

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipments

#### 3.1.1 Materials

1. Hollow silica powder (99% purity from Nanoshel, India)
2. Activated carbon (Carbokarn Co., Ltd., Thailand)
3. Ultra high purity methane ( $\text{CH}_4$ , 99.999% purity from Labgaz Co., Ltd., Thailand)
4. Deionized water

#### 3.1.2 Equipments

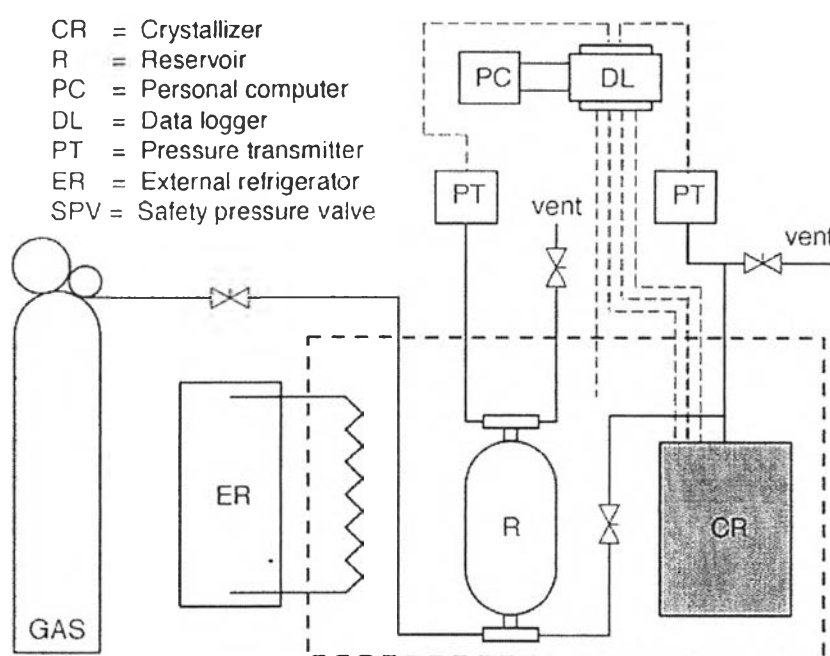
- a. Hydrate formation/dissociation apparatus
  1. Crystallizer (CR)
  2. Reservoir (R)
  3. Personal Computer (PC)
  4. Controllable water bath
  5. Pressure transducer (PT)
  6. K-type thermocouple
- b. Surface area analyzer (Autosorb-1MP, Quantachrome)
- c. Particle size analyzer (Mastersizer X, Malvern)
- d. Scanning electron microscope (TM 3000, Hitachi)
- e. Transmission electron microscope (JEM-2100, JEOL)

### 3.2 Experimental Procedures

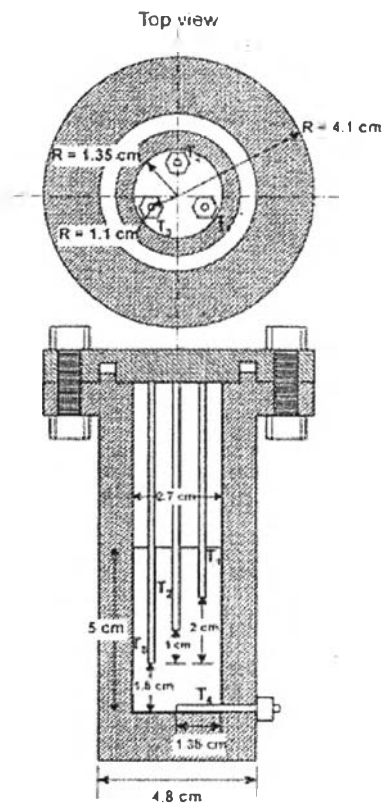
#### 3.2.1 Experimental Apparatus

The schematic diagram of the experimental apparatus is shown in Figure 3.1. The apparatus consisted of a high pressure crystallizer (CR) made by stainless steel cylindrical vessel with an internal volume of  $57.28 \text{ cm}^3$ . There was a reservoir (R) connected to the crystallizer for supplying and collecting gas. The

crystallizer and reservoir were immersed in a cooling bath. Two pressure transducers were used to detect the pressure in the system with the range of 0 - 21 MPa with 0.13% global error. Figure 3.2 shows the cross-section of the crystallizer. There were four K-type thermocouples placed in different location inside the crystallizer. Thermocouple number 1, 2 and 3 (T1, T2 and T3) were placed at the top, middle and bottom of the bed respectively. Moreover, thermocouple number 4 (T4) was placed at the bottom of the crystallizer. A Wisco data logger was connected to a computer to record the data.



**Figure 3.1** Schematic diagram of experimental apparatus.



**Figure 3.2** Cross-section of a crystallizer.

### 3.2.2 Methane Hydrate Formation

The porous medium and deionized water were placed in the crystallizer. The amount of water added into the porous medium was calculated based on the porosity of the porous medium. A rotary vacuum pump was used to evacuate the air in the crystallizer. The crystallizer was then pressurized to 0.5 MPa by the methane gas twice to ensure no more air bubble remain in the system. Methane gas was introduced into the crystallizer at the desired experimental condition (6 and 8 MPa at 4°C). The data was recorded every 10 seconds. Pressure dropped in the crystallizer marked as the gas consumption during the methane formation. The experiment was stopped when no significantly change in the pressure. The experiments were operated in the batch mode. The methane consumption at time  $t$  was calculated by Equation 3.1 (Babu *et al.*, 2013b).

$$\Delta n_{H,d} = n_{H,t} - n_{H,0} = \left( \frac{PV}{zRT} \right)_{G,0} - \left( \frac{PV}{zRT} \right)_{G,t} \quad (3.1)$$

where  $\Delta n_{H,d}$  = moles of consumed gas for hydrate formation, mol

$n_{H,t}$  = moles of hydrate at time  $t$ , mol

$n_{H,0}$  = moles of hydrate at time 0, mol

$P$  = pressure of the crystallizer, atm

$T$  = temperature of the crystallizer, K

$V$  = the volume of gas phase in the crystallizer,  $\text{cm}^3$

$z$  = compressibility factor

$R$  =  $82.06 \text{ cm}^3 \text{ atm/mol K}$

subscripts of G,0 and G,t represent the gas phase at time zero and time t respectively.

The conversion of water to hydrate is calculated by Equation 3.2 (Babu *et al.*, 2013b).

$$\text{Conversion of water hydrates (\%)} = \frac{\Delta n_{H,d} \times \text{hydration number}}{n_{H_2O}} \times 100 \quad (3.2)$$

where  $n_{H_2O}$  = moles of water in the system, mol

$\Delta n_{H,d}$  = moles of consumed gas for hydrate formation, mol

hydration number is the number of water molecules per gas molecules. Hydration number of activated carbon and hollow silica is 6.1 and 5.94 respectively (Chari *et al.*, 2014; Linga *et al.*, 2012; Prasad *et al.*, 2014).

### 3.2.3 Methane Hydrate Dissociation

After the completion of methane hydrate formation experiment, the methane hydrate was dissociated by thermal stimulation. The pressure in crystallizer was decreased from 8 MPa and 6 MPa to 6.5 MPa and 5 MPa, respectively. At this pressure the methane hydrate was still stable at the equilibrium temperature. The temperature was increased to the desired dissociation temperature ( $25^\circ\text{C}$ ). This point marked as time zero for the hydrate dissociation experiments. When the temperature in the crystallizer crossed the hydrate phase equilibrium, the methane hydrate dissociated. Thus, dissociation temperature represents the hydrate phase equilibrium. The gas released from the crystallizer was measured by the pressure transducer. The

experiments were stopped when the pressure was constant at any given experimental temperature. At any given time, the total moles of gas in the system equal to the moles of gas at time zero. The moles of methane released from the hydrate at any time during the hydrate dissociation were calculated by Equation 3.3 (Babu *et al.*, 2013b).

$$\Delta n_{H,\uparrow} = n_{H,0} - n_{H,t} = \left(\frac{PV}{zRT}\right)_{G,t} - \left(\frac{PV}{zRT}\right)_{G,0} \quad (3.3)$$

where  $\Delta n_{H,\uparrow}$  = moles of released gas from the hydrate

$n_{H,t}$  = moles of hydrate at time  $t$ , mol

$n_{H,0}$  = moles of hydrate at time 0, mol

$P$  = pressure of the crystallizer, atm

$T$  = temperature of the crystallizer, K

$V$  = the volume of gas phase in the crystallizer,  $\text{cm}^3$

$z$  = compressibility factor

$R$  =  $82.06 \text{ cm}^3 \text{ atm/mol K}$

subscripts of  $G,0$  and  $G,t$  represent the gas phase at time zero and time  $t$  respectively.

The percentage of methane recovery is calculated by Equation 3.4 (Babu *et al.*, 2013b).

$$\% \text{methane recovery} = \frac{(\Delta n_{H,\uparrow})_t}{(\Delta n_{H,\downarrow})_{t_{\text{end}}}} \times 100 \quad (3.4)$$

where  $(\Delta n_{H,\uparrow})_t$  = moles of released gas from hydrate during the hydrate dissociation at any given time.

$(\Delta n_{H,\downarrow})_{t_{\text{end}}}$  = moles of gas consumption for hydrate formation at the end of experiments.

### 3.2.4 Characterization

#### a. Surface Area Analyzer (SAA)

Surface area and pore volumes of porous medium were measured by using BET method on a surface area analyzer (Autosorb I-MP, Quantachrom). Porous medium was first outgassed to remove the humidity on the surface under vacuum at  $120^\circ\text{C}$  for 6 hours prior to the analysis. Then,  $\text{N}_2$  was purged to adsorb on the surface. The quantity of gas adsorbed was measured by static volumetric method. The volume-

pressure data was used to calculate the BET (Brunauer Emmett-Teller) surface area and pore volumes.

b. Particle Size Analyzer (PSA)

Particle size analyzer (Mastersizer X, Malvern) was used to determine size of particles and size distribution of porous medium. Mastersizer X uses Laser diffraction technique by emitting laser to particles when it reaches to particles, the laser will reflect in different angles that indicated different size of particles.

c. Scanning Electron Microscope (FE-SEM)

The sample was heated at 120°C for 6 hours to remove humidity then placed on the stub and coated with Pt prior to the analysis. The porous medium was analyzed by Scanning electron microscope (SEM, Hitachi TM3000). The SEM emits the primary electrons to the sample and detects the secondary electrons, which reflect from sample for identify the microstructure and capture the micrograph of porous medium morphology in the range of 40 to 40,000 magnifications operate at 15 kV, high vacuum condition. It is also analyze content of each substance in samples.

d. Transmission electron microscope (TEM)

The hollow silica powders were dispersed in solvent and were drop on copper grid and dried. Then, the hollow silica was observed by Transmission electron microscope (TEM, JEM-2100). The different density of sample was presented in different intensity of color.