Multidiszciplináris tudományok, 12. kötet. (2022) 4 sz. pp. 100-109 **https://doi.org/10.35925/j.multi.2022.4.10**

STORAGE OF HYDROGEN IN HYDRATES

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Abstract

The primary cause of global warming is the burning of fossil fuels. Therefore, we are looking for alternative solutions for electricity generation, such as the increased use of renewable energies such as solar, wind and hydropower. The main drawback of these energy generation methods is the high degree of weather dependence, highly unbalanced, so the creation of a complex energy storage system is of paramount importance. This system would store the excess energy as a buffer, balancing the periodicity between demand and supply. Hydrogen storage (hydrogen is produced by the electrolysis of water using renewable energy) in the form of clathrate can be one of the possible forms of energy storage. To facilitate hydrogen supply in a future with zero carbon emissions, it is necessary to examine the technical aspects and feasibility of adsorption of hydrogen in high surface area materials. The capturing of molecular hydrogen in a crystalline guest molecule, i.e., water, as a storage method is a relatively new technology. Hydrogen hydrate is a promising medium for hydrogen storage, with advantages such as low production cost, safety, lack of negative environmental effects. The aim of this study is to present the latest developments in hydrogen storage in the form of hydrates and to present the challenges of this research area.

Keywords: *green hydrogen, decarbonisation, hydrogen storage, hydrogen hydrate, renewable energy*

1. Introduction

To comply with international climate protection agreements, energy from renewable sources is playing an increasingly important role. The advantage is that the amount of greenhouse gases emitted is small, thus helping to combat climate change caused using fossil fuels. The contribution of such renewable energy sources to the energy mix has grown significantly over the last decade and has become a primary source of electricity. Hydrogen produced from renewable energy sources is considered to be an attractive renewable energy source with great potential to reduce dependence on imported energy sources. In addition to its many uses, such as fuel, fuel cell, food industry, refinery, etc., hydrogen has proven to be a secondary energy source, an important energy source. (Seo et al., 2020) Energy consumption varies according to demand (daily and seasonal changes or peak demand), while energy production can be said to be constant. To manage and control fluctuations, the excess electricity produced in the form of hydrogen must be temporarily stored so that it can be used later as consumption demands increase. Therefore, the conversion of surplus energy to hydrogen and its storage in the form of hydrates is one way to compensate for this energy shortage. The hydrogen produced can be stored in a variety of ways, such as in high pressure gas cylinders, adsorbed on high specific surface area materials, and absorbed at the interstitial sites of the host metal by covalent and ionic chemical bonding. (Zuttel, 2004; Reuß et al., 2017) Figure 1 outlines the possibilities for storing hydrogen in physical form and materials.

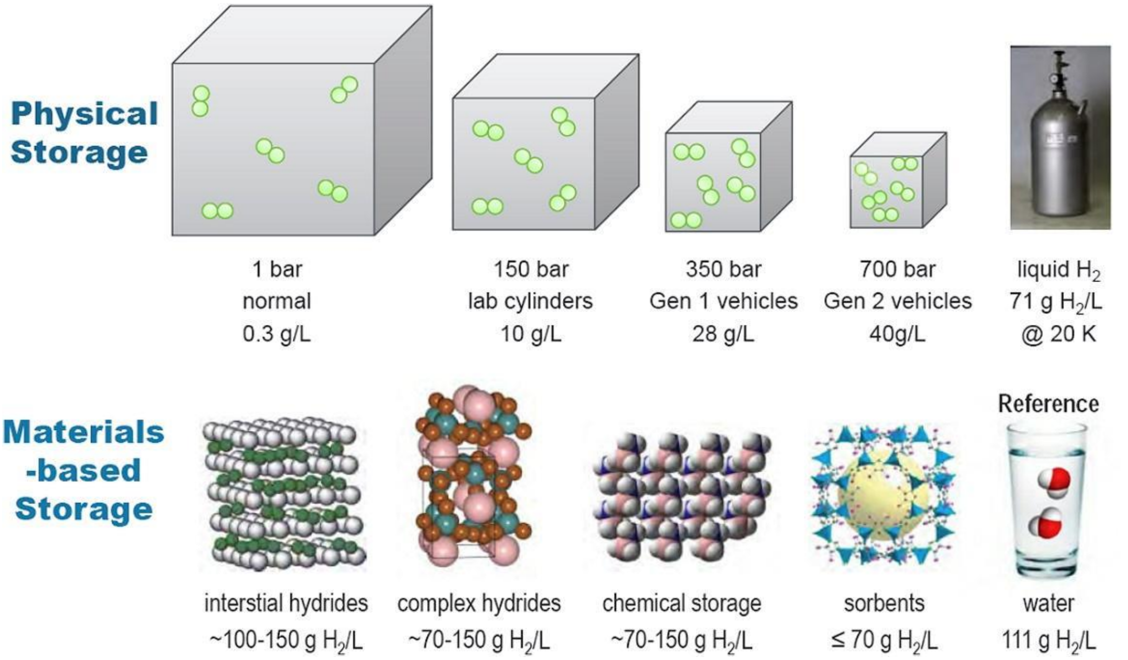

Figure 1. *Comparison of physical storage of hydrogen and material-based hydrogen storage (Ren et al., 2017)*

Because today’s intensive research is focused on developing solid-phase hydrogen storage systems. Hydrogen hydrate is a promising medium for hydrogen storage, with advantages such as low production cost, safety, lack of negative environmental effects.

2. Hydrogen as an energy carrier

Burning 1 m3 of hydrogen generates 12.7 MJ of energy, which is a high energy potential, although lower, than that of methane (40 MJ). The energy produced by hydrogen is less than the energy needed to produce a unit amount, so hydrogen is not considered an energy source. However, it can be easily converted into electricity or heat, so its ability to transmit or store energy makes it an efficient energy carrier. In addition, the loss during energy transmission is much lower using gaseous carrier (<0.1%) than using the electricity grid (8%). For non-industrial activities, hydrogen as an energy source can be considered as an efficient substitute for natural gas. (Davison et al., 2010) When blended into the existing natural gas network, this hydrogen-natural gas mixture is being explored as an energy carrier or as an alternative fuel (Mehra et al., 2017). By delivering energy to end-use devices hydrogen can be recovered or extracted by conventional separation methods (e.g., pressure fluctuation adsorption) to suit a wide range of applications. (Kura et al., 2017). It can also be injected into subsurface geological formations to meet seasonal needs. Hydrogen storage in underground structures is safer than above ground storage beyond storage capacity. According to Taylor (1986), underground storage is the cheapest method for storing large amounts of gaseous hydrogen (Taylor et al., 1986).

3. Pysical properties of hydrogen

Knowledge of the physical properties of hydrogen helps ensure safe and successful storage. Because hydrogen is less dense than natural gas, storing the same amount of hydrogen requires more pressure. The lower viscosity of hydrogen relative to methane results in greater hydrogen mobility, which can lead to lower residual hydrogen in porous media containing hydrogen and methane, and more efficient hydrogen production is expected as a result. The solubility of hydrogen is important when stored in a body of salt water or in depleted oil and gas fields. Hydrogen has a lower solubility than methane, which is an advantage because the hydrogen-methane brine system is expected to have less hydrogen loss due to dissolution. Leakage of hydrogen to the surface is likely to occur due to its low molecular weight, which may diffuse through the topcoats to a greater extent than air, carbon dioxide, or methane. At normal temperatures and pressures, the diffusion coefficient of hydrogen is three times that of methane in pure water. However, the effect of porosity on diffusion in a porous medium must be considered with tortuity, which results in an effective diffusion coefficient. (Makogon, 1997)

4. Hydrate formation

In the structure of gas hydrate, smaller and larger guest molecules are trapped in the cavities of the crosslinked network of water molecules formed by hydrogen bonds at low pressures. They are re-released from this solid phase in a gaseous state at higher temperatures and lower pressures. (Nemes, 2015) Gas hydrates were first dealt with in the history of chemistry by Joseph Priestley in 1778, bubbling sulphur dioxide in water at low temperature and atmospheric pressure. Clathrate hydrates were later described by Humphry Davy in 1810, but Davy's contemporaries were not interested. Almost a century passed on the subject until further developments: between 1778 and 1934, only 56 articles were published. However, interest suddenly picked up during the development of the U.S. oil and gas industry in the 1930s, when oil and gas began to displace coal in the energy industry. During cold winter was discovered that solid plugs formed in the gas pipelines and transport had to be stopped. Texas engineer Hammerschmidt found that the solid gas hydrate formed from the water vapor content of the gas. It was responsible for clogging the pipelines. (Makogon, 1997) Then, extensive research was started on the topic. The problem in the oil and gas industry continues to cause difficulties and costs to this day.

The third period of gas hydrate exploration began when natural gas hydrates were discovered at several sites in the 1960s. In 1963, methane hydrate was found in the 1,200 m deep layer of permafrost in Yakutia. This was the first time methane hydrate was found in nature. Since then, about 7,000 articles on natural gas hydrates have been published, and today there is a huge literature on the subject. With the discovery of naturally occurring hydrate deposits, interest has shifted to understanding the energy and environmental impact of hydrates. (Rempel and Buffett, 1997; Zatsepina and Buffett, 1997). Cha and colleagues have used the hydrates to develop natural gas storage, carbon capture, gas capture, and hydrogen storage technologies. (Cha et al., 2010).

Berecz and M. Balla-Achs stated that the stability of a gas hydrate, and consequently its dissociation temperature, are influenced considerably by the molecular size and geometrical shape of the hydrate-forming components. From the point of view of hydrate formation, a very small molecular diameter is not advantageous; thus, presumably because of the very low polarizability, independent hydrates of hydrogen, helium and neon are not known. (Berecz and Balla-Achs, 1980)

It was not until the 1990s, when the water-hydrogen system was studied by Dyadin et al., it was recognized that by raising the hydrogen pressure above 100 MPa, the kinetics of ice melting were experienced. Their observation was explained by the formation of hydrogen hydrate. Further studies were conducted to investigate the details of hydrogen hydrate formation. (Mao et al., 2002; Lokshin et al., 2004). The identification of hydrogen hydrates formed in the extreme pressure range has been a scientific success but has proved unattainable in many applications. This research on hydrogen hydrates as a possible storage system had to be done more widely. Thus, Zhang et al. concluded that the addition of tetrahydrofuran (THF) to water at ambient temperature could reduce the hydrogen hydrate formation pressure from 200 MPa to 100 MPa. (Zhang et al., 2005) By adding a small concentration (6 mol%) of THF the pressure (required to form binary H_2 = CH_4 hydrate) drops drastically from 6.5 MPa to 0.3 MPa. (Zhang et al., 2005)

The next major step in the storage of hydrogen in the form of hydrates was the introduction of semi-clathrate hydrates. The structures developed by Chapoy et al. can serve as an alternative, as they are formed and stable at atmospheric pressure and room temperature. (Chapoy et al., 2007) Hydrogen has been successfully stored in the structural cavities of semi-clathrate hydrates of quaternary ammonium salts (QAS). These hydrates are stable at atmospheric pressure and up to 30°C. During the filling of the cavities, the guest molecules are physically bound to the structure of the water.

5. Hydrogen storage capacity in hydrate

The amount and volume of a given gas hydrate is much less than the normal volume of the gas from which the hydrate was formed. This fact raised early the possibility of storing gases in hydrate form at low pressure and temperature. According to Parent's calculations, a gas mixture with a composition of 80% CH_4, 10% C_2H_6, 5% C_3H_8, 4% n. butane+isobutane and 1% inert gas has a volume of 4.42 m^3 at a temperature of 15°C and a pressure of 1.01×10^5 Pa. When stored in gas hydrate, only 1/156 of the volume is required. If an economical method can be developed to produce gas hydrates, the need for less storage space is the main advantage of this form of storage. Another significant advantage is to store the gas in the form of a much safer hydrate, which is of paramount importance from a safety point of view, than in the gaseous form or compressed into a liquid. The hydrates themselves are not inflammable and do not burn, the reconversion to gas, the evolution of gas is relatively slow, it can be controlled too. Thus, even in this process, inflammation and the explosion can be prevented. The transport of gases in the form of hydrates has untapped benefits. Such solutions are described in the patented process of Cahn et al. (Cahn et al., 1979) and Nierman (Nierman, 1976) for the transport of gases by sea.

The value of each hydrogen hydrate system as an energy source is given by its storage capacity.

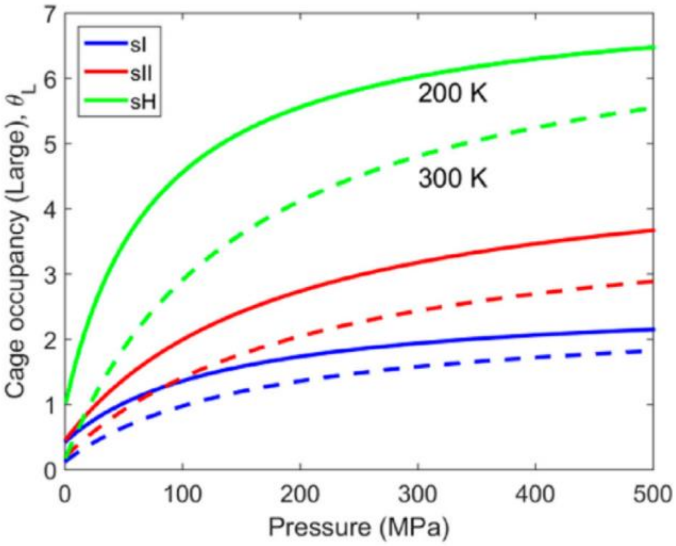

Figure 2. *Filling of the cavities belonging to the three hydrate structures as a function of pressure at the temperature of 200 and 300 K (Tsimpanogiannis et al., 2020), Copyright 2020 American Chemical Society.*

The hydrogen storage capacity (5.5% hydrogen by weight) set by the US Department of Energy encourages the development of different storage methods. The goal in these applications is to achieve high storage capacity at low pressures. Zhdanov et al. (Zhdanov et al., 2019) achieved the highest storage capacity of 4.2% without a promoter. By using promoters, the available storage capacity is reduced, as the promoter itself occupies some of the cages, thus limiting the space available to the hydrogen molecules. To leave these, extremely high pressures and very low temperatures are required. That is, by increasing the pressure and decreasing the temperature as shown in Figure 2 we can increase the storage capacity of the hydrogen hydrate, with the maximum obtained for the sH hydrates. (Guptal et al., 2021)

By using promoters, their molecular weight can have the greatest effect on the total storage capacity of hydrates. The smaller, the larger the amount of hydrogen that can be stored. For a promoter with a molecular weight of 16 g, 33% by weight is the highest available capacity for an sH-type structure. (Tsimpanogiannis et al., 2020)

Promoters are an essential component of hydrate systems and function under moderate conditions. Di Profio et al. (Di Profio et al., 2018) investigated the effect of promoters on storage capacity at presure of 10 MPa. Of the CP (cyclopentane), DHF (dihydroxyflavone), DXL (D-Xylaric acid), THP (tetrahydropyran), THT (tetrahydrothiophene), and THF (tetrahydrofuran) promoters used, THT had the largest storage capacity of 0.5%. The order it sets up from the largest to the smallest negative effect is as follows: CP <THF <DHF <THP <DXL <THT.

Dolotko et al. (Dolotko et al., 2011) studied tetra-n-butylphosphonium borohydride (TBPBH4) and tetra-n-butylammonium hydroxide (TBAOH) promoters at temperature of 285K and pressure of 12MPa. In their analysis, the storage capacity was 0.12% and 0.14%, respectively. It has been found that the addition of activated carbon can increase storage capacity.

Fang et al. (Fang et al., 2014) investigated the THF and activated carbon-modified THF promoters. Their results showed that at the same pressure, (6.4 MPa and 274 K), the storage capacity was 0.041% using activated carbon. This is higher value than THF without activated carbon. For both promoters, it has been shown that increasing the pressure can increase the storage capacity. The concentration of the promoter also has an effect on the storage capacity. Strobel et al. (Strobel et al., 2006) in their experiments supported their claim that increasing the concentration increases the storage capacity. An optimal concentration value has been identified too.

As mentioned earlier, temperature, pressure, promoter type, etc. parameters that affect storage capacity. In addition to their individual direct effects, these parameters may interact with each other, resulting in a further change in capacity value. Research shows that the choice of promoter depends on the operating pressure, and there may not be a promoter that works best in all circumstances.

Lower hydrogen storage capacity means more water. To store 1 g of H_2 in 5% by weight of clathrate hydrate, about 20 ml of water are required. With a hydrate at near atmospheric pressure, this volume of water can increase to 500 ml with 0.2% storage. This increased amount of water does not cause negativ economic or environmental impact, as the water can be reused for hydrate forming. Some studies have reported a slight improvement in the rate of formation when using recycled water. (Davoodabadi et al., 2021)

6. Hydrogen hydrate structure

Clathrate hydrates are special inclusion compounds formed from pentagonal or hexagonal water molecules with a solid crystalline structure. Van der Waals interactions between guest molecules and water molecules. Figure 3 shows the three clathrate structures in two and three dimensional forms. Of the sI, sII, and sH types, the SH type is the rarest. (Momma et al., 2011; Liang and Kusalik, 2015).

„3D structure of sI hydrate: the unit cell consists of 46 water molecules arranged into small cages with twelve pentagonal faces and large cages with two hexagonal and twelve pentagonal faces (A). 3D structure of SII hydrate with the unit cell composed of 136 water molecules arranged into small cages with twelve pentagonal faces and large cages with twelve pentagonal and four hexagonal faces (B). 3D structure of sH hydrate with the unit cell composed of 34 water molecules arranged into small cages with twelve pentagonal faces; medium cages with three hexagonal, six pentagonal, and three tetrahedral faces; and large cages with twelve pentagonal and eight hexagonal faces (C). (A), (B), and (C) are adapted with permission from (Momma et al., 2011). 2D view of hydrate structures and building blocks including small, medium, and large cages (D), adapted with permission from (Liang and Kusalik, 2015).” (Davoodabadi et al., 2021)

In all clathrate structures, water molecules and hydrogen bonds form the peaks and edges, respectively. Each structure has a specific crystallographic property. The sI type contains 46 water molecules, forming 8 cages per unit cell (Izquierdo-Ruiz et al., 2016). SII type, on the other hand, consist of 136 water molecules and sixteen small 5^{12} cages and eight larger $5^{12}6^{4}$ cages in a unit cell (Klapproth et al., 2019). Finally, SH hydrates consist of 36 water molecules, containing three 5^{12} cages, two irregular dodecahedrons, and one icosahedron per unit. (Khokhar et al., 1998; Chattaraj et al., 2011; Lee et al., 2016).

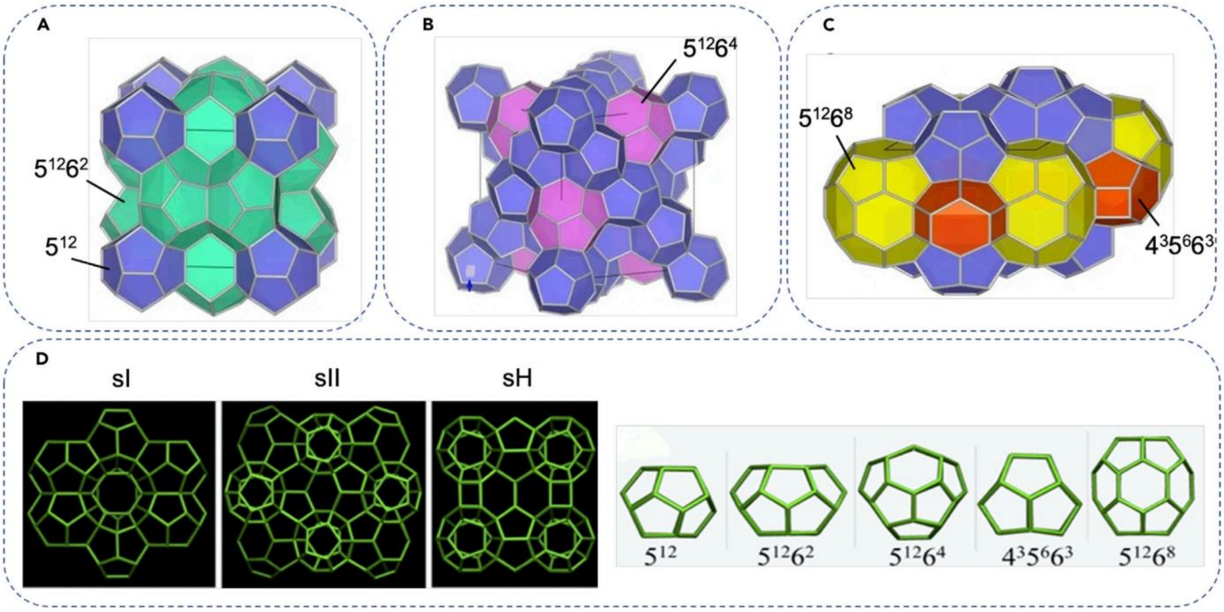

Figure 3. *Structures of hydrogen hydrate (Davoodabadi et al., 2021)*

The study of the forms and dimensions of the cavities formed on the linkage of tetrahedral water molecules is closely connected with the investigation of the structures of gas hydrates. Claussen demonstrated that, if water molecules are linked in such way that every molecule is situated approximately at the centre of the tetrahedron by the four neighbouring water molecules, cavities of various sizes can be formed. (Claussen, 1951) The thermodynamic stability of hydrates is expressed by the cohesive energy, which is the difference between the total energy of the separated monomer molecules and the energy of the hydrate. The interaction energy is used to determine the stability of the hydrogen molecule and its binding force to the hydrate. (Davoodabadi et al., 2021)

7. Summary

By 2050, humanity's energy needs are estimated to triple by the turn of the millennium, making the exploration of alternative energy sources increasingly burning and indispensable. One of the key issues to be addressed is the drastic reduction of CO_2 emissions that cause greenhouse gases. There has been a great deal of interest in the last two decades in integrating hydrogen into the energy sector, which could serve as a basis for building a hydrogen-based energy economy. According to the concept, hydrogen produced with the help of various alternative energy sources (solar energy, geothermal, wind, biomass, etc.) can be used in the so-called in fuel cells in which the chemical energy stored by hydrogen is converted into electrical energy during an electrochemical reaction. As the released hydrogen can fall away from the place of use both in space and time, it must be stored. Intensive research is currently underway to develop solid phase hydrogen storage systems. (Strobel et al., 2007) The great advantage of storage in bound form is that the hydrogen density per unit volume is the highest of all methods for these systems. In other words, in the future there is a good chance that hydrogen storage according to the presented research directions will take place.

8. Acknowledgments

The research was conducted at the University of Miskolc as part of the „Developments aimed at increasing social benefits deriving from more efficient exploitation and utilization of domestic subsurface natural resources" project supported by the Ministry of Innovation and Technology from the National Research, Development and Innovation Fund according to the Grant Contract issued by the National Research, Development and Innovation Office (Grant Contract reg. nr.: TKP-17-1/PALY-2020).

References

[1] Seo, S.-K., Yun, D.-Y., Lee, C.-J. (2020). Design and optimization of a hydrogen supply chain using a centralized storage model. *Appl. Energy*, 262, 114452. **https://doi.org/10.1016/j.apenergy.2019.114452**

[2] Zuttel, A. (2004). *Hydrogen storage methods*. Naturwissenschaften Apr 2004

[3] Reuß, M., Grube, T., Robinius, M., Preuster, P., Wasserscheid, P., Stolten, D. (2017). Seasonal storage and alternative carriers: a flexible hydrogen supply chain model. *Appl. Energy*, 200, pp. 290–302. **https://doi.org/10.1016/j.apenergy.2017.05.050**

[4] Davison, J., Arienti, S., Cotone, P., Mancuso, L. (2010). Co-production of hydrogen and electricity with CO_2 capture. *International Journal of Greenhouse Gas Control*, 4 (2), pp. 125–130. **https://doi.org/10.1016/j.ijggc.2009.10.007**

[5] Taylor, J., Alderson, J., Kalyanam, K., Lyle, A., Phillips, L. (1986). Technical and economic assessment of methods for the storage of large quantities of hydrogen. *Int. J. Hydrogen Energy*, 11 (1), pp. 5-22. **https://doi.org/10.1016/0360-3199(86)90104-7**

[6] Ren, J., Musyoka, N. M., Langmi, H. W., Mathe, M., Liao, S. (2017). Current research trends and perspectives on materials-based hydrogen storage solutions: A critical review. *International Journal of Hydrogen Energy*, 42 (1), pp. 289–311. **https://doi.org/10.1016/j.ijhydene.2016.11.195**

[7] Mehra, R. K., Duan, H., Juknelevicius, R., Ma, F., Li, J. (2017). Progress in hydrogen enriched compressed natural gas (HCNG) internal combustion engines – A comprehensive review. *Renewable and Sustainable Energy Reviews*, 80, pp. 1458–1498. **https://doi.org/10.1016/j.rser.2017.05.061**

[8] Kura, C., Kunisada, Y., Tsuji, E., Zhu, C. Y., Habazaki, H., Nagata, S., Muller, M. P., De Souza, R. A., Aoki, Y. (2017). Hydrogen separation by nanocrystalline titanium nitride membranes with high hydride ion conductivity. *Nat. Energy*, 2, pp. 786–794. **https://doi.org/10.1038/s41560-017-0002-2**

[9] Nemes, L. (2015). Methane hydrate: The promise of the future or an environmental disaster? *Chemical Panorama*, 2 (4).

[10] Makogon, Y. F. (1997). *Hydrates of Hydrocarbons*. Texas, ISBN 0-87814-718-7

[11] Berecz, E., Balla-Achs, M. (1980). *Gas Hydrates*. Budapest, ISBN 963 05 3171 2

[12] Zhang, Q., Chen, G. J., Huang, Q., Sun, C. Y., Guo, X. Q., Ma, Q. L. (2005). Hydrate formation conditions of a hydrogen + methane gas mixture in tetrahydrofuran + water. *J. Chem. Eng. Data*, 50, pp. 234-236. **https://doi.org/10.1021/je0497146**

[13] Chapoy, A., Anderson, R., Tohidi, B. (2007). Low-pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. *J. Am. Chem. Soc.*, 129, pp. 746–747. **https://doi.org/10.1021/ja066883x**

[14] Claussen, W. F. (1951). Erratum: Suggested structures of water in inert gas hydrates *J. Chem. Phys.*, 19, 662. **https://doi.org/10.1063/1.1748327**

[15] Davoodabadi, A., Mahmoudi, A., Ghasemil, H. (2021). The potential of hydrogen hydrate as a future hydrogen storage medium, 24(1), 101907. **https://doi.org/10.1016/j.isci.2020.101907**

[16] Cahn, R. P., Johnston, R. H., Plumstea, J. A. (1979). US Pat. 3,514,27 (C148-190) F17C, (6) 20 1979.

[17] Nierman, A. J. (1976). US Pat. 3,975,167 (C148) 190, F17C13 1976. **https://doi.org/10.1016/S0033-3182(76)71142-3**

[18] Tsimpanogiannis, I. N., Economou, I. G., Stubos, A. K. (2020). A practical methodology to estimate the H_2 storage capacity of pure and binary hydrates based on Monte Carlo simulations. *J. Chem. Eng. Data*, 65 (3), pp. 1289-1299. **https://doi.org/10.1021/acs.jced.9b00707**

[19] Strobel, T. A., Koh, C. A., Sloan, E. D. (2007). Hydrogen storage properties of clathrate hydrate materials. *Fluid Phase Equlib.*, 261 (1-2), pp. 382–389. **https://doi.org/10.1016/j.fluid.2007.07.028**

[20] Guptal, A., Baron, G. V., Perreault, P., Lenaerts, S., George, R., Pegie, C., Paulo, C. Mileo, G. M., Rogge, S., Van Speybroeck, V., Watson, G., Van Dervoort, P., Houlleberghs, M., Breynaert, E., Martens, J., Denayer, J. F. M. (2021). Hydrogen clathrates: Next generation hydrogen storage materials. *Energy Storage Materials*, 41, pp. 69–107. **https://doi.org/10.1016/j.ensm.2021.05.044**

[21] Di Profio, P., Arca, S., Rossi, F., Filipponi, M. (2018). Reverse micelles enhance the formation of clathrate hydrates of hydrogen. *J. Colloid Interf. Sci.*, 516, pp. 224–231. **https://doi.org/10.1016/j.jcis.2018.01.059**

[22] Dolotko, O., Karimi, A. A., Dalmazzone, D. (2011). *The phase behaviours in mixed G + tetra–N-butylphosphonium borohydride and +tetraN-butylammonium hydroxide hydrates (where G =* H_2*,* N_2*)* In Proceedings of 7th International Conference on Gas Hydrates (Scotland: Edinburgh), pp. 596–605.

[23] Fang, Y. J., Xie, Y. M., Zhou, X. F., Yan, L., Wang, S. H. (2014). Influence of activated carbon to the hydrogen storage characteristics of THF hydrate. *Advanced Materials Research*, 887-888, pp. 493–496. **https://doi.org/10.4028/www.scientific.net/AMR.887-888.493**

[24] Strobel, T. A., Taylor, C. J., Hester, K. C., Dec, S. F., Koh, C. A., Miller, K. T., Sloan, E. D. (2006). Molecular hydrogen storage in binary THF-H_2 clathrate hydrates. *J. Phys. Chem.*, B 110 (34), pp. 17121–17125. **https://doi.org/10.1021/jp062139n**

[25] Rempel, A.W., Buffett, B.A. (1997). Formation and accumulation of gas hydrate in porous media. *Journal of Gepohysical. Research,* 102 (B5), pp. 10151–10164. **https://doi.org/10.1029/97JB00392**

[26] Zatsepina, O.Y., Buffett, B.A. (1997). Phase equilibrium of gas hydrate: Implications for the formation of hydrate in the deep sea floor, *Geophysical Research Letters* 24 (13), pp. 1567–1570. **https://doi.org/10.1029/97GL01599**

[27] Shin,K., Cha,J.H., Seo, Y., Lee, H. (2010). Physicochemical Properties of Ionic Clathrate Hydrates, *Chemistry in an Asian Journal* 5 (1), 22-34. **https://doi.org/10.1002/asia.200900219**

[28] Mao, W.L., Goncharov, Struzhin, V.V., Guo, Q., Hu, J., Shu, J., Hemley, R.J., Somayjazulu, M., Shao, Y. (2002). Hydrogen Clusters in Clathrate Hydrate, Science 297 (5590), pp. 2247–2249. **https://doi.org/10.1126/science.1075394**

[29] Lokshin, K.A., Zhao, Y., He, D., Mao, W. L., Mao, H.K., Hemley, R.J., Lobanov, M.V., Greenblatt, M. (2004). Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate

Hydrate by High Pressure Neutron Diffraction, *Phys. Rev. Lett.* 93 (12), 125503. **https://doi.org/10.1103/PhysRevLett.93.125503**

[30] Ferry, A., Nugroho, A., Darmadi, I., Cusinato, L., Susarrey-Arce, A., Schreuders,H., Bannenberg, L.J., Bastos da Silva Fanta, A., Kadkhodazadeh, S., Wagner, J.B., Antosiewicz, T.J., Hellman, A., Zhdanov, V.P., Dam, B., Langhammer, C. (2019). Metal–polymer hybrid nanomaterials for plasmonic ultrafast hydrogen detection, *Nature Materials* 18, pp. 489–495. **https://doi.org/10.1038/s41563-019-0325-4**

[31] Momma, K., Ikeda, T., Nishikubo, K., Takahashi, N. (2011). New silica clathrate minerals that are isostructural with natural gas hydrates, *Nature Communications* 2, 196. **https://doi.org/10.1038/ncomms1196**

[32] Lauricella, M., Meloni, S., Liang, S., English, N.J., Kusalik, P.G., Ciccotti, G. (2015). Clathrate structure-type recognition: Application to hydrate nucleation and crystallisation, *J. Chem. Phys.* 142, 244503. **https://doi.org/10.1063/1.4922696**

[33] Izquierdo-Ruiz, F., Otero-De-La-Roza, A. (2016).Effects of the CO2 Guest Molecule on the sI Clathrate Hydrate Structure, *Materials* 9 (9), 777. **https://doi.org/10.3390/ma9090777**

[34] Klapproth, A., Piltz, R.O., Kennedy, S.J., Kozielski, K.A. (2019). Kinetics of sII and Mixed sI/sII, Gas Hydrate Growth for a Methane/Propane Mixture Using Neutron Diffraction, *J. Phys. Chem. C* 123 (5), pp. 2703–2715. **https://doi.org/10.1021/acs.jpcc.8b06693**

[35] Khokhar, A.A., Gudmundsson, J.S., Sloan, E.D. (1998). Gas storage in structure H hydrates, *Fluid Phase Equilibria* 150–151, pp. 383-392. **https://doi.org/10.1016/S0378-3812(98)00338-0**

[36] Chattaraj, P.K., Bandaru, S., Mondal, S. (2011). Hydrogen Storage in Clathrate Hydrates, *J. Phys. Chem. A* 115 (2), pp. 187–193. **https://doi.org/10.1021/jp109515adal**

[37] Sa, J., Kwak, G., Han, K., Ahn, D., Cho, S., Lee, J., Lee, H. (2016). Inhibition of methane and natural gas hydrate formation by altering the structure of water with amino acids, *Scientific Reports* 6, 31582. **https://doi.org/10.1038/srep31582**