Effect of maize starch on methane hydrate formation/dissociation rates and stability

CrossMark

Saheb Maghsoodloo Babakhani, Abdolmohammad Alamdari[*]

Dept. of Chemical Eng., School of Chemical and Petroleum Eng., Shiraz University, Shiraz, 7193616511, Iran

A B S T R A C T

The effects of maize starch on the methane hydrate formation/dissociation rates and stability were investigated in the present work. Maize starch at 5 concentrations of 200, 400, 600, 800 and 1000 ppm was tested. The results showed that maize starch at low concentrations had no significant effect on hydrate formation; however, at the concentrations higher than 400 ppm, maize starch increased the hydrate formation rates. The most effective concentration of maize starch was 800 ppm. At this concentration, methane can be stored in hydrate 2.5 times more than in the case of pure water when no maize was used. Hydrate stability was studied at ambient pressure and two temperatures below the ice point (272.2 K and 269.2 K). The results showed that for all samples the maximum dissociation rate occurred at the beginning of the process and then the rate decreased. At all concentrations, mole percentage dissociated at 272.2 K was lower than at 269.2 K and the hydrate formed at 800 ppm maize starch had the maximum stability.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Safe and cheap transport of natural gas from fields to consumption places is nowadays under the consideration due to increasing energy demand. Transport of natural gas as LNG or through pipes is unsafe or expensive. To reduce the risk in gas transport, hydrate formation technology may be employed. In this technology large volumes of hydrocarbons can be stored in cavities of hydrate matrices. For example 150–180 m^3 of methane gas at standard conditions can be stored in one m^3 of gas hydrate (Khokhar et al., 1998; Makogon, 1997).

Gas storage in hydrate needs no conditions of low temperature compared to the conditions for LNG. Additionally, hydrate formation installations may be performed on the platforms at offshore. It has been reported that transportation of natural gas through hydrate is about 18–24% cheaper than through LNG (Kim et al., 2010; Gudmundsson et al., 1994). Natural gas transportation through hydrate consists of three main steps: formation, transportation, and dissociation. Hydrate formation rate and storage capacity are the critical stages which determine the economics of the process (Hao et al., 2008). Therefore, an increase in formation rate and storage capacity is essential in hydrate research. Researchers have used additives and promoters to enhance the formation rate and

capacity (Kwona et al., 2011; Lee et al., 2010; Ganji et al., 2007).

Lee et al. (2007) investigated the effect of some cationic starches on the hydrate formation rate of methane mixture with the other natural gas components. They found that the cationic starches did not increase the formation rate. Taheri et al. (2012) studied the effects of hydroxyethyl cellulose on methane hydrate formation and stability at different temperatures. They reported the optimum concentration of 500 ppm for hydrate formation. Fakharian et al. (2012) reported a significant effect of the potato starch on methane hydrate formation and the maximum capacity of 163 volume per volume at 300 ppm concentration of the potato starch.

In the present study the effects of maize starch on the methane hydrate formation and dissociation rates and on the hydrate stability were investigated. The bottleneck for hydrate formation technique is to storage as much gas as possible in a unit volume of hydrate. Therefore, finding a good promoter for hydrate formation may help the gas industry to overcome this bottleneck. To the knowledge of authors no research on maize starch as a hydrate promoter has been reported in the literature.
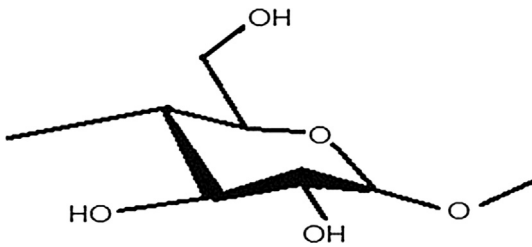
2. Experimental

2.1. Materials

High pure methane (99.9%) and deionized water were used for tests. Maize starch (100% pure) from Acros Company (Belgium) was

---

used as an additive. The formula of starch was $(C_6H_{10}O_5)_n$ and its molecular structure is (www.acros.com):

Using the method of Williams et al. (1970) for analysis, the amylose-amylopectin content of maize starch was determined as 29 and 71 percents.

2.2. Apparatus

The experiments of hydrate formation were carried out in a 250 ml cell. The maximum pressure of 34 MPa might be employed in the cell. The cell was equipped with a thermocouple of 0.1 °C accuracy, a pressure sensor of 0.1% accuracy, and an adjustable speed stirrer. The resistant torque exerted by the fluid was transferred to a computer by which the state of mixing in the fluid could be detected and a stirrer jam might be recognized. The schematic diagram of the system used for hydrate formation and dissociation is shown in Fig. 1.

2.3. Procedure

2.3.1. Hydrate formation

In order to check the cell for a leakage, it was filled with nitrogen gas to a pressure of 10 MPa. The pressure was maintained for 1 h while no pressure decline was observed. The cell was evacuated by a vacuum pump and a volume of 60 ml water containing a precise concentration of maize starch was injected to the cell. The pressure was raised to 8 MPa by methane injection and the temperature was adjusted to 275.2 K. Then, agitation was started with a stirrer speed of 300 rpm. During the course of experiments for about 24 hours, the temperature, the pressure, and the stirrer speed in the cell were recorded every 3 min. The gas consumption was calculated based on the changes in pressure and temperature as $n = PV/zRT$ where P,

T, and V are the pressure, temperature, and volume of gas, respectively. R is the gas constant and z is the compressibility factor which is calculated through Peng–Robinson equation of state (Danesh, 1998). The V was considered as the cell volume minus the water volume. Due to a very low methane solubility in water, the volume increase of liquid water due to methane absorption is quite negligible; however, the volume change of gas phase due to the volume increase of hydrate as it forms was calculated based on the hydrate density and volume difference between water and hydrate.

It is pertinent to note that the temperature chosen for hydrate formation was about 3 °C above the ice point; therefore, there was no chance for the solid phase to contain partially or entirely the ice.

2.3.2. Hydrate dissociation

The dissociation step started after the constancy of the cell pressure. First, the temperature was maintained at 269.2 K and then the cell was depressurized to the ambient pressure in two steps; a slow reduction of pressure to the equilibrium pressure of methane at 269.2 K, and a rapid reduction of pressure from the equilibrium to the ambient pressure. The variations in pressure build up were recorded for 6 h by which the quantities of gas released were calculated. This procedure was performed to avoid throttling process and also to prevent unwanted-early hydrate dissociation. Then, after the pressure build up, the cell temperature was raised to 272.2 K and the cell was depressurized again to the ambient pressure. Once again the variations in pressure buildup were recorded for 6 h. The subzero temperatures of dissociation were selected in order to eliminate the liquid water vapor pressure.

3. Results and discussion

3.1. Effects of maize starch on hydrate formation

Effects of the different concentrations of maize starch on methane hydrate formation/dissociation were studied. Quantity of methane stored in the hydrate was calculated through the variations of pressure and temperature during the course of the process.

3.1.1. Variations of pressure

Fig. 2a shows the variations of pressure during the course of hydrate formation process for 600 ppm concentration of maize starch. Fig. 2b shows the pressure variations for all the other maize starch concentrations. As Fig. 2a illustrates, the variations of pressure can be divided into four specific sections. The first section (AB) represents the injection of gas into the cell where the pressure was maintained above 80 atm almost constant. The second section (BC) demonstrates the cooling stage of the gas from the ambient temperature to 275.2 K. Due to reduction in temperature, the pressure in this stage declined from about 80 atm to about 73 atm. When the gas temperature reached 275.2 K, the stirrer was started. The pressure remained constant for a while before a sharp decline. At this pressure, the hydrate was expected to be formed but due to induction time the system came to a halt. At stage CD, the pressure declined sharply indicative of the hydrate formation progress. However, soon after this stage the pressure remained constant indicative of the end of the hydrate formation stage. Deposition of the gas in the hydrate occurs at this stage when the gas is entrapped into the hydrate cages.

Inspection of pressure drops in Fig. 2b shows that maximum gas deposition occurred at a maize starch concentration of 800 ppm. However, the starch concentrations less than and more than 800 ppm exhibited less pressure drops. At very low concentrations of maize starch (200 and 400 ppm) the pressure drop is slightly lower than that for pure water, however, the effect is very small that may be covered by experimental error; therefore, the effect was
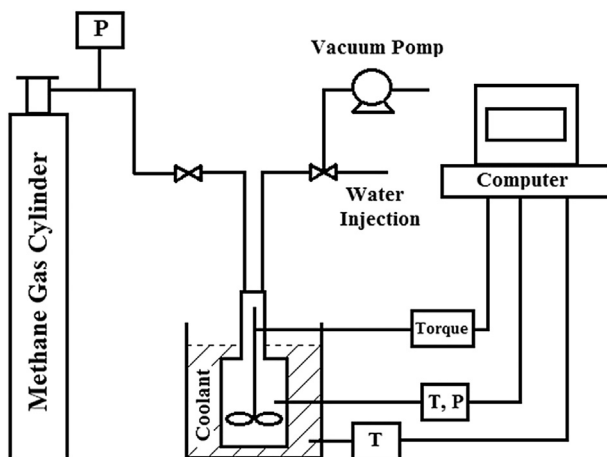

Fig. 1. Schematic diagram of the system used for the hydrate formation and dissociation.