Natural gas hydrate, fundamentals, methods of analysis of hydrate cage structures and applications as an energy source

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Abstract

Nowadays, natural gas hydrates are considered as a potential energy source capable of contributing to the global energy demand and as a possible replacement of different conventional energy sources such as coal or oil. Knowledge of the fundamental concepts, the methods of analysis of the hydrate cage structures, the growing interest of researchers and scientists to find mechanisms of exploitation of these natural resources is of relevant importance. The present article shows a comprehensive review of the main concepts of natural gas hydrates. The three types of cage structures, sI, sII and sH are defined. A reference about the distribution of clathrate hydrates worldwide and the description of the main molecular dynamic simulation algorithms, FSICA, CHILL+, GRADE, ICO and HTR that hitherto have been developed is presented. Finally, applications in the fields of energy generation and oil and gas transportation are analyzed providing an overview of the trends in the present and future applications of clathrate hydrates. The conclusions of the present work emphasize the vast amount of natural gas hydrates worldwide, mentioning it as an advantage to consider NGHs as a natural energy resource.

1 Introduction

Currently, the world is facing a global increase in energy demand. The factors influencing the rise of energy consumption are varied and cannot be plainly set forth by definite circumstances. Nevertheless, some sectors contributing to this increasing energy demand are well determined, including, globalization, massive production, increase of the global population and transportation. Certainly, these factors are advantageous for humankind and the global economy, however they imply more energy consumption and the need to create and explore new energy sources. Most of the conventional energy is carbon-based (gas, oil and coal) and, as it was projected by [1], more than 76 % of energy will come from carbon by 2040. Despite the environmental positive factors that renewable energies offer, at the present time, the amount of clean energy generated is still far from meeting the demand. In order to cover energy requirements, sundry studies and investigations have been headed towards Natural gas hydrates (NGH), which have gained more importance as a natural source of energy. As referenced by [2], since the early 1990, there has been a proliferation of research efforts on the effects of gas hydrates in the broad areas of energy and environmental applications. These Investigations have been focused on studying the fundamental physics of hydrate, hydrate formation kinetics, thermodynamic properties of hydrate, hydrate structure types, wherewith relevant information is provided for the investigations of hydrates [3]. Significant contributions for cage recognition algorithms of clathrate hydrate and their applications, explicitly on the nucleation mechanism and micro-, nano-mechanical properties of clathrate hydrate are presented in [4]. [5], presents experimental results to determine the effect of environmental conditions involving pressure, temperature, and gas flow rate on CH_4 in the sedimentary matrix, giving guidance for NGHs formation related to cold seeps.

On account of the work of several researchers and scientists, the present work aims to provide information about the fundamental concepts of Natural Gas Hydrates (NGHs), methods of analysis employed to explore sediments and important algorithms that have been used to simulate and study the behavior of clathrate hydrates. Some applications in the industrial and engineering field are presented and the application of NGHs as a potential energy source.

2 Fundamental concepts and methods of analysis of NGHs

2.1 Fundamentals

It is stated that gas hydrates were discovered in 1810, however some authors suggest that the discovery of gas hydrate has been preceded by Priestly in 1778 [2]. It has not been since approximately three decades ago that energy and environmental applications and progress in research activities with regards to gas hydrates took more relevance as shown in Fig.1.

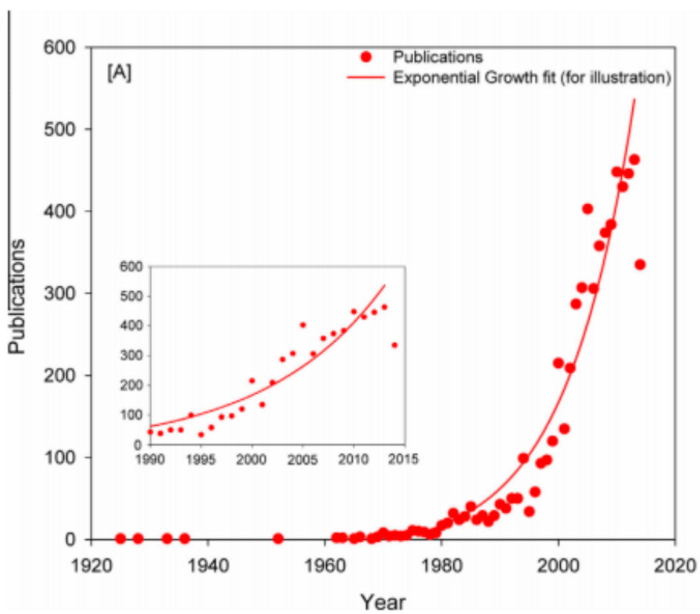

Figure 1. Progress in research activities of gas hydrates [14]

Gas hydrates, known as clathrate hydrates are solid crystalline compounds that are formed when water cages also known as hosts and small gas molecules known as guests come into contact at high -pressures and low-temperatures [6]. To illustrate, $3-10$ MPa and $275-285$ K are pressure and temperature conditions for the formation of methane hydrates respectively [2]. The most common guest molecules are methane, carbon dioxide and propane. Natural gas hydrates are distributed in on- and off-shore deposits worldwide as shown in Fig. 2, mostly distributed in marine sediment and permafrost [7,8].

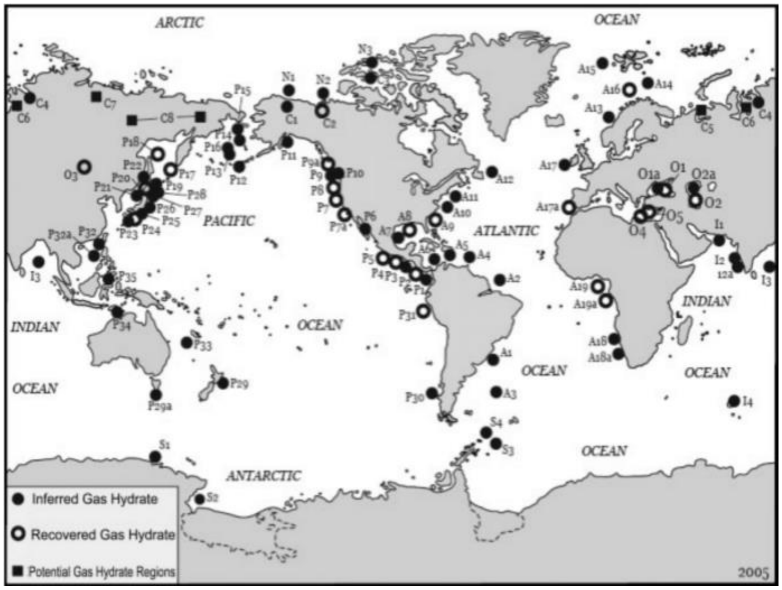

Figure 2. On-shore and off-shore gas hydrates location [2]

According to [5-8], it is estimated that the total volume present worldwide in the form of hydrate ranges from 10^{13} to 10^{17} m^3. The proportion of gas methane contained is about 164 m^3 in 0.8 m^3 of water can be obtained by dissociating 1 m^3. The most common hydrate structures are sI, sII, with cubic crystal structure and sH, with hexagonal crystal structure [2]. The clathrate hydrate cages and crystal phases can be seen in Fig.3.

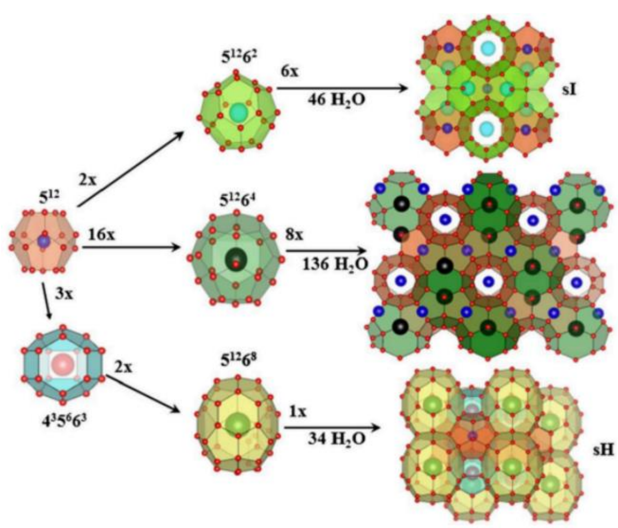

Figure 3. clathrate hydrate cages and crystal phases

2.2 Methods of analysis of hydrate cage structures

Considering the complexity to study clathrate hydrates formation and deformation at microscopic scale by experimental methods such as alternate heat transfer approaches, electromagnetic heating in situ, depressurization, in situ combustion, molecular dynamic (MD) simulations have been employed for the analysis of cage recognition [4]. By means of the application of MD simulations, micro/nano-mechanical properties, nucleation mechanism, multiple nucleation pathways, homogeneous nucleation rate and critical nucleus size of clathrate hydrates can be analyzed. These methods are called cage structure identification algorithms, including, FSICA, CHILL+, GRADE, ICO and HTR. Sundry fundamental aspects of these algorithms are mentioned in the present work, nonetheless, for thorough explanations thereof are found in [9-13].

2.2.1 FSICA

Face-saturated incomplete cage analysis is an algorithm capable of identifying complete cages (CC) and face-saturated incomplete cages (FSIC) [9]. The recognition of FSICA is high, and it can identify structures such as clusters composed of multiple hydrates, multi-guest molecular hydrates [4]. See Fig. 4 A).

2.2.2 CHILL+

CHILL +identifies water molecules belonging to either liquid or crystals using the correlation of orientational order of a water molecule with its four closest neighbors. This algorithm is an extension of the CHILL algorithm [10]. See Fig. 4 B).

2.2.3 GRADE

This method mainly uses a breadth-first search algorithm (BFS), such as identifying the connectivity of the particles of a ring by treating water as a vertex in an undirected graph to identify the ring. After determining the connection relationship between the rings, a five-membered ring is selected as the base, and five other five-membered rings connected to each edge of the ring are found and combined [11]. See Fig. 4 C).

2.2.4 ICO

Iterative Cup Overlapping, is an identification algorithm for cage structures of amorphous phase hydrates. ICO is able to identify all standard edge-saturated cages (SECs) with very low time and highest estimation efficiency in comparison with FSICA and GRADE algorithms [12]. See Fig. 4 D).

2.2.5 HTR

An algorithm proposed by [13], to identify hydrate cages based on ring topology. The principle therein, is in applying the concept that only one ring can be uniquely topology from two rings, and the topology is performed upward through the two rings on the cup. See Fig. 4 E).

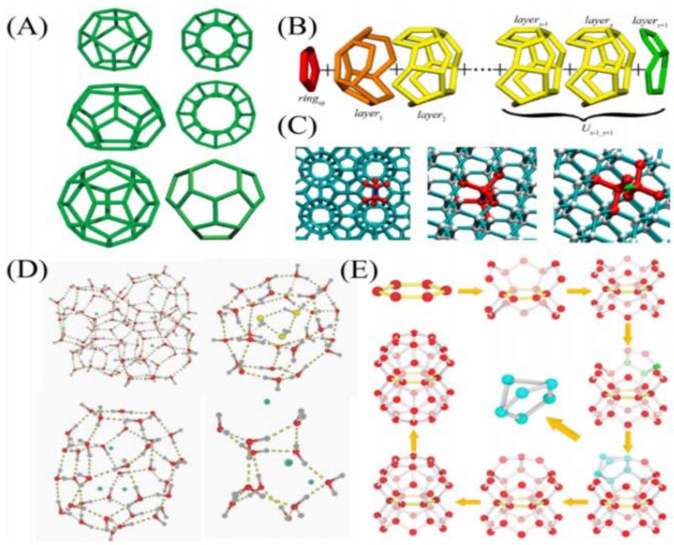

Figure 4. Identification principles of hydrate cage structure identification algorithms [4].

Table 1 presents an overview of the five algorithms presented in this section. Information regarding the recognition principle and algorithm applicable scenarios are in the table. Detailed information can be found in [4].

1. ***Table: Cage Recognition algorithms [4]***

Algorithm	*Recognition Principle*	*Applicable scenarios*
FSICA	*Grid Search*	*More in depth research on cage structure*
CHILL+	*Hydrates are determined by the type of bonds formed.*	*Number of cages and distribution in the system are required.*
GRADE	*Superposition of half-cage structures.*	Type $5^{12}, 5^{12}6^{2}, 5^{12}6^{4}$ *cages were studied.*
ICO	*Layer-by-layer iteration of the half-cage structure.*	*Do not study the behavior of guest molecules.*
HTR	*Layer-by-layer topology of ring structure.*	*Efficient identification of large system hydrates is required.*

3 Applications

Experimental and dynamic modeling studies, provide relevant information about the formation of clathrate hydrates and knowledge thereof can be utilized in different applications. One of the main uses taken into consideration at present is the applicability of gas hydrates as an energy source. In comparison to oil and coal, gas hydrates are Euclidean solids that at the time are considered as a clean fuel, moreover gas hydrates e.g., methane hydrate, has a carbon quantity twice more than all fossil fuels combined and is distributed evenly around the world [14]. It is said that the production of methane from natural gas hydrates is expected to have a higher impact on the global economy than the impact of shale gas [14]. As referenced by [2], hydrate reservoirs are a substantial future energy resource due to the large amount of hydrated gas, coupled with hydrates concentrating methane by as much as a factor of 164, and requiring less than 15 % of the recovered energy for dissociation.

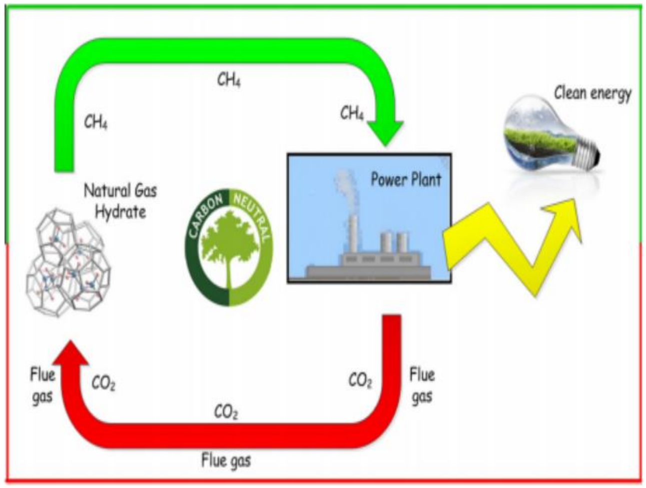

Figure 5. Identification principles of hydrate cage structure identification algorithms [4]

Another relevant application of experimental and molecular dynamic simulations is the avoidance of hydrate formation in gas and oil transportation in the subsea at water depths of more than 6000 ft, wherein exist extreme temperature and pressure conditions that are favorable for the formation of hydrates, The formation of hydrates in pipes and ducts might cause blockages, thus causing economic and ecological risks. Traditional methods to avoid hydrate formation are denominated thermodynamic methods, basically, heating systems above hydrate formation temperatures, insulation flow lines, separating free water and using thermodynamic inhibitors [2]. However, these methods are costly and require high knowledge and specialty to handle a thermodynamic control.

4 Conclusions

In the present work, a review of the fundamental concepts, definitions, techniques of analysis of cage hydrate structures and the two more important applications thereof have been discussed. Information about the progress of research in this field has been presented showing an exponential interest of researchers and scientists about natural gas hydrates. This growing interest in this field is comprehensible since, according to the studies described in this work, natural gas hydrates can offer potential benefits as an innovative source of energy. It has been claimed by some researchers that hydrates can be considered as clean energy, nevertheless, at present, there is not enough substantial information about the environmental impact that the utilization of clathrate hydrates as an energy source could occasion. One of the main advantages of considering clathrate hydrates as an energy source is that these resources can be found on and off-shore distributed evenly worldwide, explicitly in marine sediment and permafrost.

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