A review on simulation of methane production from gas hydrate reservoirs: Molecular dynamics prospective

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ABSTRACT

Hydrate reservoirs have steadily emerged as an important contributor in energy storage. To better understand the role of hydrates in gas production, it is vital to know the challenges related to the hydrate dissociation. To highlight the main technical challenges, further research and engineering investigations are needed for interactions between the molecules, phase behaviours, and detailed mechanisms of hydrate formation and dissociation. This review paper describes the gas hydrate reservoirs, hydrate dissociation, and previous research works related to gas engineering. This study briefly presents the key theoretical concepts and drawbacks of different techniques/kinetics of decomposition; consisting of depressurising, thermal stimulation, chemical injection, and gas swapping. This will be followed by the theory on the molecular dynamics simulation and its application in various decomposition methods. Owing to the limitations of existing experimental and theoretical approaches, development of more accurate theoretical models and equations of state (EOSs) is inevitable. The molecular dynamics simulation strategy has been used as a strong research tool with adequately small scales in both space and time. The practical implication of molecular dynamics (MD) simulation in hydrate dissociation methods is illustrated at the end of this study for further clarification. The complex nature of hydrates clearly implies that new potential functions for current MD tools are required to satisfactorily comprehend the hydrate molecular structure and mechanisms of hydrate decomposition.

1. Introduction

Sir Humphry Davy discovered the hydrate in 1810. He observed that a crystalline solid was created by an aqueous solution of chlorine when it was cooled. Then, in early 1820, John Faraday conducted some experiments that confirmed the Davy's results. However, it remained a matter of "academic" enthusiasm, until Hammerschmidt (1934) claimed in 1934 that hydrates (as the main reason) are responsible for obstruction of gas and oil transportation in pipeline systems. Since then, the hydrate inhibition methods have been persistently tested through various research activities by scientists across the world (Wu et al., 2007; Huo et al., 2001; Seo and Kang, 2012; Lee and Englezos, 2006; Fair, 1967; Urdahl et al., 2003; Gengliang, 2004). In this field of research, apart from the gas hydrate formation conditions, the impacts of inhibitors on the equilibrium conditions have been widely studied. The soaring cost of hydrate inhibition has been one of the important concerns in the gas and oil energy sectors since 1970.

Gas hydrates are solid ice-like substances formed from water when the natural gas (e.g., mainly methane) combines with water under high-pressure and low-temperature conditions. As the gas hydrates contain a vast quantity of methane gas and globally occur in profound water and permafrost areas, they can provide a viable (and additional) energy resource (Collett et al., 2009). Natural gas hydrates (NGHs) are non-stoichiometric compounds which are made of water molecules at particular thermodynamic conditions, depending on the temperature, pressure, and composition. Each standard cubic meter of NGH can result in approximately 160–180 cubic meters of natural gas under normal conditions (Sloan and Koh, 2007).

The best conditions required for gas hydrate formation are usually low temperatures (<300 K) and high pressures (>0.6 MPa) (Sloan, 1998, 2003). Hydrate structures are classified into three categories, depending on the size of guest molecules, and type and number of cavities that cause water molecules to change their arrangements. These three common structures are called structure (type) I (Pauling and Marsh, 1952), structure (type) II (Claussen, 1951), and structure (type) H (Ripmeester et al., 1987). The most significant structural differences between various classes of hydrates are summarized in Table 1. The unit cell of structure I hydrates includes two types of cavities; namely, two small pentagonal

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cavities known as dodecahedrons (5^{12}), and six larger cavities which are named tetrakaidecahedron ($5^{12}6^2$) (Khan, 2001). Table 1 demonstrates that the small cavity is approximately spherical, due to a low amount of change in the radius of 3.95 and 3.91 Å in types I and II of hydrates, respectively (Sloan, 2003). The structure I of hydrates is usually created by one guest molecule such as carbon dioxide, ethane, and methane. A unit cell of structure II comprises 136 water molecules which include 16 small cavities (5^{12}) and 8 large cavities ($5^{12}6^2$) (Wu, 1994). Structure H contains small, large, and $4^35^66^3$ cages. The formation of structure H hydrates requires two molecules; including, a large organic guest molecule (such as neohexane), and a help gas (such as methane) (Shin et al., 2012). Fig. 1 displays the detailed information on the hydrate crystal cell structures. In all types of hydrates, maximum one guest molecule generally can be resided in each cage. Even for severe cases (e.g., extremely high pressures), there is a possibility of having multiple-cage occupancies, with uncommon small guests like hydrogen or/and xenon (Sloan, 2003).

More than 27 percent of the land (e.g., mainly freezing rocks) and 90 percent of the sea have the potential to contain gas hydrate reserves (Kvenvolden, 1998). Moreover, the changes of pressure and temperature in longer distance especially in pipeline systems are more favorable conditions for hydrate formation. Therefore, it is vital to offer an economical, effective, and safe operation in the gas and oil production sites. Generally, the phase equilibrium of a gas hydrate is investigated through various operational strategies such as depressurising and thermal stimulation. According to this approach, the exploitation procedures of a gas hydrate can be arranged as depressurisation, thermal stimulation, chemical injection, and gas swapping (Burshears et al., 1986). Recent studies illustrate that the depressurisation method (when the pressure of the deposit is decreased to a value lower than the dissociation pressure at the dominant temperature) is the most promising technique for hydrate dissociation (Demirbas, 2010; Kurihara et al., 2008; Moridis, 2002; Liu et al., 2008). Although the hydrate formation and decomposition conditions have been investigated by some researchers at various conditions, further experimental and theoretical studies on the hydrate kinetics and gas hydrate decomposition should be carried out to understand the phenomenon mechanisms. For instance, the hydrate formation and decomposition have been studied by researchers to investigate a variety of key aspects such as synthetic seawater calculation, formation and decomposition kinetics of hydrates in different solutions (e.g., ionic and non-ionic liquids), decomposition enthalpies, formation conditions for the refrigerants in aqueous solutions, gas consumption in formations, and induction time in the bentonite clay suspension systems (Kakati et al., 2015; Kondori et al., 2013; Saw et al., 2012; Nazari et al., 2013; Saw et al., 2014; Ngema et al., 2016a; Saw et al., 2013).

Molecular dynamics (MD) is an interesting and efficient computer simulation method. A deep understanding of microscopic mechanisms can be achieved through MD simulations. MD simulation technique has been proven as a powerful research tool to analyze the behaviour of complex systems so that it gives information on structural and dynamical properties at the molecular level. It involves solving the classical equations of motion in the system. MD simulation studies of NGH have evolved during the past years (Moon et al., 2003; Zhang et al., 2008; Freer and Sloan, 2000; Storr et al., 2004).

The present work focuses on important aspects (e.g., hydrate dissociation, and methane production) of gas hydrate reservoirs which have been highlighted in the literature over recent years. In fact, it provides a brief review of hydrate dissociation under depressurisation, thermal stimulation, inhibitor injection, and gas swapping. In addition, the article investigates the various features of molecular dynamics simulations including main governing equations, assumptions, and potential functions concerning the decomposition of methane hydrate.

2. Gas hydrate reservoirs

Global energy demand is continuing to rise. There has been an increased interest in hydrates as an energy source, because gas hydrates are more available than other resources in the world and many governments/countries can benefit from them. In addition, the production cost for hydrate reservoirs is only 10–20% more than the cost for the standard (conventional) natural gas production technologies (Makogon et al., 2007). Knowing the fact that in the late 21st century there will be a sharply decline in hydrocarbon resources because of the human population growth, hydrate reservoirs seem to be a promising energy resource in the near future. Hydrates can be considered as a huge source of natural gas, because one cubic foot of solid gas hydrates contains an amount of gas which is 150–170 times higher, compared to one cubic foot of the corresponding natural gas at the standard conditions (Gudmundsson et al., 1994). Hence, by altering gas to the hydrate, a massive volume of gas can be stored under special temperature and pressure conditions (Masoudi and Tohidi, 2005).

The volume of gas hydrates and types, elastic, and petrophysical properties of the sediments/rocks appear to be vital to describe gas hydrate reservoirs (Holbrook et al., 1996). Holbrook et al. (1996) showed that the lower limit of gas hydrate stability (e.g., bottom-simulating reflector, BSR) is found in about 450 m below the seafloor (mbsf). There are diagenetic carbonates as nodules and lamina in upper and lower limits of the BSR without the mineralogical or sedimentological interruption. The mineralogy and composition of these diagenetic carbonates in equilibrium state should be used to determine the formation conditions of gas hydrates (Pierre et al., 2000). In the Blake Ridge, the thickness of diagenetic carbonate sediments (nodules or/and laminae) has been reported to be within the range of 1–10 mm (Paull et al., 1996). In addition, there are some small cubic crystals of sulfide components such as pyrite. Pierre et al. utilized scanning electron microscopy (SEM) and transmission electron microscopy (TEM) tests to characterize the crystals of smear slides (Pierre et al., 2000). Based on the tests results, they observed that the hexagonal structures in the forms of single, twinned, and aggregated crystals are smaller than 1 μm (Pierre et al., 2000). Kvenvolden et al. (Brewer et al., 1998) conducted a research work on the oxygen isotopic compositions of the diagenetic carbonates. They demonstrated that the gas hydrates formation occurs in the BSR upper limit of all sedimentary sections.

According to the geophysical methods, it has been proved that methane hydrates are available throughout the world's oceans, primarily on the continental shelves (Fig. 2) (Pinero et al., 2013). Fig. 2

Table 1
Parameters of three popular hydrate structures (modified after reference (Sloan, 2003)).

Hydrate crystal structure	I		II		H		
Crystal type	Cubic		Cubic		Hexagonal		
Space group	Pm3n (no. 223)		Fd3m (no. 227)		P6/mmm (no. 191)		
Lattice parameter	α = 12 Å		α = 17.3 Å		α = 12.2 Å, c = 10.1 Å		
	$\alpha = \beta = \gamma = 90°$		$\alpha = \beta = \gamma = 90°$		$\alpha = \beta = 90°, \gamma = 120°$		
Number of waters per unit cell	46		136		34		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Coordination number	20	24	20	28	20	36	