

CHAPTER I

INTRODUCTION

Natural gas hydrates are solid crystalline and non-stoichiometric compounds, in which gas guest molecules are trapped by hydrogen bond framework of the water lattice and stable at low temperature and high pressure (Englezos, 1993). Generally, natural gas hydrates are often found in the permafrost region and in sediments of outer continental margins (Allison, 2008). There are three well-known structures of gas hydrates, including sI, sII, and sH. Hence, the amount of gas, which can be stored in the hydrate form, depends on the available cages of the hydrate structures (Englezos, 1993; Sloan and Koh, 2008). For example, sI can host small molecules such as methane, ethane, and carbon dioxide, sII can host larger molecules like propane and isobutene, while sH hydrates rarely occur in natural gas (Carroll, 2003).

In recent years, natural gas hydrates have gained much attention not only as a new source of natural gas but also as a means for novel technologies like carbon dioxide capture, hydrogen storage and natural gas storage and transportation (Ding *et al.*, 2013; Englezos and Lee, 2005; Fan *et al.*, 2014; Kang and Lee, 2000; Kim *et al.*, 2011; Li *et al.*, 2010; Linga *et al.*, 2007; Mandal and Laik, 2008; Sloan, 2003; Veluswamy *et al.*, 2014b). Natural gas hydrates, mainly methane, contain highly concentrated methane gas. For example, 1 m³ of methane hydrate contained methane gas in the range of 150 – 170 m³ at STP, depending on the hydrate structure. (Sun *et al.*, 2003; Englezos and Lee, 2005). Although the natural gas hydrate reserve estimation is still debatable, it is widely believed that the amount of carbon in natural gas hydrates is more than twice the carbon content present in all the fossil fuels combined (Klauda and Sandler, 2005; Milkov, 2004; Sloan and Koh, 2008).

Furthermore, storing methane in the hydrate form has been challenging due to the slow kinetics of the hydrate formation, the longer hydrate formation time, and its stability (Kim *et al.*, 2011; Chari *et al.*, 2013). To overcome this specific problem, additives or promoters are commonly introduced to the hydrate systems in order to dramatically reduce the equilibrium pressure and to make hydrate technology economically more attractive. In the laboratory settings employing stirred tank

reactors, once the hydrate is formed, mass transfer resistance of gas transport to liquid and eventually to hydrates results in the low water conversion to hydrate due to the agglomeration of hydrate crystals at the interface (Erik *et al.*, 2001; Jiang *et al.*, 2008; Linga *et al.*, 2012; Fandiño and Ruffine, 2014). There are many methods to increase the hydrate formation rate and the diffusion rate between gas and water without energy intensive (stirrer system) either by employing innovative reactor designs or by using promoters (thermodynamic or kinetic) (Babu *et al.*, 2013a and 2013c; Florusse *et al.*, 2004; Linga *et al.*, 2010; Lv *et al.*, 2012). As methane hydrates form at the gas–liquid interface, it could be a suitable technique to increase the hydrate formation kinetics by increasing the adsorption of water on the activated carbon. Yan *et al.* (2005) studied the methane hydrate formation in wet activated carbon. They described that the storage capacity increased with the increase in the mass ratio of water to carbon. However, when the bulk water was higher than the carbon bed, the storage capacity was decreased. Liang *et al.* (2005) reported that methane hydrate dissociated faster with the presence of activated carbon than that of pure water. Moreover, they found the self-preservation effect in the experiment conducted at the temperature lower than the ice point. It was reported that more than 70% of water can convert to hydrates for all the hydrate formation experiments that were performed in a water saturated silica sand matrix and contacted with methane at 8.0MPa and 277.15K (Linga *et al.*, 2009a; Haligva *et al.*, 2010). Linga *et al.* (2009b) demonstrated the methane recovery from the hydrate formation in the presence of silica sand. The rate of methane released depended on the bed size of silica sand, and there were two stages of hydrate dissociation. Recent works have shown that the methane hydrate formation rate and induction time was increased in the presence of multi-walled carbon nanotubes (MWCNTs) by changing the thermodynamic phase equilibrium of methane hydrate formation (Lim *et al.*, 2014; Park and Kim, 2010; Pasięka *et al.*, 2013) Chari *et al.* (2013) investigated the methane hydrate formation and dissociation in nano silica suspension. The results showed that the rate of methane hydrate formation in the presence of silica was increased compared to the system without the silica. Moreover, they revealed that the methane hydrate formation in silica was attributed to the dispersed water phase due to the silica large surface area. Babu *et al.* (2013c) studied the morphology of

methane hydrate formation on silica sand and activate carbon. They reported that the hydrate crystals were formed in the interstitial pore space between the porous particles.

It has been well documented that tetrahydrofuran (THF) can form its hydrate with water in structure II with a stoichiometric ratio of $\text{THF} \cdot 17\text{H}_2\text{O}$ (Kim *et al.*, 2006). It acts as a help molecule for gas hydrate formation (Seo *et al.*, 2003; Zhang *et al.*, 2005). Therefore, the addition of THF shifts the hydrate phase equilibrium condition and extends the hydrate stability region as a thermodynamic promoter (Susilo *et al.*, 2008; Mohammadi and Richon, 2009; Chari *et al.*, 2012). Florusse *et al.* (2004) added THF to increase the hydrogen hydrate formation at low pressure by reducing the formation pressure from 300 MPa at 27 °C to 5 MPa at 6.6 °C. Lee *et al.* (2005) reported that the molecule of THF occupied the large cages of sII, which reduced the hydrogen storage capacity in the hydrate. Linga *et al.* (2007) used THF as a promoter for carbon dioxide capture from a flue gas. They observed that THF decreased the rates and gas consumption. Chari *et al.* (2012) investigated the methane hydrate phase equilibrium of mixed hydrate with the presence of THF. They reported that, with the certain amount, the methane hydrate was formed in two structures, sI and sII. The methane hydrate phase equilibrium was also changed after adding THF. Veluswamy and Linga (2013) formed the hydrogen hydrate by adding THF as a promoter. The result indicated that the rate of hydrate growth increased at the high concentration of THF. Another work by Veluswamy *et al.* (2014a) compared the impact of THF, tetra-n-butylammonium bromide (TBAB), and cyclopentane (CP) as a hydrate promoter on hydrogen hydrate. The results indicated that the presence of THF showed the best performance on hydrogen uptake capacity; however, it was not stable compared to the other promoters.

Surfactants are considered to be a chemical hydrate promoter as it can reduce the surface tension of gas – liquid interface, so that the diffusion resistance between two phases is reduced, and the gas molecules solubility is increased (Kalogerakis *et al.*, 1993; Karasaaran and Parlaktuna, 2000). Although surfactants are widely used as the inhibitor of gas hydrate due to the anti-agglomeration effect, the formation rates of gas hydrates can be increased with the certain amount of surfactant (Zhong and Rogers, 2000; Lin *et al.*, 2004; Ganji *et al.*, 2007b; Mandal

and Laik, 2008; Hao *et al.*, 2014). Anionic surfactant is the most effective surfactant on gas hydrate formation rates among the other kinds of surfactants (Karaasalan and Parlatuna 2000; Ganji *et al.*, 2007b). Ganji *et al.* (2007b) investigated the effect of different surfactants on methane hydrate formation. They found that SDS exhibited the maximum promotion effect on the formation rate and the stability of the hydrate. The effects of SDS on ethane hydrate were studied by Mandal and Laik (2008). They demonstrated that the presence of SDS increased the gas consumption and storage capacity of ethane and also increased the dissociation rate. Partoon *et al.* (2013) studied the low-dosage of SDS on carbon dioxide hydrate formation. They reported that the small amount of SDS increased the induction time and gas consumption of carbon dioxide hydrate formation, but the gas consumption decreased when the concentration was higher than the CMC point. Hao *et al.* (2014) reported that using SDS was efficient to enhance the methane hydrate formation rate and the storage capacity. Veluswamy *et al.* (2015) also emphasized the effect of SDS by conducting the experiment on mixed hydrogen/propane hydrates. They reported that the presence of SDS reduced the induction time even with low SDS concentration. However, the final gas uptake performed with SDS was similar to the experiments conducted without surfactant.

In order to apply the hydrate technology for gas storage and transportation, the hydrate formation and dissociation kinetics, and the storage capacity must be improved. In this work, activated carbon, THF, and SDS were used to investigate their effects on the methane hydrate formation and dissociation kinetics. The experiments were conducted in batch reactor with fixed-amount of gas and solution at the desired experimental pressure and temperature in the quiescent condition.

Scope of Research Work

Research Work 1: Improved Methane Hydrate Formation Rate Using Treated Activated Carbon

The effect of surface treatment of coconut shell activated carbon on the methane hydrate formation at 6 and 8 MPa at 4 °C was demonstrated. Sulfuric acid (H₂SO₄) and potassium hydroxide (KOH) were used in the treatment process.

Research Work 2: Investigation on the Roles of Activated Carbon Sizes on Methane Hydrate Formation and Dissociation

Different activated carbon sizes, 250-420 μm, 420-841 μm, and 841-1680 μm, were used in order to investigate their effects on the methane hydrate formation and dissociation in a quiescent fixed bed reactor. The induction time, gas consumption, and gas recovery were reported.

Research Work 3: Experimental Investigation on Methane Hydrate Formation Kinetics in the Presence of Mixed Hydrate Promoters for Gas Storage Application

Two hydrate promoters, tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS), and their mixture were investigated for their effects on the methane hydrate formation kinetics in the static condition. The induction time, gas consumption, and time to reach 90 % (t_{90}) of the final gas uptake were compared.

Research Work 4: Temperature Effects on Mixed THF-CH₄ Hydrates Formation and Dissociation Kinetics

Methane gas was pressurized into THF solution to form the hydrate at different experimental temperatures at the same pressure. Methane hydrate dissociation was employed after completion of the methane hydrate formation in each experiment. The effects of temperature on the induction time, gas consumption, t_{90} , and methane recovery were demonstrated.