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% CO_2, 10% CH_4, 10% N_2 and 60% H_2. 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% N_2 in He
b) 49.70+/-0.05% H_2 in N_2
c) 10.03+/-0.06% CO in N_2
d) 10.10+/-0.01% CH_4 in Ar
e) 9.955+/-0.01% CO_2 in N_2

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 (SiO_2) and alumina (Al_2O_3) 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	$0.4K2O{\cdot}0.6Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$	
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	$Al_2O_3 \cdot 2.0SiO_2 \cdot 4.5H_2O$	
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	$0.7CaO{\cdot}0.30Na_2O{\cdot}Al_2O_3{\cdot}2.0SiO_2{\cdot}4.5H_2O$	
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	$Na_2O{\cdot}Al_2O_3{\cdot}2.45SiO_2{\cdot}6.0H_2O$	
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)Na_2O.(0.5-10)Al_2O_3.(1.3-10)P_2O_5.(0.7-15)MxOy.(70-97)SiO_2
Structure Type	N	BEA
Major Cation	N	Na^+
Pore Size	A	7.6 x 6.4 / 5.5 x 5.5
SiO2/Al2O3, mol ratio		20±5
Crystal size, SEM	μm	< 0.5

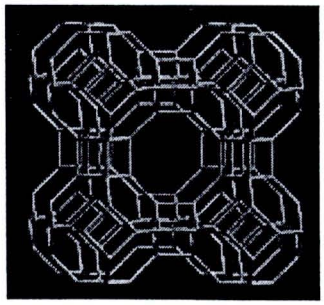

Figure 3.1 Zeolite A molecular structure

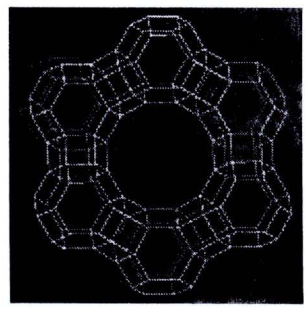

Figure 3.2 Zeolite X molecular structure

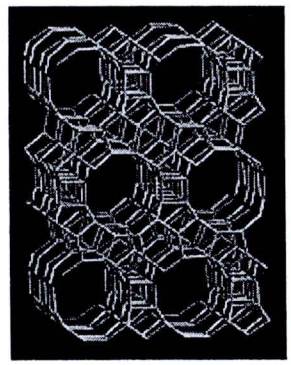

Figure 3.3 Zeolite beta molecular structure

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).

N_2 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.

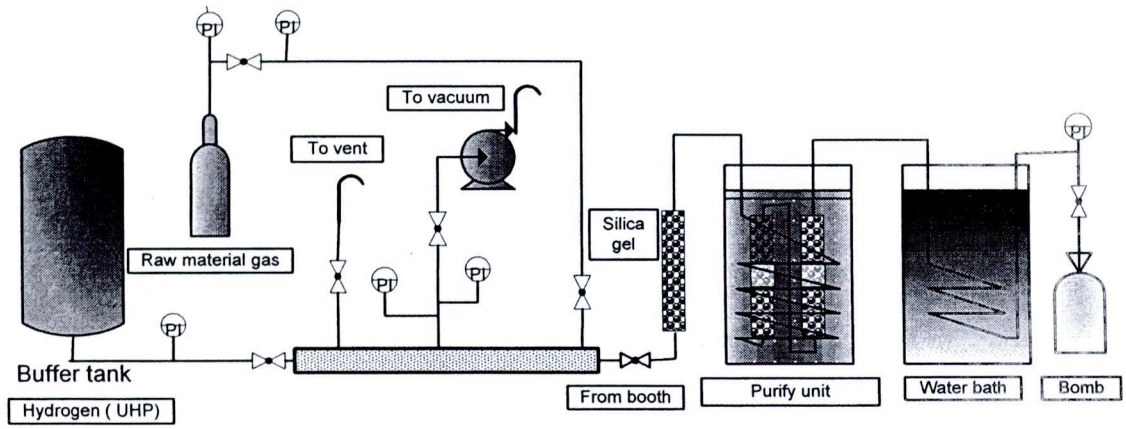

Figure 3.4 Diagram of experiment process

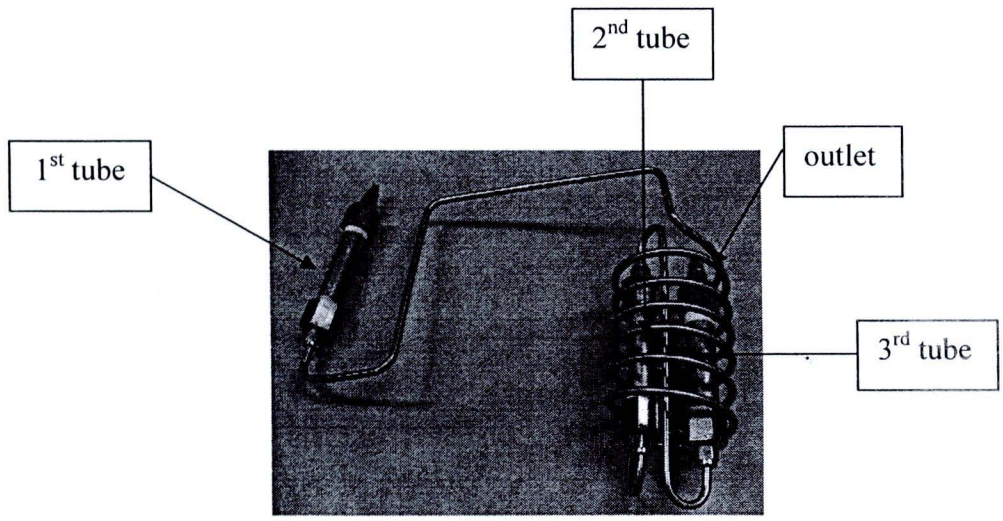

Figure 3.5 Tube apparatus

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 cm^3. 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)

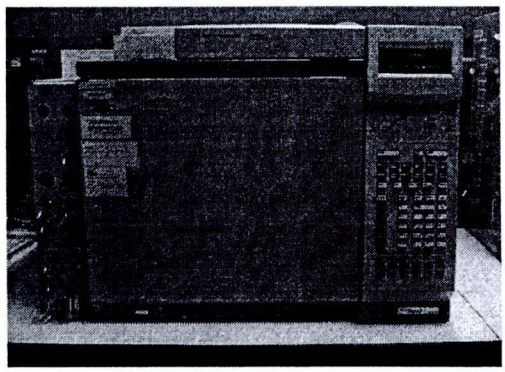

Figure 3.6 Gas Chromatography (Agilent 6890 N)

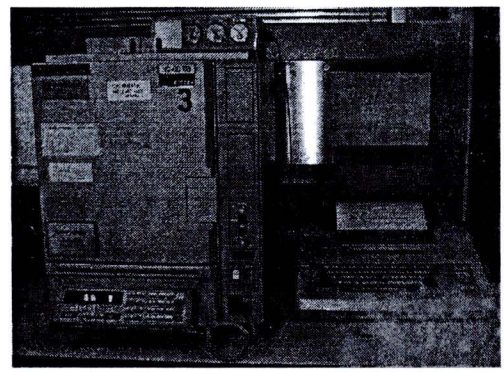

Figure 3.7 Gas Chromatograph (Shimatsu model GC 14B)

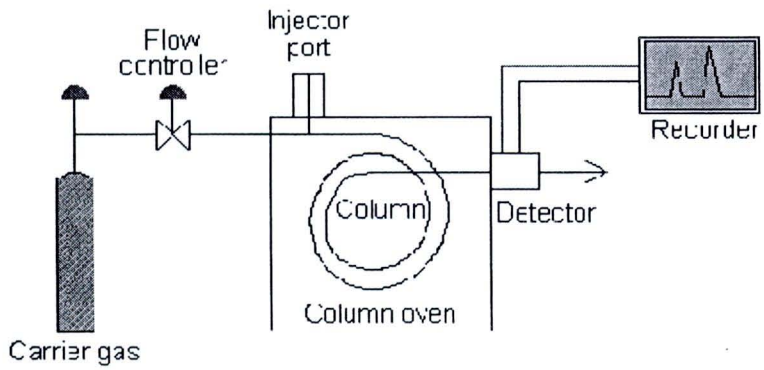

Figure 3.8 Schematic diagram of a gas chromatograph

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 use 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 H_2 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. H_2 UHP (99.9995%)
2. 1.992+/-0.003% N_2 in Ar
3. 1.04+/-0.002% CO in N2
4. 1.6+/-0.1ppm CO_2 in N_2
5. 200+/1ppm CH_4 in N_2

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 H_2 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