



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Flow characteristics and rheological properties of natural gas hydrate slurry in the presence of anti-agglomerant in a flow loop apparatus



Ke-Le Yan^a, Chang-Yu Sun^{a,*}, Jun Chen^a, Li-Tao Chen^b, De-Ji Shen^a, Bei Liu^a, Meng-Lei Jia^a, Meng Niu^a, Yi-Ning Lv^a, Nan Li^a, Zhi-Yu Song^a, Shu-Shan Niu^a, Guang-Jin Chen^{a,*}

^a State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

^b Center for Hydrate Research, Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO, United States

HIGHLIGHTS

- Hydrate slurry presents obvious shear-thinning behaviour with increase of hydrate ratio.
- Hydrate slurry is transported as a solid dispersion system with addition of AAs.
- A Herschel-Bulkley-type equation was built by considering the hydrate volume fraction.
- Shutting-down/restarting tests show that the hydrate slurry is easily and safely restarted.
- Hydrate slurry exhibits obvious thixotropic behaviour with increasing shutting-down time.

ARTICLE INFO

Article history:

Received 28 July 2013

Received in revised form

22 October 2013

Accepted 10 November 2013

Available online 19 November 2013

Keywords:

Hydrate

Slurry

Rheological properties

Flow characteristics

Anti-agglomerant

ABSTRACT

The flow characteristics and rheological properties of natural gas hydrate slurry, with initial water cuts ranging from 5 to 30 vol%, were investigated in a flow loop. The experimental results indicate that the hydrate slurry can be considered a pseudoplastic fluid and presents more obvious shear-thinning behaviour with the increase in the hydrate volume fraction. The study on the fluid morphology demonstrated that the original structure of the water-in-oil emulsion is destroyed by the formation of gas hydrate, and the hydrate slurry is ultimately transported as a solid dispersion system. An empirical Herschel–Bulkley-type equation that considers the hydrate volume fraction was developed to improve the description of the rheological properties of the hydrate slurry. The apparent viscosities of the hydrate slurry calculated by the new equation were in accordance with the experimental data. Shutting-down/restarting tests using three shutting-down times (2 h, 4 h, and 8 h) were performed. The experimental results indicate that the hydrate slurry can be easily and safely restarted from the static state after a long shutting-down period and exhibits obvious thixotropic behaviour with increasing shutting-down time.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Gas hydrates are ice-like clathrate-type crystals in which cages of water molecules are stabilised by the host molecules (Sloan and Koh, 2008). During oil/gas exploitation, light alkanes, such as methane, ethane, and propane, can form gas hydrates with the water produced in pipelines under high pressure and relatively low temperature. The hydrate particles can agglomerate into hydrate plugs, which may cause total blockage (Gao, 2009). Recently, the problem caused by natural gas hydrate blocks has become increasingly severe with the increasing water depth of the offshore oil and gas pipelines. According to a survey, the annual

cost of preventing the hydrate issue is over U.S. \$200 million (Sloan, 2003) and accounts for 5% to 8% of the total product plant cost (Sloan et al., 2010; Chandragupthan, 2011).

Many approaches are used to prevent hydrate plugs (Kelland, 2006). The most common method used is the addition of thermodynamic inhibitors, e.g., methanol or ethylene glycol, which prevent hydrate formation by shifting the hydrate equilibrium curve toward higher pressures and lower temperatures to keep the operation conditions outside the hydrate stability region. However, the concentration usually required for these inhibitors to be effective is 30 to 50 wt% of the water mass. Such a high concentration requires a large amount of additives to be used, increasing the cost of project operation and requiring the reprocessing of wastewater. Low-dosage hydrate inhibitors (LDHIs), including kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs), have been researched and developed for many years as an alternative method to control gas hydrates (Kelland, 2006;

* Corresponding authors. Tel./fax: +86 10 89733156.

E-mail addresses: cysun@cup.edu.cn (C.-Y. Sun), gjchen@cup.edu.cn (G.-J. Chen).

Arjmandi et al., 2005). KHIs are a type of water-soluble polymer with functional groups that can be accommodated into clathrate hydrate cages. Unlike thermodynamic inhibitors, they can delay hydrate nucleation (usually crystal growth as well), providing sufficient time to transport the fluids to the process facilities before hydrate plugs build up in the pipeline. KHIs have been widely applied for hydrate inhibition in gas-dominated systems in Qatar and Iran, where the subcooling is low (< 10 K) and the subcooling maximum is seasonal (Creek, 2012). However, it is well-known that they may cease to function when the subcooling is over approximately 10 K (Mehta et al., 2003). AA molecules generally have a hydrophilic head and a hydrophobic tail. They allow gas hydrates to form but keep the hydrate crystals small and dispersed in the hydrocarbon phase. The hydrate crystals can then be transported as non-sticky hydrate slurry in the pipelines (Kelland, 2006; Huo et al., 2001).

Both KHIs and AAs are added at relatively low concentrations. Approximately 0.1 to 3.0 wt% of the aqueous phase is sufficient for KHIs and AAs (Kelland et al., 2006). Generally, the best AAs can perform at higher subcooling than KHIs (Kelland, 2006). For deeper-water applications, AAs may be the only choice. A number of AAs have been developed and tested in the literature (Kelland, 2006; Kelland et al., 2006; Peng et al., 2012). A high-performance AA enables hydrates to form as a transportable flow slurry of hydrate particles dispersed in the liquid hydrocarbon phase. However, the literature on flow characteristics and rheological properties of hydrate slurry is mostly related to the aqueous phase. For example, Wang et al. (2008, 2010) investigated the flow characteristics of tetrahydrofuran (THF) and refrigerant ($\text{CH}_2\text{Cl}_2\text{F}$ or HCFC-141b) clathrate hydrate slurry and developed a model to determine the safe flow of hydrate slurries. Delahaye et al. (2008) studied the rheological characteristic of CO_2 hydrate slurry using an experimental dynamic loop, and an empirical model was developed to describe its rheological behaviour. Delahaye et al. (2011) also studied the flow properties of CO_2 hydrate slurry in the presence of additives (EO/PO copolymer). Clain et al. (2012) investigated the rheological properties of tetra-*n*-butylphosphonium bromide (TBPB) hydrate slurry flow for hydrate fractions between 0 and 28.2 vol% and shear rates between 100 and 700 s^{-1} and deduced that TBPB hydrate slurries exhibit a shear-thinning behaviour. Darbouret et al. (2005) studied the rheological properties of tetra-*n*-butyl ammonium bromide (TBAB) hydrate suspensions and determined the apparent viscosity and yield shear stress for different hydrate contents. Hashimoto et al. (2011) studied TBAB and tetra-*n*-butylammonium fluoride (TBAF) hydrate slurries and showed that both systems present pseudoplastic behaviour. They also studied the effect of the surfactant on the flow properties of TBAB and TBAF hydrate slurries. Suzuki et al. (2013) studied the flow and heat transfer characteristics of ammonium alum hydrate slurries. Recently, Joshi et al. (2013) presented a detailed analysis of hydrate formation experiments performed in a 95-m-long flowloop (9.7-cm internal pipe diameter) in high-water-cut systems. They proposed a hydrate plugging formation mechanism, which involves the transition from a homogeneous suspension (region I) of hydrate particles to a heterogeneous suspension (region II), leading to increased particle interaction and agglomeration and ultimately causing the formation of a hydrate bed and wall deposit (region III).

Gas and oil generally coexist in multiphase transportation pipelines. However, there are only a few reports of studies on the flow characteristics and rheological properties of hydrate slurries formed from the liquid hydrocarbon phase. Using a high-pressure rheology apparatus, Webb et al. (2012) studied the in situ formation and flow properties of gas hydrates from a water/crude oil emulsion. Fidel-Dufour et al. (2006) investigated the crystallisation and rheology of a methane/water/dodecane system and demonstrated that it behaves as a Newtonian fluid. According to

the studies on the rheological and flow properties of gas hydrate suspensions, Sinquin et al. (2004) demonstrated that hydrate particle formation in the liquid phase modifies the flow properties and that the pressure drop is controlled by the friction factor under turbulent flow conditions or the apparent viscosity under a laminar flow regime. Shi et al. (2011) and Gong et al. (2010) investigated natural gas hydrate formation and growth at different water cuts for a water-in-condensate oil emulsion in a flow loop. Zyliftari et al. (2013) studied the salt effects on the rheological properties of a hydrate-forming emulsion. Recently, in our group, Peng et al. (2012) investigated the flow characteristics, shutting-down/restarting behaviour, and morphology of hydrate slurries formed from a (natural gas+diesel oil/condensate oil+water) system containing an anti-agglomerant. Based on the analysis of the rheology parameters and apparent viscosity of hydrate slurry during the formation of gas hydrate, they declared that the hydrate slurry exhibits shear-thinning behaviour and is a pseudo-plastic fluid. However, the range of shear rate studied in their work (Peng et al., 2012) was only from 120 to 360 s^{-1} , which is insufficient to accurately describe the rheology of hydrate slurry for a wider range of shear rates. In addition, the restarting effect from the static state is important for flow safety assurance in the pipeline. Peng et al. (2012) studied the restarting effect of hydrate slurry, but the shutting-down time only ranged from a few minutes to less than 1 h.

In gas/oil transport pipelines, the water cut is usually less than 30 vol%. In this work, the flow characteristics and rheological properties of hydrate slurry in a flow loop were examined for initial water cuts from 5 to 30 vol% and shear rates from 50 to 350 s^{-1} . A new type of anti-agglomerant, different from that of Peng et al. (2012), was added to these systems. The flow rate and pressure drop of the hydrate slurry formed were systematically investigated. The morphologies of the hydrate slurry at different stages were recorded and analysed. Combined with the experimental data, an empirical rheological model based on Herschel-Bulkley-type equation was proposed to describe the rheological behaviour of hydrate slurry. In addition, shutting-down/restarting tests with three different shutting-down times (2 h, 4 h, and 8 h) were performed for all water-cut systems to investigate the rheological properties of the hydrate slurry.

2. Experimental

2.1. Materials and apparatus

The experimental materials include water, diesel oil, natural gas, and an anti-agglomerant. Diesel oil, with a freezing point of 253.2 K, serves as the liquid oil phase, and its composition is shown in Table 1, as analysed by a crude oil true boiling point (TBP) distillation system. The natural gas used is the associated gas from an oilfield, and its composition was analysed by a HP7890A gas chromatograph and listed in Table 2. An anti-agglomerant patented by Chen et al. (2011) was chosen in this work, and its performance was assessed using a high-pressure sapphire cell. It is well known that the produced water contains salt; therefore, a 0.81 wt% NaCl aqueous solution was prepared and used as the aqueous phase in the experiments.

The experimental flow loop illustrated in Fig. 1, similar to that described in our previous work (Peng et al., 2012; Shi et al., 2011), was used to measure the flow characteristics and rheological properties of natural gas hydrate slurries with six different initial water cuts from 5.0 to 30.0 vol%. It mainly consists of a U-bend double pipe (20 m long and 25.4-mm inner diameter) made of 316 L stainless steel, with a maximum operation pressure of 10.0 MPa. The pipes were maintained at constant temperature

Download English Version:

<https://daneshyari.com/en/article/155004>

Download Persian Version:

<https://daneshyari.com/article/155004>

[Daneshyari.com](https://daneshyari.com)