	1.7	277 ppm	0	100
	avg	93.6	4.6	1.7	277 ppm	0	100
Beta 0°C	1 st	62.6	10.4	10.3	10.4	6.6	100
	2 nd	62.0	10.3	10.1	10.1	7.3	100
	avg	62.3	10.4	10.2	10.3	7.0	100
Beta ambient	1 st	61.4	10.2	10.1	10.3	7.9	100
	2 nd	61.7	10.2	10.2	10.3	7.6	100
	avg	61.6	10.2	10.2	10.3	7.8	100

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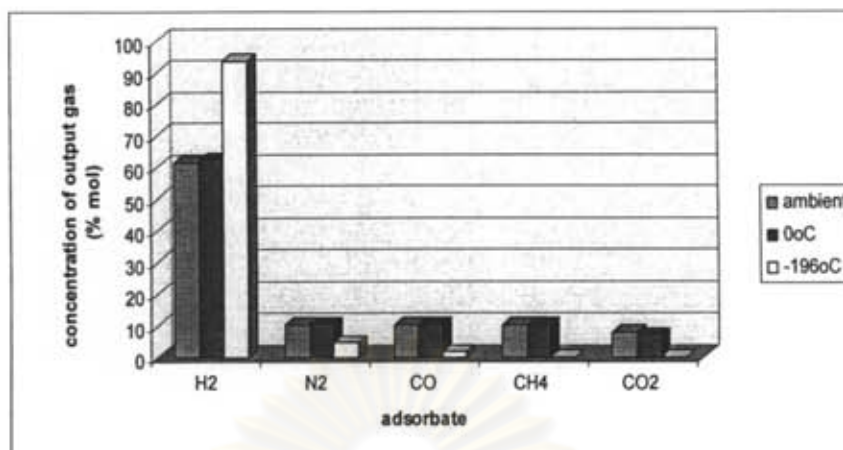


Figure 4.6 Concentration of output gas (beta zeolite/-196°C, 0°C, ambient/10 barg).

The purity of hydrogen when using beta zeolite at -196°C, 0°C, ambient are 93.6%, 62.3%, 61.6% respectively. The result at -196°C is obviously better than at 0°C and ambient. Beta zeolite does not adsorb N₂, CO, CH₄ at 0°C and ambient, only CO₂ will be adsorbed. The purity of hydrogen at 0°C are better than at ambient (25°C). This can be concluded that decreasing the temperature of the gas-solid system at a constant pressure will increase the quantity of x adsorbed.

$$X = f(t)_p$$

This is because gas molecules, upon collision with cooled surfaces, lose a significant amount of their thermal energy to the cooled surface. In general it may be said that the thermal energy of a gas molecule is determined almost entirely by the temperature of the last surface where the gas molecule desorbed from. If a surface is intentionally cooled to the temperature of liquid nitrogen (-196°C or 77K), all gas molecules which have a boiling point higher than -196°C can be cryo-condensed on this surface. These gas molecules will literally freeze, transforming from a gas to a solid. As solid material, these condensed gases are capture [15]. Table 4.5 shows boiling and melting point of CO, CO₂, CH₄, N₂ and H₂ respectively. At -196°C, solid property of CO₂ is more than CH₄ and liquid property of CO is more than N₂ which correspond to the results that CO₂ can be adsorbed more than CH₄ > CO > N₂. According to the result

decreasing the temperature will increase gas adsorption. This corresponds to Vithitsan's experiment which reported that adsorption of moisture on zeolite 3A at 90°C is better than 110°C [11] and Peiyuan Li which reported that with beta zeolite, the kinetic separation factors are very small at high temperatures for all system studied (CH_4/N_2 , CH_4/O_2 , N_2/O_2 , N_2/CO_2 , O_2/CO_2) [8].

Table 4.5 boiling and melting point of CO, CO₂, CH₄, N₂ and H₂

Gas type	Boiling point (°C)	Melting point (°C)	State at -196°C
CO	-192	-205	liquid
CO ₂	-78	-57	solid
CH ₄	-161.6	-185.5	solid
N ₂	-195.79	-210	liquid
H ₂	-252.87	-259.14	gas

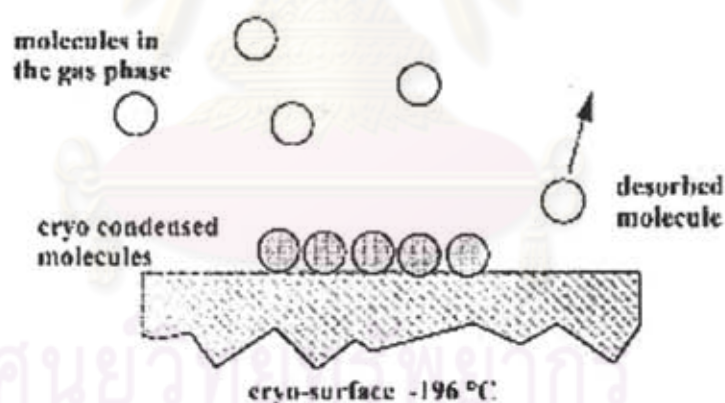


Figure 4.7 Molecules in the gas phase, upon contact with a liquid nitrogen temperature surface, condense on that surface. The residence time for molecules is dependent upon the species of gas, the temperature of the cryo-surface and the heat of adsorption.

From the temperature study, the temperature of -196°C was chosen for the next experiments.

4.4 Effect of the inlet pressure

Effect of the initial pressure was determined by using the following conditions.

The results are shown in the table 4.6.

Feed gas	:	standard mixed gas
Zeolite	:	Beta
Inlet pressure	:	5, 10, 15, 20 barg
Temperature	:	-196°C
Pellet size	:	2.5-5 mm.
Alumina : Zeolite : Alumina (g.)	:	4.5 : 3 : 4.5

Table 4.6 Concentration of output gas (beta zeolite/-196°C/5, 10, 15, 20 barg)

Molecular sieve	Number run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
5 barg	1 st	94.3	4.3	1.4	258	0.4	100
	2 nd	93.2	4.7	1.7	282	0.6	100
	avg	93.8	4.5	1.6	270	0.5	100
10 barg	1 st	93.5	4.6	1.7	278	0	100
	2 nd	93.7	4.6	1.7	277	0	100
	avg	93.6	4.6	1.7	278	0	100
15barg	1 st	91.3	6.0	2.7	439	1.3	100
	2 nd	90.9	6.2	2.8	528	1.0	100
	avg	91.1	6.1	2.8	484	1.2	100
20barg	1 st	89.8	6.9	3.3	627	1.0	100
	2 nd	91.3	6.0	2.7	467	1.6	100
	avg	90.6	6.5	3.0	547	1.3	100

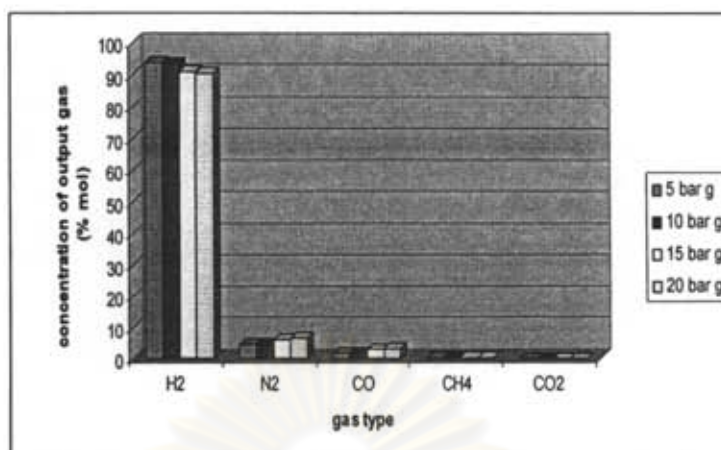


Figure 4.8 Concentration of output gas (beta zeolite/-196°C/ 5, 10, 15, 20 barg).

Purity of hydrogen will be increased when decreasing the inlet pressure. The purity of hydrogen at 5, 10, 15, 20 barg are 93.8, 93.6, 90.9, 90.6% respectively. This is explained by the adsorption time. At low pressure, the flow rate is also low. Therefore, there is much time for adsorption. This corresponds to Vithitsan's experiment which reported that adsorption of moisture on zeolite 3A at 1 mL/min. is better than 2 mL/min [11].

The adsorption pressure can be fixed by either available feed pressure or the required product pressure. Although a high feed gas pressure is always preferred for high hydrogen recovery and low investment costs but the purity of hydrogen is decreased.

In this experiment, the purity of hydrogen at 5 and 10 barg are not much different. To increase the productivity, pressure 10 barg was chosen for the next experiments.

4.5 Effect of the pellet size

In order to utilize the adsorption characteristics of zeolites in separation processes, commercial molecular sieve adsorbents are prepared as pelleted agglomerates containing a high percentage of the crystalline zeolite together with the necessary amount of an inert binder. The effect of pellet size was studied by using the 2.5-5 mm. and 1-2 mm. of zeolite 3A. The condition is below. The results are shown in the table 4.7.

Feed gas	:	standard mixed gas
Zeolite	:	3A

Initial pressure	:	10 barg
Temperature	:	-196°C
Pellet size	:	2.5-5 mm., 1-2 mm.
Alumina : Zeolite : Alumina (g.)	:	4.5 : 3 : 4.5

Table 4.7 Concentration of output gas (2.5 mm.,1-2 mm. of zeolite 3A/-196°C/10 barg)

Molecular Sieve	# run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
Beta (2.5-5 mm.)	1 st	93.5	4.6	1.7	278	0	100
	2 nd	93.7	4.6	1.7	277	0	100
	avg	93.6	4.6	1.7	278	0	100
3A (2.5-5 mm)	1 st	91.3	6.0	2.7	434	0	100
	2 nd	91.3	5.9	2.8	461	1.1	100
	avg	91.3	6.0	2.8	448	0.6	100
3A (1-2 mm)	1 st	91.0	6.0	2.9	511	0.4	100
	2 nd	90.9	7.2	1.8	557	1.8	100
	avg	91.0	6.6	2.4	534	1.1	100

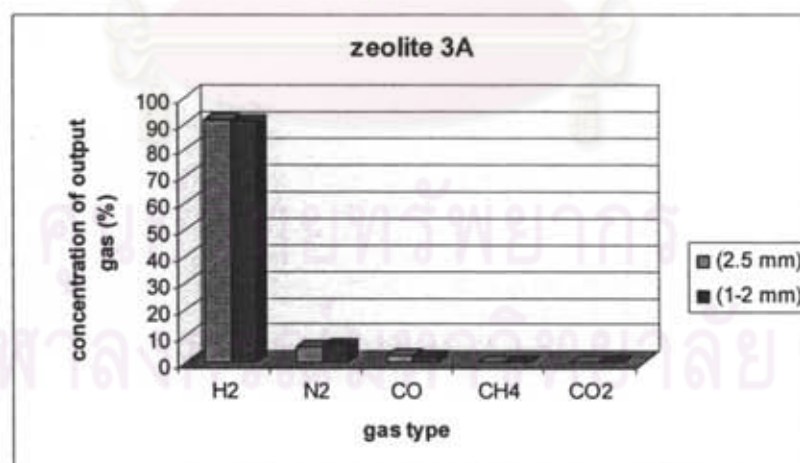


Figure 4.9 Concentration of output gas (2.5 mm.,1-2 mm. of zeolite 3A/-196°C/10 barg).

Purity of hydrogen when use 2.5-5 mm. and 1-2 mm. of zeolite 3A, -196°C are 91.3% and 91.0% respectively. The results are not much different. This is because adsorption is a matter of pore filling. The external surface area which takes a few percent of the total area doesn't play an important role in adsorption for this case.

4.6 Effect of ratio between alumina and zeolite

In this experiment alumina and zeolites were used to adsorb gas impurities of hydrogen. Effect of ratio between alumina and zeolite was studied. The condition is following. The results are shown in the table 4.8.

Feed gas	:	standard mixed gas
Zeolite type	:	3A, beta
Inlet pressure	:	10 barg
Temperature	:	-196°C
Pellet size	:	2.5 mm.
Adsorbent ratio		
Alumina:Zeolite:Alumina (g.)	:	0 : 12 : 0
	:	6 : 0 : 6
	:	4.5 : 3 : 4.5
	:	2.5 : 7 : 2.5

Table 4.8 Concentration of output gas by vary ratio of alumina and zeolite.

Molecular sieve	Ratio(alumina: zeolite:alumina) (g)	# run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
Beta	(0:12:0)	1 st	93.7	4.4	1.8	422	0	100
		2 nd	94.5	3.8	1.6	441	0	100
		avg	94.1	4.1	1.7	432	0	100
3A	(0:12:0)	1 st	87.7	7.2	4.7	1361	0	100
		2 nd	87.8	7.3	4.7	1377	0	100
		avg	87.8	7.3	4.7	1369	0	100
Alumina	(6:0:6)	1 st	92.0	5.7	2.4	370	0.1	100
		2 nd	92.1	5.4	2.4	322	0.1	100
		avg	92.1	5.6	2.4	346	0.1	100

Molecular sieve	Ratio (alumina: zeolite: alumina) (g.)	# run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
beta	(4.5:3:4.5)	1 st	93.5	4.6	1.7	278	0	100
		2 nd	93.7	4.6	1.7	277	0	100
		avg	93.6	4.6	1.7	278	0	100
	(2.5:7:2.5)	1 st	93.5	4.7	1.7	380	0	100
		2 nd	93.5	4.8	1.7	292	0	100
		avg	93.5	4.8	1.7	336	0	100
3A	(4.5:3:4.5)	1 st	91.3	6.0	2.7	434	0	100
		2 nd	91.3	5.9	2.8	461	1.1	100
		avg	91.3	6.0	2.8	448	0.6	100
	(2.5:7:2.5)	1 st	89.9	6.5	3.6	691	0	100
		2 nd	89.8	6.4	3.7	746	1	100
		avg	89.9	6.5	3.7	719	0.5	100

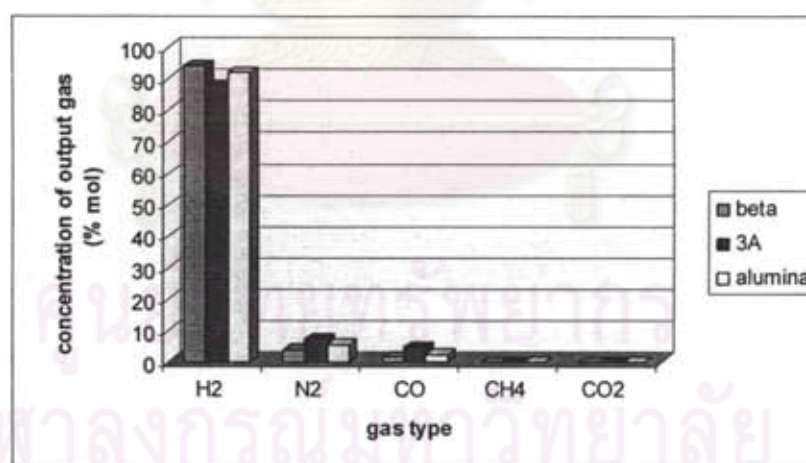


Figure 4.10 Concentration of output gas (zeolite 3A, beta, alumina (12g.)/-196°C/10 barg.).

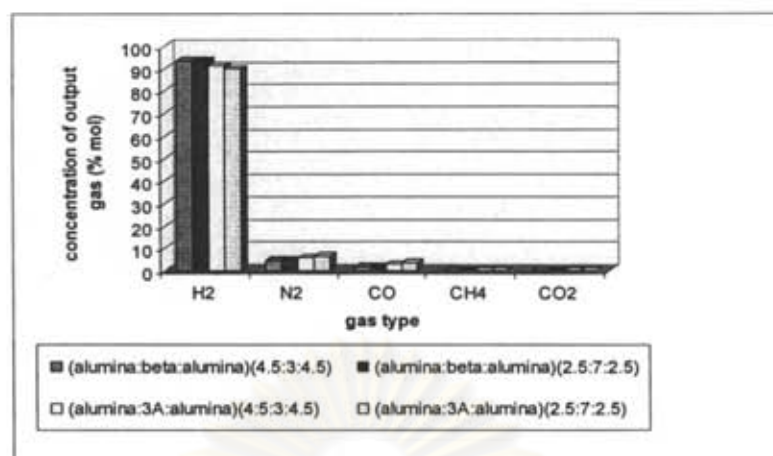


Figure 4.11 Concentration of output gas (zeolite 3A, beta/alumina:zeolite; 9:3, 5:7/-196°C/10 barg).

Purity of hydrogen when use 100% of zeolite beta, 3A and alumina are 94.1, 87.8, 92.1 respectively. The adsorption ability of zeolites and alumina are shown below.

N₂ beta > alumina > 3A
 CO beta > alumina > 3A
 CH₄ alumina > beta > 3A
 CO₂ beta = 3A > alumina

Alumina can adsorb CH₄ well, when beta can adsorb N₂, CO and CO₂ well. Increasing the alumina content would make CH₄ adsorption much better. This result corresponds to mixing alumina and zeolite adsorbent. At higher alumina content adsorbent, it exhibits lower CH₄ content of outlet gas in both cases of beta and 3A zeolites. However the most appropriate ratio is 4.5 : 3 : 4.5 of alumina : zeolite : alumina which makes the hydrogen purity to be 93.6% in case of beta zeolite is an adsorbent.

Activated alumina does not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameters within the adsorbent particles may be narrow (20 to 50 Å) or it may range widely (20 to several thousand Å). Hence, all molecular species, with the possible exception of high molecular weight polymeric materials, may enter the pores. The major use of activated alumina as a sorbent

is in drying. The moisture content can be reduced to below 1 ppm using activated alumina in suitable designed adsorbers.

Zeolite molecular sieves have pores of uniform size (3Å to 10Å) which are uniquely determined by the unit structure of the crystal. These pores will completely exclude molecules which are larger than their diameter [6].

4.7 Life time of adsorbents

All adsorption systems are cyclic in nature i.e. there is an adsorption cycle followed by regeneration cycle, which enables repeated use of adsorbent. In this experiment, the thermal was employed for regeneration and the stability period of the zeolite was studied. Four times of calcination (300°C for zeolite beta and 180°C for alumina, 3 hours) are done and hydrogen purification are repeated by using the following condition. The results are in the table 4.9 and figure 4.12.

Feed gas	:	standard mixed gas
Zeolite	:	beta
Initial pressure	:	10 barg
Temperature	:	-196°C
Pellet size	:	2.5-5 mm.
Alumina : Zeolite : Alumina (wt):		4.5 : 3 : 4.5

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Table 4.9 Concentration of output gas after each calcination (beta zeolite/-196°C/10 barg).

	# run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total
Calcination 1st	1 st	93.5	4.6	1.7	278	0	100
	2 nd	93.7	4.6	1.7	277	0	100
	avg	93.6	4.6	1.7	278	0	100
Calcination 2nd	1 st	91.9	5.5	2.5	319	0.1	100
	2 nd	91.6	5.6	2.8	422	0	100
	3 rd	92.8	5.0	2.2	322	0	100
	avg	92.1	5.4	2.5	354	0.05	100
Calcination 3rd	1 st	92.8	5.0	2.1	262	0	100
	2 nd	91.9	5.4	2.6	326	0.07	100
	avg	92.4	5.2	2.4	294	0.04	100
Calcination 4th	1 st	92.7	5.2	2.1	264	0	100
	2 nd	92.3	5.4	2.3	332	0	100
	avg	92.5	5.3	2.2	298	0.00	100

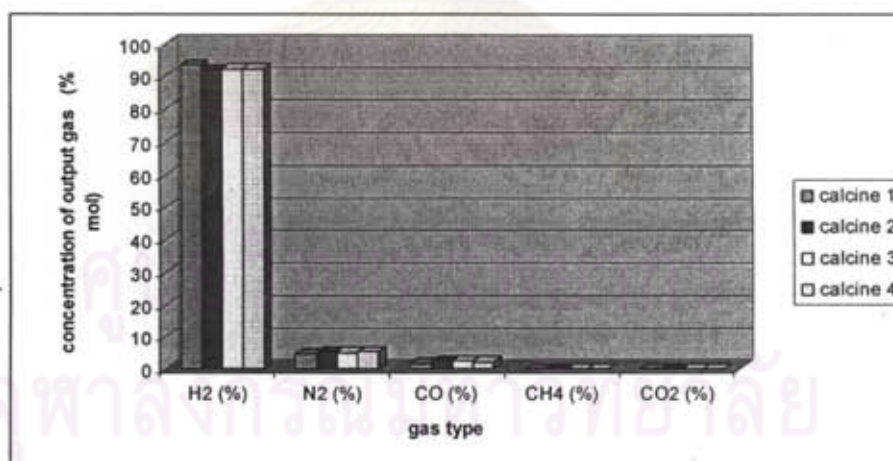


Figure 4.12 Concentration of output gas after each calcination (beta zeolite/-196°C/10barg).

Hydrogen concentration of output gas after 1st, 2nd, 3rd, 4th calcinations is 93.6, 92.1, 92.4, 92.5 respectively. The concentration of hydrogen after the second time of regeneration is less than the first one around 1.6%. The concentration of hydrogen after the 2nd, 3rd, 4th of regeneration is not much different. This result corresponds to the Shang-Bin Liu's experiment which reported that the structure of beta zeolite is a small destruction at 400°C [12].

4.8 Comparison the best and present condition.

The present and the best condition are compared by using standard mix gas and hydrogen (industrial grade) as an inlet gas. The condition is below. The results are in the table 4.10.

	Best condition	Factory condition
Feed gas	: standard mixed gas	
	: H ₂ industrial grade	
Zeolite	: beta	4A (Factory)
Inlet pressure	: 10 barg	15 barg
Temperature	: -196°C	-196°C
Pellet size	: 2.5-5 mm.	2.5-5 mm.
Alumina:Zeolite:Alumina (g.)	: 4.5:3:4.5	4.5 : 3 : 4.5

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Table 4.10 Compare concentration of output gas by present factory condition and best condition.

Feed Gas	Condition	# run	H ₂ (%)	N ₂ (%)	CO (%)	CH ₄ (ppm)	CO ₂ (ppm)	Total	
Standard Mixed Gas	Factory Condition	1 st	90.3	6.6	3.1	482	0.9	100	
		2 nd	90.3	6.4	3.3	641	0.6	100	
		avg	90.3	6.5	3.2	562	0.8	100	
	Best Condition	1 st	93.5	4.6	1.7	278	0	100	
		2 nd	93.7	4.6	1.7	277	0	100	
		avg	93.6	4.6	1.7	278	0	100	
Feed Gas	Condition	# run	O ₂ (ppm)	N ₂ (ppm)	CO (ppm)	CH ₄ (ppm)	CO ₂ (ppm)	Impurity (ppm)	H ₂ purity (%)
H ₂ Ind.			5.8259	1.7145	2.3011	0	1.2459	9.8415	99.9990
H ₂ Industrial Grade (99.8%)	Factory Condition	1 st	2.0341	0.5369	1.5297	0	0	4.1007	99.9996
		2 nd	2.0886	0.6152	1.7105	0	0	4.4143	99.9996
		avg	2.0614	0.5761	1.6201	0	0	4.2576	99.9996
	Best Condition	1 st	0.7716	0.3019	0.2913	0	0	1.3648	99.9999
		2 nd	1.3346	0.1957	0.2894	0	0	1.8197	99.9998
		avg	1.0531	0.2488	0.2903	0	0	1.5922	99.9999

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Table 4.11 Product specification of hydrogen

Gas	Typical Level	Production Specification	Selling Specification
Hydrogen, industrial grade (99.8%)	Purity 99.8%min	Purity 99.8%min	Purity 99.8% min
	O ₂ < 200 ppm	O ₂ < 200 ppm	
	H ₂ O < 200 ppm	H ₂ O < 200 ppm	
	N ₂ < 1000 ppm		
Hydrogen, UHP (99.999%)	Purity 99.999%min.	Purity 99.999%min	Purity 99.999%min
	O ₂ < 2 ppm	O ₂ < 2 ppm	O ₂ < 2 ppm
	H ₂ O < 3 ppm	H ₂ O < 3 ppm	H ₂ O < 3 ppm
	THC as CH ₄ < 1 ppm	THC as CH ₄ < 1 ppm	THC as CH ₄ < 1 ppm
	N ₂ < 4ppm		
	CO < 0.5ppm		
	CO ₂ < 1ppm		

source : Thai Industrial Gases (Public) Co.,Ltd.

The hydrogen concentration of output gas after using standard mixed gas as a feed gas with the present factory condition and our best condition are 90.3% and 93.3% respectively. When hydrogen industrial grade was used as a feed gas with the present and our best condition, the hydrogen concentration are 99.9996 and 99.9999% respectively. The purity of hydrogen after using our best condition is better than the specification. Especially, O₂ and CO levels are lower than maximum limit of UHP H₂ gas specification. This beta zeolite adsorbent exhibits the superior property than the present factory condition. Therefore, it can be concluded that the suitable zeolite for hydrogen purification by absorption process is beta zeolite. The inlet pressure is 10 barg and the temperature is -196°C. The pellet size is 2.5-5 mm. and the ratio of alumina:zeolite:alumina is 4.5:3:4.5. By this condition hydrogen purity would increase up to 99.9999%. This would raise the product quality and make it is valuable.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

Beta is a good adsorbent for all of studied impurity gases. The result shows that not only pore size affects the adsorption ability. They are also zeolite structure and surface area. Temperature was studied at -196°C , 0°C , ambient (25°C). Decreasing temperature would increase H_2 purity. The outlet gas has a grate concentration of H_2 at -196°C . Adsorption is an exothermic reaction so it occurs easily at low temperature. At -196°C , All gases which have boiling point higher than -196°C will condense to liquid and literally freeze. As solid material, these condensed gases are capture. H_2 purity is not much significant difference when using 1-2 and 2.5-5 mm pellet size of beta zeolite. During the subsequent adsorption or occlusion of various substances, the micropores can be filled and released reversibly. Therefore, adsorption is a matter of pore filling and the usual surface area concepts as they are applied to other solid adsorbents. The suitable ratio of alumina:zeolite is 9:3. Alumina has a great potential for methane adsorption while beta zeolite has a great potential for CO , CO_2 , N_2 adsorption. The inlet pressure was studied at 5, 10, 15 and 20 barg. Decreasing inlet pressure would increase H_2 purity because there is a longer time of adsorption. At inlet pressure of 5 and 10 bar g does not show much difference in H_2 purity. Therefore inlet pressure of 10 bar g was chosen to increase productivity. By this selected condition, hydrogen industrial grade was used as a feed gas, hydrogen purity would increase up to 99.9999%. Beta zeolite was tested its stability. After four times of adsorption cycles, this adsorbent can be reused without a significant changing in H_2 purity.

This would raise the product quality and make it is valuable to meet the today's application such as PEM fuel cell which needs the hydrogen with trace impurities.

5.2 Suggestion

It was concluded that beta zeolite is a good candidate for applications of hydrogen purifications. Anyway, the test in industrial scale should be done

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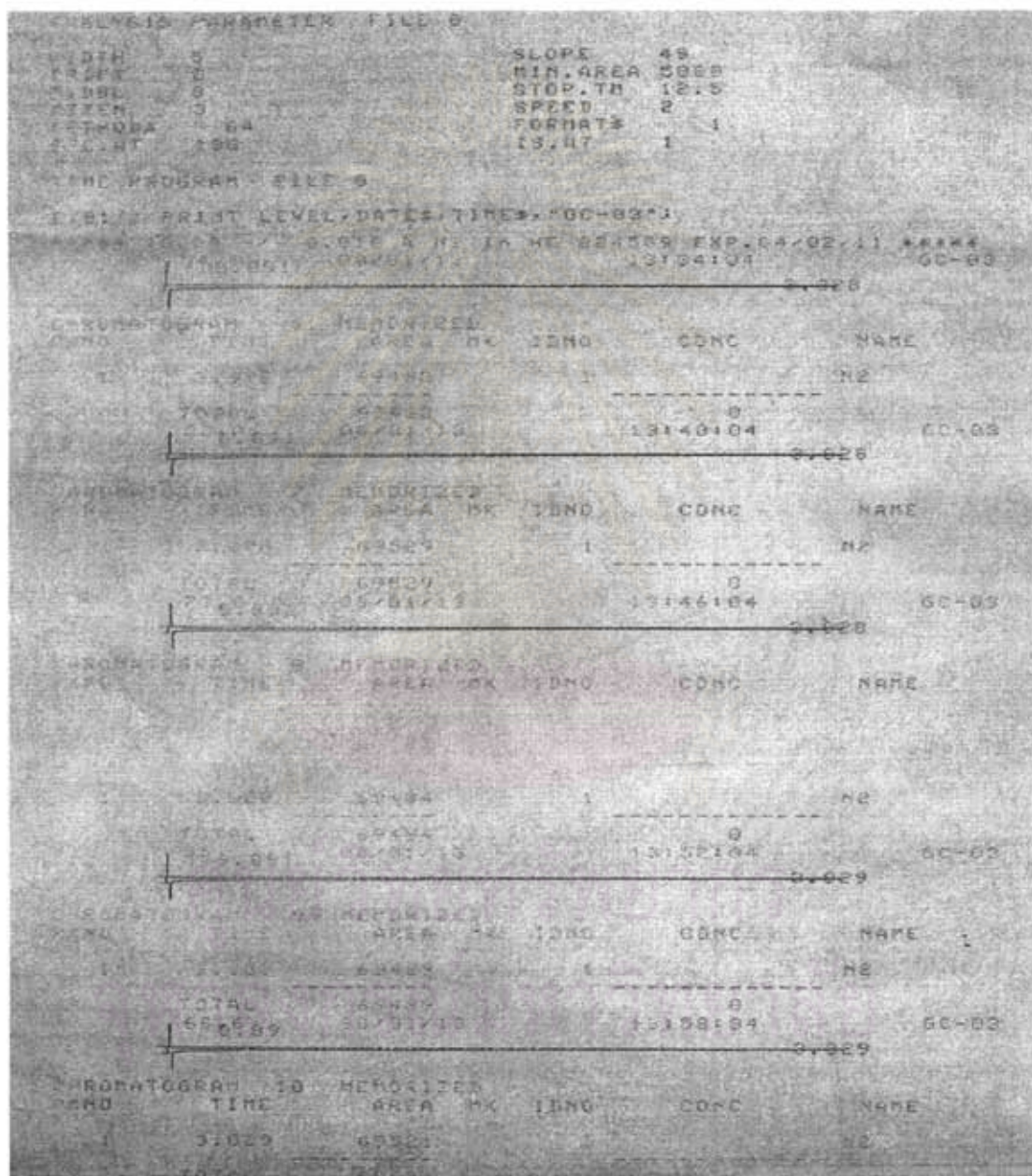
APPENDICES

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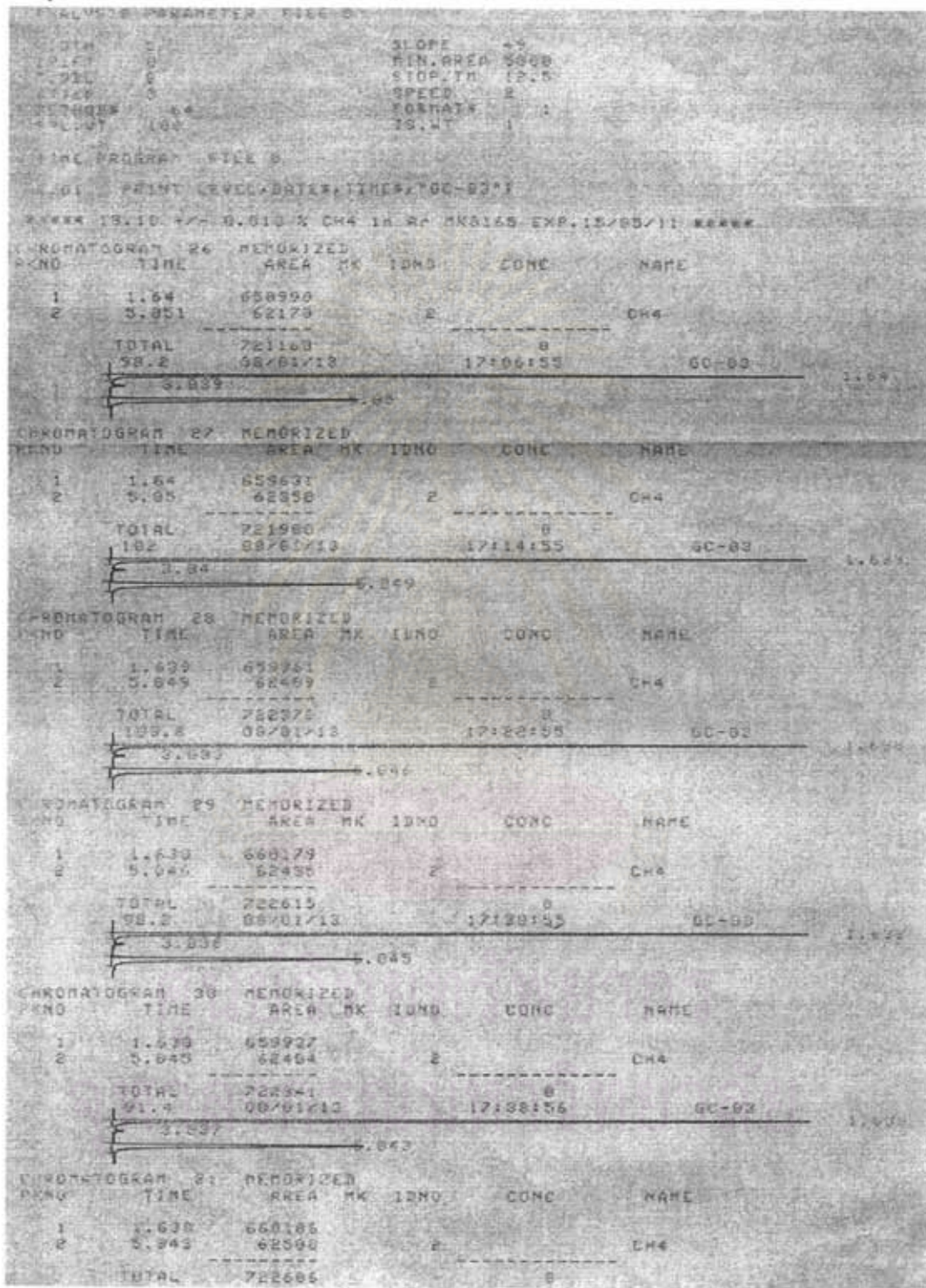
APPENDIX A

1. Chromatogram of standard mixed gas.

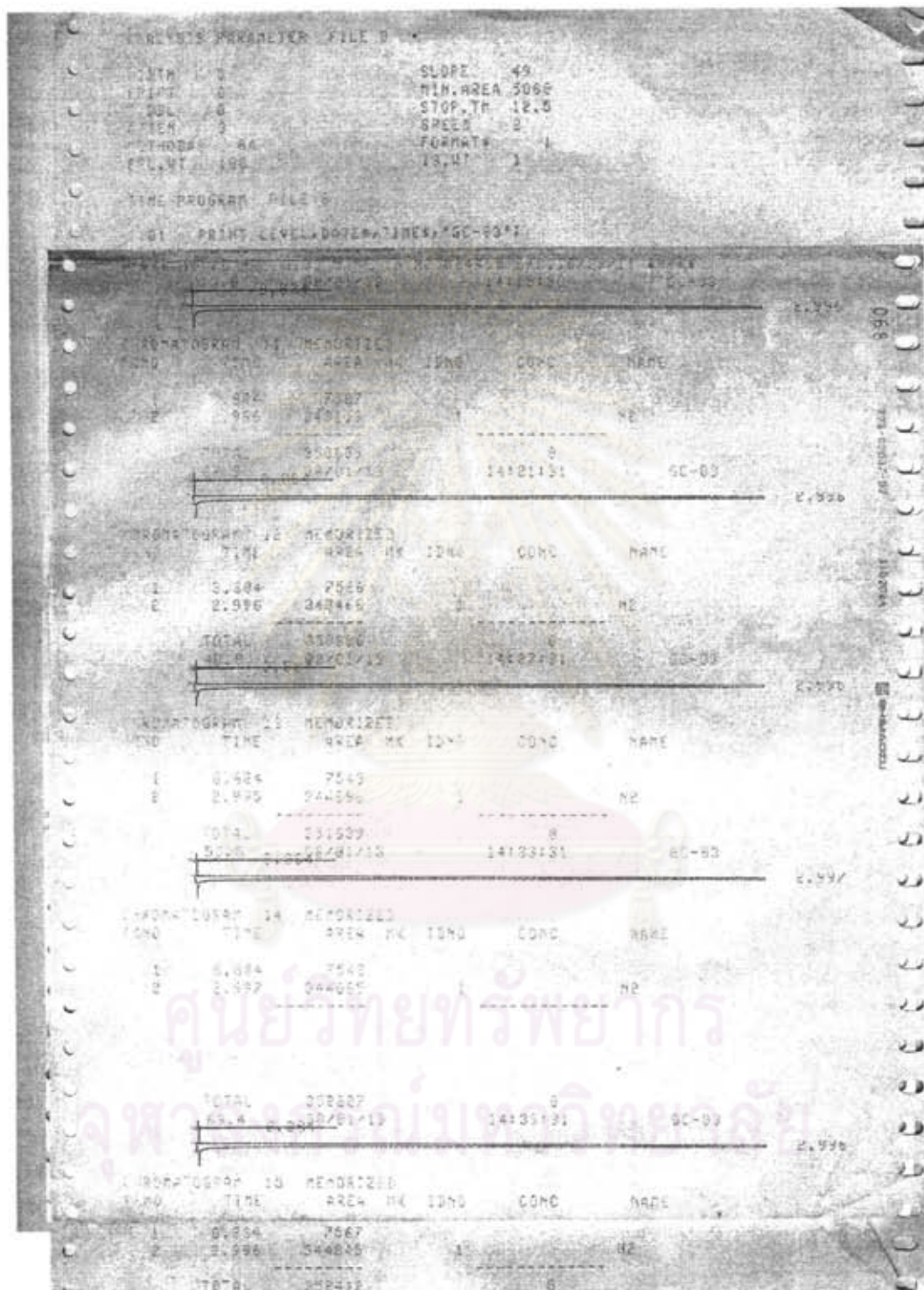
- Reference standard $10.09 \pm 0.010\%$ N_2 in He



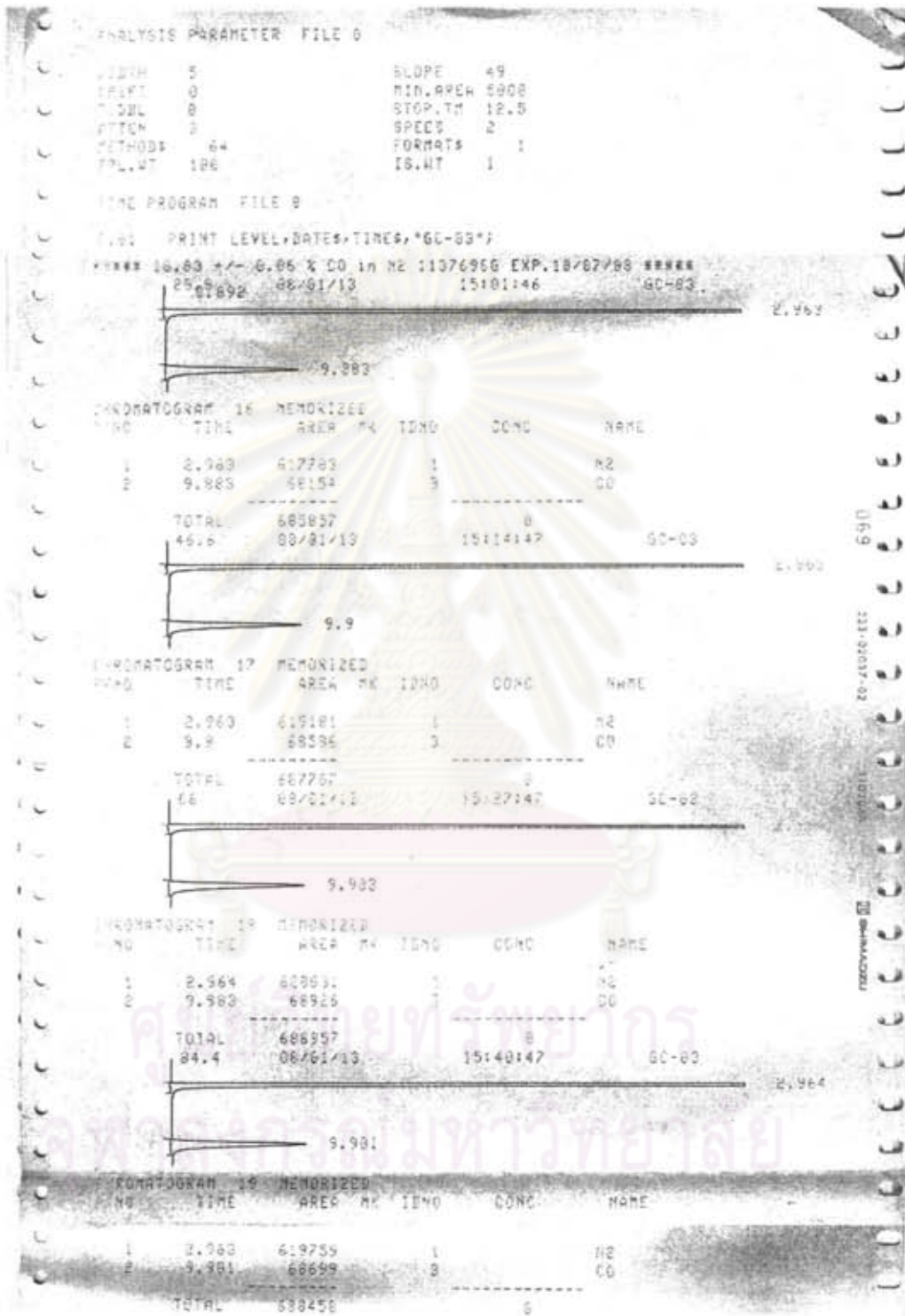
- Reference standard 10.10 ± 0.010% CH₄ in Ar



- Reference standard $49.70 \pm 0.05\% \text{H}_2$ in N_2



- Reference standard 10.03±0.06% CO in N₂



- Reference standare 9.955±0.010% CO₂ in N₂

ANALYSIS PARAMETER FILE 0

WIDTH 5 SLOPE 47
 DRIFT 0 MIN.AREA 5000
 T.DBL 0 STOP.TM 3.5
 ATTEM 5 SPEED 2
 METHOD# 61 FORMAT# 1
 SPL.WT .100 IS.WT 1

METHOD NO. SG-00-04
 CHANGE:

TIME PROGRAM FILE 0

0.01 PRINT LEVEL,DATE#,TIME#,"GC-03"

***** 9.955 +/- 0.010 % CO2 in N2 MK0227 EXP.01/11/10 *****

83.8 08/01/15 17:56:38 GC-03 U.669
 1.816

CHROMATOGRAM 1 MEMORIZED

PKNO TIME AREA MK IDNO CONC NAME

1 0.669 641324 88.6317
 2 1.816 82259/ 11.3683

TOTAL 723583 100

84.4 08/01/15 18:00:38 GC-03 U.668
 1.816

CHROMATOGRAM 2 MEMORIZED

PKNO TIME AREA MK IDNO CONC NAME

1 0.668 642346 88.6352
 2 1.815 82361/ 11.3648

TOTAL 724707 100

82.2 08/01/15 18:04:38 GC-03 U.668
 1.814

CHROMATOGRAM 3 MEMORIZED

PKNO TIME AREA MK IDNO CONC NAME

1 0.668 641713 88.6356
 2 1.814 82277/ 11.3643

TOTAL 723990 100

81.4 08/01/15 18:08:38 GC-03 U.668
 1.814

CHROMATOGRAM 4 MEMORIZED

PKNO TIME AREA MK IDNO CONC NAME

1 0.669 641615 88.6384
 2 1.814 82241/ 11.3616

TOTAL 723856 100

79.6 08/01/15 18:12:38 GC-03 U.668
 1.813

CHROMATOGRAM 5 MEMORIZED

PKNO TIME AREA MK IDNO CONC NAME

1 0.668 642334 88.6343
 2 1.813 82367/ 11.3657

TOTAL 724702 100

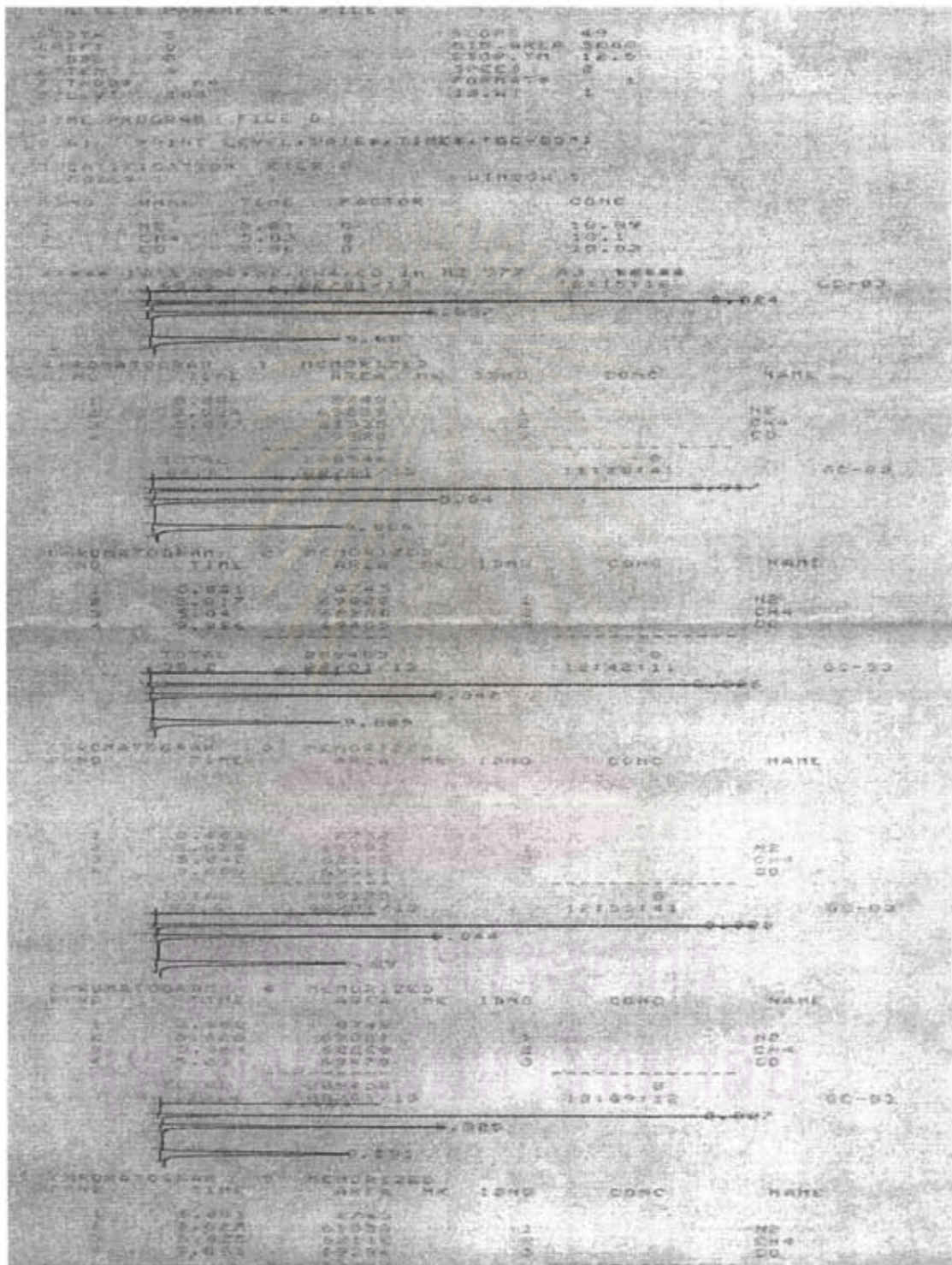
IDENTIFICATION FILE 0
 MODE# 1

WINDOW 5

COMPONENT :
 CO2
 5
 51.9006
 0.0727
 24.301
 9.955±0.010%
 11.3683
 11.3648
 11.3643
 11.3616
 11.3657

060
 223-02037-02
 310704

- Standard mixed gas (59.8% H₂, 10.0% N₂, 10.1% CO, 10.1% CH₄, 9.5% CO₂)



- Standard mixed gas (59.8% H₂, 10.0% N₂, 10.1% CO, 10.1% CH₄, 9.5% CO₂)

***** 10% CO2, CH4, CO, H2 in He 377 RJ *****
 23.4 598 08/21/75 19199125 0.691 GC-13

CHROMATOGRAM 11 MEMORIZED

PKT NO	TIME	AREA	PK	IDNO	CONC	NAME
1	0.349	5967				
2	0.691	147100	V			
3	1.003	61144	V			
4	1.911	82288		1		CO2
TOTAL		299350			0	
23.4 598 08/21/75					19199125	0.691 GC-13

CHROMATOGRAM 12 MEMORIZED

PKT NO	TIME	AREA	PK	IDNO	CONC	NAME
1	0.339	5917				
2	0.691	147278	V			
3	1.003	61279	V			
4	1.909	82363		1		CO2
TOTAL		296838			0	
23.4 598 08/21/75					19199125	0.691 GC-13

CHROMATOGRAM 13 MEMORIZED

PKT NO	TIME	AREA	PK	IDNO	CONC	NAME
1	0.337	5926				
2	0.691	146397	V			
3	1.004	61167	V			
4	1.9	82198		1		CO2
TOTAL		295591			0	
23.4 598 08/21/75					19199125	0.691 GC-13

CHROMATOGRAM 14 MEMORIZED

PKT NO	TIME	AREA	PK	IDNO	CONC	NAME
1	0.338	5937				
2	0.7	146163	V			
3	1.003	61297	V			
4	1.889	82175		1		CO2
TOTAL		295491			0	
23.4 598 08/21/75					19199125	0.691 GC-13

CHROMATOGRAM 15 MEMORIZED

PKT NO	TIME	AREA	PK	IDNO	CONC	NAME
1	0.337	5934				
2	0.7	145675	V			
3	1.034	61375	V			
4	1.809	82194		1		CO2
TOTAL		295156			0	

มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

092-256
 23.4 598 08/21/75
 19199125 0.691 GC-13
 ANALYST LP
 99.0192
 0.1117
 92106
 9.96 ± 1.1%

2. Chromatogram of best condition at 1st, 2nd, 3rd, 4th adsorption cycle.

- Reference standard 200.2±1.0 ppm CO, 200.0±1.0 ppm CH₄, 200.1±1.0 ppm CO₂ in N₂

0803192
Statistic Report

Sequence table: C:\HPCHEM\1\DATA\090319_2.S
 Data directory path: C:\HPCHEM\1\DATA\1010325
 Operator: Seksan
 Method file name: C:\HPCHEM\1\METHODS\ACC-ME~1\ACC-ME~2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	19/3/2008 10:31:15 AM	08031920.D	ALVY644
2	Vial 1	2	19/3/2008 10:39:55 AM	08031921.D	ALVY644
3	Vial 1	3	19/3/2008 10:48:35 AM	08031922.D	ALVY644
4	Vial 1	4	19/3/2008 10:57:15 AM	08031923.D	ALVY644
5	Vial 1	5	19/3/2008 11:05:56 AM	08031924.D	ALVY644
6	Vial 1	6	19/3/2008 11:14:38 AM	08031925.D	ALVY644

Compound: Carbon Monoxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	3028.98657
2	3019.94775
3	3025.14648
4	3026.46021
5	3023.67651
6	3022.66846

Mean: 3024.48100
 S.D.: 3.13506
 RSD: 0.10366
 95% CI: 3.29005

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	2962.26831
2	2970.05029
3	2973.38647
4	2975.57593
5	2974.85132
6	2974.67041

Mean: 2971.80046
 S.D.: 5.06436
 RSD: 0.17041
 95% CI: 5.31472

Compound: Carbon Dioxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	2976.14307
2	2984.67700
3	2988.66309
4	2991.15161
5	2990.35596

- Reference standard 1.6 ± 0.1 ppm CO, 1.7 ± 0.1 ppm CH₄, 1.6 ± 0.1 ppm CO₂ in N₂

0810100
S t a t i s t i c R e p o r t

Sequence table: C:\HPCHEM\1\DATA\081010_0.S
 Data directory path: C:\HPCHEM\1\DATA\1009261
 Operator: Seksan
 Method file name: C:\HPCHEM\1\METHODS\ACC-ME-1\ACC-ME-2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	10/10/2008 8:34:41 AM	08101000.D	ALWA7148
2	Vial 1	2	10/10/2008 8:43:21 AM	08101001.D	ALWA7148
3	Vial 1	3	10/10/2008 8:52:02 AM	08101002.D	ALWA7148
4	Vial 1	4	10/10/2008 9:00:43 AM	08101003.D	ALWA7148
5	Vial 1	5	10/10/2008 9:09:24 AM	08101004.D	ALWA7148
6	Vial 1	6	10/10/2008 9:18:06 AM	08101005.D	ALWA7148

Compound: Carbon Monoxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	16.62586
2	15.67266
3	15.98224
4	15.61271
5	15.58857
6	25.61274
Mean:	17.51580
S.D.:	3.98591
RSD :	22.75609
95% CI:	4.18296

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	16.84346
2	16.83319
3	16.84682
4	16.91287
5	16.88065
6	16.87641
Mean:	16.86557
S.D.:	0.02990
RSD :	0.17731
95% CI:	0.03138

Compound: Carbon Dioxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	17.63055
2	16.79604
3	16.55412
4	16.45318
5	16.43300

- Reference standard 1.992+/-0.003% N₂ in Ar
- H₂ UHP

ANALYSIS PARAMETER FILE 0

WIDTH 5 SLOPE 300
 DRIFT 0 MIN.AREA 5000
 T.BBL 0 STOP.TM 12
 ATEN 4 SPEED 2
 METHOD# 61 FORMAT# 1
 SPL.WT 100 IS.WT 1

TIME PROGRAM FILE 0

0.01 PRINT LEVEL,DATE#,TIME#, "GC-02"

*** 1.992+/-0.003% N2 IN AR ***

73 1.442 08/02/16 19:05:00 GC-02

4.338

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.338	18156			100	

TOTAL	AREA	CONC	NAME
84.6	18156	100	GC-02

08/02/16 19:11:01

4.375

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.375	18249			100	

TOTAL	AREA	CONC	NAME
83.8	18249	100	GC-02

08/02/16 19:17:35

4.342

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.342	18203			100	

TOTAL	AREA	CONC	NAME
84.6	18203	100	GC-02

08/02/16 19:24:35

4.333

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	4.333	18186			100	

TOTAL	AREA	CONC	NAME
100	18186	100	GC-02

*** H2 UHP ***

100 08/02/16 20:06:57 GC-02

1.694

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.694	9312641			100	

TOTAL	AREA	CONC	NAME
101.4	9312641	100	GC-02

08/02/16 20:13:57

1.693

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.693	9283577			100	

TOTAL	AREA	CONC	NAME
	9283577	100	

- Chromatogram of output gas by best condition at 1st adsorption cycle.
- Carbon monoxide, methane , carbon dioxide

0802160
Statistic Report

Sequence table: C:\HPCHEM\080216_0.S
 Data directory path: C:\HPCHEM\1\DATA\SANGSOM
 Operator: Sangsom
 Method file name: C:\HPCHEM\1\METHODS\ACC-ME~1\ACC-ME~2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	16/2/2008 6:29:02 PM	08021600.D	BETA 1ST
2	Vial 1	2	16/2/2008 6:37:44 PM	08021601.D	BETA 1ST

Compound: Carbon Monoxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	279860.18750
2	279629.06250

Mean: 279744.62500
 S.D.: 163.43005
 RSD : 0.05842
 95% CI: 1468.36068

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	4336.78955
2	4334.28174

Mean: 4335.53564
 S.D.: 1.77329
 RSD : 0.04090
 95% CI: 15.93239

Statistic results for compound Carbon Dioxide not available.

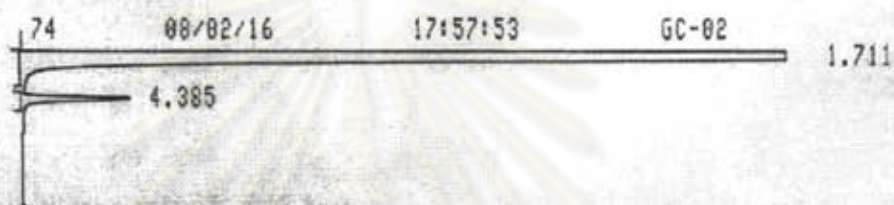
- Hydrogen and nitrogen

ANALYSIS PARAMETER FILE 0

WIDTH	5	SLOPE	300
DRIFT	0	MIN.AREA	5000
T.DBL	0	STOP.TM	12
ATTEN	4	SPEED	2
METHOD#	61	FORMAT#	1
SPL.WT	100	IS.WT	1

TIME PROGRAM FILE 0

0.01 PRINT LEVEL,DATE\$,TIME\$,"GC-02")



CHROMATOGRAM 1 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.711	9011040			99.512	
2	4.385	44193			0.488	

TOTAL	9056040	100		
102.2	00/02/16	18:10:53	GC-02	1.717



CHROMATOGRAM 2 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.717	9017927			99.511	
2	4.387	44316			0.489	

TOTAL	9062243	100
-------	---------	-----

- Chromatogram of output gas by best condition at 2nd adsorption cycle.
- Carbon monoxide, methane and carbon dioxide

Sequence table: C:\HPCHEM\1\DATA\081015_1.S
 Data directory path: C:\HPCHEM\1\DATA\SANGSOM
 Operator: Sangsom

Method file name: C:\HPCHEM\1\METHODS\ACC-ME~1\ACC-ME~2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	15/10/2008 7:51:07 AM	08101510.D	HEAT 2
2	Vial 1	2	15/10/2008 7:59:49 AM	08101511.D	HEAT 2

Compound: Carbon Monoxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	369251.12500
2	368955.12500
Mean:	369103.12500
S.D.:	209.30361
RSD :	0.05671
95% CI:	1880.51817

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	4697.45215
2	4694.64307
Mean:	4696.04761
S.D.:	1.98632
RSD :	0.04230
95% CI:	17.84638

Compound: Carbon Dioxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	2.60465
2	2.75388
Mean:	2.67927
S.D.:	0.10552
RSD :	3.93855
95% CI:	0.94810

- Hydrogen and nitrogen

ANALYSIS PARAMETER FILE 0

WIDTH	5	SLOPE	300
DRIFT	0	MIN.AREA	5000
T.DBL	0	STOP.TM	12.5
ATTEN	4	SPEED	2
METHOD\$	61	FORMAT\$	1
SPL.WT	100	IS.WT	1

TIME PROGRAM FILE 0

0.01 PRINT LEVEL,DATE\$,TIME\$,"GC-02";

*** HEAT 2 ***



CHROMATOGRAM 1 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.576	3848325			99.1708	
2	3.972	21948			0.5656	
3	10.062	10230			0.2636	

TOTAL	3880503	100
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CHROMATOGRAM 2 MEMORIZED

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.576	3847815			99.1562	
2	3.969	22292			0.5729	
3	10.041	10511			0.2709	

TOTAL	3880558	100
-------	---------	-----

- Chromatogram of output gas by best condition at 3rd adsorption cycle.
- Carbon monoxide, methane and carbon dioxide

0810230
Statistic Report

Sequence table: C:\HPCHEM\1\DATA\081023_0.S
 Data directory path: C:\HPCHEM\1\DATA\SANGSOM
 Operator: Sangsom
 Method file name: C:\HPCHEM\1\METHODS\ACC-ME-1\ACC-ME~2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	23/10/2008 12:09:21 PM	08102300.D	HEAT3
2	Vial 1	2	23/10/2008 12:18:02 PM	08102301.D	HEAT3

Compound: Carbon Monoxide (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	330418.81250
2	330107.96875
Mean:	330263.39062
S.D.:	219.79972
RSD :	0.06655
95% CI:	1974.82202

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	3998.82910
2	3994.14673
Mean:	3996.48792
S.D.:	3.31094
RSD :	0.08285
95% CI:	29.74759

Statistic results for compound Carbon Dioxide not available.

- Hydrogen and nitrogen

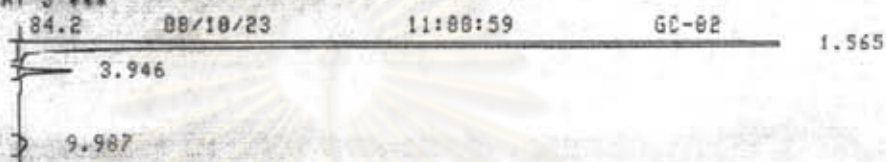
ANALYSIS PARAMETER FILE 0

WIDTH	5	SLOPE	300
DRIFT	0	MIN. AREA	5000
T.DBL	0	STOP. TH	12.5
ATTEN	4	SPEED	2
METHOD#	61	FORMAT#	1
SPL. WT	100	IS. WT	1

TIME PROGRAM FILE 0

0.01 PRINT LEVEL, DATE#, TIME#, "GC-02":

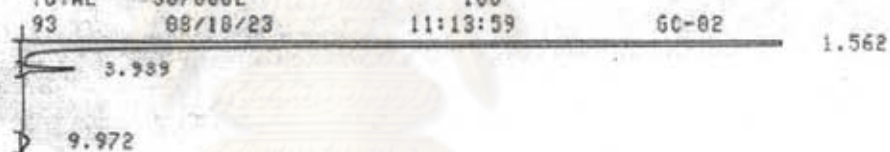
*** HEAT 3 ***



CHROMATOGRAM 1 MEMORIZED

PKNO	TIME	AREA	HK	IDNO	CONC	NAME
1	1.565	3848695			99.2939	
2	3.946	19475			0.5024	
3	9.987	7893			0.2036	

TOTAL	3876062	100
-------	---------	-----



CHROMATOGRAM 2 MEMORIZED

PKNO	TIME	AREA	HK	IDNO	CONC	NAME
1	1.562	3860871			99.2912	
2	3.939	19481			0.501	
3	9.972	8081			0.2078	

TOTAL	3888432	100
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CHROMATOGRAM 3 MEMORIZED

PKNO	TIME	AREA	HK	IDNO	CONC	NAME
1	1.565	3851357			99.3826	
2	3.94	19666			0.5071	
3	9.978	7382			0.1983	

TOTAL	3878405	100
-------	---------	-----

- Chromatogram of output gas by best condition at 4nd adsorption cycle.
- Carbon monoxide, methane and carbon dioxide

0810250
Statistic Report

Sequence table: C:\HPCHEM\1\DATA\081025_0.S
 Data directory path: C:\HPCHEM\1\DATA\SANGSOM
 Operator: Sangsom
 Method file name: C:\HPCHEM\1\METHODS\ACC-ME~1\ACC-ME~2.M

Run #	Location	Inj #	Inj. Date/Time	File Name	Sample Name
1	Vial 1	1	26/10/2008 11:23:49 AM	08102500.D	HEAT 4
2	Vial 1	2	26/10/2008 11:32:31 AM	08102501.D	HEAT 4

Compound: Carbon Monoxide (Signal: FID2 B,)

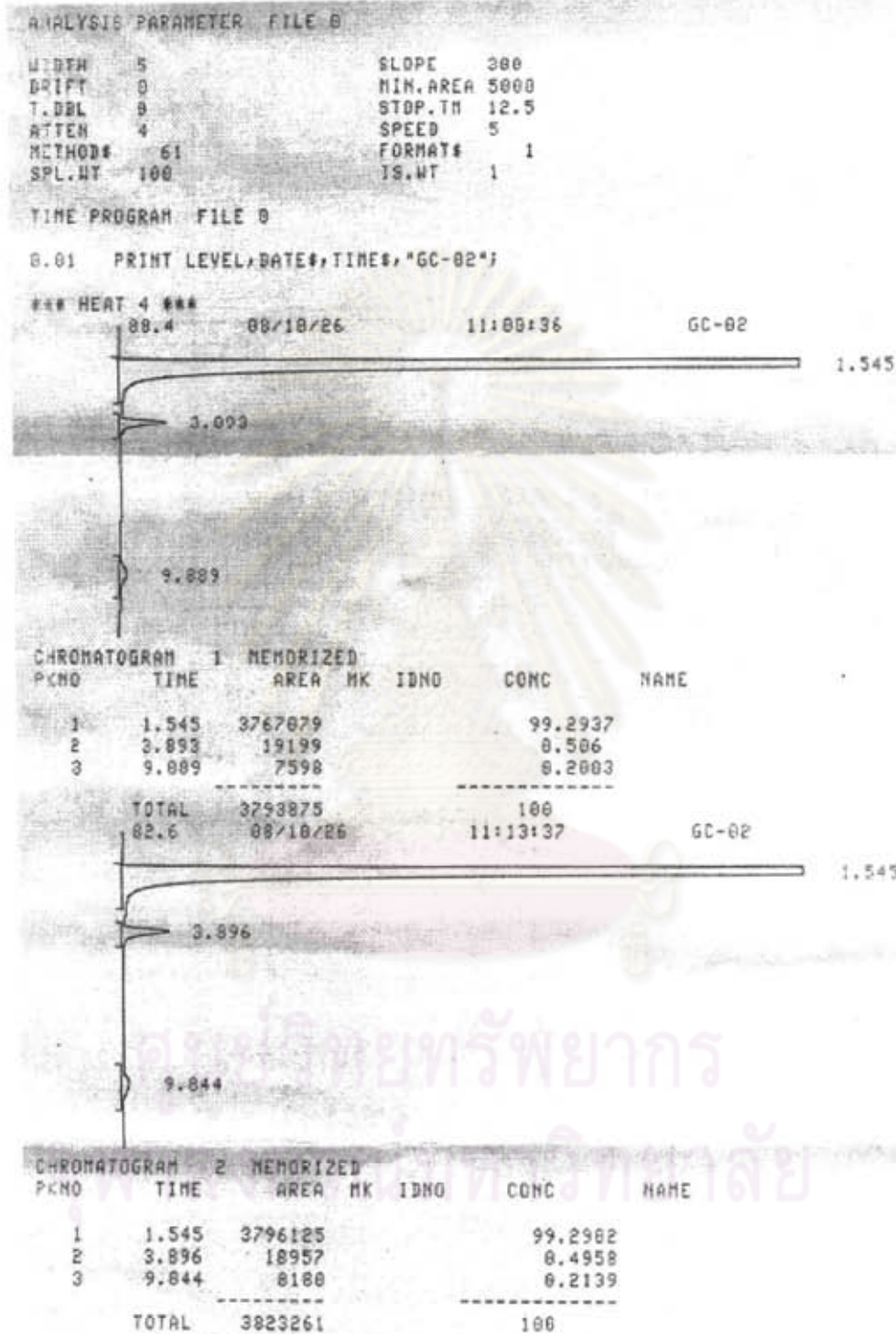
Run #	Peak area [pA*s]
1	310594.28125
2	310156.71875
Mean:	310375.50000
S.D.:	309.40341
RSD :	0.09969
95% CI:	2779.87915

Compound: Methane (Signal: FID2 B,)

Run #	Peak area [pA*s]
1	3930.42139
2	3928.19312
Mean:	3929.30725
S.D.:	1.57563
RSD :	0.04010
95% CI:	14.15644

Statistic results for compound Carbon Dioxide not available.

Hydrogen and nitrogen



APPENDIX B

1. N₂ adsorption / desorption isotherm of zeolite 13X

[Adsorption / desorption isotherm]

File Name	13X(1).DAT
Date of measurement	17/4/2009
Time of measurement	7:14:11
COMMENT1	13X(1)
COMMENT2	
COMMENT3	
COMMENT4	
Serial number	154
Version	

Sample weight	3.99E-02	[g]
Standard volume	9.043	[cm ³]
Dead volume	12.98	[cm ³ g ⁻¹]
Equilibrium time	100	[sec]
Adsorptive	N2	
Apparatus temperature	0	[C]
Adsorption temperature	77	[K]

Saturated vapor pressure	100.98	[kPa]
Adsorption cross section area	0.162	[nm ²]
File name of walladsorption		
Wall adsorption correction value 1		
Wall adsorption correction value 2		
Number of adsorption data	44	
Number of desorption data	26	

No	p_i /kPa	p_e /kPa	p_{e2} /kPa	p_0 /kPa	p/p_0	V_a /cm ³ (STP) g ⁻¹
ADS						
1	0	0.0040601	0	101.26	0.000040096	12.914
2	0	0.0040601	0	101.28	0.000040088	23.784
3	0	0.0081201	0	101.28	0.000080175	34.584
4	0	0.01218	0	101.28	0.00012026	45.351
5	0	0.0203	0	101.27	0.00020045	56.124
6	0	0.0203	0	101.25	0.00020049	66.816
7	0	0.02842	0	101.23	0.00028075	77.485
8	0	0.036541	0	101.22	0.00036101	88.044
9	0	0.1015	0	101.22	0.0010028	98.119
10	0	0.3289	0	101.19	0.0032499	107.03

11	0	0.8161	0	101.21	0.0080631	113.65
12	0	1.4007	0	101.22	0.013838	117.72
13	0	2.1112	0	101.21	0.02086	120.84
14	0	3.9829	0	101.17	0.039368	125.89
15	0	5.6922	0	101.21	0.056241	128.89
16	0	7.3162	0	101.17	0.072316	131.15
17	0	8.5627	0	101.16	0.084645	132.66
18	0	10.844	0	101.19	0.1072	135
19	0	13.39	0	101.14	0.1324	137.26
20	0	14.75	0	101.12	0.1459	138.31
21	0	16.236	0	101.15	0.1605	139.49
22	0	18.201	0	101.2	0.1799	140.87
23	0	22.428	0	101.2	0.2216	143.73
24	0	25.57	0	101.17	0.2527	145.72
25	0	30.491	0	101.18	0.3014	148.69
26	0	35.558	0	101.13	0.3516	151.51
27	0	40.629	0	101.19	0.4015	154.36
28	0	45.647	0	101.16	0.4512	157.33
29	0	50.674	0	101.22	0.5006	160.43
30	0	55.745	0	101.16	0.5511	163.74
31	0	60.747	0	101.15	0.6006	167.18
32	0	65.753	0	101.1	0.6504	170.85
33	0	71.019	0	101.12	0.7023	174.94
34	0	75.777	0	101.07	0.7497	179.05
35	0	81.055	0	101.06	0.802	184.39
36	0	85.809	0	101.01	0.8495	190.73
37	0	89.882	0	100.98	0.8901	199.17
38	0	90.925	0	101.02	0.9001	202.25
39	0	95.627	0	100.91	0.9476	226.89
40	0	96.264	0	100.97	0.9534	232.78
41	0	97.847	0	100.94	0.9694	254.96
42	0	98.887	0	100.85	0.9805	284.49
43	0	99.402	0	100.8	0.9861	310.3
44	0	99.715	0	100.78	0.9894	332.63
DES						
1	0	98.574	0	100.73	0.9786	303.99
2	0	97.912	0	100.76	0.9717	281.64
3	0	97.372	0	100.75	0.9665	269.02
4	0	96.016	0	100.73	0.9532	246.42
5	0	95.383	0	100.75	0.9467	240.11
6	0	91.636	0	100.75	0.9095	211.36

7	0	90.21	0	100.73	0.8956	205.39
8	0	86.934	0	100.71	0.8632	195.3
9	0	85.545	0	100.68	0.8497	192.31
10	0	81.108	0	100.72	0.8053	185.68
11	0	80.409	0	100.72	0.7983	184.8
12	0	75.314	0	100.67	0.7481	179.96
13	0	70.511	0	100.7	0.7002	176.4
14	0	65.448	0	100.68	0.6501	173
15	0	60.288	0	100.66	0.5989	170.25
16	0	55.184	0	100.68	0.5481	167.88
17	0	50.162	0	100.7	0.4981	165.56
18	0	45.688	0	100.69	0.4537	159.47
19	0	45.237	0	100.7	0.4492	158.59
20	0	40.097	0	100.73	0.3981	153.55
21	0	35.172	0	100.76	0.3491	150.67
22	0	30.113	0	100.76	0.2989	147.81
23	0	25.067	0	100.75	0.2488	144.93
24	0	20.04	0	100.75	0.1989	141.82
25	0	15.022	0	100.76	0.1491	138.41
26	0	10.045	0	100.76	0.099692	134.2

[BET plot]

File Name	Zip_bag(1).DAT
Date of measurement	17/4/2009
Time of measurement	7:14:11
COMMENT1	13X(1)
COMMENT2	
COMMENT3	
COMMENT4	
Serial number	154
Version	

Sample weight	3.99E-02 [g]
Standard volume	9.043 [cm ³]
Dead volume	12.98 [cm ³ g ⁻¹]
Equilibrium time	100 [sec]
Adsorptive	N2

Saturated vapor pressure	100.98 [kPa]
Adsorption cross section area	0.162 [nm ²]
File name of walladsorption	
Wall adsorption correction value 1	
Wall adsorption correction value 2	

Apparatus temperature	0 [C]
Adsorption temperature	77 [K]

Number of adsorption data	44
Number of desorption data	26

Starting point	4	
End point	17	
Slope	0.0081965	
Intercept	2.7811E-06	
Correlation coefficient	1	
V _m	121.96	[cm ³ (STP) g ⁻¹]
a _{s,BET}	530.84	[m ² g ⁻¹]
C	2948.2	
Total pore volume (p/p ₀ =0.989)	0.5142	[cm ³ g ⁻¹]
Average pore diameter	3.8746	[nm]

No	p/p ₀	p/V _a (p ₀ -p)
1	0.000040096	0.000003105
2	0.000040088	1.6856E-06
3	0.000080175	2.3184E-06
4	0.00012026	2.6521E-06
5	0.00020045	3.5723E-06
6	0.00020049	3.0013E-06
7	0.00028075	3.6243E-06
8	0.00036101	4.1018E-06
9	0.0010028	0.00001023
10	0.0032499	0.000030464
11	0.0080631	0.000071524
12	0.013838	0.0001192
13	0.02086	0.0001763
14	0.039368	0.00032554
15	0.056241	0.00046236
16	0.072316	0.00059438
17	0.084645	0.00069706
18	0.1072	0.00088909
19	0.1324	0.0011117
20	0.1459	0.0012347
21	0.1605	0.0013707

22	0.1799	0.0015567
23	0.2216	0.0019809
24	0.2527	0.0023211
25	0.3014	0.0029009
26	0.3516	0.0035791
27	0.4015	0.0043462
28	0.4512	0.0052264

2. N₂ adsorption / desorption isotherm of beta zeolite

[Adsorption / desorption isotherm]

File Name	Beta zeolite(1).DAT
Date of measurement	17/4/2009
Time of measurement	4:50:34
COMMENT1	Beta zeolite(1)
COMMENT2	
COMMENT3	
COMMENT4	
Serial number	154
Version	

Sample weight	3.58E-02 [g]	Saturated vapor pressure	101.08 [kPa]
Standard volume	9.043 [cm ³]	Adsorption cross section area	0.162 [nm ²]
Dead volume	12.005 [cm ³ g ⁻¹]	File name of walladsorption	
Equilibrium time	100 [sec]	Wall adsorption correction value 1	
Adsorptive	N2	Wall adsorption correction value 2	
Apparatus temperature	0 [C]	Number of adsorption data	42
Adsorption temperature	77 [K]	Number of desorption data	20

No	p_i /kPa	p_e /kPa	p_{e2} /kPa	p_0 /kPa	p/p_0	$V_a/cm^3(STP)$ g ⁻¹
ADS						
1	0	0.01626	0	101.27	0.00016056	13.505
2	0	0.01626	0	101.27	0.00016056	24.909
3	0	0.01626	0	101.25	0.00016059	36.384
4	0	0.02439	0	101.29	0.00024079	47.754

5	0	0.01626	0	101.27	0.00016056	59.2
6	0	0.020325	0	101.25	0.00020074	70.592
7	0	0.012195	0	101.23	0.00012047	82.022
8	0	0.01626	0	101.25	0.00016059	93.398
9	0	0.020325	0	101.21	0.00020082	104.75
10	0	0.028455	0	101.21	0.00028115	116.17
11	0	0.020325	0	101.21	0.00020082	127.48
12	0	0.028455	0	101.21	0.00028115	138.68
13	0	0.126	0	101.19	0.0012454	149.2
14	0	0.7154	0	101.2	0.0070697	156.65
15	0	2.1626	0	101.19	0.021372	160.24
16	0	3.9797	0	101.21	0.039321	162.04
17	0	5.6667	0	101.19	0.056001	163.06
18	0	7.252	0	101.12	0.071717	163.77
19	0	8.7927	0	101.2	0.086884	164.33
20	0	10.829	0	101.16	0.107	164.9
21	0	13.35	0	101.2	0.1319	165.55
22	0	14.923	0	101.12	0.1476	165.92
23	0	16.439	0	101.19	0.1625	166.24
24	0	18.459	0	101.19	0.1824	166.63
25	0	22.439	0	101.19	0.2218	167.31
26	0	25.52	0	101.2	0.2522	167.85
27	0	30.5	0	101.13	0.3016	168.64
28	0	35.541	0	101.17	0.3513	169.4
29	0	40.589	0	101.19	0.4011	170.18
30	0	45.667	0	101.19	0.4513	170.95
31	0	50.715	0	101.17	0.5013	171.73
32	0	55.744	0	101.19	0.5509	172.59
33	0	60.784	0	101.15	0.6009	173.52
34	0	65.788	0	101.16	0.6503	174.58
35	0	70.805	0	101.21	0.6996	175.82
36	0	76.215	0	101.15	0.7535	177.62
37	0	81.207	0	101.2	0.8024	179.75
38	0	86.097	0	101.18	0.8509	183.03
39	0	91.199	0	101.19	0.9013	188.81
40	0	96.374	0	101.03	0.9539	203.33
41	0	98.414	0	101.09	0.9735	215.96
42	0	100.12	0	101.02	0.9911	239.83
DES						
1	0	97.549	0	101	0.9658	219.37
2	0	95.248	0	100.96	0.9434	208.26

3	0	90.443	0	100.93	0.8961	194.19
4	0	86.207	0	100.96	0.8539	188.27
5	0	85.634	0	100.96	0.8482	187.65
6	0	80.756	0	100.96	0.7999	184.2
7	0	75.54	0	100.9	0.7487	181.61
8	0	70.37	0	100.85	0.6978	179.8
9	0	65.614	0	100.83	0.6507	178.5
10	0	60.528	0	100.81	0.6004	177.3
11	0	55.435	0	100.83	0.5498	176.29
12	0	50.394	0	100.79	0.5	174.19
13	0	45.211	0	100.81	0.4485	171.58
14	0	40.301	0	100.8	0.3998	170.58
15	0	35.215	0	100.8	0.3494	169.69
16	0	30.146	0	100.79	0.2991	168.94
17	0	25.102	0	100.78	0.2491	168.18
18	0	20.073	0	100.75	0.1992	167.37
19	0	15.053	0	100.75	0.1494	166.42
20	0	10.077	0	100.69	0.1001	165.21

[BET plot]

File Name	Plastic Bottle(1).DAT
Date of measurement	17/4/2009
Time of measurement	4:50:34
COMMENT1	Plastic Bottle(1)
COMMENT2	
COMMENT3	
COMMENT4	
Serial number	154
Version	

Sample weight	3.58E-02 [g]
Standard volume	9.043 [cm ³]
Dead volume	12.005 [cm ³ g ⁻¹]
Equilibrium time	100 [sec]
Adsorptive	N ₂
Apparatus temperature	0 [C]

Saturated vapor pressure	101.08 [kPa]
Adsorption cross section area	0.162 [nm ²]
File name of walladsorption	
Wall adsorption correction value 1	
Wall adsorption correction value 2	
Number of adsorption data	42

Adsorption temperature	77 [K]
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Number of desorption data	20
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Starting point	5	
End point	16	
Slope	0.0063913	
Intercept	6.7173E-07	
Correlation coefficient	1	
V _m	156.45	[cm ³ (STP) g ⁻¹]
a _{s,BET}	680.93	[m ² g ⁻¹]
C	9515.7	
Total pore volume (p/p ₀ =0.990)	0.3684	[cm ³ g ⁻¹]
Average pore diameter	2.1644	[nm]

No	p/p ₀	p/V _a (p ₀ -p)
1	0.00016056	0.000011891
2	0.00016056	6.4469E-06
3	0.00016059	4.4145E-06
4	0.00024079	5.0436E-06
5	0.00016056	2.7126E-06
6	0.00020074	2.8442E-06
7	0.00012047	1.4689E-06
8	0.00016059	1.7197E-06
9	0.00020082	1.9175E-06
10	0.00028115	2.4208E-06
11	0.00020082	1.5756E-06
12	0.00028115	2.0279E-06
13	0.0012454	8.3575E-06
14	0.0070697	0.000045452
15	0.021372	0.00013629
16	0.039321	0.0002526
17	0.056001	0.00036381
18	0.071717	0.00047174
19	0.086884	0.00057903
20	0.107	0.00072699
21	0.1319	0.00091793
22	0.1476	0.0010434

23	0.1625	0.0011668
24	0.1824	0.001339
25	0.2218	0.001703
26	0.2522	0.002009
27	0.3016	0.0025606
28	0.3513	0.0031968
29	0.4011	0.0039357
30	0.4513	0.0048113



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

VITA

Miss Sangsom Chongsotichat was born on January 7, 1979 in Bangkok, Thailand. She graduate at Suksanaree School in 1997. She received the Bachelor Degree of Science in chemistry, Srinakarinwirot University in 2001. She continued her Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2005 and completed the program in 2009.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย