

Constant-volume vapor-liquid equilibrium for thermal energy storage: investigation of a new storage condition for solar thermal systems

Abdullah Bamoshmoosh¹, Gianluca Valenti^{1*}

¹Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4A, 20156, Milano, Italy

Abstract. The sector of thermal energy storage shows a number of alternatives that could have a relevant impact on the future of energy saving as well as renewable energy technologies. Among these, latent heat thermal energy storage technologies show promising results. Technologies that exploit solid-liquid phase change have already been widely proposed, but those technologies show common drawbacks limiting their application, such as high cost, low energy storage density and particularly low heat transfer properties. This work proposes to exploit the liquid-vapor phase transition in closed and constant volumes because it shows higher heat transfer properties. Consequently, the objective is to assess its energy storage performances in target temperature ranges. With respect to previous activity by the authors, this work proposes an exergy analysis of these systems, gives a methodology their deployment, and proposes a comparison between a new storage condition for solar thermal domestic hot water systems exploiting vapor-liquid equilibrium and conventional technologies. The exergy analysis is performed in reduced terms in order to have a generalized approach. Three hypothetical fluids with increasing degree of molecular complexity are considered in order to have a complete overview of the thermodynamic behavior of potential heat storage fluids. The analysis shows that the increased pressure of liquid systems has a major impact on exergy, resulting in vapor-liquid systems having less than 50% of the exergy variation of pressurized liquid systems. This is proven to have no impact on thermal energy storage. For the case study, the proposed methodology indicates that water itself is a strong candidate as a heat storage fluid in the new condition. Comparison shows that the new condition has a higher energy storage capacity at same volume. The useful temperature range is increased by 108% by setting a 10.5% volume vapor fraction at ambient temperature. The resulting improvement gives a 94% higher energy storage, with a maximum operating pressure of the system of less than 5 bar.

1 Introduction

Energy storage technologies are crucial in the transition to a sustainable energy infrastructure because they allow to accommodate the mismatch of energy supply and demand by storing the excess energy that is produced and releasing it at need [1]. Research on thermal energy storage systems has shown three main mechanisms that can be used in order to improve primary energy savings, as explained by Arce and Kalaiselvam [2, 3]: sensible heat storage, latent heat storage and thermochemical heat storage.

Latent thermal energy storage is based on phase change phenomena. When matter undergoes phase change, phase transition energy is either absorbed or released by matter itself. The increase or decrease of energy in the system is given by the direction of the phase transition. This behavior is exploited by solid-liquid phase change materials that are already available.

The materials are charged in thermal energy during liquefaction and are discharged during solidification. These materials have already been considered for the design of industrial heat storage units [4, 5, 6], but show a number of limitations that are mainly related to the low heat transfer parameters of the solid-liquid phase change materials that make the process less effective [7].

The objective of this work is to assess the possibility and the performances of a pure fluid vapor-liquid based latent thermal energy storage system and to develop a methodology to select working fluids and operating conditions in order to increase thermal storage at same volume of conventional technologies. An exergy analysis of these systems is added to the existing work by the authors [8]. As a case study, a new condition for a solar domestic water heating system that exploits vapor-liquid equilibrium for thermal energy storage is proposed.

* Corresponding author: gianluca.valenti@polimi.it

This work presents a review of vapor-liquid equilibrium thermal storage first, then a generalized exergy analysis of the analyzed systems, then the methodology for the deployment of this technology. A presentation of the case study of a new condition of use of domestic water heating is then given, which uses water itself as vapor-liquid heat storage fluid, and last the results of the case study itself are shown.

2 Thermodynamic modeling

This section describes the thermodynamic modeling of pure fluid vapor-liquid systems employed for the latent thermal storage. It illustrates first the generalized approach, then the phenomenology of the system, and later the analysis from an exergy perspective.

2.1 Generalized thermodynamic approach

A generalized approach is adopted to have a complete overview of the behavior of potential heat storage fluids. The three-parameters Corresponding State Principle is used to model different fluids at different conditions [9]. The formulation of Lee and Kesler in temperature and specific volume is used to assess the thermodynamic properties of these systems [8, 10, 11]. The three-parameters Corresponding State Principle states that the residual properties of a fluid are a function of its critical temperature, critical pressure and molecular complexity. The molecular complexity is represented by the acentric factor (also called Pitzer factor [12]) ω , defined as

$$\omega = -1 - \log_{10} \frac{P^{sat}(T_r = 0.7)}{P_c} \quad (1)$$

At same reduced conditions, the properties of fluids differ only because of their molecular complexity, *i.e.* the value of ω . Three hypothetical fluids are considered and compared with each other at same reduced coordinates: simple fluids, with ω of 0, intermediate complexity fluids, with ω of 0.2, and complex fluids, with ω of 0.4. These values are taken in order to cover the spectrum of the Lee-Kesler formulation of the Corresponding State Principle, which takes fluids with ω up to 0.398, which is the value of the acentric factor of n-octane. This value is also the highest among fluids that are of interest for thermal storage purposes.

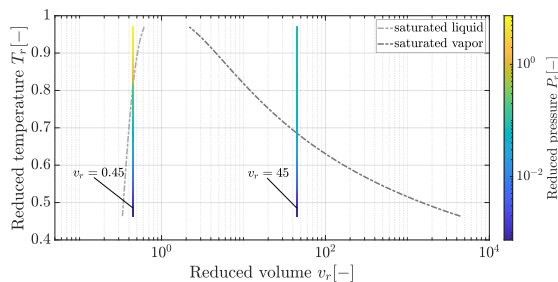


Figure 1. Reduced temperature T_r , as a function of reduced specific volume v_r , at reduced specific volume of 0.45 and 45, taken as example, for a hypothetical intermediate complexity fluid with acentric factor ω equal to 0.2, with colorbar for reduced pressure P_r [8].

2.2 Phenomenology

Vapor-liquid phase change shows mass-based energy storage densities that are almost an order of magnitude higher than solid-liquid transitions. Nevertheless, since the vapor phase has much lower density than the liquid phase, the constant-volume energy storage density could be affected negatively. A higher fraction of vapor in the system decreases its overall mass, and thus increases its specific volume. Vapor-liquid systems on the other hand show much higher heat transfer coefficients than solid-liquid ones. The previous work by the authors [8] presents the energy storage density of fluids of different complexity at different values of specific volume, alongside the specific energy storage variation of these systems over a fixed range of temperatures. Internal energy on volume basis is evaluated at a fixed temperature range in the previous work. An analysis of the pressure variation of these systems is also given.

Figure 2 depicts a schematic of the proposed system. The charging is done through heat transfer between the solar collector circuit, or primary circuit, on the left, and the storage vessel, in the center. The discharge is given by heat transfer from the storage vessel to the domestic hot water circuit, or secondary circuit, on the right.

The process is isochoric, or in other words at constant specific volume. This means that the variation of volume of the closed vessel given by thermal expansion is neglected and the volume of the fluid is thus constant during the process. Figure 1 depicts the process on the specific volume-temperature diagram for the hypothetical fluid of intermediate complexity in reduced coordinates for a general representation of these processes. In detail, Figure 1 shows two isochoric processes at different values of reduced specific volume, specifically at reduced specific volume of 0.45 and 45. After the saturation curve is crossed, the two curves show different behavior: the one on the right shows a steady increase of the vapor title, while the one on the left has an initial increase of the vapor title, but it eventually goes to zero in a process that will be referred to as *countercondensation*. This process occurs only for systems with specific volume lower than critical. The curve on the left shows the steep increase in pressure after crossing the saturated liquid line, typical of constant-volume single phase liquids, while the curve on the right shows a much smoother increase in pressure after crossing the saturation curve in the vapor phase.

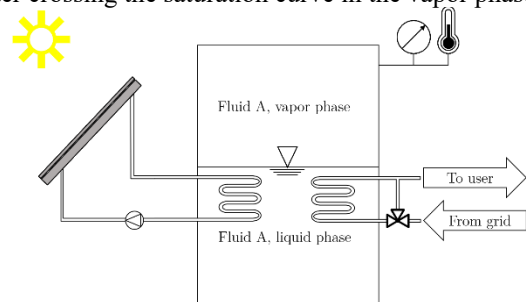


Figure 2. Schematic of the pure fluid vapor-liquid thermal energy storage system with primary circuit on the left and secondary circuit on the right.

Figure 3 depicts the vapor fraction as a function of temperature for the two processes in Figure 1. At the reduced volume of 0.45, the system has a low vapor fraction on the mass basis, which initially increases with temperature, but goes to zero at higher temperatures. The vapor fraction on the volume basis, at the lowest temperature, is around 0.30. Almost a third of the volume of the system is filled with vapor. At the reduced volume of 45 on the other hand, when the fluid is almost completely in its vapor phase at the lowest temperature, the vapor title increases monotonically until it reaches unity when it crosses the saturated vapor curve.

The vapor fraction in the initial conditions defines the total density of the system. The lower the free surface, the lower the density of the system since more of the volume is filled with vapor instead of liquid. Hence, different systems with different free surface levels, at the same total volume, have different masses. Considering the processes with countercondensation, increasing the specific volume leads to delaying it to higher temperatures. As in Figure 1, translating curves to the right shifts the crossing point with the saturation curve at higher temperatures, as long as the specific volume is below the critical one. This leads to an increased range of available temperatures since the steep pressure increase that occurs after countercondensation moves to higher temperatures.

2.3 Exergy analysis

For defining the exergy of the system in Figure 2, the environmental conditions need to be stated. Figure 4 shows the generic energy-entropy relationship for a closed and constant volume system, showing the equilibrium entropy given by the second law of thermodynamics [13, 14]. In this plot, temperature of the stable system is the slope of the equilibrium entropy curve. Two stable equilibrium states have been highlighted as examples: one with higher temperature than environment, and one at environmental temperature. Hence, the exergy difference would be defined as the energy difference between the two points, subtracting the entropic contribution that needs to be extracted from the system in order to reach equilibrium:

$$\Delta b = \Delta e - T_{env} \Delta s \quad (2)$$

where Δb , Δe and Δs are the exergy, energy and entropy differences between the two states and T_{env} is the temperature of the environment.

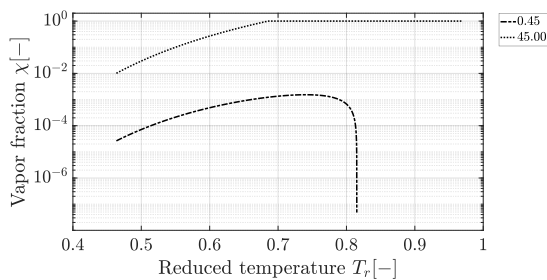


Figure 3. Vapor fraction χ as a function of reduced temperature T_r , at reduced volume v_r , of 0.45 and 45 for a hypothetical fluid with acentric factor ω equal to 0.2 [8].

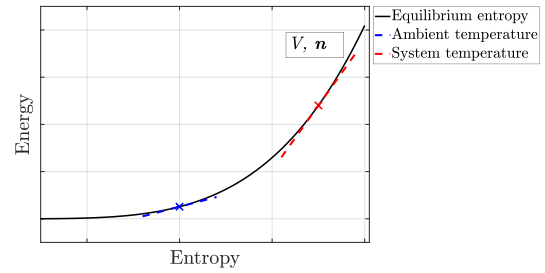


Figure 4. Generic energy-entropy diagram for a closed and constant volume system showing the second law equilibrium entropy curve and highlighting the temperature of a generic system and the environment temperature.

Pressure equilibrium with the environment is not required in the formulation. This can be seen in two ways. First, since there is no volume variation in the system, it is meaningless to define an energy potential such as pressure. Considering the definition of pressure

$$P = - \left. \frac{\partial E}{\partial V} \right|_T \quad (3)$$

it is clear that the potential related to the variation of volume cannot be exploited in a thermodynamic process with no volume variation. The second way of explaining why pressure equilibrium is not necessary is using the Gibbs phase rule. For a pure component, such as in the considered system, once one specific property π is defined, either temperature or pressure can be set *a priori*, but not both. In this case, the generic property is specific volume, since both total volume and mass are fixed in the process. Since the system is not adiabatic, heat interactions with the environment require equilibrium to be reached at the environmental temperature T_{env} . This leads to having pressure as an invariant of equilibrium with the environment.

Excluding chemical reactions or other mechanical phenomena that could affect the energy of the system, the total energy is the internal energy u , leading to

$$\Delta b = \Delta u - T_{env} \Delta s \quad (4)$$

which differs from the typical formulation of exergy in terms of specific enthalpy h as pressure equilibrium with the environment is not required in this type of system.

Figure 5 shows the variation of exergy on a volume basis $\Delta \hat{b}$ for the three classes of fluids that have been defined in Subsection 2.1. The variation is considered for systems at constant volume at different values of reduced specific volume. These processes are of the same kind as the ones represented in Figure 1. Each of these plots represents how much mechanical energy could be extracted from the analyzed systems. Unlike for thermal energy storage, which is analyzed in previous work by the authors [8], there is no major advantage for mechanical production in vapor-liquid systems with respect to pure liquid systems. There is also no major impact of fluid complexity on the performances of these systems.

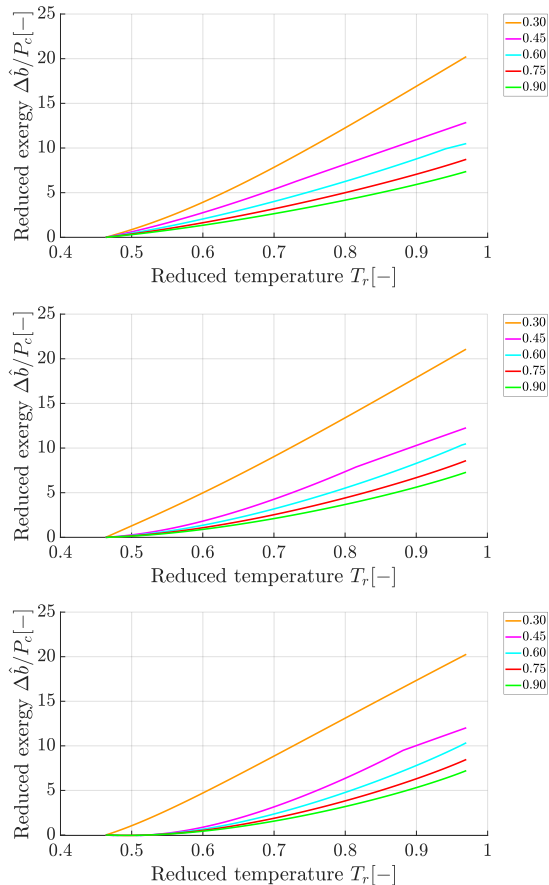


Figure 5. Reduced exergy on volume basis $\Delta\hat{b}_r$ as a function of reduced temperature T_r for hypothetical fluid with acentric factor ω equal to 0 (top), 0.2 (middle) and 0.4 (bottom) with reduced volume from 0.3 to 0.9.

Moreover, the curve in Figure 5 with reduced volume equal to 0.3 represents the pure liquid system, *i.e.* the pressurized liquid system at constant volume. It is still a constant-volume process, but unlike the processes in Figure 1 it starts on the left of the saturated liquid curve. Other curves represent vapor-liquid systems that face countercondensation in the considered temperature range. The main reason for which exergy variation of vapor-liquid systems is less than half of the exergy variation of pure liquid systems is the effect of entropy on exergy in Equation 2. After countercondensation occurs the system is fully liquid and highly pressurized in order to keep density constant. The pressure increase has an important impact on entropy of these systems, increasing the extractable mechanical energy from them. For the system at reduced volume equal to 0.3, countercondensation can be seen as occurring at temperatures lower than the considered range, thus showing this effect on a higher scale.

3 Case study

This section describes the case study. It outlines a conventional solar thermal storage, and then gives an explanation of the new storage conditions that are used for the analysis of the case study itself. At last, it provides the methodology for deployment of vapor-liquid thermal energy storage systems.

3.1 Conventional solar thermal storage

Solar thermal storage is a technology that uses solar radiation as the energy source for thermal loads [15]. It draws high attention because of its high integrability in many fields, such as domestic water heating. Solar energy is gathered via a solar collector and transferred to a hot water tank. At different temperatures, the variation of density, and thus expansion of the liquid, is higher than the thermal expansion of the tank. In order to avoid steep increases of pressure similar to the ones in Figure 1 for the curve with v_r equal to 0.45, expansion vessels are used to create extra volume to accommodate the expansion of the liquid. The system is considered to be a perfectly stirred tank. A schematic of the conventional system is given in Figure 6.

3.2 Design parameters

The values used in order to estimate the performances of a conventional storage tank and of the proposed system are summarized in Table 1.

Values in Table 1 originate from legislation on domestic hot water systems or from market analysis of available products. In the case of domestic hot water, Italian legislation sets the maximum temperature of water to the user to 48 °C as a compromise between disinfection from bacteria such as Legionella and safety of users from burns [16].

Table 1. Design parameters for conventional solar heat storage technologies and the proposed technology.

Common parameters	
Domestic hot water maximum temperature	48 °C
Maximum operating pressure (absolute)	9 bar
Conventional technology	
Maximum operating temperature	90 °C
New storage conditions	
Safety temperature difference from countercondensation temperature	25 °C
Pinch point temperature difference with secondary circuit	15 °C

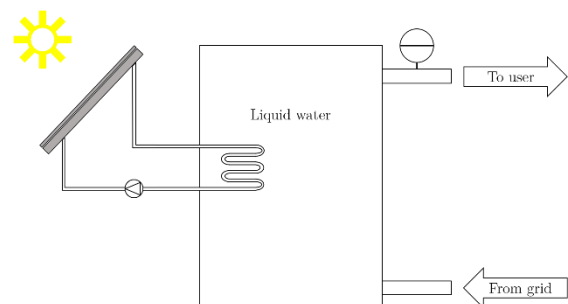


Figure 6. Schematic of a conventional solar thermal energy storage system, with heat transfer from the heat transfer fluid to the storage system and expansion vessel on the delivery line to the user.

The maximum operating temperature of conventional systems is a typical value for commercial calorifiers. It is mainly given by the expansion vessel limitations. Since hot water expands much faster at higher temperatures, the use of the extra expansion volume would be more critical at higher temperatures. It is also set to have a safety factor from unwanted boiling. Maximum pressure is given by material limitations.

Moreover, the temperature difference from countercondensation for the proposed technology is set in order to have a safety factor from the countercondensation point, after which expansion of the liquid would not be accommodated. The pinch point temperature difference is set in order to account for non-ideal heat transfer between the storage and the secondary circuit. It is used to define the minimum operating temperature T_{min} of the proposed system, which is the sum of the domestic hot water maximum temperature and the pinch point temperature difference.

The methodology for calculating the performances of vapor-liquid thermal energy storage systems for any application consists in the following steps:

1. the heat storage fluid is chosen;
2. the saturation temperature T_{max}^{sat} at the maximum operating pressure is calculated;
3. the saturated liquid specific volume at T_{max}^{sat} , v_{max}^{sat} is calculated;
4. the maximum allowable temperature T_{max} is obtained by difference between T_{max}^{sat} and the safety temperature difference;
5. the minimum operating temperature T_{min} is computed;
6. the internal energy difference between the two thermodynamic states, one at T_{max} and v_{max}^{sat} and the other at T_{min} and v_{max}^{sat} is computed.

The choice of the storage fluid is related strictly to the temperature range at which the heat storage must be deployed. Optimal temperature ranges for a given fluid have been shown to be between 0.4 and 0.8 of the critical temperature T_c of the fluid itself [8]. This leads to a good compromise between the risk of pressure increase and the advantage of using two-phase heat storage instead of sensible heat storage.

The specific volume of the saturated liquid phase at T_{max}^{sat} , v_{max}^{sat} is the constant specific volume at which the system operates. It is the maximum density at which the system can work while abiding the maximum limit on pressure. The system will thus work in a two-phase state throughout the whole process.

4 Results

As a first step, the heat storage fluid is chosen. In this work, water is used as the heat storage fluid. This is given both for good margin of application in terms of temperature range and for simplicity of comparison with conventional technologies. Thermodynamic properties of water are calculated using the 1997 IAPWS industrial formulation for water [17].

Table 2 reports the results of the analysis. The new storage condition shows a relevant margin of improvement for thermal energy storage with respect to conventional technologies. The main reason for this is the increased temperature range of the system, which is 108% larger. Although the storage mass is lower, since the useful temperature difference is more than doubled, the energy storage on volume basis of the proposed system is 94% higher than the conventional technology, which is almost twice the energy stored at same volume.

Figure 7 illustrates the two processes on the temperature-specific volume diagram. The conventional technology shows the volume variation that needs to be allocated in the expansion vessel, while the new one does not need any extra space. The conventional process is considered at constant pressure for simplicity. The considered pressure is the maximum operating pressure of the conventional system. This has no impact on the heat storage because neither specific heat nor specific volume of liquid water are relevantly affected by pressure itself in the considered range.

Figure 8 shows the two processes on the volume-based internal energy-temperature diagram. The slightly higher slope of the heat storage with conventional technologies with respect to new conditions can be seen. This difference is around 5% with respect to the proposed system. This difference is largely compensated by the much higher operating range than conventional solar heat storage systems.

Table 2. Results of the case study of conventional solar thermal storage and the proposed technology using water as thermal storage fluid.

Conventional technology	
Maximum useful temperature difference	42.0 °C
Minimum density	965.5 kg/m ³
Maximum density	989.3 kg/m ³
Mass-based internal energy difference	175.8 kJ/kg
Volume-based internal energy difference	169.7 MJ/m ³
New storage conditions	
Countercondensation temperature	175.4 °C
System density	891.9 kg/m ³
Maximum operating temperature	150.4 °C
Maximum operating pressure	4.8 bar
Maximum useful temperature difference	87.4 °C
Mass-based internal energy difference	369.7 kJ/kg
Volume-based internal energy difference	329.7 MJ/kg
Vapor volume fraction at ambient temperature	10.5%

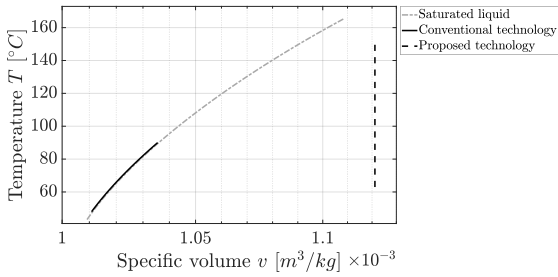


Figure 7. Temperature T as a function of specific volume v for the conventional solar heat storage process and the proposed technology.

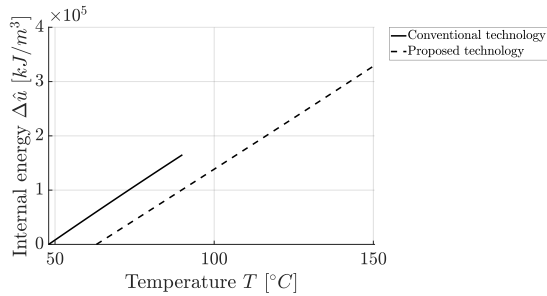


Figure 8. Volume-based internal energy difference $\Delta\hat{u}$ as a function of temperature T for the conventional solar heat storage process described and the proposed technology.

There are two main disadvantages of using these systems. The first is related to mechanical stress of the vessel. Since the system is saturated throughout its operating range, pressure inside the system is set univocally by temperature. While in a vapor-liquid state, pressure decreases exponentially with temperature. Temperature cycles lead to pressure cycles that could be a relevant factor in structural issues of the vessel.

The second disadvantage is related to the heat transfer with the primary circuit. Albeit higher temperatures are an advantage from an energy storage perspective, they pose a heat transfer problem related to the primary circuit fluids. Use of more flexible, more expensive heat transfer fluids is required. The minimum operating temperature is the same as the conventional technologies because it is set by anti-freeze properties that are needed during winter. The maximum operating temperature of the heat transfer fluid on the other hand needs to be higher since the maximum operating temperature of the system itself is higher.

5 Conclusions

This work presents an analysis of constant-volume vapor-liquid systems for thermal energy storage applied to solar thermal storage using water but in different working conditions. Conclusions are as follows.

- An exergy analysis of constant-volume processes is performed. Vapor-liquid systems do not show better performances from an exergy point of view with respect to pressurized liquid systems. Over the considered temperature range, the exergy variation of vapor-liquid systems is less than 50% of the variation of pure liquid systems.

- A methodology for the deployment of vapor-liquid heat storage systems is developed. Six steps are highlighted, and the rationale for the choice of the heat storage fluid is described.
- A comparison between conventional solar heat storage technologies and the new proposed storage condition is given for the case study of industrial calorifiers. Albeit in the same range of temperatures differences are not noticeable, the proposed system has a much higher margin of application because it does not have volume variation effects that limit conventional technologies. The temperature range of application is increased by 108%. Energy storage capacity on volume basis is increased by 94%.

Future work will include the analysis of multicomponent systems. A deeper heat transfer analysis will be conducted, both on the primary circuit and on the secondary circuit. Mechanical stress of the vessel due to pressure cycles will be investigated.

Nomenclature

b	Specific exergy on mass basis	V	Total volume
\hat{b}	Specific exergy on volume basis	π	Generic property specific to mass
e	Specific energy on mass basis	ρ	Density
E	Total energy	χ	Vapor fraction
h	Specific enthalpy on mass basis	ω	Acentric factor
P	Pressure	Superscripts	
s	Specific entropy on mass basis	sat	Saturation
T	Temperature	Subscripts	
u	Specific internal energy on mass basis	c	Critical
\hat{u}	Specific internal energy on volume basis	env	Environment
v	Specific volume	r	Reduced

References

- [1] I. Dincer and M. A. Rosen, *Thermal Energy Storage, Systems and Applications*, Wiley, 2011.
- [2] P. Arce, M. Medrano, A. Gil, E. Oró and L. F. Cabeza, "Overview of thermal energy storage (TES) potential energy savings and climate change mitigation in Spain and Europe," *Applied Energy*, vol. 88, pp. 2764-2774, 2011.
- [3] S. Kalaiselvam and R. Parameshwaran, *Thermal Energy Storage Technologies for Sustainability*, Academic Press, 2014.
- [4] A. Sharma, V. V. Tyagi, C. R. Chen and D. Buddhi, "Review on thermal energy storage with phase change materials and applications," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 2, pp. 318-347, 2009.
- [5] S. Dusek and R. Hofmann, "Modeling of a Hybrid Steam Storage and Validation with an Industrial Ruths Steam Storage Line," *energies*, vol. 6, no. 1014, 2019.
- [6] G. Valenti, A. Seveso, C. N. Bonacina and A. Bamoshmoosh, "Assessment of a phase change regenerator for batch industrial dryers," *AIP Conference Proceedings*, vol. 2191, no. 1, 2019.
- [7] Z. A. Qureshi, H. M. Ali and S. Khushnood, "Recent advances on thermal conductivity enhancement of phase change materials for energy storage systems: A review," *International Journal of Heat and Mass Transfer*, vol. 127, pp. 838-856, 2018.
- [8] A. Bamoshmoosh and G. Valenti, "Constant-volume vapor-liquid equilibrium for thermal energy storage: Generalized analysis of pure fluids," in *75° Congresso Nazionale ATI*, 2020.
- [9] R. Rota, *Fondamenti di Termodinamica dell'Ingegneria Chimica*, Pitagora, 2015.
- [10] B. I. Lee and M. G. Kesler, "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," *AIChE Journal*, vol. 21, no. 3, pp. 510-527, 1975.
- [11] U. Plöcker, H. Knapp and J. Prausnitz, "Calculation of High-Pressure Vapor-Liquid Equilibria from a Corresponding-States Correlation with Emphasis on Asymmetric Mixtures," *Industrial & Engineering Chemistry Process, Design and Development*, vol. 17, no. 3, pp. 324-322, 1978.
- [12] K. S. Pitzer, D. Z. Lippmann, R. F. Curl Jr., C. M. Huggins and D. E. Petersen, "The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *Journal of the American Chemical Society*, vol. 77, no. 13, pp. 3433-3440, 1955.
- [13] E. P. Gyftopoulos and G. P. Beretta, *Thermodynamics: Foundations and Applications*, Dover, 2005.
- [14] M. J. Moran and H. N. Shapiro, *Fundamentals of Engineering Thermodynamics*, Wiley, 2010.
- [15] A. Jamar, Z. A. A. Majid, W. H. Azmi, M. Norhafana and A. A. Razak, "A review of water heating system for solar energy applications," *International Communications in Heat and Mass Transfer*, vol. 76, pp. 178-187, 2016.
- [16] *DPR N° 412 dd 26/893*.
- [17] The International Association for the Properties of Water and Steam, "Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam," IAPWS, Lucerne, 2012.