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## APPENDICES

### Appendix A Calculation for the Methane Consumption

From;

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

where,  $\Delta n_{H,\downarrow}$  = 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

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

#### Properties of methane

Critical Temperature ( $T_c$ ) = 190.45 K

Critical Pressure ( $P_c$ ) = 4596 kPa

Acentric Factor ( $\omega$ ) = 0.00115

#### Properties of adsorbent

Density of activated carbon =  $0.4426 \text{ g/cm}^3$

Density of hollow silica =  $0.0657 \text{ g/cm}^3$

**Step 1:** To find pressure reduced ( $P_r$ ) and temperature reduced ( $T_r$ )

Data: Experimental number 1

At time 0, Pressure (P) = 8000 kpa = 78.95 atm

Temperature (K) = 277 K

At time  $t$ , Pressure (P) = 7121 kpa = 70.28 atm

Temperature (K) = 277 K

Solution;

$$T_r = \frac{T}{T_c} = \frac{277 \text{ K}}{190.45 \text{ K}} = 1.45$$

$$\text{At time } 0, \quad P_r = \frac{P}{P_c} = \frac{8000 \text{ kpa}}{4596 \text{ kpa}} = 1.74$$

$$\text{At time } t, \quad P_r = \frac{P}{P_c} = \frac{7121 \text{ kpa}}{4596 \text{ kpa}} = 1.55$$

**Step 2:** To find volume of adsorbent ( $V_{\text{ads}}$ ) and volume of gas phase ( $V_{\text{cr}}$ )

Data:

Volume of reactor with reservoir ( $V_{\text{reactor}}$ ) = 158.63 cm<sup>3</sup>

Use activated carbon 10.0053 g

Weight of adsorbent ( $W_{\text{ads}}$ ) = 10.0053 g

$$V_{\text{ads}} = \frac{\text{Weight}_{\text{ads}}}{\text{Density}_{\text{ads}}} = \frac{10.0053}{0.4426} = 22.6057 \text{ cm}^3$$

Volume of gas phase =  $V_{\text{reactor}} - V_{\text{ads}} = 158.63 - 22.61 = 135.75 \text{ cm}^3$

**Step 3:** To find compressibility factor ( $z$ )

$$\beta^0 = \frac{0.083-0.422}{T_r^{1.6}} = \frac{0.083-0.422}{1.45^{1.6}} = -0.19$$

$$\beta^1 = \frac{0.139-0.172}{T_r^{4.2}} = \frac{0.139-0.172}{1.45^{4.2}} = -6.9 \times 10^{-3}$$

$$\text{Time } 0; Z = 1 + \beta^0 \frac{P_r}{T_r} + \omega \beta^1 \frac{P_r}{T_r} = 1 + (-0.19) \left( \frac{1.74}{1.45} \right) + (0.00115) (-6.9 \times 10^{-3}) \left( \frac{1.74}{1.45} \right) = 0.77$$

$$\text{Time } t; Z = 1 + \beta^0 \frac{P_r}{T_r} + \omega \beta^1 \frac{P_r}{T_r} = 1 + (-0.19) \left( \frac{1.55}{1.45} \right) + (0.00115) (-6.9 \times 10^{-3}) \left( \frac{1.55}{1.45} \right) = 0.80$$

**Step 4:** To find the methane consumption

$$\begin{aligned} \Delta n_{\text{H}_2} &= n_{\text{H}_2,t} - n_{\text{H}_2,0} = \left( \frac{PV}{zRT} \right)_{G,0} - \left( \frac{PV}{zRT} \right)_{G,t} \\ &= \left( \frac{78.95 \text{ atm} \times 135.75 \text{ cm}^3}{0.77 \times 82.06 \text{ cm}^3 \text{ atm/mol K} \times 277 \text{ K}} \right)_{G,0} - \left( \frac{70.28 \text{ atm} \times 135.75 \text{ cm}^3}{0.80 \times 82.06 \text{ cm}^3 \text{ atm/mol K} \times 277 \text{ K}} \right)_{G,t} \end{aligned}$$

$$= 0.6123 - 0.5264 = 0.0859$$

So, the methane consumption = 0.0859 mol

The calculation for the methane released has similar step with the methane consumption, but the equation is calculated by

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

where  $\Delta n_{H,t}$  = 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

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



**Appendix B Calculation for the Conversion of Water to Hydrate**

From;

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

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

$\Delta n_{H_2O}$  = moles of consumed gas for hydrate formation, mol

Data:

Hydration number of activated carbon = 6.1

$n_{H_2O}$  = Weight water/ Molecular weight water = 10 g /18 M.W. = 0.56 mol

$\Delta n_{H_2O}$  = 0.0859 mol

Thus, conversion of water hydrates (%) =  $\frac{0.0859 \times 6.1}{0.56} \times 100 = 93.57\%$

### Appendix C Calculation for the Percentage of Methane Recovery

From;

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

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.

Data:  $(\Delta n_{H,\uparrow})_t = 0.0588 \text{ mol}$

$(\Delta n_{H,\downarrow})_{t_{\text{end}}} = 0.0859 \text{ mol}$

Thus,  $\% \text{methane recovery} = \frac{0.0588}{0.0859} \times 100 = 68.45\%$

## Appendix D Methane Uptake Capacity

**Case 1:** Convert to mol of gas/ g of dry adsorbent + water

Data: Experimental number 8

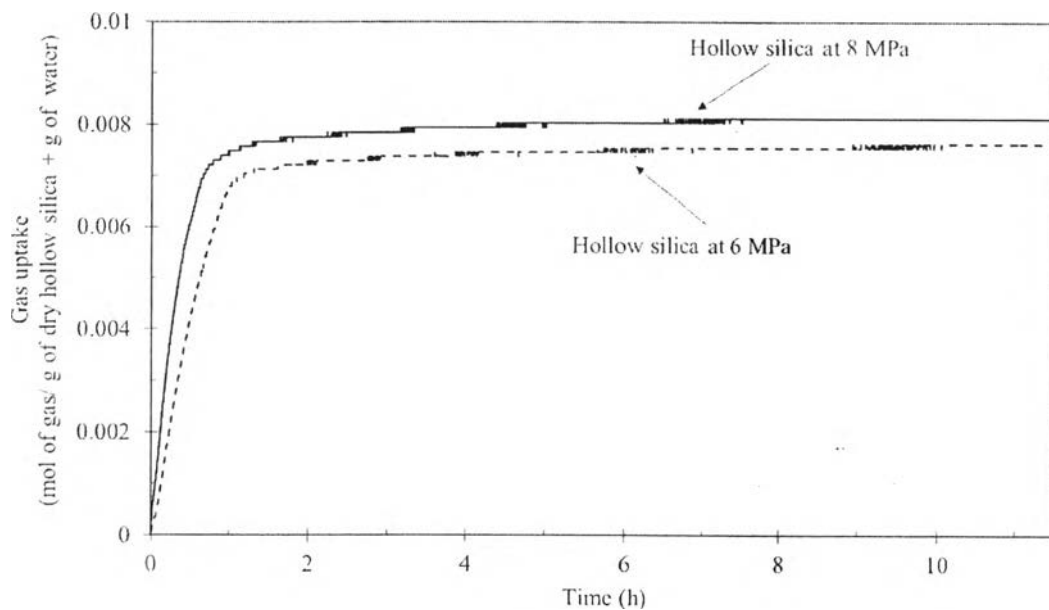
Calculate along Appendix A;  $\Delta n_{H_2O} = 0.0934$  mol

Weight of hollow silica (HS) = 1.5032 g

Weight of water = 10 g

Hence,

$$\text{mol of gas/ g of dry HS + water} = \frac{0.0934}{1.5032+10} = 0.008119 \frac{\text{mol of gas}}{\text{g of dry HS + g water}}$$



**Figure D1** Comparison of gas uptake during the methane hydrate formation in the systems of HS/H<sub>2</sub>O/CH<sub>4</sub> at 8 MPa and 6 MPa. Time zero in the figure corresponds to the first point of hydrate growth.

**Case 2:** Convert to mol of gas/ g of dry adsorbent

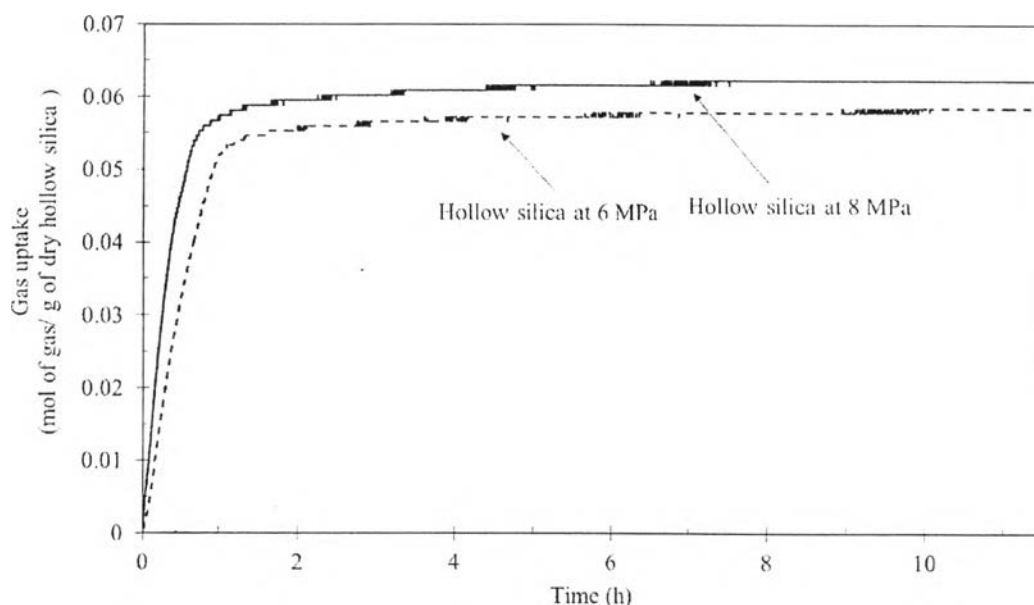
Data: Experimental number 8

Calculate along Appendix A;  $\Delta n_{H_2O} = 0.0934$  mol

Weight of hollow silica (HS) = 1.5032 g

Hence,

$$\text{mol of gas/ g of dry HS + water} = \frac{0.0934}{1.5032} = 0.0621 \frac{\text{mol of gas}}{\text{g of dry HS}}$$



**Figure D2** Comparison of gas uptake during the methane hydrate formation in the systems of HS/H<sub>2</sub>O/CH<sub>4</sub> at 8 MPa and 6 MPa. Time zero in the figure corresponds to the first point of hydrate growth.

**Case 3:** Convert to mol of gas/ volume of dry adsorbent

Data: Experimental number 8

Calculate along Appendix A;  $\Delta n_{H_2O} = 0.0934$  mol

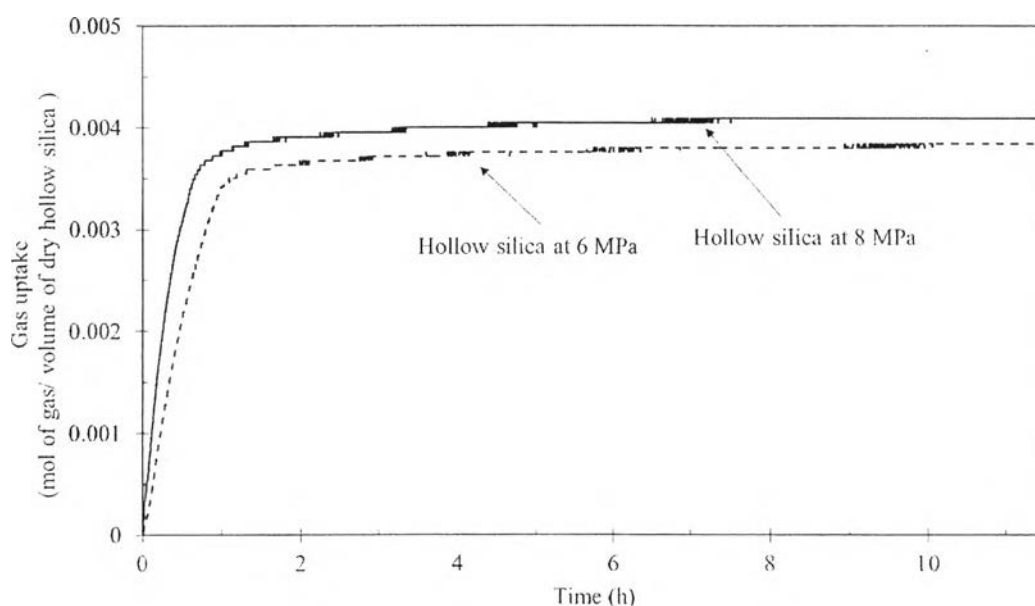
Weight of hollow silica (HS) = 1.5032 g

Density of hollow silica = 0.0657 g/cm<sup>3</sup>

$$\text{Volume of hollow silica} = \frac{1.5032 \text{ g}}{0.0657 \text{ g/cm}^3} = 22.8798 \text{ cm}^3$$

Hence,

$$\text{mol of gas/ volume of dry HS} = \frac{0.0934}{22.8798} = 0.004082 \frac{\text{mol of gas}}{\text{volume of dry HS}}$$



**Figure D3** Comparison of gas uptake during the methane hydrate formation in the systems of HS/H<sub>2</sub>O/CH<sub>4</sub> at 8 MPa and 6 MPa. Time zero in the figure corresponds to the first point of hydrate growth.

**Case 4:** Convert to volume of gas/ volume of dry adsorbent

Data: Experimental number 8

Final pressure = 6876.1 kPa = 67.86 atm

Temperature = 277 K

Volume of hollow silica = 22.8798 cm<sup>3</sup>

Calculate along Appendix A; Compressibility factor (z) = 0.8542

$$\Delta n_{H,1} = 0.0934 \text{ mol}$$

$$\begin{aligned} \text{Volume of methane gas} &= \frac{nzRT}{P} \\ &= \frac{0.0934 \text{ mol} \times 0.8542 \times 82.06 \text{ cm}^3 \frac{\text{atm}}{\text{mol}} \text{K} \times 277 \text{K}}{67.86 \text{ atm}} \\ &= 26.7241 \text{ cm}^3 \end{aligned}$$

$$\text{Thus, volume of gas/ volume of dry HS} = \frac{26.7241}{22.8798} = 1.1680 \frac{\text{volume of gas}}{\text{volume of dry HS}}$$

## CURRICULUM VITAE

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1. Suesuan, R.; Rangsunvigit, P.; and Kulprathipanja, S. (2015, April 21) Comparative Study on the Effects of Hollow Silica and Activated Carbon on Methane Hydrate Formation and Dissociation. Paper presented at The 6<sup>th</sup> Research Symposium on Petroleum, Petrochemicals and Advanced Materials and The 21<sup>st</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers. Bangkok, Thailand.
2. Suesuan, R.; Rangsunvigit, P.; and Kulprathipanja, S. (2015, May 20 - 23) Effect of Hollow Silica/Activated Carbon on CH<sub>4</sub> Hydrate Formation. Paper presented at EST - the International Conference and Exhibition on Energy, Science & Technology. Karlsruhe, Germany. (Poster presentation)