

Application of Gas Hydrates as an Alternative Dehydration Method



Yaqub S, Partoon B, Mellon N, Shariff AM and Bhajan Lal*

Chemical Engineering Department, Universiti Teknologi Petronas, Malaysia

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*Corresponding author: Bhajan Lal, Chemical Engineering Department, University Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia, Email: bhajan.lal@utp.edu.my

Abstract

Natural gas is the cleanest, safest and most economical fossil fuel. Similar to other type of fossil fuel resources, natural gas required treatments and conditioning prior to industrial applications. The presence of water vapors as an impurity, limits its applications in energy sector. Moreover, natural gas having water vapor is not feasible for gas conditioning i.e. cryogenic process. There are several commercially available processes for natural gas dehydration. However, the high operational and capital cost made these processes uneconomical. Therefore, this short review is an attempt to insight alternative and economical natural gas dehydration method by gas hydrate formation. The aim of this paper is to demonstrate the necessity of fundamental studies of gas hydrate such as; thermodynamic, kinetic and vapor-hydrate two-phase equilibrium that is essential to know for the development of dehydration application.

Keywords: Natural gas; Dehydration; Gas hydrate

Introduction

Gas hydrates were first discovered by Sir Humphry Davy in 1810 [1]. Clathrate hydrates are crystalline compounds, formed by the smaller molecules (guest), entrapped within the cavities of a rigid "cage-like" lattice of water molecules (host) at low temperature (typically less than 300K) and high pressure (typically more than 0.6MPa) conditions [2]. The small molecules of gasses, such as methane (CH₄), carbon dioxide (CO₂), hydrogen Sulfide (H₂S), ethane (C₂H₆), propane (C₃H₈), iso-butane (i-C₄H₁₀) and n-butane (n-C₄H₁₀) act as a former or guest molecule in clathrate hydrates. The former are physically trapped inside a three-dimensional lattice structure formed by the hydrogen bonding of water molecules. Arctic permafrost and subsea are two major environments that naturally confine gas hydrates [3,4]. Particularly large clathrate hydrate deposits occur along Siberia Arctic Shelf and Nankai trough, off Japanese east coast [5,6]. Recently (2012), recovery efforts have been made to extract natural gas from such gas hydrate deposits in Alaska's North Slope [7]. The structure of gas hydrate is composed of about 85mol% of water. Based on gas molecules and the formation conditions, gas hydrate crystalline structures can be classified into three categories: a body-centered cubic structure I (sI), a diamond cubic structure II (sII), and a hexagonal structure H (sH). Each crystalline structure contains geometrically different water

cages with different size cavities. The cavities normally adapt only one guest molecule ranging in diameter from 0.40-0.90nm. Methane hydrates typically accommodate in structure I [8,9].

The application of gas hydrates in energy production, and natural gas storage is gaining attention. The amount of energy trapped in gas hydrates is twofold then that of all fossil fuel reserves. For the standard gas application where the amount of produced gas is not enough to build a liquefied natural gas plant, the storage of natural gas in the form of gas hydrate pellets is spectacular [3]. The transportation of natural gas by solidification (SNG) tends to be energy conservative compared to liquefied natural gas [10]. However, efforts have also been made to develop gas hydrates for hydrogen storage applications. Gas hydrates have their vast applications in separation processes including separation of flue gases and desalination of seawater/wastewater. The former application includes CO₂ separation and storage which is helpful in reducing greenhouse gas emissions and prevents global warming [11]. Desalination process is a technology for separating gaseous or water solutions [12]. The use of gas hydrates in purification of wastewater or fresh water generation is attractive, because the salts ions present in waste or sea water form hydrates and can easily be removed. On the contrary, gas hydrates now days are causing more problems than solutions. In oil and gas

transportation and processing equipments gas hydrates are considered a nuisance. In flow assurance gas hydrates are responsible for causing huge obstacles in the pipe line which either disturbs the flow continuity or damage the whole pipeline. In these cases, hydrate formation can be prevented by maintaining the temperature and pressure of pipeline, by injecting thermodynamic or kinetic inhibitors or by dehydrating the gas [13]. Having immense utility of gas hydrates, this paper is focused on introducing a new application of gas hydrate i.e. gas dehydration.

Gas Dehydration

Gas dehydration is the method of removing water vapor from a gas stream. It lowers the temperature at which water will condense from the stream; this temperature is called "dew point" of the gas [14]. If the temperature in the pipeline or storage tank decreases below the dew point, water vapors begin to condense on the cold surfaces and the problems such as; Methane hydrates formation, natural gas corrosiveness, slug flow, erosion can emerge. Moreover the natural gas having water vapors is difficult to operate on cryogenic plant [15]. To address these problems, it is necessary to remove water vapors from the natural gas stream by dehydration method. In previous studies various dehydration methods have been used

- (i) dehydration by liquid desiccants (absorption),
- (ii) dehydration by solid desiccants (adsorption),
- (iii) dehydration by refrigeration,
- (iv) dehydration with calcium chlorides,
- (v) dehydration by membrane permeation and
- (vi) supersonic dehydration.

The conventional dehydration methods have certain benefits in terms of very low dew point depression and are suitable to deal with large water content. However, they tend to have various drawbacks such as; energy consumption, chemical losses/degradation, operational and maintenance cost. Dehydration by gas hydrate can be considered as an alternative dehydration method. It is a green technology of separating water vapors from the natural gas without the expense of any chemicals.

Description of the Proposed Method

The basic principle of gas hydrate formation is to create a contact interface for dissolving the gas in liquid water at appropriate thermo baric conditions [16]. However, in dehydration process usually the incoming gas is saturated or wet gas, so there might be no need of liquid water for gas hydrate formation. The rest of the mechanism of gas hydrate formation is similar to the one used in previous studies [17]. In previous studies, no work has been done on the formation of gas hydrates from the wet gasses having vapor water instead of liquid water. Some work on the vapor-hydrate region has been

done on ethanegas but till date, there is no published work on wet natural gas. The cold stream from cryogenic separation can be used as cooling media for gas hydrate formation. The dried gas by dehydration is sent to the cryogenic separation for further gas conditioning of natural gas. Hence, two gas conditioning steps i.e. dehydration and cryogenic separation accommodate each other.

The development of thermodynamic equilibrium data for critical analysis of vapor hydrate region of gas hydrates for dehydration is necessary. Subsequently, there is a need to determine the rate of gas hydrates formation, induction time and moles of gas consumption. The development of gas hydrate kinetic data is essential to adopt alternative dehydration method. This paper is to deliberate the necessity of thermodynamic and kinetic data for the vapor-hydrate region of wet gas.

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