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Gas hydrate formation condition: Review on experimental and modeling approaches

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ABSTRACT

Hydrate behavior has been under continuous investigation and so far numerous experimental and modeling examinations have been published since its discovery. In addition, the emergence of new hydrate applications – e.g. energy recovery, gas separation, storage, and transportation – had led scientists toward conducting new and more detailed studies on different aspects of it. It is estimated that in the months at the very beginning of 2013, over 150 hydrate entitled papers were published. In case of studying each hydrate related fields; the issue which should be considered first is formation condition of hydrate. Therefore, this topic has allocated an immense number of articles to itself. This review is intended to overview and classifies the critical studies on hydrate equilibrium condition and reveals the aspects in which still further investigations are required.

1. Introduction

Importance of overcoming flow assurance problems in pipelines ignited interest of researchers to start serious studies on various aspects of gas hydrate. After that, novel applications, such as energy recovery [1–3], storage and transportation [4,5], and gas separation [6,7] caused gas hydrate to be under continuous investigations during the past century. Fig. 1 depicts how number of publications increased significantly over the 20th century [8]. According to this figure that was provided by Sloan [8], each application of hydrate would considerably increase the number of publications and with extrapolating the plot into current date the number of publications will go beyond 11,000 per decade, which means more than 3 publications per day. Therefore, authors of this paper feel that there is ever-increasing demand for reviewing critical areas in hydrate studies such as its thermodynamic behavior.

Hydrate was first discovered by Sir Humphry Davy in 1810 and then approved by experiments done by John Faraday in early 1820 [9]. However, it remained only an academic and laboratory matter of interest, until Hammerschmit [10] mentioned hydrate as the responsible component for oil and gas transport line blockage in 1934. Since then, hydrate prevention methods have been under constant investigations by scientists [11–17]. In this field of study, besides the formation condition of gas-hydrate, the effects of inhibitors on equilibrium conditions have been widely investigated. One of the main concerns in oil and gas industry has been the increasing cost of hydrate inhibition since 1970. With a simple rule of thumb Koh et al. [18] showed that five million dollars per year is needed for methanol injection to prevent hydrate formation in flow lines.

The Greek word “Khlatron” meaning barrier is the main origin of term “Clathrate” [19]. Clathrate hydrates are crystalline solids formed by cage-like water molecules combined with guest gas molecules (i.e. methane, ethane, propane, and carbon dioxide). The hydrate guest molecules usually have small size (<0.9 nm). Nevertheless, there are 130 gas molecules known to form hydrate [20]. The ideal conditions for hydrate formation are usually high pressure (>0.6 MPa) and low temperature (<300 K) [21,22]. Fig. 2 demonstrates the phase diagram for some gas hydrate formers. The pressure–temperature stability zone of gas-hydrate for each system is shown in this phase envelope as if in left section of each line (that represents low temperature and high pressure), the gas hydrate exists.

Three different structures of hydrate are known, based on the type and number of cavities and various sizes of guest molecules which causes the different arrangements of water molecules in turn. These three structures are named structure I (sI) [23], structure II (sII) [24], and structure H (sH) [25]. Table 1 summarizes the major differences between various types of hydrate structures [22]. Couple types of cavities are present in one unit cell of hydrate sI hydrate, two small pentagonal dodecahedron (5^{12}) and six larger cavities which are called tetrakaidecahedron ($5^{12}6^2$) [26]. Hydrates in the category sI are formed by a single guest molecule such as methane, ethane or carbon dioxide. In sII, 136 water molecules

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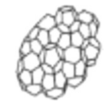
Table 1
Main properties of three common hydrate structures [22].

Hydrate crystal structure	I		II		H		
							
Cavity	Small	Large	Small	Large	Small	Medium	Large
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (A)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Coordination number	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		
Crystal type	Cubic		Cubic		Hexagonal		

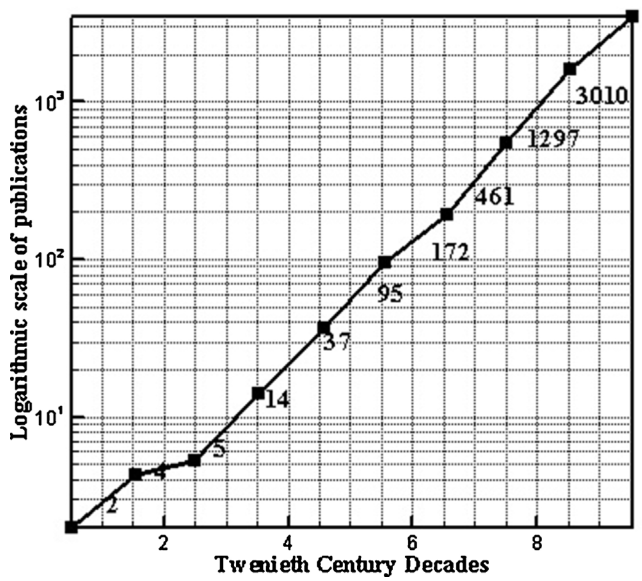


Fig. 1. Logarithmic demonstration of hydrate related publication per decade in the 20th century [8].

form 16 small (5^{12}) and 8 large cavities ($5^{12}6^2$) [27]. Structure H consists of 5^{12}, $5^{12}6^8$ and $4^35^66^3$ cages. The coexistence of a help gas and a large organic guest molecule is required for formation of sH hydrate [28].

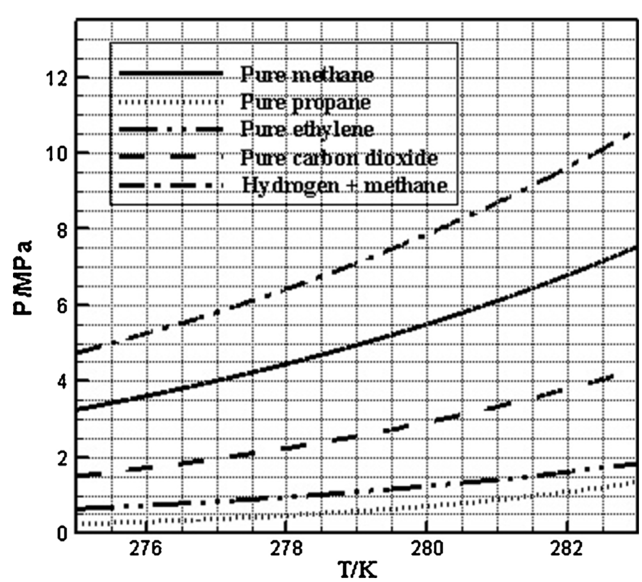


Fig. 2. Phase diagram of pure methane [21], propane [41], ethylene [65], carbon dioxide [76], and mixture of hydrogen and methane hydrate [75].

Over the past decade studies on hydrate were conducted, not only on its prevention but also on investigating the most efficient methods to use it as gas storage [29–32] and transmission method [33], or even as separation technology [7,6,34–37]. However, due to the slow rate of gas-hydrate formation and the need for low temperature and high pressure for its formations, industrial units are facing major difficulties in order to utilize hydrate in abovementioned applications [38]. Therefore, study on hydrate promoters has become one of great research interest. These promoters are classified into water soluble and insoluble groups. Detailed description of these groups is not in scope of this paper, although could be found widely in the literature [39–45].

Moreover, there has been an increasing interest in studying hydrate as energy resource recently [46]. Firstly, because it is more distributed than other resources and many countries can benefit from them. Secondly, producing from hydrate reservoirs cost only 10–20% more than conventional gas fields in the same area [3]. Furthermore, considering this fact that until the late 21st century there will be significant decrease in fossil fuels due to increasing number of population, many researchers have studied hydrate reservoirs as promising future energy resources.

Hydrate could be considered as one method for large-scale gas storage. This is because in standard condition, the volume that gas hydrate occupies is 150–170 times less than the volume of gas hydrate former [47]. Therefore, by bringing the gas to the hydrate condition, huge amount of it could be stored in that specific pressure and temperature condition. In addition, by hydrate self-preservation property which makes it possible to remain stable even in atmospheric pressure, the gas transportation also could be considered [48].

Following the dramatic increase in fossil fuels consumption, not only energy crisis is a great matter of concern, but also the accumulation of CO_2 in atmosphere, which is becoming the main threat for earth habitats. For reducing the concentration of carbon dioxide in atmosphere, its capture and disposal by hydrate has been studied by several researchers recently [6,49–57]. Carbon dioxide and water are combined at the hydrate formation condition in this technology and after hydrate formation occurred the solid will be transported to the depths of the ocean.

In addition to the aforementioned areas, hydrate is also considered as a geohazard that can threaten human welfare, because in profound layers of earth methane and water are free to move along the porous media before hydrate formation. However, after hydrate formation each layer will be clogged by solid hydrate. These phenomena take place as deep as the layer with a temperature at which solid hydrate is not stable in it. Therefore, there will be an unconsolidated layer under those occupied by hydrate and can be overpressured due to newly released gas. Failure could be triggered by gravitational loading or seismic disturbances [58].