INTERNATIONAL JOURNAL OF REFRIGERATION 59 (2015) 84–90

Available online at www.sciencedirect.com

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Experimental and computational study on clathrate hydrate of tetrahydrofuran formation on a subcooled cylinder

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ARTICLE INFO

Article history:
Received 3 March 2015
Received in revised form 15 July 2015
Accepted 16 July 2015
Available online 23 July 2015

Keywords:
Hydrate formation
Heat transfer
Phase-change material
THF

ABSTRACT

In the present work, formation of tetrahydrofuran (THF) hydrate on a subcooled cylinder is experimentally investigated. Then it is modeled using a latent-heat based, heat transfer with phase change model. Formation and growth of a THF hydrate layer from a liquid solution having the same composition as the hydrate have been observed in a one-dimensional cylindrical heat-transfer system. Our model simplifies equations and corresponding solutions for a moving boundary phase change problem using two simple yet accurate assumptions. This model successfully changes a "moving boundary phase change" problem to a "simple single phase transient heat transfer" problem. This model describes the hydrate formation process for different boundary and initial conditions. The effects of many operating conditions like subcooling temperature on hydrate formation rate are evaluated.

Etude expérimentale et numérique sur la formation d'hydrate de clathrate de tétrahydrofurane sur un cylindre sous-refroidi

Mots clés : Formation d'hydrates ; Transfert de chaleur ; Matériau à changement de phase ; THF

1. Introduction

Gas hydrates are a class of clathrates which are composed of water and certain molecules called guest molecules (Sloan and Koh, 2007). These molecules can be gases such as methane, ethane, propane, some refrigerants and carbon dioxide as well as liquids such as tetrahydrofuran (THF) (Maryam and Varaminian, 2014; Maryam et al., 2014; Sloan and Koh, 2007). Gas hydrates are one of the cold storage materials under study (Darbouret et al., 2005; Delahaye et al., 2010; Jerbi et al., 2010; Li et al., 2012; Wenji et al., 2009). Some hydrates can be formed at atmospheric pressure with suitable phase change temperature for air-conditioning and large fusion heat (Li et al., 2012). Also studies show that gas hydrate has high potential for storage of natural gas, water desalination, concentration of solutions, and separation of gases (Eslamimanesh et al., 2012; Hao et al., 2008; Javanmardia and Moshfeghian, 2003; Mazraeno and

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http://dx.doi.org/10.1016/j.ijrefrig.2015.07.024
0140-7007/

Nomenclature

α	the fraction of phase after transition
θ	$1-\alpha$
α_L	heat diffusivity
β_L	thermal expansion coefficient
γ	ratio of specific heats
ρ	density
υ_L	kinematic viscosity
Cp	heat capacity at constant pressure
D_H	hydraulic diameter
g	acceleration of gravity
H	enthalpy
k	thermal conductivity
L	latent heat
T_i	solution temperature
T_{eq}	equilibrium temperature

Varaminian, 2013; Naeiji et al., 2014; Tomlinson, 1982). The potential of gas hydrates to be used in industrial applications encourages researchers to find a better understanding of its formation and dissociation. Better understanding of this phenomenon helps industry and research and also makes possibilities to introduce new technologies.

In spite of its importance, many facts about hydrate formation are not well understood and mathematical models are very scarce (Karimi et al., 2014; Roosta et al., 2013). Many authors have shown the benefits of hydrate formation in purification of mixtures. In particular, the technique seems well adapted in seawater desalination plants. Compared to vaporization, hydrate formation requires less energy during phase change. Moreover, the process of hydrate formation could be used as a storage system of cold thermal energy to resolve the peak demand in electric power of air conditioners.

Tetrahydrofuran (THF) hydrate is not a naturally formed hydrate. Among all hydrate formers, it has gained attention of researchers interested in hydrate due to its unique properties (Lida et al., 2001). THF forms hydrate at atmospheric pressure. It is also a liquid hydrate former. These two properties facilitate experiments. THF forms structure II hydrate with 17 water molecules per THF guest molecule (Sloan and Koh, 2007). If THF–water solution is composed of THF and water at the stoichiometric composition of THF hydrate, then no mass transfer occurred in liquid during hydrate formation. In described system, the formation rate can be controlled by heat transfer or by hydrate formation reaction at the surface. Most researches on hydrates have been conducted such that heat or mass transfer mechanisms are not well understood (e.g. stirred vessels). Thus, it makes mathematical modeling almost impossible. Beside scientific issue, hydrate formation is considered to be a candidate for cooling systems. To increase the coefficient of performance (COP) of the refrigerators in thermal energy storage systems, it is necessary to select a thermal energy-storing material that undergoes a phase change at a temperature close to the desired temperature value, i.e., 7–12 °C. THF hydrate is an enticing potential analog material because it forms at atmospheric pressure and moderate temperatures (below 4.4 °C) (Karamoddin and Varaminian, 2015; Lida et al., 2001).

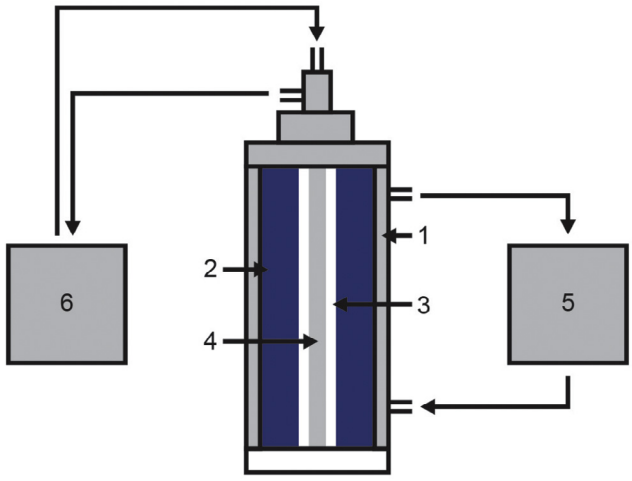

Fig. 1 – Setup schematics, 1: constant temperature jacket. 2: THF–water solution, 3: hydrate layer, 4: subcooled cylinder, 5: jacket temperature control circulation, 6: refrigeration system.

Solving moving boundary phase change problem is a mathematical challenge and several numerical solutions have been introduced for it (Fikiin, 1996; Karamoddin and Varaminian, 2015). The classical approach assumes that solidification occurs at a sharp phase interface. Approximate analytical solutions have been introduced based on this (Fikiin, 1996; Karamoddin and Varaminian, 2015). The difficulties are related to localization of the interface which makes solutions slow and complicated. These semi-analytical techniques are not useful in multi-dimensional systems or systems with simultaneous heat and mass transfer. Numerical solutions for PDEs are powerful tools for fluid dynamics and thermal design in industrial applications, as well as in academic research activities (Ettouney et al., 2005; Tay et al., 2012). Formation of hydrate can be considered as a moving boundary heat transfer with phase change problem. Special care must be taken when modeling these systems taking into account the effect of latent heat in heat transfer rate (Ettouney et al., 2005; Tan et al., 2009; Tay et al., 2012).

In this research, a static hydrate formation geometry that has not mathematically or experimentally studied for hydrate formation in previous literature is investigated. A heat transfer model was developed to analyze transient heat transfer during the phase change process of THF–water on a subcooled cylinder. Hydrate formation rate and final width are evaluated and compared with experimental results.

2. Static crystallization of hydrate on a subcooled cylinder

A simplified pilot of static hydrate formation is illustrated in Fig. 1. This pilot is used for THF hydrate formation at different initial and boundary conditions. The apparatus consists of a vertical stainless steel tube and a jacketed tank. The hydrate is formed on the wall of the vertical tube. Inside this subcooled cylinder, a refrigerant is evaporating at constant temperature (T_{cold}) and pressure. While the refrigerant is in saturated