

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Activated carbons were used as a porous media to increase the methane hydrate formation rates. Initially, the chemical treatment method, using sulfuric acid (H_2SO_4) and potassium hydroxide (KOH), was employed for treatment and modify the surface of activated carbons. All treated activated carbons and untreated one were used to conduct the methane hydrate formation in the quiescent condition. The results indicated that the chemical treatment method did not significantly improve the surface area and pore volume of activated carbons. However, the impurities or carbon dust on the surface of activated carbon could be removed after the treatment. It can be noted that the methane hydrate formation kinetics was improved at 6 and 8 MPa and 4 °C by adding the untreated- and treated-activated carbons in the system compared the pure water, where the methane hydrate formation was not observed for 48 h. Moreover, the treated activated carbon enhanced the methane hydrate formation rates at both experimental pressure of 6 and 8 MPa unlike the untreated one, which was affected only at 8 MPa. This is because the impurities or dust covering on the activated carbons surface were removed after the chemical treatment. The results indicated that the methane hydrate was formed in the interstitial space between activated carbon particles, where the impurities and dust were removed. The highest water conversion to hydrates was achieved at 64.9 % in the system with H_2SO_4 treated activated carbon.

To further clarify the methane hydrate formation region, coconut shell activated carbons with different particle sizes, 250-420 μm , 420-841 μm , and 841-1680 μm , were used in order to investigate their effects on methane hydrate formation and dissociation kinetics. The methane hydrate formation experiments were conducted at 6 and 8 MPa at 4 °C. The results showed that all particle sizes of activated carbon enhanced the methane hydrate formation kinetics compared to pure water. In addition, the methane hydrate formation rate depended on the experimental. In other words, the kinetics of methane hydrate formation was slow when decreasing

the experimental pressure. The small particle size of activate carbon (250-420 μm) enhanced the methane hydrate formation due to the high interconnectivity space between the particle packed in the crystallizer, which increased the contact area between methane gas and water. Therefore, the limitation of interconnected space in the larger size of activated carbon resulted in a slower methane hydrate formation rate than that of the small one. Furthermore, the large particle size of activated carbon (841-1680 μm) exhibited the highest average water conversion to hydrate at about 96.5 % at 8 MPa and 4 °C due to large interstitial space between the activated carbon particles, where the subsequent hydrate can be formed. The dissociation experiments were conducted at initial pressure of 4.5 and 6 MPa and increased the temperature to 25 °C. The results showed that the use of the largest particle size of activated carbon resulted in the highest water conversion to hydrate. However, it showed the lowest methane recovery, which formed the large hydrate particles led to decrease the methane recovery. The methane recovery for all experiments was in the range of 79.2 – 99.1 % was obtained.

Furthermore, the two different hydrate promoters and their mixture including tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS) were also investigated for their effects on methane hydrate formation kinetics. The concentrations were prepared at 1, 3, and 5.56 mol% for THF and 1, 4, and 8 mM for SDS. The experiments were conducted in a quiescent condition in a fixed volume crystallizer at 8 MPa and 4 °C. The results showed that all concentrations of SDS and THF enhanced the methane hydrate formation kinetics and methane consumption compared to pure water, except 1 mol% of THF, which did not form the hydrate until 48 h. Considering the experiments conducted with SDS solution, the induction time at SDS concentration of 8 mM was the shortest due to the presence of SDS decreased the surface tension of the solution, leading to the increase in the solubility of gas in water. On the other hand, THF influenced the thermodynamics of methane hydrate formation. In other words, the presence of THF shifted the methane hydrate phase equilibrium to lower pressure and high temperature, which increased the driving forces of methane hydrate formation, thereby, formed methane hydrate faster compared to pure water. In addition, based on the assumption that THF hydrate could be formed in sII. It was found that, at THF concentration lower than 5.56 mol%, the

methane hydrate could form in both structures, including sI and sII. However, the small amount of THF in the solution (1 mol% THF) did not result in the methane hydrate formation. Nevertheless, the mixture of 1 mM SDS and 1 mol% THF showed the synergetic effects on the methane hydrate formation kinetics by decreasing the surface tension of water, which reduced the induction time and enhanced the storage capacity. From the experimental results, it can be noted that SDS or THF can be used as a hydrate promoter for gas storage and transport applications.

Later, the effects of temperature on methane hydrate formation and dissociation kinetics in 5.56 mol% THF solution were investigated. The experiments were conducted at different temperatures including 4, 7, 10, and 15 °C in the quiescent condition at 8 MPa. The results showed that the methane hydrate formation in THF solution was observed in all experimental temperatures compared to pure water. The fastest induction time was observed in the experiment conducted at 4 °C due to the higher driving force temperature. However, in the case of rapid methane hydrate formation at 4 °C, the stiff and high density hydrate was observed, thereby decreased the gas diffusion to grow the hydrate crystals. Therefore, the water conversion to hydrate of experiment conducted at 4 °C was lower than that at 15 °C, which obtained the highest water conversion to hydrate due to the porous hydrate formation. Therefore, the methane gas can diffuse through the porous hydrate to grow the hydrate crystal and increased the water conversion to hydrate. On the other hand, the methane hydrate formation at high temperature was not stable and can be rapidly dissociated when increasing the temperature. In addition, the methane gas can be recovered in the range of 75.1 – 91.4 % from its hydrate by increasing the temperature to 34 °C.

7.2 Recommendations

There are several possible promoters to enhance the methane hydrate formation kinetics including the porous media such as carbon nanotubes, silica sand, nanosilica, and clay, surfactants, and non-polar chemicals such as cyclopentane and tetra-n-butylammonium bromide (TBAB). To apply gas hydrate technology to store and transport gas, the condition to form gas hydrate should be moderate such as high temperature, low pressure, and no mixing system.

Methane hydrate was formed in porous media in the interstitial space between particles; therefore, this space should be optimized to increase the rate of methane hydrate formation and dissociation, and also the methane consumption capacity.

During the methane hydrate dissociation in the experiment conducted with SDS, the formation of foam was developed and moved out in the tube of apparatus. To avoid this problem, the gas hydrate apparatus should be redesigned. In addition, preparing the THF concentration should be considered about the THF evaporation before connecting to the apparatus.

Importantly, in CHAPTER VI, more experiments should be done to clarify the effects of experimental temperature on methane hydrate formation with the presence of 5.56 mol% THF. That is because, at lower temperature (4, 7, 10 °C), the hydrate could form in two structures (sI and sII), while at 15 °C, the hydrate forms only in sII.

For further investigation of gas hydrate formation kinetics, a crystallizer with an observation window should be applied in order to observe the mechanism of gas hydrate formation in the crystallizer. For an economic interest, the induction time, the rate of methane hydrate formation, methane storage capacity, and the time required to complete the methane hydrate dissociation should be taken into account.