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A review of solidified natural gas (SNG) technology for gas storage via clathrate hydrates

Hari Prakash Veluswamy[a], Asheesh Kumar[a], Yutaek Seo[b], Ju Dong Lee[c], Praveen Linga[a,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore
[b] Department of Naval Architecture and Ocean Engineering, RIMSE, Seoul National University, Seoul 08826, Republic of Korea
[c] Offshore Plant Resources R&D Center, Korea Institute of Industrial Technology, Busan, Republic of Korea

HIGHLIGHTS

- First review on Solidified Natural Gas (SNG) Technology via clathrate hydrates.
- Prospects for improving the kinetics and storage capacity is presented.
- Critical examination of 'self-preservation' and 'tuning' effect in hydrates is presented.
- Challenges and future directives for commercial deployment of SNG technology are outlined.

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ABSTRACT

Natural gas (NG), the cleanest burning fossil fuel, plays a crucial role in meeting the global energy demand, contributing to 24% and is projected to grow at a rate of about 2% until 2040. Natural gas is also considered as the bridging fuel to transition into a carbon-constrained world with reduced carbon dioxide emissions whilst catering to the huge energy demand. Efficient and effective modes of NG storage/transport are dire need in the current golden era of natural gas. A plethora of advantages offered by storing NG in the form of hydrates carve a niche for this novel technology. Termed as solidified natural gas (SNG) technology, it has remarkable potential to store multi-fold volumes of natural gas in compact hydrate crystals offering the safest and the most environmental friendly mode of NG storage. This review provides an account on the research efforts put forth in this technology. Hydrate formation and storage aspects have been examined thoroughly with a subtle account on the gas recovery. The review encompasses studies conducted using different promoters (thermodynamic, kinetic or a combination of both) in different reactor configurations, novel/innovative approaches and hybrid processes adopted to improve the kinetics of hydrate formation and to increase the gas storage capacity. Detailed sections on the 'self-preservation' and 'tuning' effect in hydrates have been included due to their significance in SNG technology. Process chain of the SNG technology, underlying challenges and measures adopted to deploy the SNG technology for large-scale NG storage applications are included in this review.

1. Introduction

Natural gas (NG) is the cleanest burning fossil fuel and is abundantly available in nature both in conventional and in unconventional forms (Shale gas, natural gas hydrates, tight gas, etc.). Natural gas predominantly contains methane (approximately 90% and above in most cases) along with a small percentage of higher hydrocarbon gases like ethane, propane and butane. Natural gas may also contain small amounts of carbon dioxide, nitrogen, hydrogen sulfide and trace amounts of water vapour [1]. Amongst fossil fuels, the share of natural gas towards primary energy will continue to increase for at least another twenty years until 2040 [2]. With this inevitable shift to a natural gas based economy globally, there is an ever-increasing need to develop effective technologies to store and transport natural gas efficiently. Improved power generation efficiency, high calorific value and low carbon emission (compared to coal and gasoline) favor the increased utilization of natural gas for power generation application. In fact, using natural gas for power generation results in about 50% and 33% reduction in CO_2 emission in comparison to using coal and oil, respectively [3]. Natural gas is also used extensively for other industrial and manufacturing applications.

Several approaches have been considered worldwide for the

* Corresponding author.
E-mail address: praveen.linga@nus.edu.sg (P. Linga).

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transportation of natural gas. The most common approach is transportation through gas pipeline which is not always practical considering the distance, cost, feasibility and accessibility of the delivery location. Another approach for NG transportation and storage at a much smaller volume is through compressed natural gas (CNG). However, safety concern and the poor volumetric storage capacity are the characteristic drawbacks for this approach. Transportation of NG in liquid form, Liquefied Natural Gas (LNG) has been considered the most suitable approach for large scale and long distance transportation due to the high volumetric storage capacity (600 v/v compared to STP conditions). Currently, LNG tankers are used to transport natural gas from source to the areas of demand. Adsorbed natural gas (ANG) is another possible approach to transport NG by adsorbing on to sorbents like carbon nanotubes (CNTs), graphene, metal organic frameworks (MOFs), etc. US Department of Energy (DOE) target for on-board vehicular methane transport/storage requirement is 263 v/v at STP and 0.5 g/g of adsorbent gravimetric storage capacity. Few MOFs are reported to have higher gravimetric and considerable volumetric storage capacities with the potential to meet DOE target for methane storage/transport [4]. It is noted that a number of materials for ANG are under active research and development phase for usage in automobiles as an alternative to CNG powered vehicles.

Natural gas can be stored either in gaseous, liquid or solid forms. Available pathways for NG storage and transport are provided in Fig. 1. Underground inventory is one of the most common methods that includes storing natural gas in depleted reservoirs of oil and/or natural gas fields, aquifers, and salt cavern formations. Characteristic aspects of these storage modes include the capacity and the ease of deliverability of NG. For achieving a volume reduction of about 200 times, it is noted that CNG has a very high pressure requirement (200 bars and above), practically making it not suitable for large scale NG storage due to the extremely high cost involved in the design of high pressure, large volume storage tanks and the inherent explosive nature of CNG.

Though considered the best mode of NG transport, the extreme low temperature requirement (−162 °C) to keep LNG stable as well as the continuous boil-off issues associated with LNG deters its use for large-scale, long term storage applications. Gravimetrically, the storage capacity for ANG is higher due to the relatively larger surface area and higher porosity. However, volumetric storage capacity observed in these materials is lower and this volumetric storage capacity is a key driver for practical applications [4]. Volumetric storage capacity calculations for MOFs reported in literature were performed based on density of a single crystal. However, when calculated on the basis of bulk powder (when used in large scale), there will be a substantial reduction in volumetric storage capacity. Further, other factors like mechanical stability, thermal conductivity, presence of impurities and most importantly the high cost of the material will impede the deployment of MOFs for large-scale NG storage [5]. Storing and transporting natural gas in clathrate hydrates, referred as Solidified Natural Gas (SNG) from now on, is a promising alternative due to several characteristic advantages that include

(i) Clathrate hydrate formation process is environmentally benign as it uses only water and very low concentration of promoters (used when required to improve the operating conditions of storage)
(ii) Guest gas (methane) is stored in its respective molecular form, almost complete recovery or utilization is possible just by simple depressurization or minimal thermal stimulation
(iii) Moderate temperature and pressure conditions required during formation and storage (in the presence of low concentration of promoters)
(iv) Highly compact mode of storage with relatively high energy content per unit volume and
(v) It is extremely safe mode of storage due to its non-explosive nature.

Table 1 presents the comparison of different technologies available for storage of natural gas in molecular form. Formation, storage conditions along with advantages and disadvantages of each of these methods have been included. From the table, it is clear that the proposed SNG method cannot meet the DOE targets envisaged for on-board vehicular transportation. Thus, SNG technology can cater only to stationary applications that require natural gas and it can also enable natural gas storage suited for power generation applications.

2. Scope of the review

Despite the substantial research in storing methane (natural gas) in hydrates for past three decades, there is no comprehensive review paper summarizing the hydrate-based technology for storing and transporting methane/natural gas. This review attempts to summarize the experimental work conducted till date to store methane /natural gas in the form of hydrates and presents the current status of solidified natural gas

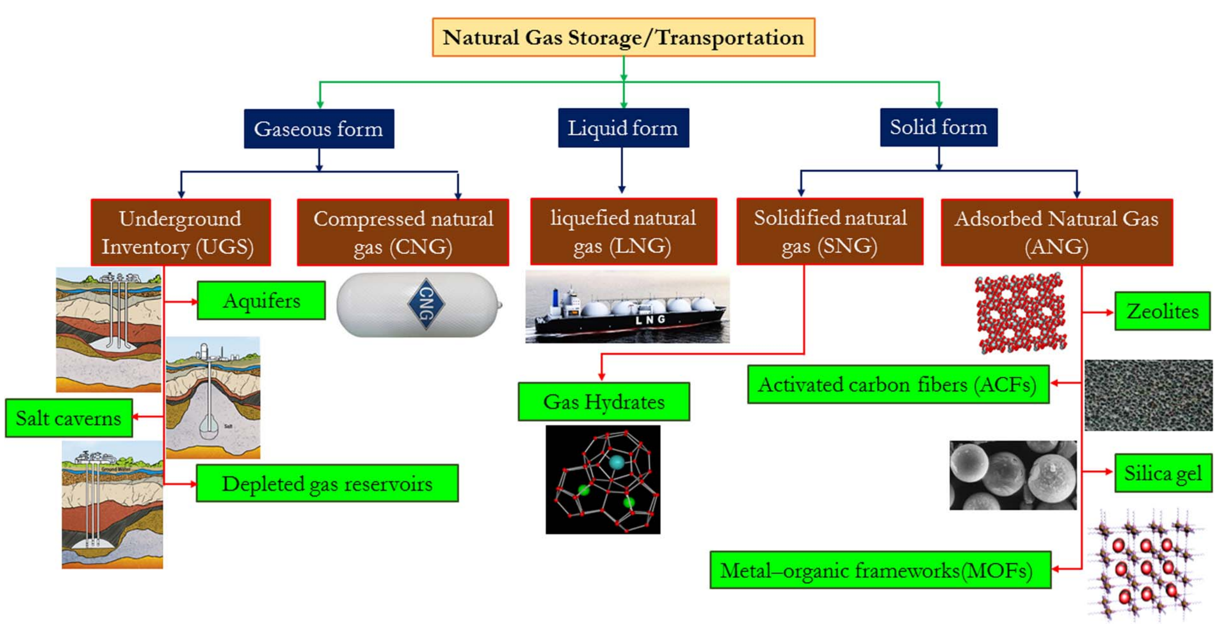

Fig. 1. Pathways for natural gas storage and transportation (Images on UGS obtained from http://www.energyinfrastructure.org/energy-101/natural-gas-storage).