Ocean Engineering 112 (2016) 16–24

Contents lists available at ScienceDirect

Ocean Engineering

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

Simulation of gas bubbles with gas hydrates rising in deep water

Changjun Li [a,b], Ting Huang [a,*]

[a] School of Petroleum and Natural Gas Engineering, Southwest Petroleum University, Chengdu 610500, China
[b] CNPC Key Laboratory of Oil and Gas Storage and Transportation, Southwest Petroleum University, Chengdu 610500, China

ARTICLE INFO

Article history:
Received 28 February 2015
Accepted 6 December 2015
Available online 17 December 2015

Keywords:
Gas bubbles
Hydrate shell
Deep water
Models
Longevity
Hydrate-coated area ratio

ABSTRACT

It is essential to evaluate the effect of gas bubbles rising in deep water from the place where thermodynamic conditions are favorable for gas hydrates formation. Considering the bubble surface morphology, a gas bubble fate simulation model was established which integrated bubble hydrodynamics, gas dissolution, the thermodynamic and kinetic stability of gas hydrates. Hydrate-coated area ratio was a key parameter. The model was applied to simulate methane bubbles in 1500–5000 μm radii released at 1000–2000 m in Monterey Bay Canyon and South China Sea. Reliable simulation results were helpful for further research on deep water environment.

1. Introduction

In recent years, because of the blowouts of offshore oil and gas drilling, the leakage of pipeline transportation and the instability of submarine gas hydrate resources, gas bubbles rising in deep water began to attract wide attention. Specifically, with the development of onshore oil and gas fields going into the semi-late period (Maggio and Cacciola, 2012), emphasis of fossil fuel exploration has transferred to ocean, especially to the deep and ultra-deep water regions where water depths are larger than 400 m (Muehlenbachs et al., 2013). Leakage happened during the production process due to the unavoidable pipeline corrosion, the undetected welding defects and other uncertain factors. Gas bubbles would form and ascend under such circumstances. On the other hand, it was estimated that the global amount of hydrate-bound methane gas ranged from 0.2×10^{15} to 3053×10^{15} m^3 at standard temperature and pressure (STP), and about 98% of the gas hydrates distributed in seafloor areas (Milkov, 2004; Sloan and Koh, 2007; Song et al., 2014). Free gases, which are similar to that of gas hydrates in magnitude, exist below the hydrate stability fields (Buffett and Archer, 2004). Factors like gas hydrate resources exploitation, climate change and earth plate movement could lead to gas hydrates decomposition and the release of free gases (Egorov et al., 2014; Fischer et al., 2013). Consequently, gas bubbles come up and rise in the deep water.

The process of gas bubbles rising in deep water is quite complicated because: (1) thermodynamic condition changes along the whole journey; (2) gas bubble velocity in vertical direction varies with radius; (3) gas expansion happens in the period of getting close to water surface; (4) gas dissolution in seawater leads to the bubble mass reduction. However, the most dramatic effect is gas hydrates formation.

Gas hydrates are crystalline inclusion compounds in which water cages trap light hydrocarbon species (e.g., CH_4, C_2H_6, C_3H_8). Gas hydrates mainly have three structures: structure I, structure II and structure H (Sloan and Koh, 2007). Three basic conditions for hydrate formation are: water-saturated gas, low temperature and corresponding high pressure. Fig. 1 presentes the three-phase equilibrium line of methane gas hydrate in deep water. Also shown were the relationships between water temperature and depth in Monterey Bay Canyon (Rehder et al., 2009) and South China Sea. These two places are both particularly rich in oil, gas and gas hydrate resources. The intersection point of temperature line and three-phase equilibrium line is defined as the critical point. Depths of the two critical points in Fig. 1 are 637 m and 548 m for South China Sea and Monterey Bay, respectively. If a gas bubble is released below the critical point, it is considered that hydrate formation conditions are satisfied.

Some researchers have made efforts to understand gas bubble behaviors with hydrates for years. Initially, stationary natural gas bubbles in 0.8–2.7 cm diameters were generated in an opposing water flow to simulate the process of gas bubbles ascending in deep water (Maini and Bishnoi, 1981). Later, more and more experiments verified the phenomenon that gas bubbles rising in deep water would couple with hydrate particles (Egorov et al., 2014). Several mathematical models were also presented to simulate hydrocarbon gas bubbles rising in ocean based on experiments (Topham, 1984; Yapa and Chen, 2004; Yapa et al.,

---

[*] Corresponding author.
E-mail address: huangtingswpu@163.com (T. Huang).

http://dx.doi.org/10.1016/j.oceaneng.2015.12.002
0029-8018/© 2015 Elsevier Ltd. All rights reserved.

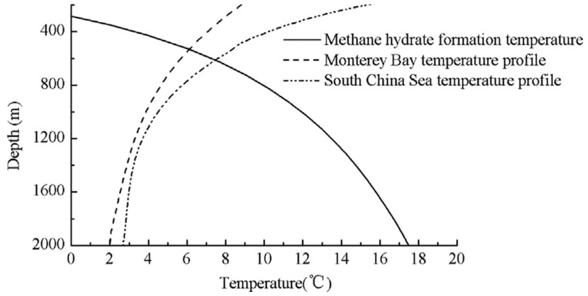

Fig. 1. Three-phase equilibrium line of methane gas hydrate in seawater. Also shown are the temperature profiles in Monterey Bay Canyon and South China Sea.

2001; Zheng and Yapa, 2000, 2002). Among them, a comprehensive model established by Yapa et al. (2010) included the initial jet/plume stage. Numerical bubble-propagation models generally involved factors like kinetics of gas hydrate formation and decomposition, mass and heat transfer, bubble shapes and gas dissolution. The bubble release depths extended from several hundred meters to about 1500 m (Rehder et al., 2002, 2009). Agreement was reached that in gas hydrate stability field, the formation of gas hydrates enhanced gas bubble lifetime markedly (McGinnis et al., 2006; Römer et al., 2012; Rehder et al., 2002, 2009). However, limited by current achievements in intrinsic mechanism of gas hydrates formation on the surface of gas bubbles under deep water condition, most models were not able to consider bubble surface features. Recently, focus is put on the complex bubble surficial mechanism that governs gas hydrates formation and dissociation (Warzinski et al., 2014). New insight was obtained about the synergistic feedbacks between gas bubble hydrodynamics, hydrate morphology and coverage characteristics.

In this paper, based on the latest experimental observations on bubble rise process and achievements in underlying mechanism of gas hydrate formation, a model was established to simulate the fate of individual methane bubbles rising in deep water coupled with gas hydrates. Our model considered gas bubble hydrodynamics, the thermodynamics and kinetics of gas hydrate, gas non-ideal and dissolution properties. Hydrate-coated area ratio was put forward as a key parameter. This model was applied to simulate gas bubbles in 500–5000 μm radii released at depths of 1000–2000 m. Model simulation results were compared to experimental data obtained by previous researchers (Maini and Bishnoi, 1981; Rehder et al., 2002, 2009; Warzinski et al., 2014). Our research subject was one separate gas bubble, not a gas bubble cluster. So, this model is not for jet/plume stages.

2. Gas bubble behavior description

When gas blows out in deep water, gas bubbles appear in radii of 500–5000 μm (Leifer, 2010). Gas hydrates are supposed to form on the surface of gas bubbles if they are released below the critical depths as mentioned in Section 1. In some cases, there is a delay before gas hydrates begin to grow macroscopically (Englezos et al., 1987). The delay can be explained as the induction time for nucleation which is strongly related to the degree of super-cooling. But when the depth was greater than 1511.4 m while the corresponding super-cooling was larger than 12.3 °C, no delay was observed in Monterey Bay Canyon (Rehder et al., 2009). Following are phenomena observed in experiments (Chen et al., 2013; Egorov et al., 2014; Rehder et al., 2002; Warzinski et al., 2014).

Gas hydrates presented on bubble surface in the shape of hydrate shells or hydrate needles/plates (Chen et al., 2013). Whether hydrate shells form or not is determined by hydrate formation rate and hydrate dissolution rate (Servio and Englezos, 2002). If the dissolution rate is higher than the formation rate, hydrate shells would not form. Moreover, gas hydrate dissolution rate is determined by the chemical potential difference of gas in hydrate and water phase, while the chemical potential is strongly related to gas concentration. So, full hydrate shells are not likely to grow in ambient seawater because of the low gas concentration. For example, methane concentration in seawater is on the order of 1 nmol/L, much lower than the required value of 0.0018 mol fraction for hydrate formation under methane-water-hydrate three phase equilibrium at 8.8 °C, 6.59 MPa (Tsimpanogiannis et al., 2014). Instead, hydrate needles and plates form at the edge of gas bubbles.

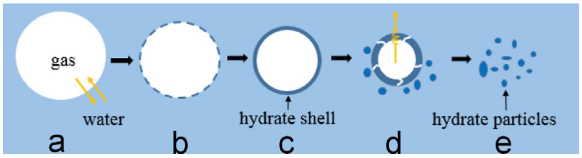

Fig. 2. Schematic diagram of gas bubble behaviors with gas hydrates in rising process.

However, when the driving force for hydrate formation is pretty strong, shells can still form (Egorov et al., 2014). The formation driving force is commonly defined as the fugacity difference of dissolved gas in operation and three-phase equilibrium thermodynamic conditions (Sloan and Koh, 2007). At first, discrete clusters grow and float on the bubble surface (Fig. 2(b)). After a while, these clusters fuse into a thin hydrate shell surrounding the bubble (Fig. 2(c)). As the shell thickens, small hydrate particles begin to shed (Fig. 2(d)). Cracks appear as soon as the hydrate shell forms. These cracks are hypothesized to play an important role in latter mass transfer. During the ascending process, even if the environmental pressure is higher than the three-phase equilibrium pressure to about 2 MPa, increased cracking happens because of bubble movement (Warzinski et al., 2014). Hydrate shells separate into distinct, plate-like structures. So, the hydrate-free bubble surface area enlarges.

Gas in the bubble is consumed in two ways: hydrates formation and gas dissolution. Since gas hydrates are porous and can not isolate gas from water completely (Chen et al., 2013), we guess that gas molecules can still dissolve in water even if hydrates cover on the bubble. But compared to no hydrate condition, gas molecules have to travel through a tortuous path (Fig. 2(d)), thus the gas dissolution rate reduced to a large degree. It is hard to quantify the interaction between hydrates formation and gas dissolution. For better simulation, hydrate-coated area ratio was introduced in our model to describe gas bubble surface feature.

When gas bubbles enter into the hydrate instability zone, hydrates begin to decompose. If hydrate shells exist, cracking becomes more severe. Hydrate shells separate into distinct, plate-like structures dramatically (Warzinski et al., 2014). Furthermore, hydrate needles and plates break into many small particles. Released gas molecules from hydrates soon dissolve in water. Less gas hydrates cover on the bubble surface, which leads to a faster gas dissolution rate. Eventually, the remained free gas is consumed through dissolution and gas bubble disappears (Fig. 2(e)).

3. Model description

This section derived a model to simulate the fate of gas bubbles with gas hydrates rising in deep water. The model considered in-situ temperature condition and transient bubble velocity in vertical direction instead of supposing the two parameters to be fixed values. Assumptions were made that: (1) heat transfer resistance was negligible; (2) no pressure gradient existed between gas