Transient Study of THF Hydrate in Cylindrical Reactor

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Abstract

This work presents the THF hydrate formation growth dynamics in cylindrical reactor. This paper starts with brief introduction to THF hydrate and then in next section we provide experimental details in fabrication of experimental cell and then procedure adopted for experiment. Later we show the exothermic nature of reaction and hydrate growth with the help of images and temperature distribution at various points. Experiments demonstrated Heat generation and insulating effects of THF hydrate layer.

Keywords: *exothermic; Heat generation; Insulating*

1.0 INTRODUCTION

Clathrate Hydrates are crystalline inclusion compounds in which guest molecules are trapped in cages formed by hydrogen bonded water molecules. Recently natural gas hydrates have received a lot of attention due to ever increasing energy demands and need for cleaner fuel. They are found in natural sites generally in permafrost and ocean. Besides an energy resource gas hydrates also have other applications like desalination of sea water (Wang et. al, 2013), energy storage (Veluswamy and Linga, 2013). Methane hydrate production requires high pressure and low temperatures.THF(Tetrahydrofuran) can form clathrate hydrate at atmospheric pressure and can serve as a substitute for clathrate hydrate research. THF and water mixed at the stoichiometric 1:17 (17 water molecules per THF molecule) has equilibrium melting point 4.4°C at .1MPa. Larsen et.al(1998) investigated THF hydrate single crystal growth and found THF hydrate sII crystals grown from the melt (the stoichiometric solution) exhibit (111) crystallographic planes, in the form of regular octahedral. M.Karamoddin et.al(2014) investigated the kinetic behaviour of THF hydrate formation in the presence of electrolytic inhibitors and observed inhibition potentials. Wilson et. al (2005) investigated statistics of liquid-to-crystal nucleation for clathrate-forming mixtures of tetrahydrofuran (THF) and water using an automatic lag time apparatus (ALTA) and demonstrated stochastic nature of nucleation. Iida et.al (2000) investigated hydrate growth between two copper plates subjected to various conditions and compared hydrate film thickness with from the mathematical model and found good match between two. Bollovaram et.al (2000) studied growth kinetics of single hydrate crystal hydrates and comparing the observed crystal growth rates with corresponding predicting from forced convection from crystal surfaces that surface reactive restraints may not be overlooked when the heat transfer coefficient is much increased. Prasad et.al (2007) carried out Raman spectroscopy of THF hydrate, its spectra provide vital details of THF hydrate structure and conformation of its formation. Ricaurte et. al (2014) studied THF as kinetic hydrate promoter and concluded that THF supersaturation produced at the injection point induces crystallization of a first hydrate rich in THF, which then triggers that of second hydrate rich in gas hydrate former phase. There is not enough literature available to show how THF hydrate will grow in cylindrical maintained against a cooled isothermal wall. So here we have investigated THF hydrate cooling and growth process at two locations in cylindrical reactor and also calculated hydrate thickness during growth of hydrate.

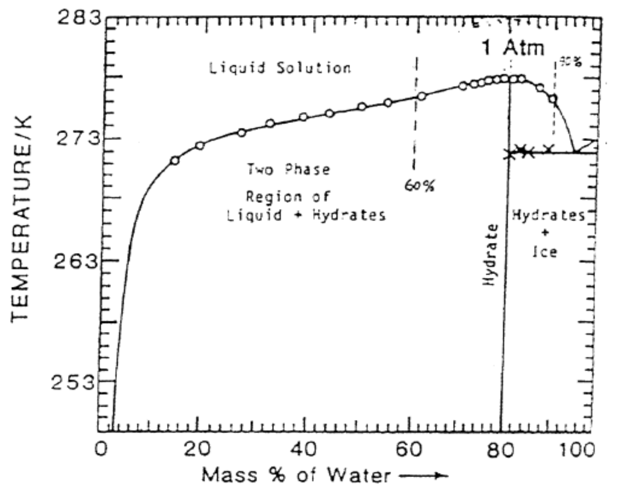

Figure 1: THF hydrate phase diagram(Dyadin et.al(1973))

2.0 METHODOLOGY

2.1 Experimental Details

Experiment cell (Figure 3) was designed in a way to allow cooling of solution by providing a jacket around the main reactor chamber. Outside chamber was made of Plexiglas with dimensions 37cm*37cm* 26cm and inner chamber was made up of glass of 13.5cm diameter, height 20cm and volume 3L. Secondary tank is added to ensure always a certain level of height of coolant is present in the experimental cell. Windows are attached to allow the visualization. During experiments the cell was covered with a lid which also contains probes for temperature measurement and outer body was covered with insulation for preventing heat coming inside the system. Entire experimental set up is shown in figure 5. Temperature probes coming from inner cell is connected to data acquisition system where data is acquired at every 4 seconds and temperature probes are T type thermocouples. We have used ice-water mixture to maintain the low temperature near the wall which remains mostly around 1°C. Schematic diagram is given in figure 4 has following parts 1-inner cell, 2-outer chamber,3-connecting pipe (for connecting windows to outer tank),4,5-window,6-lower block.

Figure 3 : Experimental cell with parts

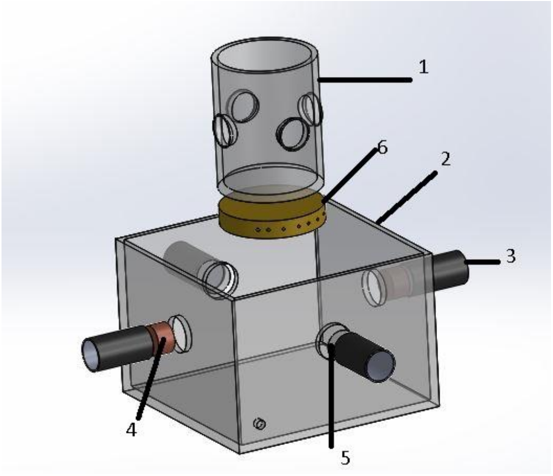

Figure 4 :Schematic diagram of reactor vessel

2.2 Experimental Procedure

THF was purchased of 99.5% purity and deionized water was added to it at stoichiometric ratio (19.06%wt THF). However, 1% extra THF was added to compensate the evaporation losses. Then solution was stirred by hand stirrer for about 7 minutes and placed in the inner cell. Temperature probes are placed and connected to data acquisition system(DAQ). Data was collected with the help of LabVIEW program. Wall of reactor is maintained at constant temperature 1.2°C. Photographs are also collected to see hydrate front moving and calculate hydrate thickness. The reaction for 81% water by mass (stoichiometric concentration) is

$$THF + 17H_2O \rightarrow THF\cdot17H_2O + \Delta H$$

At above concentration the equilibrium temperature of THF hydrate solution is reported to be 4.4 °C which can be observed in phase diagram of THF hydrate in figure 1.

3. RESULTS AND DISCUSSION

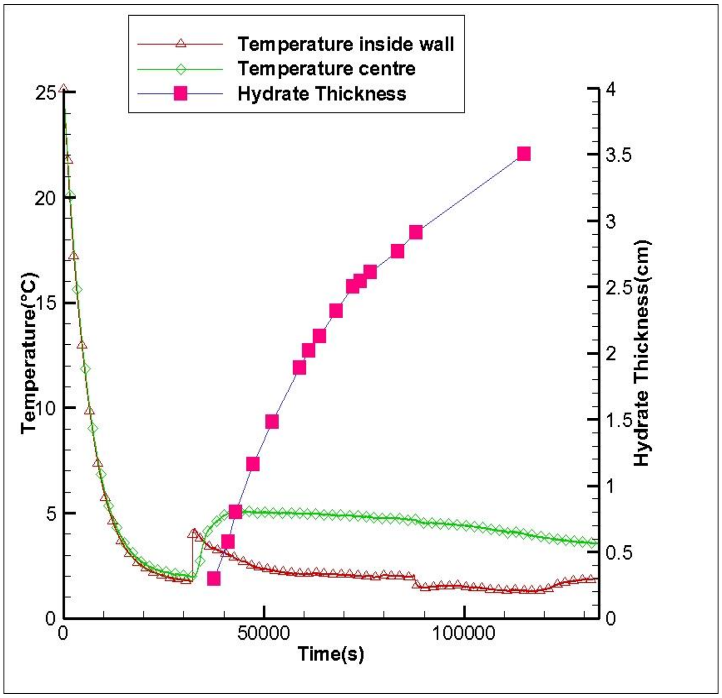

Figure 5 : Temperature time profile for inner cell at various locations.

Temperature time study is shown in figure 5. Temperature is monitored at close to the wall and at the centre of the reactor. Cooling curve becomes less steep as we reach closer to wall temperature which is expected because of reduction in temperature gradient. The difference in temperature at both these two locations is then 2°C throughout run. Temperature continue to fall in cooling period however the temperature jumps to nearly 4.4 °C after nucleation happens. Temperature at centre nearly remains constant due to heat generation and insulating effect of hydrate layer at periphery of inner cell but starts dropping after long interval of time. Movement of hydrate front can be clearly seen in figure 6. Hydrate thickness is calculated by analysing the images at various time intervals, slope become less steep as hydrate thickness increases after some time. One of the reasons is because hydrate growth slows down with time due to decreased heat transfer because of insulating effect of hydrate layer. Temperature close to the wall starts dropping after initial rise due to nucleation due to its proximity to the wall. The decrease in temperature at the wall is strongly dependent on the boundary condition and temperature distribution at the centre of the reactor depends on the properties of the THF solution and hydrate. Thermal diffusivity of THF solution plays an important role in this transport of energy. Growth of THF hydrate is quite axisymmetric in the reactor. THF hydrate thickness growth is nonlinear in nature as we can expect from a Stefan problem. This problem may be modelled as one dimensional transient conduction problem in cylindrical coordinates for cooling part and interface boundary condition may be used for modelling of growth of THF hydrate. The nature of temperature variation may change if we change concentration of THF as equilibrium temperature will change but overall trend may remain same.

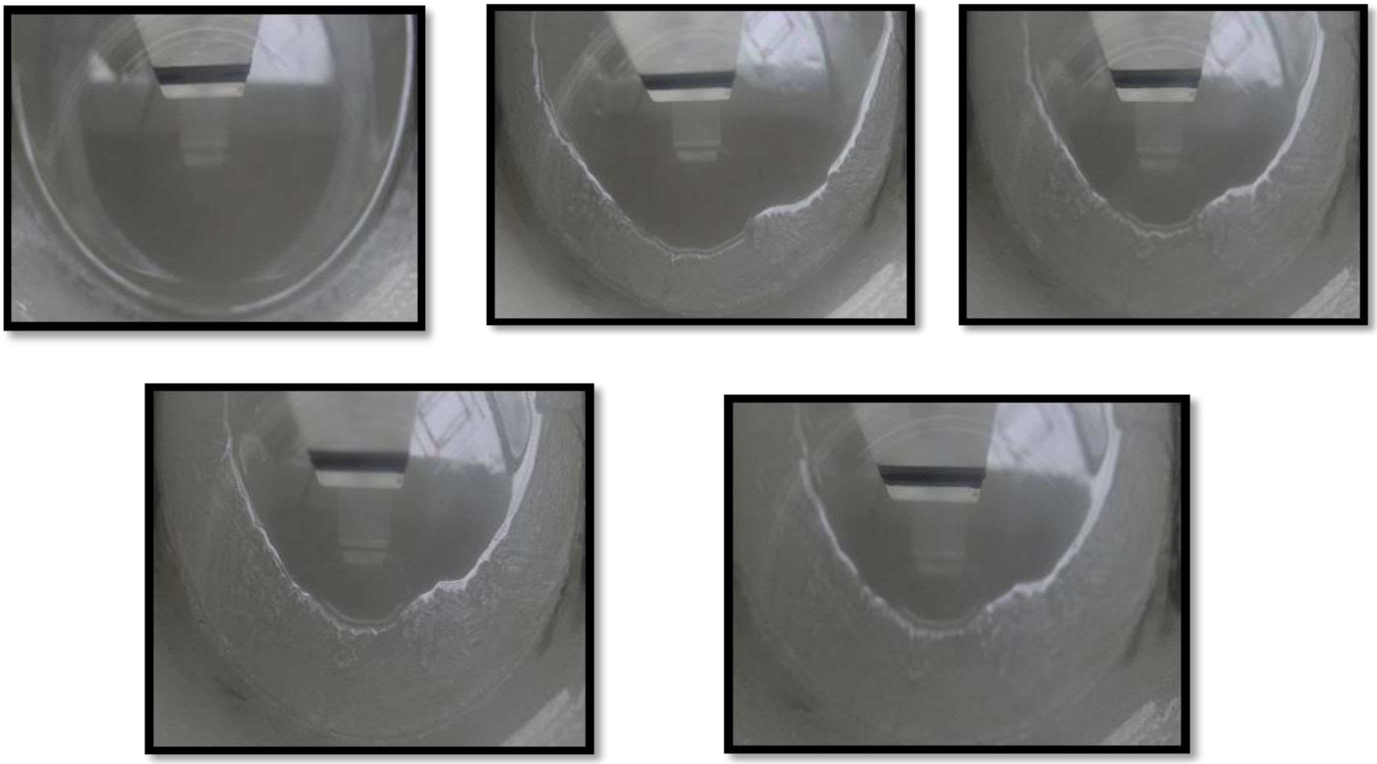

Figure 6: THF hydrate formation at various time intervals (from top, LHS): - t= 10:28h ,16:23h, 17:1h, 17:46 h, 18:54h

CONCLUSIONS

This work shows dynamics of THF hydrate growth inside a cylindrical cell with the help of temperature distribution and images. We found that at approximately 2.5 cm of hydrate growth, the growth in thickness of hydrate slows down. Natural gas hydrates tend to block pipelines the above work may help us understanding the growth dynamics of in pipeline, however natural gas hydrate growth dynamics may differ significantly from it. Heat generation and insulating effects can be significant in understanding THF hydrate growth in various geometries. Finally, testing the above results with numerical simulation may provide interesting insights

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