

Article

Cold Energy Storage via Hydrates Production with Pure CO₂ and CO₂/N₂ (70/30 and 50/50 vol%) Mixtures: Quantification and Comparison between Energy Stored and Energy Spent

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Abstract: Gas hydrates represent an attractive opportunity for gas storage. These ice-like structures can be produced both for the final disposal of greenhouse gases such as carbon dioxide in the solid form and for the storage of energy gases, such as methane, propane, and others, with the possibility of reaching energy densities comparable with those of pressurised vessels, but at lower pressures. In addition, gas hydrates can be directly produced for their capability to act as phase change materials at temperatures higher than 0 °C. This research deals with cold energy storage via the production of gas hydrate into a lab-scale apparatus. Hydrates were produced with pure carbon dioxide and with CO₂/N₂ mixtures (70/30 and 50/50 vol%). For each mixture, the amount of energy spent for hydrates production and cold energy stored were calculated, and the results were compared among each other. The addition of nitrogen to the system allowed us to maximise the energy stored/energy spent ratio, which passed from 78.06% to 109.04%; however, due to its molecular size and the consequent impossibility to stabilise the occupied water cages, nitrogen caused a reduction in the total quantity of hydrates produced, which was obviously proportional to the energy stored. Therefore, the concentration of nitrogen in the mixtures need to be carefully determined in order to optimise the Estored/Escent ratio.



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1. Introduction

Gas hydrates are ice-like and non-stoichiometric crystalline compounds where water molecules are hydrogen-bonded among each other and produce polyhedral cavities containing gaseous guest molecules [1]. Various gas species can form hydrates, among them being methane, ethane, propane, iso-butane, carbon dioxide, nitrogen, hydrogen sulphide, and others [2–4]. The possibility of producing hydrates with a specific species is mainly a function of its size and geometry; however, the chemical properties also play a crucial role. In particular, the molecular size of guests leads to the production of different hydrate structures: the cubical sI (which typically hosts molecules as methane and carbon dioxide), the cubical sII (propane, hydrogen) and the hexagonal sH (iso-pentane, neohexane). Probably the main common property of guest species is their hydrophobicity, even if some exceptions exist, such as carbon dioxide and hydrogen.

Gas hydrates need relatively high pressures and low temperatures to be formed; the specific values required are a function of the guest compound involved in the process.

Within the crystalline framework, gas molecules are considered to be physically but not chemically trapped [5]. Between gas and water molecules, only van der Waals bonds are established, while water molecules are hydrogen-bonded among each other. The energy required to break hydrogen bonds is equal to 5 kcal/mol, while 0.3 kcal/mol is enough to

break van der Waals bonds. Therefore, the chemical interaction between hosts and guests can be neglected [5].

The main source of interest in gas hydrates consists of their huge and widespread natural reservoirs: approximately 10^{15} – 10^{17} m³ of methane can be recovered from the currently known natural gas hydrates reservoirs [6], which are mainly distributed in deep oceans and continental margins; approximately 97% of discovered reservoirs exist in those places, while the remaining 3% belongs to permafrost regions [7]. The techniques used to recover methane from these reservoirs are based on altering the local conditions in order to make them no longer suitable for the stability of hydrates, whose dissociation causes the release of gas molecules trapped within their lattice. The most widespread solutions are depressurisation [8,9], thermal stimulation [10], and the injection of chemical inhibitors [11–13].

In addition to the production of energy, the formation of dissociation processes of gas hydrates find effective applications in several fields. Probably the most attractive option is the final disposal of carbon dioxide in solid form. Carbon dioxide can be injected into appropriate marine environments, where the favourable pressure and temperature conditions allow for the production of hydrate structures containing it [14]. To produce CO₂ hydrates, at least 30 bar are required at temperatures higher but approaching 0 °C. It means that the process can be carried out at a depth of equal to or greater than 300 m [15]. Depending on depth, the sites suitable for CO₂ storage can be divided into three main groups: shallow (<300 m), deep (300–3700 m), and ultra-deep (>3700 m) seafloor [16]. In general, the deeper the reservoir is, the larger the amount of CO₂ it is possible to store [17]. Lake Superior was tested for carbon dioxide storage under the form of hydrates. It is approximately 800 m deep, and the quantity of CO₂ storable in it was estimated to be equal to 256 Gt [18].

Similarly, hydrates can be produced for the storage and transportation of energy gases. The most diffused techniques are high-pressurised vessels [19], cryogenic technologies [20], the usage of porous materials [21], and metal hydrides [22].

The production of hydrates allows for the storage of energy gases at pressures lower than those required for the previously mentioned techniques and at temperatures higher than 0 °C [23]. Moreover, the energy density of the formed lattice, if considering cage occupancy approaching 100%, is comparable with that of pressurised vessels. For instance, one cubic meter of hydrates can contain up to 172 m³ of methane (evaluated at standard conditions) [24]. The energy density theoretically achievable is a function of the molecular size of guests. For that reason, the storage of hydrogen into hydrates, proposed for the first time in the 1990s, is difficult to perform [25]. Small molecules can fit the polyhedral cavities of hydrates, but without providing the needed stability for the lattice; therefore, their enclathration is possible only at extremely high pressures, comparable with those used for pressurised vessels [26]. The hindrance of pressure can be overcome with two different solutions: (i) the usage of chemical additives, capable of making the formation process feasible also at a pressure lower of more than one order of magnitude; and (ii) forming hydrates with gas mixtures instead of pure species [27,28].

Similar to ice, ions dissolved in water, impurities, and others cannot be involved in the production of hydrates and remain in the aqueous phase. Therefore, the process can be considered as a viable alternative to the conventional separation and purification procedures, such as evaporation, crystallisation, and filtration [29]. The production of clathrates allows for the obtainment of fresh water (from the melting of solid structures) and for the concentration at the same time of contaminants and impurities in the residual liquid water, thus facilitating the following purification processes [30]. Electrolytes are capable of lowering the activity of water and consequently its capability to form clathrate structures. The removal efficiency of these species from water depends on their size and charge: larger sizes and lower charge numbers enhance the process efficiency [31–33].

The same property can be exploited for the concentration of liquid foods, such as juices [34,35].

In addition to the storage of energy gases, gas hydrates can be directly exploited for the storage of energy. In particular, their production for the storage of cold energy is gaining continuously growing attention [36]. Compared with cold storage using water, ice slurries show high energy capacity, with their latent heat being approximately equal to 333 kJ/kg (water) [37]. However, the application of ice as a phase change material is limited due to its freezing point (273.15 K), which is beyond the range of application temperatures. For that reason, semiclathrate hydrate slurries were proposed as a viable alternative to ice [38]. Semiclathrate hydrates can be produced by reacting quaternary salts with water. These compounds can be produced at atmospheric pressure, and the range of phase change temperatures is nearly 5–14 °C. Unfortunately, the heat capacity of semiclathrate hydrates is lower than that of ice as the corresponding latent heat is close to 200 kJ/kg.

In this context, carbon dioxide hydrates gained the interest of researchers due to their latent heat and gas storage capacity in addition to the wide phase change temperature range [36]. The latent heat of carbon dioxide hydrates is higher than that of ice, at up to 500 kJ/kg [39,40]. In contrast to semiclathrates, at the operating temperatures, these compounds cannot be formed at room pressure; however, the operating thermodynamic region is attractive, with a pressure equal to 25–43 bar and the corresponding temperature being about 6–9.8 °C. In addition, such a range can be widely modified with the addition of chemical additives (thermodynamic promoters) to the system [41].

However, the production of pure carbon dioxide for the scope consists of an expensive process that can be avoided by using CO₂/N₂ gas mixtures. These mixtures can be easily produced from industrial flue gases (exhausts). In addition to the minor costs, the presence of nitrogen molecules, whose diameter is shorter than carbon dioxide molecules, allows for the increase in cage occupancy in the whole hydrate lattice. The exhausts of fossil-fuelled power plants consist of mixtures containing, in order of concentration, nitrogen, carbon dioxide, water, oxygen, and possible traces of further species [42–44]. The content of carbon dioxide usually does not exceed 15% [45] but with some exceptions, as one such case had the concentration grow up to 95% [46].

This experimental study deals with the storage of cold energy into gas hydrates, produced with pure carbon dioxide and with CO₂/N₂ mixtures with different concentrations, respectively (70/30 and 50/50 vol%). The two specific concentrations were selected in order to keep the role of carbon dioxide predominant, thus favouring the comparison with pure carbon dioxide, and at the same time observe the role of nitrogen with accuracy, both in terms of hydrates formation and the energy stored/energy spent ratio. This research was carried out on a lab-scale device. For each guest mixture, the hydrates production process was thermodynamically characterised. The quantity of energy stored was quantified globally and as a function of the time needed for its storage. Based on the energy inputs and based on the materials involved in the process, the energy spent was also measured and compared with the previous quantity. Therefore, the energy stored/energy spent ratio was determined for each guest species, and the results were finally compared. The results allow us to understand the role of nitrogen during cold energy storage processes via clathrate hydrates production.

2. Materials and Methods

2.1. Experimental Apparatus and Materials

Hydrates were formed in a lab-scale apparatus consisting of a cylindrical-shape stainless steel (316SS) reactor with an internal volume equal to 1000 cm³. Detailed descriptions of this apparatus are already available in the literature [47,48]; therefore, only a brief description of its main components is provided here.

The main details of the experimental apparatus are provided in Figure 1.

The upper flange allows us to easily inspect the internal volume and, if required, to quickly extract hydrate samples. It hosts the sensors used to measure pressure and temperature. The first consists of a digital manometer, model MAN-SD, having a class accuracy equal to ±0.5% of full scale. Temperature is measured using Type K thermocouples, having

class accuracy 1 and positioned at different depths (5, 10, and 15 cm from the upper flange) in order to detect the possible occurrence of internal gradients, mainly during the formation process. The flange also hosts a safety valve (model E10 LS/150) and a gas ejection channel, which has a dual function: the fast and massive ejection of the whole internal gaseous phase and the possibility of taking small gas samplings for gas chromatographic analyses. The injection of guest species occurs from the bottom to enhance the permeation of guests through the aqueous phase. The whole system was inserted within a cooling room in order to control the temperature from the outside with an accuracy equal to ± 0.1 °C and also to define specific temperature trends over time.

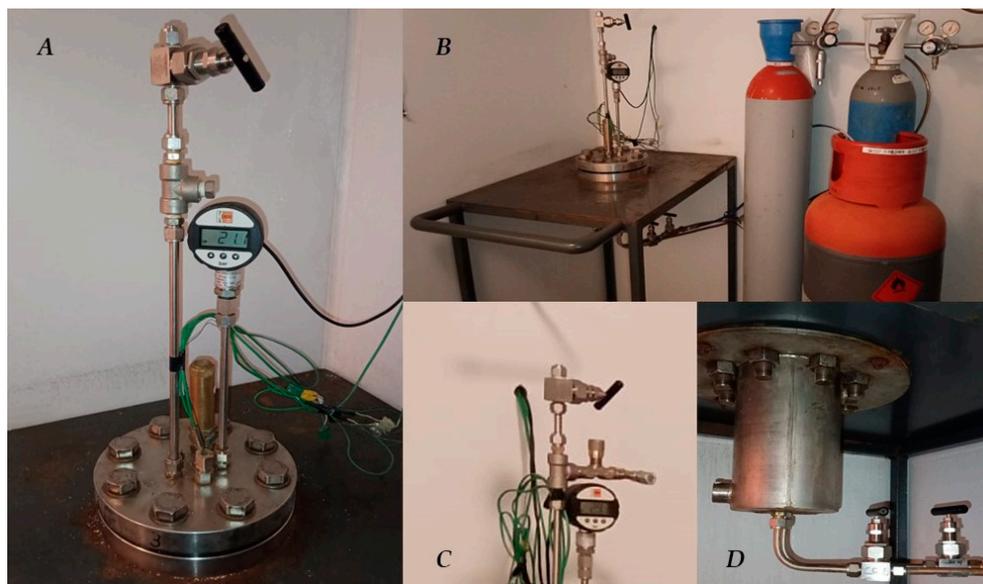


Figure 1. Main details of the experimental apparatus used for the production of hydrates: (A) upper flange and sensors used to measure pressure and temperature; (B) picture of the assembled system; (C) enlargement of the gas ejection channel; and (D) perimetral walls and gas injection channels.

The reactor was filled with porous sand, pure demineralised water, and ultra-high purity (UHP, purity degree equal to 99.99%) gases. Based on the available literature [49], the mean hydration number was considered to be equal to 6; therefore, 13 moles of water and 2.2 moles of gas were used in each test. The porous sediment consisted of 744 cm³ pure quartz spherical grains, with diameters ranging between 0.09 and 0.15 mm and the mean porosity being equal to 34% (measured with a porosimeter; Thermo Scientific Pascal 140, by Thermo Fisher Scientific, Milan, Italy). The sediment was used to ensure the production of hydrates along the whole internal volume and not only in proximity of the gas–liquid interface.

The experiments were carried out with pure carbon dioxide and with two CO₂/N₂ mixtures, having concentrations equal to 70/30 and 50/50 vol%, respectively.

2.2. Methodology

Gas hydrates were formed according to the procedure followed in previous studies [50]: The reactor was initially filled with the sand/water mixture and with the guest species; then, it was closed, and its internal temperature started gradually decreasing. The production of hydrates began after the system entered within the hydrate stability zone and caused a decrease in pressure. The formation process continued until the pressure stabilised in correspondence with the lowest temperature fixed in the reactor. The cooling room was then switched off, and the consequent increase in pressure caused the melting of hydrates and the consequent release of guest molecules in the gaseous phase. The dissociation process ended as soon as the internal pressure reached its initial value, meaning that the whole hydrate phase had completely melted.

The quantity of energy spent during the process was calculated by considering, for each material present within the reactor, the corresponding quantity, specific heat, pressure increase, and temperature drop. For the porous sediment, the specific heat was considered to be equal to 0.83 kJ/kgK. For the gas mixture, it was defined by considering the composition used in each test; in particular, it was equal to 0.86 kJ/kgK for pure carbon dioxide, 0.98 kJ/kgK for the binary CO₂/N₂ (70/30 vol%) mixture, and 1.01 kJ/kgK for the CO₂/N₂ (50/50 vol%) mixture. The increase in pressure was calculated by considering a three-stage adiabatic compression with intercooling.

The quantity of energy stored was calculated as a function of the moles of hydrates formed and their corresponding enthalpy of dissociation, which is approximately equal to 58 kJ/kg when pure carbon dioxide is used, while it assumed lower values (51.7–53.0 kJ/kg) when binary mixtures were used [51].

Both quantities (energy spent and stored) were defined globally and as a function of time. The time dependency of energy spent was related to the drop in temperature measured. For the amount of energy stored, the amount of moles of hydrates formed was considered.

Finally, the two energy values were compared in order to define the process's Estored/Espent ratio globally and as a function of time.

3. Results and Discussion

Hydrates were produced with pure carbon dioxide and with binary CO₂/N₂ gaseous mixtures having composition equal to 70/30 and 50/50 vol%. The main parameters describing the formation process are indicated in Table 1, while the thermodynamic evolution of each test is shown in Figure 2.

Table 1. Main parameters describing the hydrates production process: pressure (P) and temperature (T) at the beginning (i) and ending (f) of production; moles of gas inserted within the reactor (mol_{INJ}), and moles of hydrates formed (mol_{HYD}).

Parameter	Pure CO ₂	CO ₂ /N ₂ (70/30 vol%)	CO ₂ /N ₂ (50/50 vol%)
Pi [bar]	44.23	45.20	41.02
Ti [°C]	9.76	5.03	5.45
Pf [bar]	14.91	19.74	22.84
Tf [°C]	0.79	1.35	2.37
mol _{INJ} [mol]	0.622	0.527	0.479
mol _{HYD} [mol]	0.345	0.349	0.215

To produce the diagrams, more tests were carried out (with the same gas–water mixtures and the same procedure) in order to define a reliable and reproducible P–T trend. Conversely, the data shown in Table 2 refer to a single test for each group, or the ones taken as references, whose data were then used for energy evaluations.

Table 2. Energy spent for the production of hydrates (cooling + compression), cold energy stored into water cages, and Estored/Espent ratio.

	Cooling [kJ]	Compression [kJ]	Energy Spent [kJ]	Energy Stored [kJ]	Estored/Espent [%]
Pure CO ₂	15.72	9.91	23.63	20.00	78.06
CO ₂ /N ₂ (70/30 vol%)	6.39	10.01	16.41	18.04	109.94
CO ₂ /N ₂ (50/50 vol%)	5.38	9.06	14.44	11.40	78.91

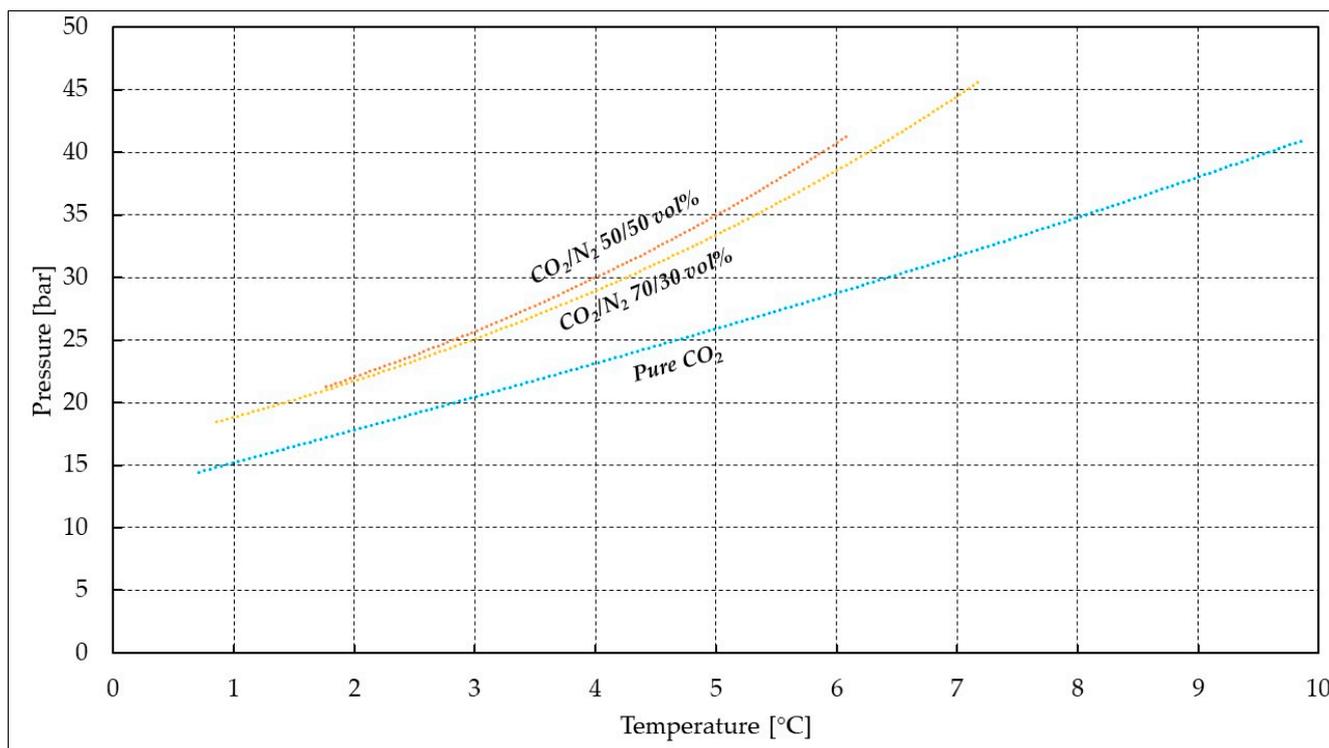


Figure 2. Thermodynamic description of gas hydrates production, carried out with pure CO₂ (blue line) and with the CO₂/N₂ binary mixtures having concentration equal to 70/30 (light orange) and 50/50 (dark orange) vol%.

As expected, the addition of nitrogen shifted the P–T curves to higher pressures and/or lower temperatures, and the deviation from the CO₂ hydrates curve is proportional to the concentration of nitrogen. It should be noted that these curves were depicted with formation data; therefore, they cannot be considered representative of the phase equilibrium boundary of the system. Formation rather than dissociation data were considered as the scope is to evaluate the quantity of energy spent for the production of hydrates.

Both carbon dioxide and nitrogen molecules can form sI hydrates; moreover, the first species preferentially fits the large cavities (5¹²6²), while nitrogen molecules, due to their lower molecular diameter, occupy the small cages (5¹²). Therefore, the addition of nitrogen could lead to higher cage occupancies or to a greater quantity of gas stored per unit of volume. However, the molecule of nitrogen is not large enough to stabilise the small cavities and, as a consequence, higher pressures are required for the overall production of hydrates. In the range of temperatures considered for the experimentation, the capture of pure nitrogen would require pressures of up to one order of magnitude higher than those required for the capture of pure carbon dioxide [52–54].

In mixtures with carbon dioxide, its capture into hydrates is possible at far lower pressure as large/small cages ratio in the unit cell of sI is 3:1 and the capture of carbon dioxide provides stability to the whole lattice.

Based on this concept and on the data of Table 1, the use of pure carbon dioxide allows (if considering equal thermodynamic conditions) for a more abundant production of hydrates, which is obviously proportional to the amount of energy stored. However, it does not automatically mean a higher energy stored/energy spent ratio, which is the first parameter to take into consideration. Moreover, pure carbon dioxide is an expensive raw material due to the purification processes required for its production, while CO₂/N₂ mixtures can be considered as a waste material, with consequent lower costs, which will not be deepened in this study.

The quantity of energy spent for the production of hydrates and cold energy stored were calculated for the three different mixtures, and the results are shown in Table 2. The same parameters are also plotted in Figure 3.

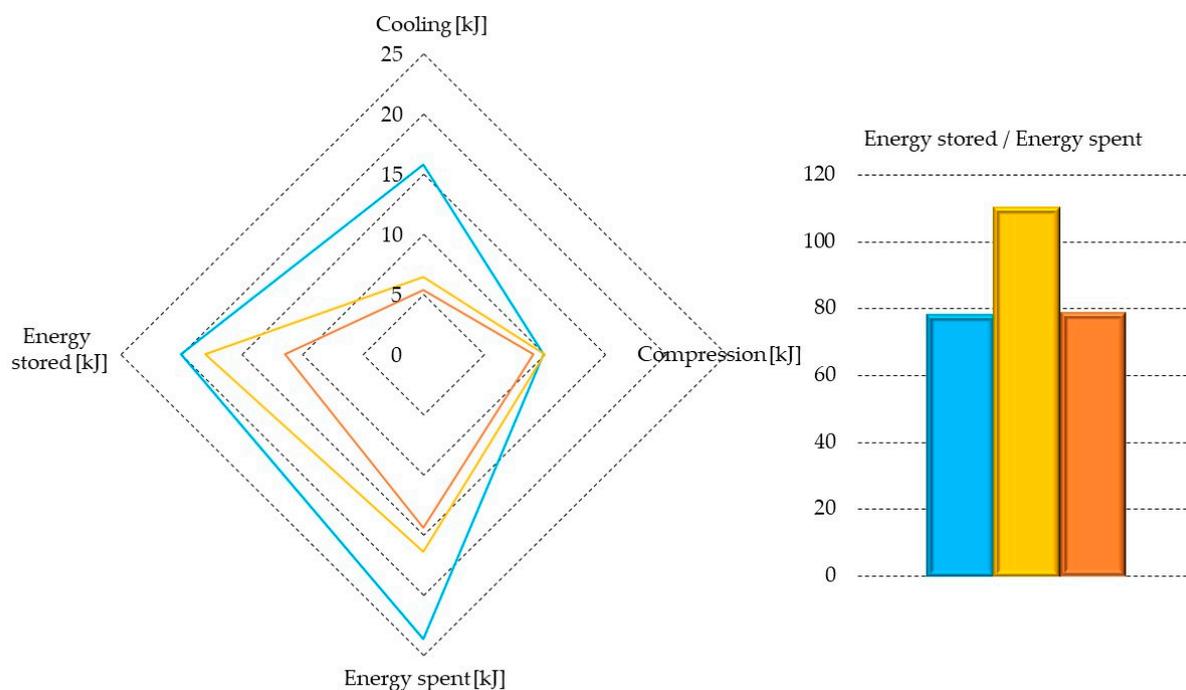


Figure 3. Definition of energy spent and energy stored into hydrates as a function of the guest mixture used: pure CO₂ (blue line), CO₂/N₂ binary mixtures having concentration equal to 70/30 (light orange) and 50/50 (dark orange) vol%.

The energy spent for the production of hydrates was calculated by considering the compression of gas mixtures and the subcooling of the whole system (gas–water–sediment). Conversely, the cold energy stored is based on the quantity of hydrates produced and the respective enthalpy of dissociation.

Due to the greater production of hydrates, the highest quantity of cold energy stored was achieved with pure carbon dioxide (20.00 kJ). The mixture, having 30 vol% nitrogen, reached a slightly lower value (18.04 kJ), while the 50/50 mixture remained widely below these values (11.40 kJ), as visible in Figure 3. Similarly, the production of hydrates with pure carbon dioxide also registered the highest energy spent value. The amount of energy required for the production of hydrates gradually decreased with the growing concentration of nitrogen in the mixture. The values obtained were equal to 23.63, 16.41, and 14.44 kJ, respectively.

Such a difference in terms of energy spent between pure CO₂ and N₂-containing gas mixture can be attributed to the cooling phase. The production process involved a wider thermodynamic region when carried out with pure CO₂; therefore, the drop in temperature to reach before reaching process completion was significantly higher (8.97 °C vs. 3.08–3.65 °C). Conversely, the greatest contribution to the total energy spent for the CO₂/N₂ mixtures was related to the compression stage.

Regarding these latter mixtures, similar results in terms of energy spent were reached. However, the quantity of energy stored widely differed: a total of 18.04 kJ was stored with the 70/30 vol% mixture, while only 11.4 kJ was stored when the 50/50 vol% mixture was tested. This explains the relevant difference in the energy stored–energy spent ratio between the two mixtures, whose values were equal to 109.94% and 78.91%, respectively. The same parameter was equal to 78.06% for pure carbon dioxide.

These results prove that CO₂/N₂ mixtures can be advantageously exploited for cold energy storage via clathrate hydrates formation. In particular, the 70/30 vol% mixture

allowed for the storage of a quantity of energy similar to the one obtained with pure CO₂; however, at the same time, the overall quantity of energy spent during the process was significantly lower, thus making the process globally more effective. It should also be considered that pure carbon dioxide is expensive to produce due to the required purification process, and its cost cannot be neglected. Conversely, CO₂/N₂ mixtures can be obtained from flue gases or exhausts coming from industrial processes with consequent lower (or negligible) costs.

The results showed in this study also highlighted that the N₂ concentration must be selected carefully. Starting from the Estored/Espent ratio achieved with pure CO₂, a marked positive benefit was obtained with the 70/30 vol% mixture (from 78.06 to 109.94%); meanwhile, when the concentration of nitrogen was still increased and reached 50 vol%, such a ratio approximately turned back to its previous value, or 78.91%. While this research aimed to define the possibility of advantageously using CO₂/N₂ mixtures for cold energy storage, further studies were exclusively dedicated to define the optimal concentration of the two species in order to optimise the process and maximise the Estored/Espent ratio.

Finally, the following Figures 4–6 describe the trend over time of energy spent, energy stored, and Estored/Espent ratio for each mixture tested in this study.

The diagrams reveal that the difference between energy stored and energy spent did not remain constant over time, mainly due to the formation phase and its stochastic nature, which makes the production of hydrates not perfectly linear during time. The quantity of energy stored continuously increased over time in all tests. Such a quantity is strongly dependent on the moles of hydrates formed, and the trend of these two parameters were obviously similar between each other. Conversely, the energy spent mainly increased during the initial portion of the formation process and then stabilised. The total energy spent includes the work required for gas compression, which is spent at the beginning of the process and does not vary anymore during the tests; and the cooling phase, which increases during time until the system reaches the lowest pressure fixed for the tests. This quantity also remains constant.

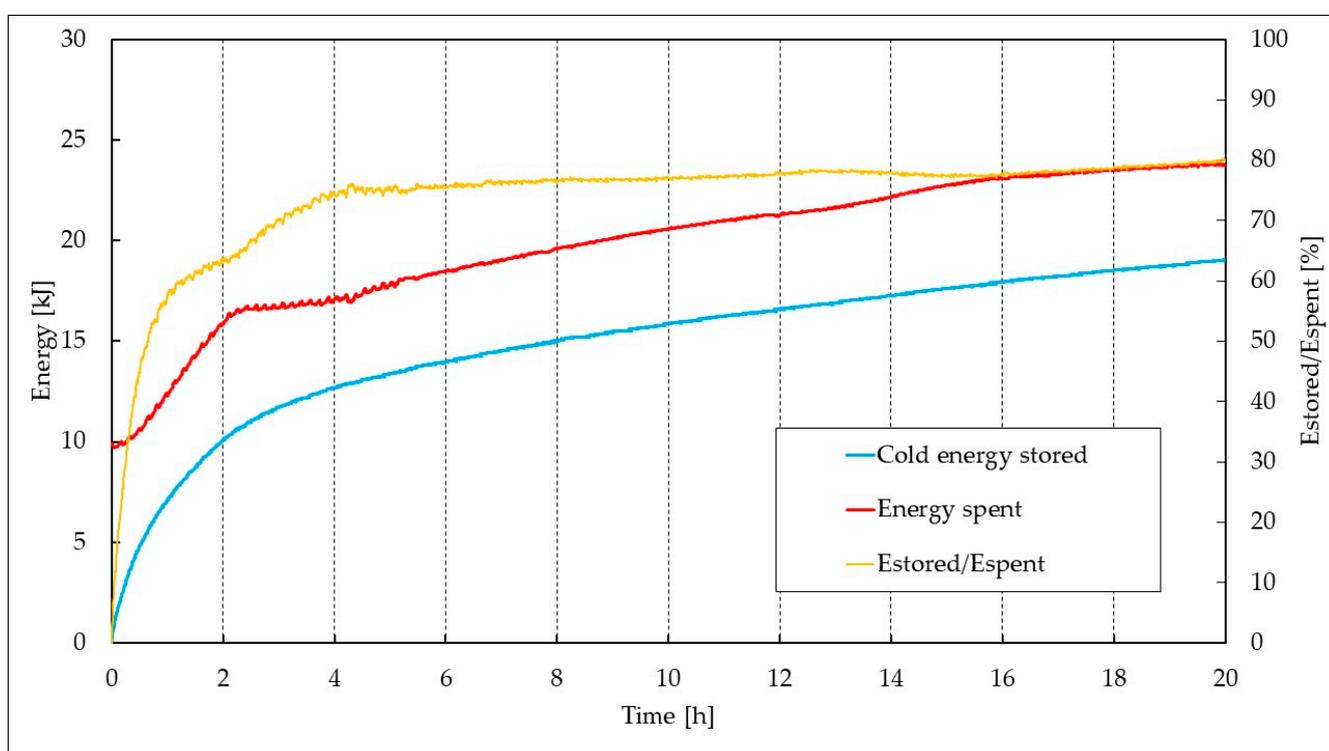


Figure 4. Trend over time of energy spent, energy stored, and Estored/Espent ratio for hydrates formed with pure CO₂.

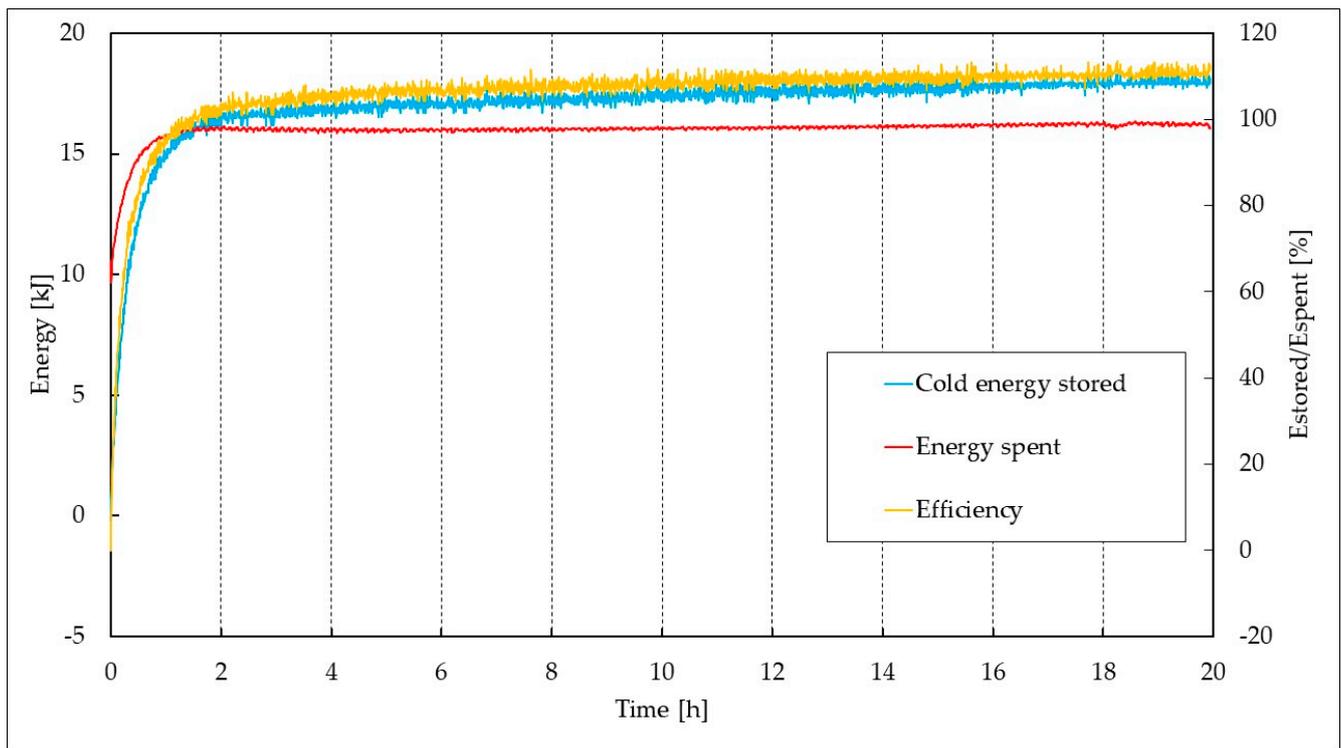


Figure 5. Trend over time of energy spent, energy stored, and Estored/Escent ratio for hydrates formed with CO₂/N₂ (70/30) vol%.

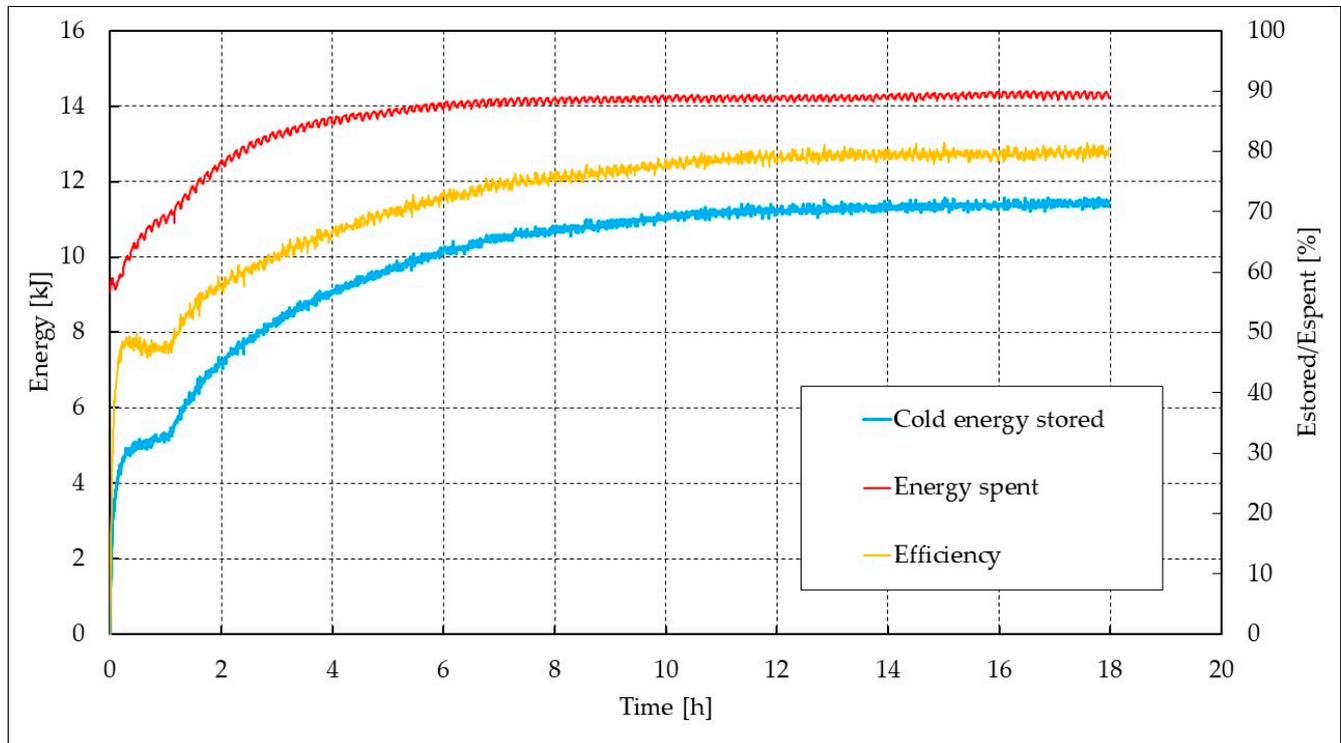


Figure 6. Trend over time of energy spent, energy stored, and Estored/Escent ratio for hydrates formed with CO₂/N₂ (50/50) vol%.

In particular, the trend of energy stored obtained with the binary (50/50 vol%) gas mixture confirmed the variability of hydrates production. The massive production of hydrates did not occur immediately and caused a temporary reversal in the trend of the Estored/Espent ratio. To make the production process more predictable, some strategies can be pursued instead of using chemical additives which, due to their related critical aspects, such as costs, availability, environmental sustainability, and so on, were not considered in this study. For instance, the memory effect, or the capability of the system to retain memory of previous formation, thus reducing the stochastic degree of the initial nucleation phase, could be established during hydrates production [55–57].

Based on the results showed in Figures 4–6, it can be concluded that the best option to optimise the process is to carry out the production of hydrates until its completion, not interrupting it in advance with the aim of maximising the Estored/Espent ratio. The reason is the different trend between the two respective energies: the amount stored continuously increased with time, while the quantity spent mainly varied during the initial stage of the process and then remained approximately constant.

4. Conclusions

In this study, gas hydrates were produced with pure carbon dioxide and CO₂/N₂ mixtures having concentrations equal to 70/30 and 50/50 vol%. Hydrates were produced to deepen their possible usage for cold energy storage in the absence of chemical additives, commonly used for this kind of application. The possibility of using flue gas-derived mixtures instead of pure CO₂ was characterised in terms of both the energy required for the production of hydrates and the energy stored into clathrate structures. Based on the followed experimental procedure, the three mixtures (in order: pure CO₂ and CO₂/N₂ 70/30 and 50/50) allowed us to produce 0.345, 0.349, and 0.215 moles of hydrates, respectively. The energy required for gas compression and cooling was quantified and was overall equal to 23.63, 16.41, and 14.44 kJ, while the corresponding energy stored was 20.00, 18.04, and 11.40 kJ. The use of pure CO₂ led to the largest amount of energy stored; however, it required more energy for the cooling process, and the overall Estored/Espent ratio (78.06) was significantly lower than what was observed with the 70/30 vol% binary mixture (109.04). Conversely, the same ratio for the remaining mixture was equal to 78.91. The addition of nitrogen to the system effectively enhanced the process, especially when considering that CO₂/N₂ mixtures are widely less expensive than pure carbon dioxide; however, the concentration of nitrogen must be carefully determined in order to ensure the mass-production of hydrates at still favourable thermodynamic conditions.

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