Fuel 94 (2012) 356–360

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Potato starch as methane hydrate promoter

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ARTICLE INFO

*Article history:*
Received 25 April 2011
Received in revised form 25 September 2011
Accepted 17 October 2011
Available online 31 October 2011

*Keywords:*
Gas hydrates
Potato starch
Formation rate
Dissociation rate
Storage capacity

ABSTRACT

In this study the effects of water-soluble biological starch from potatoes on methane hydrate formation rate, stability and storage capacity have been investigated and compared with the hydrate formed in pure water and aqueous sodium dodecyl sulfate (SDS) solution. Methane hydrate was formed in 100, 200, 300 and 500 ppm starch and 500 ppm SDS aqueous solutions. Hydrate stability tests were performed at two temperatures of 263.2 and 268.2 K with and without additives at two pressures of 1 and 10 bar. It has been found that potato starch in all tested concentrations increases the hydrate formation rate and at 500 ppm it has maximum acceleration effect comparable to SDS at similar concentration. Maximum hydrate storage capacity of 163 was achieved at 300 ppm starch solution and the best operating condition for storage was the pressure of 10 bar and temperature of 268.2 K.

## 1. Introduction

Natural gas hydrates (NGH) are crystalline solids composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules. There are three known hydrate structures (I, II and H) depending principally on the molecular size of the guest molecule [1,2]. In recent years gas hydrates have received much attention not only as a new natural energy resource but also as a new means of natural gas storage and transportation [3–6]. Natural gas storage in hydrates has been investigated because hydrates store large quantities of natural gas (e.g. 180 volumes per each volume of hydrate at standard condition) [1,6]. Gudmundsson et al. [7] demonstrated that the hydrate can be stored at −15 °C under atmospheric pressure for 15 days, retaining almost all the gas. They also showed a substantial cost saving (24%) for the transport of natural gas in the form of hydrates compared to liquefied natural gas (LNG). NGH also will be a cheaper method that will require less energy and equipment for forming/dissociating the hydrate and safer than the traditional methods of LNG and compressed natural gas (CNG) [8].

Slow formation rate of natural gas hydrate has been considered to be a critical problem hindering the industrial application of gas hydrates for storage and transportation of natural gas. Some researchers applied water spraying into a guest–gas phase as a practical means of rapid hydrate formation [9]. Among the solutions to increase the hydrate formation rate and the storage capacity of gas in the hydrate, additives as promoter were often used. In recent years, researchers have reported the promotion effect of some additives on gas hydrate formation rate and its gas content [10–16]. These studies have verified that some anionic, cationic, and non-ionic surfactants could promote the hydrate crystallization whereas polymers further were used as hydrate inhibitors.

Fast formation rate and gas content of gas hydrates are important in commercializing their use in storage and transportation, but also the stability of the hydrate formed is vital for long distance transportation and long period of storage. Lin et al. [17] studied the stability of methane hydrate with and without SDS as hydrate promoter and found that it decreases the hydrate stability below the ice point. Ganji et al. [15] have also shown that surfactants decrease the stability of methane hydrate compared to pure water–methane hydrates.

The effect of starch as chemical additive on gas hydrate formation and dissociation rates has been scarcely reported. Lee et al. [18] have investigated the kinetic inhibiting effect of a number of cationic starches in hydrate formation experiments with methane and methane/ethane and methane/propane gas mixtures and found that they are hydrate formation inhibitors. Also Ganji et al. [19] have reported that starch can decrease the dissociation rate of methane hydrate formed in SDS aqueous solution.

The promotion effect of starches on gas hydrate formation rate has not previously been reported in the literature. In this study the effect of different concentrations of water-soluble biological starch from potatoes on the hydrate formation/dissociation rate and its storage capacity has been investigated. The objective of this study is to find suitable conditions for rapid hydrate formation with desirable stability and storage capacity.

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doi:10.1016/j.fuel.2011.10.029

## 2. Experimental

### 2.1. Materials

High purity methane gas (99.9%) was used to form hydrate with de-ionized water. Additives used in the experiments were: sodium dodecyl sulfate (>99% purity) from Merck with chemical formula of ($C_{12}H_{25}SO_4Na$) and potato starch from Fluka with chemical formula of $(C_6H_{10}O_5)_{162.14}$ and an assay of about 80%.

### 2.2. Apparatus

The experimental setup used in this research was the same as it was described before [15,19], except that the temperature and pressure were recorded by a computer during the process as a function of time (Fig. 1).

The setup consisted of a high-pressure stainless steel reactor with an internal diameter of 6.2 cm, a height of 10 cm and a total volume of 300 $cm^3$. The reactor was equipped with a four-blade mixer. A J model thermocouple with scale of 0.1 °C, at an accuracy within 0.4% of full scale and an Ashcroft model pressure transducer with scale of 0.5 psi, at an accuracy within 0.5% of full scale, were connected to the reactor for temperature and pressure measurements. The reactor had valves for injecting and venting the gas. It was placed into a water/ethylene glycol cooling medium and the temperature was adjusted using a controllable circulator.

### 2.3. Procedure

#### 2.3.1. Hydrate formation

The reactor pressure have been raised to 1600 psi with nitrogen inert gas and left for 24 h at 20 °C to ensure that the system pressure remains constant and consequently the reactor has no leak. Then the reactor was washed and rinsed with de ionized water and 75 $cm^3$ aqueous solution with specified concentration was charged into the reactor. The reactor was pressurized with methane to 1600 psi at room temperature. After reaching equilibrium at the initial temperature and pressure, the system was cooled to the hydrate formation temperature (275.2 K). The mixer was then started at a rate of 200 rpm to initiate hydrate formation. To obtain the amount of gas consumed during the process Eq. (1) was used:

$$n = \frac{PV}{ZRT} \tag{1}$$

P, V and T are the gas pressure, volume, and temperature respectively. R is the gas universal constant and Z is the compressibility factor obtained by Peng Robinson equation of state. For all experiments the hydrate formation was monitored for 30 h.

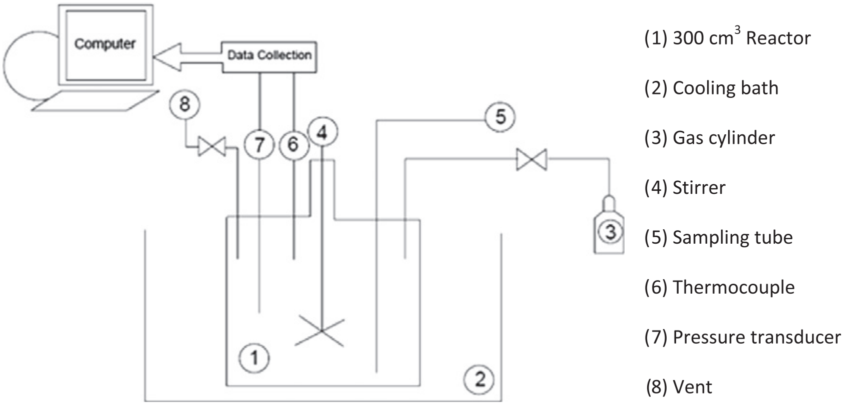

**Fig. 1.** Schematic diagram of the experimental apparatus.

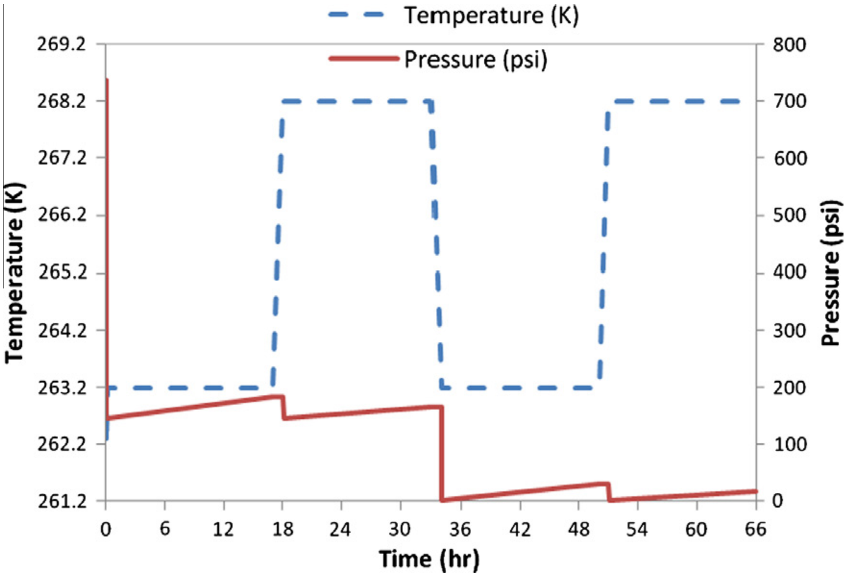

**Fig. 2.** Schematic diagram of the hydrate dissociation procedure.