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Viscosity investigation of natural gas hydrate slurries with anti-agglomerants additives

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HIGHLIGHTS

- Viscosity of natural gas hydrates slurry is investigated with anti-agglomerants.
- Hydrates slurry viscosity model is developed based on Einstein effective medium theory.
- Empirical correlations for non-Newtonian coefficient is extracted from experimental data.
- Aggregation and broken of hydrates particles was considered by four dimensionless parameters.

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ABSTRACT

The viscosity of natural gas hydrates slurry in high-pressure hydrates slurry rheological measurement system is investigated, which is meaningful for hydrates risk management to solve flow assurance issues in deep-water offshore field. Based on an appropriate stirring speed and time, a relatively uniform and stable hydrates slurry were formed from a water-in-oil emulsion to study the hydrates formation and slurry viscosity under different water cuts, bath temperatures and AAs concentrations. The influence of water cut on hydrates formation and hydrates slurry viscosity is much more significant than that of bath temperature and AAs concentration. Results indicate that the hydrates volume fraction, the continuous liquid phase viscosity and the dispersion degree of hydrates particles in the slurry are the critical factors to affect the viscosity of natural gas hydrates slurry. Considering both of aggregation and breakage of hydrates particles, a natural gas hydrates slurry viscosity semi-empirical model is developed based on the Einstein effective medium theory. The key parameter non-Newtonian coefficient K of this model is determined by several empirical correlations according to the experimental conditions and fluid properties. The consistence of predicted and experimental data demonstrates the feasibility of this model.

1. Introduction

Gas hydrates consist of light molecules or volatile liquid molecules (e.g., methane, ethane, hydrogen sulfide, nitrogen, cyclopentane and so on) encaged by water molecules at a certain pressure and temperature condition [1,2]. With the increase of the exploitation depth of petroleum resources in deep-water from 100 m in the 1970 s to 3500 m in 2012 [3], the complex environment of high pressure and low temperature in subsea pipeline is an ideal condition for hydrates formation. Once hydrates form in the petroleum transportation system, the risks of plug and blockage in pipelines, valves or other processing equipment will increase because of the agglomeration and deposition of hydrates particles [4].

The traditional method to avoid hydrates problems in petroleum industry is mainly to prevent hydrates formation by thermodynamic inhibitors injection or insulation [2,4]. However, the high cost and obvious technical limitation of the traditional methods are serious with the increase of depth in offshore petroleum exploitation [5]. An alternative method of hydrates risk management has been proposed to prevent hydrates plugging in the subsea gathering and transportation system by cold flow without additives or

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Nomenclature

a	coefficient of correlation
b	coefficient of correlation
d	diameter, m
f	function of non-Newtonian coefficient
f_1	sub function of non-Newtonian coefficient
f_2	sub function of non-Newtonian coefficient
K	non-Newtonian coefficient
M	molecular weight, g/mol
N	dimensionless number
n	accumulated natural gas consumption at time t, mol
p	pressure, MPa
R	gas constant, J/(mol·K)
t	time, s
T	temperature, K
V	volume, m^3
z	the compressibility factor in real gas law

Greek symbols

β	hydration number
η_r	relative viscosity
μ	viscosity, Pa·s
ρ	density, kg/m^3
φ	hydrates formation volume fraction
ϕ	water cut
$\dot{\gamma}$	shear rate, 1/s

Subscript/superscript

0	initial point of time, at t = 0 s
A	agglomerate
eq	equilibrium
g	natural gas
H	hydrates
L	liquid phase
num	number
max	maximum volume
Re	Reynolds number
s	hydrates slurry
t	time
t_Hyd	time for hydrates formation onset
o	continuous oil
w	water
We	Weber number

injecting low dosage hydrates inhibitors, including Kinetics Hydrates Inhibitor (KHI) and Anti-agglomerants (AAs) [6–8]. The objective of cold flow or with AAs injection is to allow the hydrates formed and transported with the liquid fluid as hydrates slurry. However, the viscosity of hydrates slurry will increase with the presence of hydrates particles in the liquid phase, which will affect the transmission capacity of multiphase system. Therefore, it is important to investigate the hydrates slurry viscosity for the application of hydrates slurry technology to prevent hydrates plugging in subsea pipelines.

Many researchers [9–14] investigated the viscosity of hydrates slurry formed by using TBAB, TBAF, TBPB, and THF as guest molecules for the application of hydrates technology in refrigeration field at a lower pressure condition. All the results manifested that a shear thinning phenomenon for the TBAB, TBAF, TBPB, and THF hydrates slurry was observed, which could be described by different rheological models such as Bingham or Power Law or Herschel-Bulkley models. Because of the tough hydrates formation condition of natural gas, high pressure equipment is required to study the rheological property of natural gas hydrates slurry by experimental method, such as high pressure flow loop or high pressure rheometers. Generally, the Hagen-Poiseuille equation and Rabinowitsh-Mooney equation were used to calculate the viscosity of natural gas hydrates slurry in different high-pressure flow loops [15–22]. And, different high-pressure rheometers, such as Physica UDS200 [23,24], Physica MCR500 [23], AR-G2 [25–27], Physica MCR301 [28], were used to measure the viscosity of natural gas hydrates slurry directly. Based on the experimental data of high-pressure apparatus, the behavior of shear thinning even thixotropy of natural gas hydrates slurry were found. And, the Power Law [19–21,23–25], Herschel-Bulkley [28], and Cross [27] constitutive equations were widely used to develop the viscosity model for natural gas hydrates slurry, where the consistency coefficient or rheological index of the constitutive equations were regressed based on the experimental data.

Being as a complex suspension system, the influence of aggregation and breakage of the hydrates particles under flow condition was critical and could not be ignored to study the viscosity of natural gas hydrates slurry, because the natural gas hydrates agglomerates with the size of nearly 100 μm were observed in the system consisting of natural gas hydrates particles about 30–40 μm [24]. Based on the classical Einstein's calculation of the viscosity for a dilute suspension of spheres [29], lots of efforts had been devoted to the extension of the Einstein viscosity equation with the effective medium theory for considering the particle correlations in concentrated suspensions of natural gas hydrates slurry [10,30–37]. Camargo and Palermo [22] put forward a viscosity prediction method by taking the aggregation of natural gas hydrates particles into account, where the size of the hydrates particle agglomerates was determined by the balance of shear stress and the cohesion force between particles. An improved model with a population balance model was developed by Palermo et al. [33] and Fidel-Dufour et al. [34] for describing the coalescence process of the hydrates particles. Colombel et al. [35] proposed a model considering both of aggregation and breakage of hydrates particles. A bimodal model for predicting the emulsion-hydrate mixture viscosity in high water cut systems was developed by Moradpour et al. [38] modified the Mills [32] equation based on the Pal [39] equation with the anti-agglomerants concentrations ranging from 0.15 wt% to 2 wt%. However, the influence mechanism of agglomeration and breakage of hydrates particles on the viscosity of natural gas hydrates slurry should be investigated further to make it clear.

In this paper, a high-pressure hydrates slurry rheological measurement system have been designed to measure the viscosity of natural gas hydrates slurry containing AAs, including a gas pressurization system, a high-pressure mixing autoclave reactor, a hand metering pump and a high-pressure rheometer. Based on an appropriate stirring speed and time, a relatively uniform and stable hydrates slurry were formed from a water-in-oil emulsion to study the hydrates formation and slurry viscosity under different water cuts, bath temperatures and AAs concentrations. And, a semi-empirical viscosity prediction model of natural gas hydrates slurry is developed based on the effective medium theory considering the influence of the agglomeration and breakage of hydrates particles on the viscosity of natural gas hydrates slurry.