



Impact of pressure on the dynamic behavior of CO₂ hydrate slurry in a stirred tank reactor applied to cold thermal energy storage



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HIGHLIGHTS

- CO₂ hydrate storage was studied in a stirred tank reactor under pressure.
- CO₂ hydrates can store three times more energy than water during the same time.
- Increasing CO₂ hydrate pressure decreases charge time for the same stored energy.
- CO₂ hydrate storage allow average power exchange to be maintained along the process.

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ABSTRACT

Phase change material (PCM) slurries are considered as high-performance fluids for secondary refrigeration and cold thermal energy storage (CTES) systems thanks to their high energy density. Nevertheless, the efficiency of such system is limited by storage dynamic. In fact, PCM charging or discharging rate is governed by system design (storage tank, heat exchanger), heat transfer fluid temperature and flow rate (cold or hot source), and PCM temperature. However, with classical PCM (ice, paraffin...), phase change temperature depends only on material/fluid nature and composition. In the case of gas hydrates, phase change temperature is also controlled by pressure. In the current work, the influence of pressure on cold storage with gas hydrates was studied experimentally using a stirred tank reactor equipped with a cooling jacket. A tank reactor model was also developed to assess the efficiency of this storage process. The results showed that pressure can be used to adjust phase change temperature of CO₂ hydrates, and consequently charging/discharging time. For the same operating conditions and during the same charging time, the amount of stored energy using CO₂ hydrates can be three times higher than that using water. By increasing the initial pressure from 2.45 to 3.2 MPa (at 282.15 K), it is also possible to decrease the charging time by a factor of 3. Finally, it appears that the capacity of pressure to increase CO₂-hydrate phase-change temperature can also improve system efficiency by decreasing thermal losses.

1. Introduction

In the current context of energy network improvement, there is an urgent need in Electrical Energy Storage (EES), in order to manage electricity production and demand, especially for intermittent renewable-energy integration. To be effective, such EES systems must meet various criteria of flexibility. Ulbig et al. [1] proposed a quantification of the flexibility of power systems in terms of power, energy capacity and charging/discharging time. Many methods can be chosen for implementing electricity storage as mentioned by Chen et al. [2], such as

Pumped Hydroelectric Storage (PHS), Compressed Air Energy Storage (CAES), Flywheel, Metal Battery and Thermal Energy Storage (TES). The choice of storage method depends on application requirements, and more specifically on energy services, which can be classified as energy management or power quality. In the case of space heating and cooling, which represent almost 60% of energy consumption in buildings, TES appears as an environmentally-friendly and good choice for energy management. In fact, TES can offer relatively high energy density, suitable power level, good life cycle, and low cost [3]. Furthermore, contrary to PHS and CAES, TES systems do not depend on geographical

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Nomenclature

C_p	specific heat, $\text{J kg}^{-1} \text{K}^{-1}$
m	weight, kg
n	mole number, mol
P	pressure, MPa
T	temperature, K
nbh	hydration number
t	times, s
Q	energy, J
\dot{Q}	power, W
Z	compression factor

Greeks symbols

ΔH	phase change enthalpy, J kg^{-1}
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φ	hydrates mass fraction
ϕ	flux, W
σ	solubility

Subscripts

av	average
l	liquid
h	hydrate
w	water
c	supercooling break
hs	hydrate slurry

criterion.

TES is used in many application fields as electricity generation [4,5], cogeneration [6] or building [7], as well as for heating or cooling applications. In literature, there are many examples of the positive impact of TES and cold thermal energy storage (CTES) on CO₂ mitigation and energy savings [8–11]. Stinner et al. [12] applied the classification of Ulbig et al. [1] to study the impact of the size of a TES tank on a heating process with sensible heat. The authors showed that the volume of the storage tank has little influence on the flexibility of the system. This behavior can be due to the scenarios considered by the authors, in particular with similar thermal conditions for both energy storage and use. On the contrary, for CTES applications, energy can be stored during the night with favorable thermal conditions for the cooling device (lower temperature and thus better coefficient of performance-COP). Therefore, the impact of CTES on system efficiency depends on day/night scenarios, and consequently on storage capacity. In fact, Ruddell et al. [13] showed that the design of a CTES installation is crucial to optimize the energy consumption, environmental impact and economic benefits. According to Dincer, the impact of CTES on system efficiency depends on size, storage capacity, lifetime, cost, efficiency, safety, installation, environmental standards and control [14]. In addition, Sun et al. [15] showed that the impact of CTES depends on the choice of the control strategies of the storage tank as full storage or load levelling. Other authors studied the impact of TES on chiller's efficiency [16,17] or on whole systems including demand scenarios [18–22].

Nevertheless, most of the CTES devices which base on annual peak

demand which is reached generally only few hours/days in a year are oversized. The design issue leads many authors to study the impact of storage capacity on system efficiency. Zhang et al. [23] and Upshaw et al. [24] compared the cost, energy saving, peak shaving as a function of water system size. Both authors had the same conclusion on payback period, but not on energy saving since Zhang et al. [23] found electricity saving for all tank sizes, while Upshaw et al. [24] reported an increase in electricity consumption with storage device.

In order to overcome the problem of storage device size, various authors worked on phase change materials (PCM) to replace water. Indeed, the presence of PCM allows the size of the storage device to be decreased thanks to a higher energy density (related to latent heat of melting). Many PCMs are then studied in literature for CTES applications [25,26]. Moreover, systems using PCM show an improvement in charging and discharging rate [27–31]. In particular, the main factors impacting the charging/discharging dynamic are inlet HTF (Heat Transfer Fluid) temperature or mass flow rate [28,32], and also phase change temperature of the PCM. For some materials, as TBAB hydrate or ice slurries, phase change temperature depends on solute concentration [33,34]. Wang et al. [35] presented an overview on slurries and showed the advantages of having a secondary fluid with a high energy density. Ice slurry was used to improve secondary refrigeration loops [36,37] thanks to suitable thermodynamic properties. Nevertheless, the temperature range of applications using ice slurry requires the chiller to work at low temperature ($< 273.15 \text{ K}$) and less efficient (low COP) [38,39]. Various slurries appear to be good candidate to replace ice slurry [40,41]. Some authors already studied the feasibility

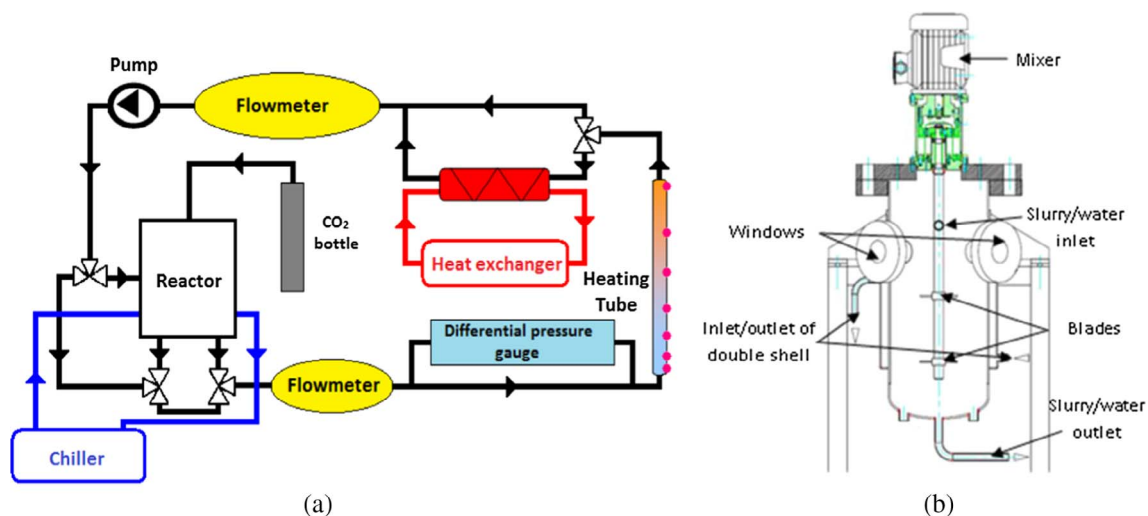


Fig. 1. Pilot loop and tank reactor (a: pilot loop; b: tank reactor).

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