

Review

Review on the Usage of Small-Chain Hydrocarbons (C₂—C₄) as Aid Gases for Improving the Efficiency of Hydrate-Based Technologies

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Abstract: This review article aims to describe the main applications of gas hydrates in industrial processes and the related advantages and limitations. In particular, gas storage, energy storage, gas transportation, final disposal of greenhouse gases, desalination, wastewater treatments, food concentration, and other technologies are described in detail. Similarly, the benefits and disadvantages of the solutions, currently adopted to improve the process efficiency, are discussed in the text. A particular focus on the use of additives and their capability to intervene during the formation of hydrates and on the replacement process is provided. The second part of the article deals with the use of small-chain hydrocarbons as aid gases during formation, to improve the efficiency and the competitiveness of hydrate-based processes. First, the thermodynamic properties of hydrates, containing only these compounds, are described. Then, based on a collection of experimental data available elsewhere in the literature, their effect on the hydrate formation process, when present in the mixture, is shown and detailed. Finally, direct and experimental applications of these gases during hydrate-based processes are described to definitively prove the possibility of solving, partially or completely, most of the main limiting problems for the diffusion of hydrate-based technologies.

Keywords: gas hydrates; hydrocarbons as guests; hydrate-based technologies; process efficiency



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1. Introduction

Gas hydrates are ice-like and non-stoichiometric crystalline compounds where, in the presence of the appropriate thermodynamic conditions, hydrogen-bonded water molecules form solid cavities around specific typologies of gas species. Water molecules are referred to as “hosts”, while the molecules of gas are referred to as “guests” [1]. Numerous species were found capable of forming hydrates; among them, the most relevant are methane and other small-chain hydrocarbons (ethane, propane, butane, and pentane), carbon dioxide, hydrogen, nitrogen, hydrogen sulfide, and noble gases [2]. Guest species have in common their hydrophobicity, with only the exceptions of carbon dioxide and hydrogen [1]. The relation between hosts and guests occurs only on a physical level: gas molecules are mechanically but not chemically trapped within water cages. More in depth, only van Der Waals forces are established between gas and water molecules; however, the energy required to break the van Der Waals bonds, or 0.3 kcal/mol, is more than one order of magnitude lower than the one required to break hydrogen bonds, which is equal to 5 kcal/mol [3]. In this context, the natural reservoirs diffused worldwide are known as “natural gas hydrates” (NGH) and contain small molecules of alkanes (methane, ethane, propane, and butane) [4,5] and traces of other species, such as carbon dioxide, hydrogen, and nitrogen. In the hydrate lattice, the hydrogen-bonded water molecules lead to the formation of five different typologies of cavity, whose size and morphology mainly depend on the shape and size of the guest species, and the mutual aggregation of these cavities generates three different unit cells of the hydrate framework: the cubic structure I (sI), the

cubic structure II (sII), and the hexagonal structure H (sH). More details about the cavities and the unit cells they produce will be provided in the text.

The history of gas hydrates can be grouped in three main periods. The first period dates back to the human discovery of gas hydrates, definitively established between 1778 and 1810 [3]. In those years, hydrates were mainly considered as a scientific curiosity due to the possibility to obtain a solid by mixing liquid water with gases. In 1934, gas hydrates were discovered as the main causes of gas blockages in natural gas pipelines. In order to avoid this highly expensive phenomenon, the natural gas industries financed the research in this field. In this second period, the research was mainly focused on finding solutions to avoid their formation in pipelines, such as the addition of chemical inhibitors. The third period began in the mid-1960s, when hydrates were finally taken under consideration for the enormous opportunities they consist of. Natural hydrate reservoirs were discovered worldwide; moreover, these structures were found capable of storing high quantities of gas per unit of volume and started being considered high-energy-density systems. One cubic meter of methane hydrates contains approximately 164 m³ of guest (evaluated at standard conditions) and only 0.8 m³ of water [6]. It means that the combustion of one cubic meter of methane hydrates approximately produces 35.79 MJ. If multiplying this value for the estimated quantity of methane diffused worldwide in the form of hydrate, which ranges from 10¹⁵ to 10¹⁷ m³ [7], the quantity of energy obtained is more than twice the energy that can still be produced from all the conventional energy sources still available [8,9].

Natural reservoirs are mainly distributed along continental margins and deep oceans: approximately 97% of the whole findings belong to these areas and were discovered mainly in the South China Sea, Gulf of Mexico, Japan Sea, Indian Ocean, and Bering Strait [10]. The remaining 3% has been located in permafrost regions (Alaska, Siberia, and the Qinghai-Tibet Plateau) [11].

The abundance of methane in natural hydrate reservoirs explains why the attention of researchers was mainly focused on their exploitation for energy production. However, during this third period, the hydrate formation and dissociation processes, together with their chemical and physical properties, were widely studied, and several strategic applications of them were established. Based on the capability of these structures to host great quantities of gas in relatively contained volumes, their usage for gas storage was proposed and immediately validated [12,13], both for the energy gases and for the final disposal of waste gases, such as carbon dioxide. The possibility to store gas in solid form makes hydrates the safest option for gas transportation [14]. The selectivity of the process allows one to obtain high-efficiency gaseous mixtures separated into single components [15]. In addition, being the structure composed by hydrogen-bonded water molecules, it hardly involves other species diffused in the liquid phase; thus, the formation of hydrates is an excellent technique for seawater desalination [16], wastewater purification [17], food concentration, and others. A more detailed description of the applications, as cited later, is provided in the next paragraph. First, these hydrate-based applications are characterized and their potentialities discussed; then, a further section is dedicated to their main limitation or the reason why the diffusion of these processes is still limited and their competitiveness with traditional technologies has not been established yet.

The manuscript continues with the description of the strategies currently adopted to improve the efficiency of hydrate-based processes, together with the benefits and the advantages they introduce. Finally, the usage of small-chain hydrocarbons in this process is proposed and validated. The promoting effect of these compounds for the production of hydrates is first explained, with the auxilium of data collected from the current literature; then, experimental applications of these species in hydrate-based processes were described, in order to definitively validate the feasibility of their usage as promoting additives.

2. Main Application of Gas Hydrates

The main cause of interest clearly remains the production of energy from natural reservoirs. In the past years, several strategies for methane recovery were performed [18]; the most accredited are depressurization [19,20], thermal stimulation [21,22], chemical inhibitor injection [23,24], or a combination of these [25]. These techniques are far from the ones used for natural gas extraction from conventional natural gas reservoirs, which are mainly based on fracturing the impermeable rocks containing the gas and creating a channel for its extraction. The recovery of methane contained in hydrates requires the initial rupture of water cages and the following capture of the released gas. The first step consists of shifting the local thermodynamic conditions outside from the region of stability for methane hydrates. Depressurization and thermal stimulation directly intervene on these local conditions; conversely, the injection of chemical inhibitors allows one to make the local pressure and temperature no more suitable for the stability and permanence of hydrates.

More in depth, the depressurization technique is based on lowering the local pressure while keeping the temperature constant, thus causing hydrate dissociation. The saturation degree, diffusion of pressure, and permeability are key parameters during depressurization and must be carefully controlled [2]. Thermal stimulation acts in the opposite manner: the local pressure is increased at a constant pressure. Different strategies were considered for this scope, i.e., water injection, steam injection, microwave radiation, and electrical heating [26–28]. Depressurization and thermal stimulation are often carried out together, in order to obtain high-efficiency methane recovery from hydrates.

The final disposal of carbon dioxide under the form of hydrates in deep oceans is currently considered one of the most promising solutions for its removal from the atmosphere: these areas have suitable pressures and temperatures, and the self-protective properties of hydrates make the process safer than CO₂ storage in inland aquifers [29]. In case of losses, CO₂ molecules would completely dissolve in water, and the quantity released again in the atmosphere would be negligible [30]. As a function of depth, three different typologies of sites for CO₂ hydrate storage can be distinguished: shallow seafloor (<300 m), deep seafloor (300–700 m), and ultra-deep seafloor (>3700 m) [31]. On one side, the density of water favors the sequestration process increases with depth; unfortunately, the depth is also proportional to the overall costs, mainly associated to the gas injection phase. In addition, the thickness of the area suitable to host hydrates must be considered. It is clearly wider when water is deep [32] and determines the feasibility of realizing a plant for CO₂ hydrate formation and storage in a specific site. For instance, the CO₂ hydrate stability zone in Lake Superior was found to be approximately equal to 800 m, with a consequent storage capacity equal to 256 Gt of carbon dioxide [33].

The storage of energy gases in the form of hydrates is considered one of the most promising strategies for the near future. The increasing consumption of methane, together with the expected greater production and usage of green hydrogen, are focusing the interest of researchers on the usage of clathrate hydrates as vectors for the storage and transportation of these gases [34]. The storage of methane in liquid form requires –83 °C and 5 MPa [35,36]. At the same pressure, methane can be easily stored into clathrate structures also at temperatures higher than 0 °C [37].

Differently, the formation of hydrates containing pure hydrogen is difficult and absolutely not competitive. The most common techniques for hydrogen storage consist of high-pressure vessels [38], usage of porous materials [39], metal hydrides [40–42], and cryogenic technologies [43]. The main difficulties in storing hydrogen lie in its extremely low density (0.089 kg/m³) and the consequent need for large volume or extreme thermodynamic conditions [44]. The problem is partially solved with high-pressure vessels, where hydrogen is stored at pressures between 35 and 70 MPa. These high pressures lead to high energetics costs; in addition, the vessels must be realized with specific and expensive materials, in order to avoid any leaks [45,46]. Similarly, the cost of raw materials represents the main limiting factor for metal hydrides [47], even if this technology offers the highest

performances in terms of energy density. With cryogenic technologies, the problem of raw materials is solved, but the liquefaction of hydrogen requires extremely low temperatures (up to 20 K), and the energy required for hydrogen cooling is more than one-third of the total energy stored [48].

The proposal to store gaseous hydrogen in the form of hydrates dates back to the 1990s [49]. The pressures required for this application were immediately considered, as previously asserted, not competitive with the traditional techniques. In fact, more than 200 MPa are needed to form hydrogen hydrates at room temperature [50]. The problem was overcome by using appropriate additives, capable of promoting the process, thus obtaining the same results but at significantly lower pressures [51,52]. On its own, the use of an additive does not solve the problem definitively: first, the selected compound must be widely available, low-cost, safe for human usage, and environmental friendly. Moreover, further separation and recovery phases must be considered. The enclathration of hydrogen molecules can be enhanced also with the addition of complementary gases [53,54]. The introduction of a second guest, having a more appropriate size for hydrate formation, was proved to reduce the equilibrium pressure up to one order of magnitude. Appropriate complementary gases are carbon dioxide and small-chain hydrocarbons (C2—C5) [55].

Similar to ice, the crystalline structures of hydrates do not include in their lattice the impurities present in the aqueous solution, such as salts, ions, and pollutants. This property allows one to obtain fresh water, with the following dissociation of hydrates, and to concentrate these contaminants in the remaining aqueous phase, thus facilitating their further treatment. The use of clathrate hydrates for this scope is gaining a growing interest as a competitive alternative of the traditional techniques or evaporation, membrane, and crystallization [56]. Two main differences exist between ice and hydrates in this field: first, the possibility of carrying out desalination and/or the removal of pollutants at temperatures higher than 0 °C, and then, the difference between the formation and dissociation of hydrate crystals, which can be advantageously exploited. The presence of salts and ions in the aqueous solution reduces the activity of water (thus its capacity of hydrogen bonding with the surrounding molecules of water) and hinders the process by lowering the formation rate of clathrates [57]. However, these contaminants do not affect the dissociation of hydrates, causing this process to depend exclusively on the physical and chemical properties of the hydrate lattice [58]. The removal efficiency depends on the ion size and their charge [59]: lower charge numbers and larger ionic sizes improve the removal efficiency [60,61]. In fact, ions with high charges also have higher hydration free energy, and the resulting hydrated ions are more stable, with a consequent lower separation efficiency [62,63]. Differently, a larger size makes the diffusion of ions in water more difficult; thus, their inhibiting effect is lower, and their removal is consequently favored [64]. Nowadays, the most suitable hydrate formers, for water treatments, are R141b, R22, CHClF₂, HCFCs, HFCs, and CFCs, due to the high stability they confer to the hydrate structures, their non-toxicity for humans, and their immiscibility with water [65].

The same property exploited for desalination can be also advantageously applied for the concentration of food [66]. To obtain concentrated juices, the removal of water is often carried out by means of evaporation. This process represents one of the most cost-effective phases of the whole supply chain [67]. In addition, the evaporation cannot be applied in the presence of volatile species, which must be preserved within the final product. Another possibility consists of the use of membranes. This technique is rarely used because of problems related to the frequent obstruction of filters and membranes. In this sense, gas hydrates are a promising alternative due to the low energy required and to the high water removal efficiency they are allowed to reach [68,69]. Among the potential applications of clathrate hydrates, the storage of cold energy is gaining the growing interest of researchers and industrialists. Cold storage technologies probably represent the most efficient solutions to reduce the gap between electricity consumption and production [70]. Researchers are mainly focused on their applications in buildings, to reduce the related energy consumption

and the emissions of carbon dioxide [71]. Different cold storage techniques exist: water cold storage, ice cold storage, eutectic salt cold storage, and hydrate cold storage. The first method has low storage capacity and needs large volumes to be considered. The other techniques belong to the phase change cold storage options. Regarding ice cold storage, the main problem is the necessity of reaching low temperatures (up to $-10\text{ }^{\circ}\text{C}$) and the related costs [72]. Eutectic salts are often expensive and cause corrosion [73,74]. On the other side, hydrate cold storage can be performed at temperatures higher than $0\text{ }^{\circ}\text{C}$ and is less energy intensive than the other techniques; moreover, corrosion is avoided. The competitiveness of the process is highly dependent on the guest species selected. The most accredited options are carbon dioxide, methane, tetrabutylammonium bromide (TBAB), and cyclopentane [75].

3. Reasons behind the Low Diffusion of Hydrate-Based Technologies

Despite the enormous potentialities related to the natural reserves of hydrates and to the numerous possible applications of their intrinsic properties, their effective exploitation is still marginal and mainly classified as a field test. All these applications are still not competitive with the traditional solutions and are in need of further scientific and technologic development to fill the gap.

In terms of energy production from natural hydrate reservoirs, two main problems are identified: the high costs for the recovery of methane and the environmental sustainability of the process. The exploitation of marine reservoirs, which represent up to 97% of the whole reserves, implies the need to reach and work on deep oceans. Similarly, the mining activity required for the exploitation of terrestrial deposits presents different but equally relevant problems. Several field tests were carried out to verify the feasibility and economical sustainability of the process. The main field applications were/are carried out in the Alaska North Slope, western Siberia, the Mackenzie Delta, the Nankai Trough, and Messoyakha. In particular, Messoyakha is sited in the Arctic on the eastern border of west Siberia. The hydrate deposit in this region was discovered in 1967 [76], and the quantity of gas stored in the form of hydrates was estimated to be equal to $9\text{--}12 \times 10^9\text{ m}^3$. At the end of 2011, the quantity of gas recovered from hydrates was equal to $45 \times 10^6\text{ m}^3$, and the water produced from the dissociation of water cages was $48 \times 10^3\text{ m}^3$. The main advantage of these reservoirs remained in the stability of the pressure, which kept the recovery efficiency unchanged for many years. During gas production, the internal drop of pressure is balanced by the dissociation of hydrates and the following release of further methane. At the same time, the water production was contained enough to not affect the process significantly.

However, the Messoyakha site is still considered a unique example of a commercially successfully hydrate deposit, confirming that the feasibility of worldwide exploitation of hydrate reservoirs is far from being truly possible [11]. In addition, over the years, some doubt about the effective provenience of recovered gas from hydrates and not from the adjacent free gas zones has emerged [77].

Considering all the field tests carried out between 1997 and 2013, the continuous time of methane production rarely exceeded six days; moreover, the production of sand always represented a serious problem to overcome. The single-well system emerged as the preferable solution, compared with dual or multi-well configurations. However, the single-well system led to a production efficiency lower than that of the other solutions.

Gas hydrates harden the compactness of sediments; their decomposition would lead to losses of shear strength and instability of the well [78,79]. The release of gas could also increase the pore pressure, thus producing failures and deformation of soils [80]. The mechanical deformation of sediments cannot be accepted to ensure the environmental preservation; moreover, it could also negatively act on the assessment of the gas yield from the hydrate deposits [81].

The final disposal of carbon dioxide in the form of hydrates in deep oceans and in continental margins is feasible, but the associated costs cannot be absolutely neglected. The complexity of CO₂ storage is drastically dependent on some key parameters, which must be carefully determined and often make the specific site and/or procedure selected unavailable. The thermodynamics and kinetics of CO₂ hydrate formation (mainly) and dissociation are clearly the two most effective variables for the process. Both the phases must be determined: it has been established that the dynamic process of hydrate decomposition is simultaneous to the formation of hydrates in the sediment layers. The storage capacity of a specific area is a function of the phase boundary equilibrium conditions of hydrates. Moreover, the gap between local and phase equilibrium conditions is proportional to the quantity of gas effectively destined to the area and is also crucial for ensuring the stability of the hydrate lattice, thus avoiding the release of carbon dioxide in the atmosphere with time. In this sense, the effect of salts and ions dissolved in water is crucial and must be verified. Ions dissolved in water affect the formation of hydrates, while they do not have a relevant influence on the dissociation phase. Experimental results proved that even in presence of salts, the sequestration of carbon dioxide in deep oceans and in continental margins is possible [82,83]; however, the variations in terms of the storage capacity, process efficiency, and costs cannot be neglected.

Gas hydrates can be exploited for energy storage: energy carriers, such as methane or hydrogen, can be stored in their cavities, and high energy densities can be theoretically achieved. Moreover, hydrates can be directly used for thermal energy storage (cold energy). Similar to the previous applications, the efficiency is still low also for these kinds of applications. The advantages of using hydrates as storage carriers are highly attractive: water is an inexpensive material, the transportation phase is easier and less expensive when the storage is solid, it is safe for humans and for the environment, and so on. Unfortunately, the usage of hydrates for this proposal is still far from technical maturity [84]. The first variable is the stochastic nature of the process: the same processes, carried out with the same experimental conditions and with the same apparatuses, often produce different results [85]. In fact, parameters such as the typology and diffusion of nucleation sites, the level of mixing between water and guest molecules, the presence of impurities and their chemical composition, the presence, concentration, and typology of ions or other substances in water, and so on can drastically intervene on the process, mainly during the nucleation phase [86]. The storage capacity can be expressed as a function of the hydration number or the proportion between the molecules of gas and water in the hydrate cell. In the presence of gases and conditions suitable for the production of sI hydrates, this number is on average equal to 5.75 if the guest species can occupy only the small cages, while it is equal to 7.67 if both types of cavities can be filled. In addition, the complete cage occupancy is highly improbable to reach; for that reason, the hydration number can vary from 5.75 to 19, with consequent enormous differences in terms of storage capacity.

Regarding the storage of thermal energy, the main problem is, as predicted, the required costs and the environmental impact. On one hand, the first can be solved by using specific refrigerants; unfortunately, these refrigerants consist of highly harmful greenhouse gases, and their usage cannot be accepted anymore. Conversely, environmentally friendly species can be involved in the process, with benefits in terms of sustainability and, on the other hand, a still not acceptable increase in costs. The current research is focused on defining solutions capable of completely solving, or reducing, both the problems. Apart from this, the cold storage technology still suffers from relevant problems, which must be addressed in order to make its large-scale diffusion feasible. In particular, the internal structure of the hydrate cold storage needs to be optimized [70]. Moreover, the efficiency of cold storage systems must be defined prior to their construction, and the current simulation software must be improved and made more accurate [70].

Finally, HDB techniques are a particularly promising application for gas hydrates, mainly in geographic regions where low temperatures persist for the whole year. In addition, for this technology, maturity has not yet been reached, and their application on the industrial scale is not competitive [87,88]. The low kinetics clearly represents the first hindrance to overcome. One of the most affecting problems consists of the separation of hydrate crystals from the residual brine: the currently used apparatuses do not achieve good efficiencies in this sense [89]. The usage of additives could solve the kinetic issue; unfortunately, chemicals showing the best performances for HBD techniques are often poisonous for the environment and toxic for humans, and their cost cannot be neglected [90,91].

The main advantages and limitations of the applications, described in this section and in the previous one, are summarized in Table 1.

Table 1. Main advantages and limitation of the hydrate-based applications described in Section 2 and in Section 3.

Application	Advantages	Limitations
Energy production	Abundancy (10^{15} – 10^{17} m ³ CH ₄)	Risks for the environment: deformations, soil failures, and landslides
	Potential carbon-neutral energy source	Risks for the atmosphere: gas leaks
	Higher distribution of natural reservoirs (if compared with conventional energy sources)	High energy spent/energy recovered ratio Technical maturity still not reached
CO ₂ disposal in deep oceans	Suitable pressures and temperatures	Complexity of the CO ₂ injection phase
	Unlimited availability of space	Too elevated costs (without the contemporary production of energy)
	Environmentally friendly	
Storage of energy gases	Ease of transportation	Low efficiency for small-size molecules (H ₂)
	Energy density similar to that of pressurized vessels	Necessity of using gas mixtures to improve the storage efficiency
	Safety for operators	
	Safety for the environment	
Desalination, wastewater treatment, and food concentration	High efficiency (up to 98%)	Need for chemical additives
	Possibility for CO ₂ reuse prior to final disposal	Recovery of additives from water
	Mature technology	Overall costs
		Separation of hydrates from residual brine
Cold storage	Possibility for CO ₂ reuse prior to final disposal	Technical maturity still not reached
	High energy density	Elevated plant costs
	Promising application in key sectors (nuclear plants)	Need for chemical additives
	Use for security systems	

4. Strategies for Improving the Process Efficiency

In order to make the processes described next effectively competitive with the traditional procedures, during the last decades, several integrative solutions have been proposed and practically validated. Problems such as low storage efficiency, slow kinetics, high energy costs, and so on can be drastically reduced or completely solved. However, in most cases, the resolution of one problem leads to the appearance of another one.

The main answer to most of weaknesses related to hydrate-based processes consists of the usage of chemical additives, capable of acting as promoters or inhibitors (or both) for gas hydrates, depending on the required performances. Promoters can be used to improve the process kinetics by lowering the induction period and favoring the formation of the

first hydrate nuclei and also to perform the thermodynamics of the process, allowing the formation of hydrates at milder thermodynamic conditions than those naturally required. Conversely, chemical inhibitors lead to the opposite results: some of these additives can lower the process kinetics, while some others shift the needed pressures and temperatures to more severe values.

Chemical inhibitors can be advantageously applied in the energy sector: the injection of inhibitors, within the natural gas hydrate deposit, facilitates the release and recovery of gaseous methane. Promoters could help in reducing the energy required to form hydrates in applications such as desalination, cold storage, food concentration, wastewater treatments, and so on. In addition, the storage of energy gases can be enhanced in this way. On the other side, these additives introduce further variables to consider. Environmental sustainability, safety for humans, availability, and costs are the main hindrances. Moreover, their subsequent separation and recovery often represents a complex and too expensive procedure.

Inhibitors are divided into thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs) [92,93]. The first group shifts the phase boundary equilibrium of gas hydrates to higher pressures and/or lower temperatures; the second is capable of enhancing or delaying the nucleation phase and the growth rate of hydrates. THIs form hydrogen bonds with water molecules, thus avoiding their participation in the production of hydrates [94]. KHIs are included in the wider group of low-dosage hydrate inhibitors (LDHIs), together with anti-agglomerants (AAs). A further group of additives consists of ionic liquids (ILs), organic salts existing in the liquid phase at room conditions [95]. To affect the formation of hydrates, ILs must be hydrophilic, in order to interact with water [96]. The most widespread organic inhibitors are amino acids, organic compounds forming the building blocks of proteins [97]. Amino acids are not poisonous for the environment and for humans, are largely available and inexpensive, and do not cause corrosion [98,99].

Similarly, promoters are divided into thermodynamic hydrate promoters (THPs) and kinetic hydrate promoters (KHPs). The first group lowers the phase boundary equilibrium conditions to lower pressures and/or higher temperatures, while the second group acts on the nucleation phase and, more generally, on the induction period. Tetrahydrofuran (THF) is the most known THI, while sodium dodecyl sulfate (SDS) is the same for KHIs. Some of these additives, for instance THF, lead to the formation of sII hydrates, a structure showing higher gas density and better forming conditions than the cubic sI [100]. This transition is possible also with ketone compounds, such as cyclobutanone and cyclohexanone [101]. Differently, TBA-Halides allow the formation of semi-clathrates and have found large applications in cold storage, gas separation, and gas storage hydrate-based techniques [102,103]. The main problems related to these chemical compounds are corrosion and the environmental impact. In this sense, halogen-free semiclathrates provide good performances, especially in terms of biocompatibility [104]. Biocompatible promoters, such as potato starch and glycolipid-type surfactants, are gaining growing space [105]: they offer good performances as promoters; however, the effect is proportional to the concentration, and the costs are often too elevated and not competitive. It was also established that the contemporary use of different promoters, i.e., THF and SDS, produces a synergistic effect and further improves the water-to-hydrate conversion [106,107].

In addition to costs, availability, and environmental issues, these additives must be recovered after their usage in order to reuse them and reduce their impact.

Probably the most promising solution to improve the efficiency of energy production and greenhouse gas storage processes is to carry them out contemporarily via replacement techniques. For the first time, in 1980, it was proposed to couple the recovery of methane with the storage of carbon dioxide, with a triple benefit: improving the efficiency of methane recovery, avoiding the dissociation of water cages and, the CO_2/CH_4 exchange ratio being theoretically equal to one, obtaining a carbon-neutral energy source [108]. The only recovery

of methane from hydrates inevitably allows the dissociation of structures; the replacement of methane with carbon dioxide molecules ensures the stability of the crystalline framework and avoids consequences such as soil deformation and failures [109]. Moreover, the process increases the structural strength of hydrate reservoirs: the contemporary presence of both the gaseous species within the unit cells improves the mechanical properties of the lattice [110].

The replacement process is feasible because both species form the same typology of hydrate structure (the cubic sI). In addition, the capture of carbon dioxide is more favored than that of methane at the same thermodynamic conditions: the enthalpy of formation is equal to -57.98 kJ/mol for CO₂ hydrates and -54.49 kJ/mol for CH₄ hydrates. This latter condition is crucial for the feasibility of the replacement process because it defines the existence of a narrow thermodynamic region where the exchange can occur spontaneously [111]. The current replacement strategies are based on modifying the local conditions in order to drive the system within such a region.

Two different replacement mechanisms are possible: (i) the initial dissociation of methane hydrates and the re-formation of the hydrate lattice with carbon dioxide as a guest species [112,113] and (ii) the CO₂/CH₄ exchange directly within the already existing water cages [114,115]. The real evolution of the process probably stays in the middle between these two mechanisms. Due to the difference in size between the two guests, the replacement mainly occurs in the large 5¹²6² cavities. The formation of binary CO₂/CH₄ hydrates causes the microscopic rearrangement of the crystalline structure and thus the partial rupture of cells and their reorganization.

The main hindrances occurring during the process are methane hydrate re-formation, competition between ice and hydrates [116], and pure CO₂ hydrate formation [117], which are responsible for the overall low kinetics. Moreover, the maximum exchange efficiency cannot exceed 75%. As previously asserted, carbon dioxide molecules preferentially fit the large cavities of the sI structures. For that reason, part of the molecules of methane present in hydrates are not involved in the process.

The maximum theoretical efficiency can be enhanced by using CO₂-based mixtures instead of pure carbon dioxide. The exchange can be advantageously carried out with CO₂/N₂ mixtures or directly with flue gas mixtures. Due to its lower size, the molecule of nitrogen can easily take the place of the molecule of methane under the geometrical point of view. Therefore, when using flue gas mixtures, theoretically, a 100% exchange efficiency can be reached. Unfortunately, by itself, nitrogen requires drastically more severe thermodynamic conditions to form hydrate; thus, flue gas mixtures require higher pressures and/or lower temperatures to form hydrates if compared with pure carbon dioxide streams. In order to carry out the process at conditions outside of the stability region for methane hydrates, only a small quantity of nitrogen can be mixed with carbon dioxide. At these low N₂ concentrations, the flue gas mixture coming from industrial processes can rarely be exploited. As an alternative, the replacement process can be realized within the stability region of methane hydrates. However, this latter possibility implies higher energy costs.

In order to visualize the effect on the thermodynamics of hydrates, due to the use of nitrogen in mixture with carbon dioxide, the following diagrams show the phase boundary equilibrium for pure carbon dioxide, methane, and nitrogen hydrates (Figure 1) and the same for hydrates containing binary CO₂/N₂ mixtures (Figure 2).

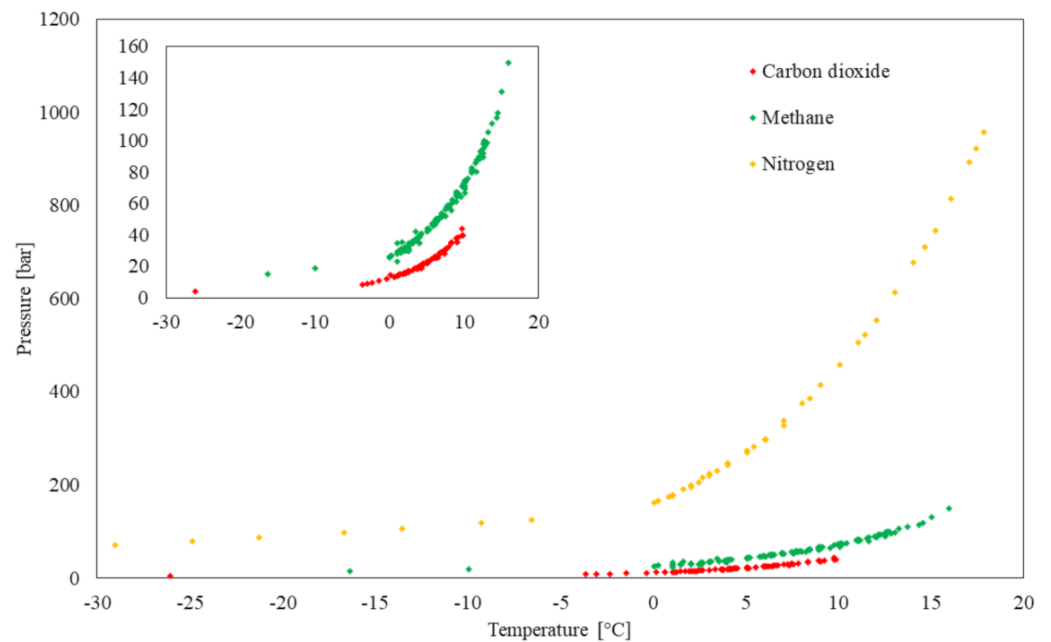


Figure 1. Phase boundary equilibrium diagrams for pure carbon dioxide (red), methane (green), and nitrogen (orange) hydrates [118–127].

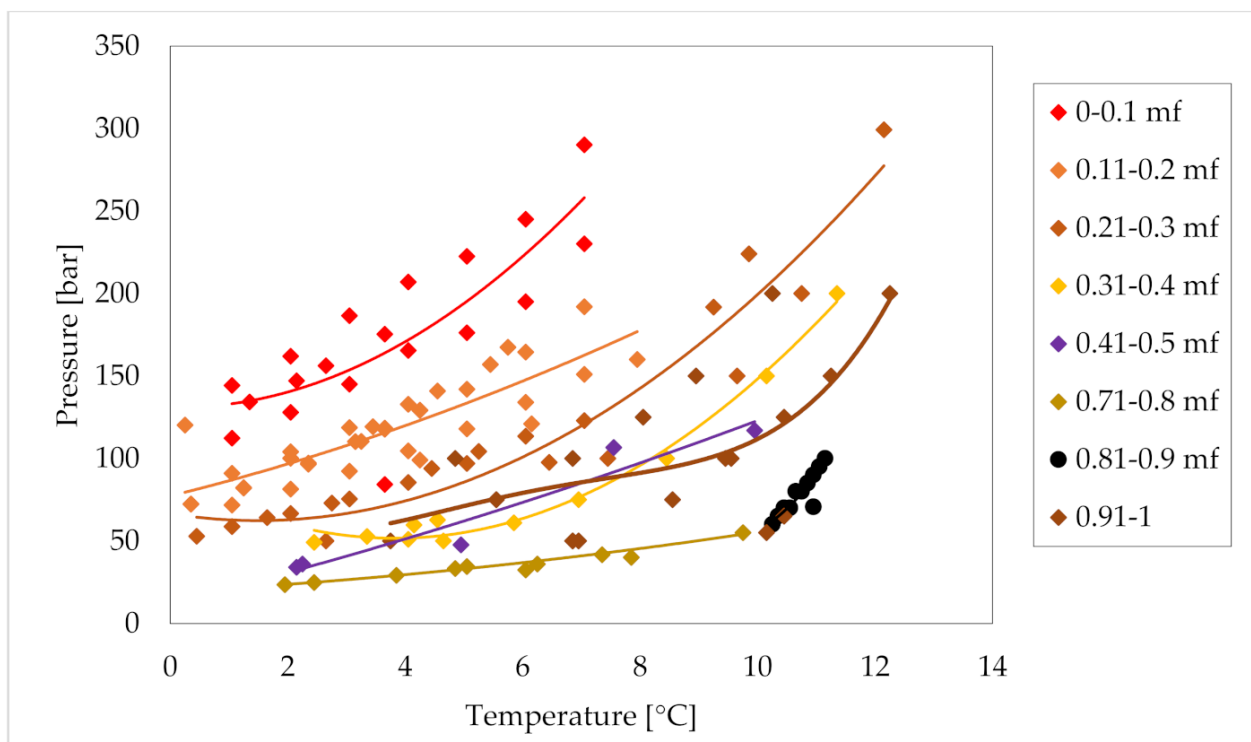


Figure 2. Phase boundary equilibrium diagrams for hydrates containing binary CO_2/N_2 mixtures. The legend indicates the initial CO_2 concentration, expressed as molar fraction (mf) [128–131].

Using this binary mixture, the recovery of methane is improved due to the selective replacement of methane molecules in the small cavities with nitrogen molecules. This strategy was tested for the first time in the natural hydrate reservoir in the Alaska North Slope. The test was carried out by Conoco Phillips, in collaboration with the US-DOE [132]. A binary CO_2/N_2 (23/77 mol%) was used for the scope. Park and co-workers asserted that the usage of this kind of mixture allows the attainment of replacement efficiencies

up to 85% [133]. Conversely, they affirmed that with pure carbon dioxide, the maximum recovery efficiency is 64%. The greater production of methane with CO₂/N₂ mixtures was also proved by Lim and colleagues [134].

The further development of hydrate-based technologies must be focused on the following specific key areas: process efficiency, process operation, related costs, environmental sustainability, and scale of the apparatuses.

The process efficiency is probably the most relevant theme to deepen, and more scientific effort is required to better control the stochastic nature of the hydrate formation process and, more generally, its kinetics. Some technologies are already mature, but most hydrate-based techniques have to be performed or re-designed. Chemical additives represent an invaluable opportunity to improve the competitiveness of these applications; to be completely sustainable, these additives should be inexpensive, environmentally friendly, widely available, effective at low concentrations, and non-toxic for humans. In this regard, the research is still far from defining the optimal solutions. A higher role of field and experimental tests is mandatory to reduce the scattering and inconsistency in currently available kinetics and equilibrium data for hydrate systems. The scale of hydrate production systems is often too contained, and the scaling up of these systems is not studied enough. The environmental sustainability has a key role in the energy production processes since the impact of mining operations still has dramatic consequences on the surrounding environment. Moreover, as previously asserted, most of hydrate-based applications require the adoption of chemical additives to be competitive and attractive. These chemicals are often poisonous for the environment, and the definition of highly sustainable additives must be carefully planned and pursued. Finally, the main limitation for the diffusion of hydrate-based technologies remains the high operative costs, which must be definitively reduced through the possible implementations as described later and by defining novel applications and the most performant solutions.

In this sense and based on the evidence described in the previous paragraphs, a promising solution to solve or partially reduce the main problems affecting hydrate-based applications consists of using CO₂ small-chain hydrocarbons in most of the applications shown in Section 2. The term “small-chain hydrocarbons” mainly refers to C₂–C₅ HCs, such as propane and pentane. The main reasons behind their usage are the extremely low pressures required for their enclathration and the ease of separation from carbon dioxide. The formation of hydrates with CO₂/HC mixtures could improve the process efficiency of desalination and wastewater treatment. These mixtures could be also used for energy production and storage: a higher replacement efficiency could be reached, while a higher energy stored/energy spent ratio would be established in cold storage applications.

5. Mixtures Containing Small HCs in Gas Hydrates Production

The presence of small-chain HCs in the gaseous mixture leads to the formation of sII instead of sI hydrates, with consequent benefits in terms of the thermodynamic conditions required for the formation of hydrates and gas storage capacity. The reason can be found in the cage occupancy ratio and in the capability of these molecules to better fit the larger cavities of sII instead of those belonging to sI. In this sense, small-chain HCs act as sII hydrate-forming additives [135,136]. Three different typologies of hydrate structures were found to exist in nature: the cubic structure I (sI), the cubic structure II (sII), and the hexagonal structure H (sH) [137]. These structures differ from each other in the typology and number of cavities they involve. The cavities are defined with the nomenclature “ $n_i^{m_i}$ ”, where “ n_i ” is the number of edges in the specific face, while “ m_i ” is the number of faces having n_i edges. Five different cavities exist: pentagonal dodecahedron (5¹²), tetrakaidecahedron (14-hedra, 5¹²6²), hexakaidecahedron (16-hedra, 5¹²6⁴), irregular dodecahedron (4³5⁶6³), and icosahedron (5¹²6⁸). The unit cell of sI contains two small 5¹² cavities and six 5¹²6² cavities. It can host molecules having diameters between 4.2 and 6 Å. Methane and carbon dioxide naturally form this kind of structure; for that reason, sI is the most diffused structure in natural reservoirs. The reason why the replacement efficiency cannot

exceed 75% can be explained with the filling ratio for the two guest species of the two different cavities forming sI. The filling ratio consists of the ratio between the molecule and the cavity diameters. In the small 5^{12} cavity, this ratio is equal to 0.855 for methane and 1.00 for carbon dioxide. Therefore, carbon dioxide can fit this small cavity but with greater difficulties than the molecule of methane. The unit cell of sII contains sixteen small pentagonal dodecahedrons and eight 16-hedra. Molecules having diameters between 6 and 7 Å can form this type of structure. Common examples are ethane and propane. Since some molecules can easily form both of the two types of cubic structures, the transition between sI and sII is possible and mainly depends on pressure. Finally, the hexagonal sH includes three pentagonal dodecahedrons, one icosahedron, and two irregular dodecahedrons. To be formed, this structure needs guests having diameters larger than 9 Å, together with small-size molecules, such as hydrogen.

As previously asserted, the presence of small-chain HCs favors the formation of sII hydrates, with relevant benefits in terms of the energy required for hydrate production and gas storage capacity [1].

Molecules such as ethane, propane, and butane are capable of forming hydrates at pressures up to one order of magnitude lower than those required for methane and carbon dioxide at the same temperatures. This is clearly visible in Figure 3, where the phase boundary equilibrium conditions of C_2H_6 , C_3H_8 , and C_4H_{10} hydrates are shown.

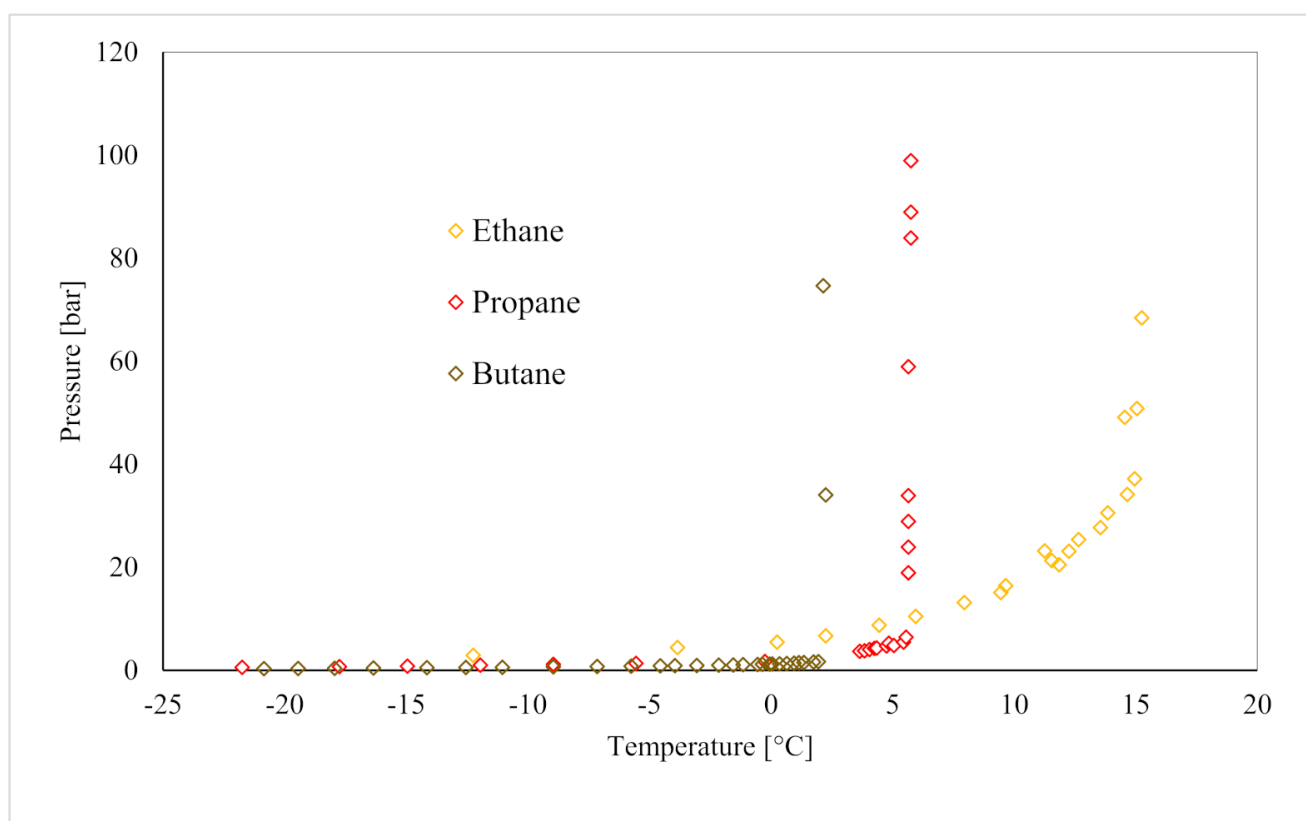


Figure 3. Phase boundary equilibrium diagrams for pure ethane [138], propane [139], and butane hydrates [140].

At temperatures below 280 K, these species can form hydrates at pressures extremely close to the atmospheric value. This is possible thanks to their size, which is particularly appropriate to fill the 14-hedra and 16-hedra cavities with a filling ratio approximately equal to one, with a consequent high stability for the whole hydrate lattice.

Their size makes them a suitable option also for the storage of energy gases, such as hydrogen, whose storage is highly expensive and represents one of the most limiting

barriers for its diffusion. The thermodynamic conditions required for hydrogen enclathration are absolutely not competitive; however, the addition of small concentrations of other gases, such as propane, allows the lowering of the needed pressure by about one order of magnitude. In the presence of propane, Babu and colleagues capture hydrogen into hydrates at temperatures between 275.3 and 283.2 K and pressures ranging from 2.51 to 7.9 MPa [141].

The next section shows some experimental results, extrapolated from the current literature, showing how the phase boundary equilibrium for gas hydrate may significantly change when the guest species is mixed with small-chain hydrocarbons.

6. Phase Equilibrium Boundary Conditions for Gas Mixtures Containing Low Concentrations of C₂—C₄ HCs

This section shows a brief collection of phase boundary equilibrium conditions for gas hydrates made with methane as the main guest component, mixed with minor concentrations of small-chain hydrocarbons (ethane, propane, and iso- and normal-butane). The scope of this section is to highlight the lowering of pressures required for hydrate formation, even in the presence of small concentrations of these added hydrocarbons. Figure 4 shows a diagram describing the equilibrium conditions for hydrates containing binary or ternary mixtures containing methane and aid gases, at temperatures within 0–25 °C and pressures from 0 to 170 bar.

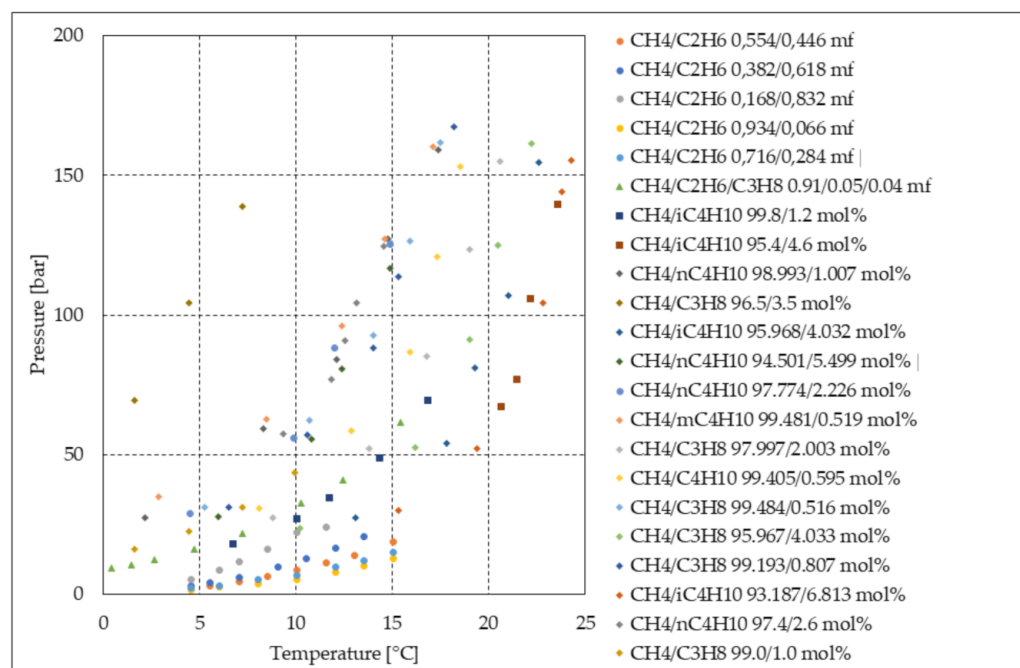


Figure 4. Phase boundary equilibrium diagrams for hydrate systems containing methane and small concentrations of C₂H₆, C₃H₈, and (iso- and normal-) C₄H₁₀ [138,142–145].

The comparison between the diagrams shown in Figure 4 and the phase boundary equilibrium conditions for pure methane hydrates, illustrated in Figure 1, immediately proves the advantageous effect due to the introduction of these small-chain HCs in the system.

This paragraph does not represent a detailed collection of the experimental results produced and shared in the literature; however, it allows the validation of the main thesis proposed in this article: small-chain hydrocarbons can be considered an alternative to chemical additives in most hydrate-based processes.

Figure 4 deals with the enclathration of an energy carrier such as methane. Similar positive results can be also obtained for the capture of waste gases, such as carbon dioxide.

The diagram in Figure 5 describes the formation of CO₂ hydrates in a small-scale reactor (whose detailed description can be found in [146,147]) filled with pure silica sand, in order to simulate a natural marine deposit. With this configuration, Figure 5 describes the formation of pure carbon dioxide hydrates and the same process carried out with a binary CO₂/C₃H₈ mixture, with a concentration equal to (0.95/0.05 mf).

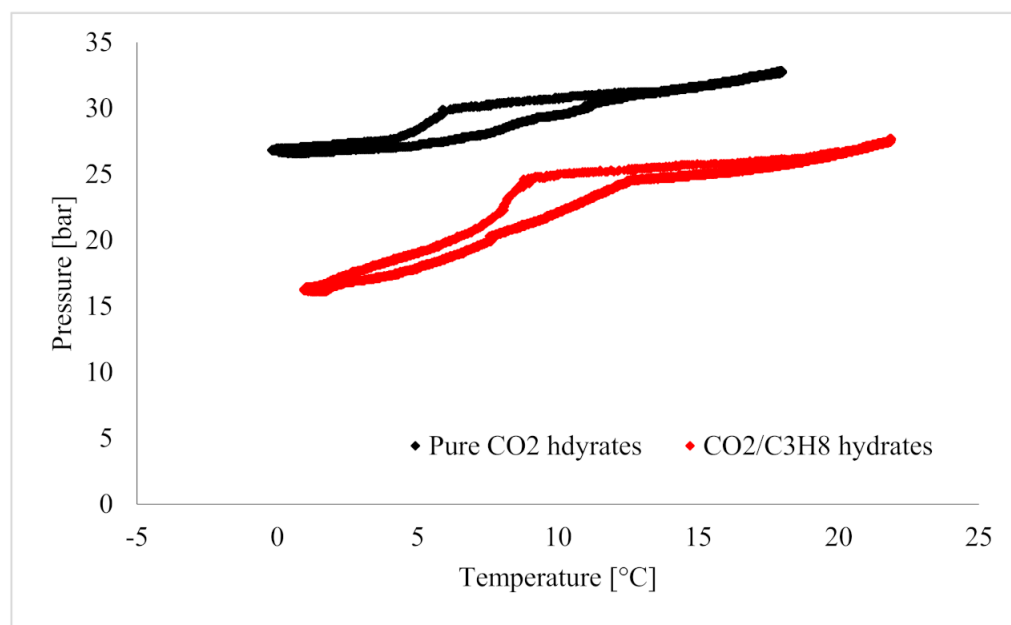


Figure 5. Formation and dissociation of pure carbon dioxide hydrates, made with the apparatus described in [146,147] and in the presence of pure silica sand.

These diagrams cannot be used to define the phase boundary equilibrium conditions for the mixture, being the process depending on the properties of the reactor and, mainly, the shape, typology, and porosity of sand. However, these experimental values clearly prove the benefit due to the introduction of 0.05 mf propane in the system.

Based on the data shown in this section, small-chain hydrocarbons can be used to improve the capture and storage of both energy and waste gases. Moreover, they can be involved in all the processes where the massive and rapid formation of hydrates is desirable, such as desalination and wastewater treatment. Conversely, there is not enough evidence regarding the possibility of improving the gas mixture separation, via hydrate formation, with the auxilium of these aid species.

In this section, the theoretical convenience of using these compounds for improving the aforementioned process has been proved. To provide a further validation, in the next section, some experimental evidence will be shown and briefly described.

7. Practical Applications of Small-Chain HCs in Hydrate-Based Processes

This last paragraph shows and describes some experimental results, published in the literature in recent years, regarding the usage of small-chain HCs in the hydrate-based key activities described in Section 2. Probably the most widespread application consists of seawater desalination and, more generally, wastewater treatment. Montazeri and Kolliopoulos explained that since one cubic meter of hydrates has a water content between 85 and 94%, the formation of clathrates represents an excellent solution for seawater desalination. In their study [63], they proved that based on the data available in the literature, the hydrate-based process can be considered the less energy intensive and, at the same time, one of the most effective solutions, in terms of removal efficiency. The addition of small-chain HCs allows, in this sense, the improvement of the formation of hydrates and, consequently, the achievement of the practical feasibility and competitiveness of the process.

Babu and colleagues [89] studied the formation of hydrates with a ternary gaseous mixture containing carbon dioxide (38.1%), hydrogen (59.4%), and propane (2.5%) and in a silica sand bed. They observed that propane molecules attract the water molecules dispersed in the sand bed toward the hydrate formation area, thus increasing the production of crystalline structures. They also proposed a practical application, capable of carrying out at the same time seawater desalination and carbon dioxide storage and final disposal. According to it, seawater would be pumped through a crystallizer filled with sand. The formation of hydrates, with the mixture previously described, would lead to the formation of hydrates above sand, while salts would remain trapped within the sediment.

Saline water is also considered a serious hindrance in mining activities. It is commonly referred to as “produced water” and is a waste product, containing salts, heavy metals, dispersed oils, organic compounds, suspended solids, lipids, and other substances. The high concentrations of salts often limit the application of traditional desalination techniques, such as distillation or reverse osmosis. Yousefi and co-workers [148] proved that the formation of hydrates with a binary $\text{CO}_2/\text{C}_3\text{H}_8$ mixture, containing 10% propane, allows the perfect balance of the inhibiting effect of 12 wt% NaCl on hydrate formation. Thus, the mixture can be used to obtain high-efficiency removal of salts.

Sludges are sub-products of biological treatments of wastewater; these compounds often contain several toxic species, which must be removed and correctly disposed. Wu and colleagues [149] proposed a method to obtain sludges’ dehydration and their following depuration, via hydrogen hydrate production. It was concluded that the organic substances of sludges act as promoters for hydrate formation. This peculiarity, together with the usage of propane as a guest, allowed the drastic reduction of the water content of sludges, thus facilitating their following treatments. The water obtained from the dissociation of hydrates does not need further treatments. Finally, the present solution was proved to be less energy intensive than common techniques such as mechanical dehydration and thermal drying.

Hydrate-based gas separation processes can be highly improved with the use of small-chain HCs as guest species. The production and combustion of syngas leads to the formation of carbon monoxide. This species can be separated from the gaseous mixtures via hydrate formation. The presence of small-chain HCs strongly promotes this process. Jeong et al. [150] concluded that in presence of aid gases, it is possible to capture carbon monoxide in the form of sII hydrates and not sI, with consequent high storage capacities and minor energy requirements. In this structure, CO molecules would occupy the small-size cavities. Similarly, these hydrocarbons can be also advantageously applied for the separation of carbon dioxide from hydrogen in processes related to the production of blue hydrogen from fossil fuels [151].

Finally, the storage of energy gases takes great advantages from the usage of small-chain HCs. This concept was already explained in the text for the storage of hydrogen [55,141]. The proposed solution was also tested for the storage and transportation of natural gas. Even small percentages of these gases lead to the production of sII, instead of sI, hydrates, with consequent benefits for the process kinetics and also for the stability of hydrates [152]. It was observed that natural gas molecules occupy more than one-third of large-cage cavities and up to 100% of small-cage cavities; therefore, high storage capacity is ensured in the presence of these aid gases.

8. Conclusions

Even if the production of energy remains the main area of application for gas hydrates, due to the enormous reserves diffused worldwide in deep oceans and in permafrost regions, the formation of these structures can be advantageously applied in several technological applications, such as gas storage and transportation, desalination, wastewater treatment, energy storage, and others. In particular, the hydrate-based technology promises to reach the same or higher efficiencies than the traditional methods, while requiring lower energy inputs.

In the present review, the main hydrate-based processes have been enounced and described, together with their advantages and main limitations. In the past years, several solutions have been proposed to overcome such limitations, mainly based on the use of additives and on the contemporary application of more than one technique (i.e., replacement processes), in order to improve the overall efficiency. These solutions were discussed in detail, together with the main hindrances related to their applications. A brief overview on hydrate-forming additives and their cataloguing, specific usage, and consequences, both on the process and on the environment, was provided.

Finally, the usage of small-chain hydrocarbons as aid guests in hydrate-based processes was proposed and argued. Based on the experimental data collected from the literature, the thermodynamic properties of hydrates containing pure C2–C4 and mixtures, formed with these aid gases and other species commonly involved in the hydrate-based technologies, were described in the text. The benefits related to the usage of these gases were theoretically proved. Finally, direct applications of these gases in hydrate-based processes, such as gas storage, gas transportation, desalination, wastewater and sludge treatments, and CO₂ disposal, were collected and described in detail. Therefore, thanks to a deepened study and cataloguing of the experimental evidence available in the literature, the benefits associated to their usage in hydrate-based processes were definitively established.

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