Energy and Exergy Analyses of an Open Thermochemical Energy Storage System: Methodology and Illustrative Application

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Abstract: Thermal energy storage (TES) is a developed technology for storing thermal energy that can diminish environmental impacts and provide more efficient and environmentally friendly energy systems. Among various types of TES systems, thermochemical TES is an advanced method with the potential for higher energy storage densities and more compact systems. The evaluation of such systems is improved significantly when exergy analysis is used to complement energy analysis. Here, a general open thermochemical TES is investigated using energy and exergy analyses. An example using experimental data is presented to illustrate the analyses. Efficiencies are determined for the overall TES cycle and its charging, storing and discharging processes. The overall energy and exergy efficiencies for system considered in the illustrative example are determined to be 69% and 23%, respectively. This result indicates that the efficiency of the thermochemical TES based on exergy is much lower than that based on energy, and that there is a significant margin for loss reduction and efficiency improvement.

1. INTRODUCTION

Societal energy demands are presently increasing while fossil fuel resources, which dominate most national energy systems, are limited and predicted to become scarcer and more expensive in coming years [1, 2] Furthermore, many concerns exist regarding the environmental impacts associated with increasing energy consumption, such as climate change and atmospheric pollution. Greenhouse gas (GHG) emissions are considered the main cause of climate change, and agreements to limit them, such as the Kyoto Protocol, have been developed [3].

Thermal energy storage (TES) systems are one of developed technologies that can provide to achieve advanced energy systems. There are three main types of TES: sensible, latent and chemical [4]. Sensible TES systems store energy by changing the temperature of the storage medium. Latent TES systems store energy through phase change. In thermochemical energy storage, energy is stored after a dissociation reaction and then recovered in a chemically reversed reaction. Thermochemical energy storage has a higher storage density than the other types of TES, allowing large quantities of energy to be stored using small amounts of storage substances. Thermochemical TES systems can be classified as closed or open [5]. In closed systems, internal substances are separate from the heat transport fluid while in open systems, internal substances are not separate from the heat transport fluid. Closed systems can provide higher output temperature than open systems in heating applications [6]. Charging

processes in closed systems usually need higher temperatures than open systems [7]. In open thermochemical energy storage, the basic operating principle is the same as for closed thermochemical TES. The main chemical reaction can be expressed as follows:

$$C + heat \leftrightarrows A+B \qquad (1)$$

In this reaction, a thermochemical material (TCM) absorbs energy and is converted chemically into two components (A and B), which can be stored separately. The reverse reaction occurs when A and B are combined together and C is formed. Energy is released during this reaction and constitutes the recovered thermal energy from the TES. The storage capacity of this system is the heat of reaction when C is formed.

In open thermochemical TES, the heat transport fluid is not separate from materials A, B and C. Open thermochemical TES systems operate in an open loop coupled to the ambient conditions and an air stream transports water vapor and heat in and out of the packed bed of thermochemical materials [8]. Open sorption storage is a type of open thermochemical TES. Open sorption systems operate at the atmospheric pressure and the working fluid vapor is released to the environment [8, 9]. Two examples of applications of open sorption TES in energy systems follow. Sorption systems in the Monosorp project have been examined by the Institute of Thermodynamics and Thermal Engineering at the University of Stuttgart [10]. Sorption energy storage as part of a district heating grid in Munich [11] has been studied by the Bavarian Center for Applied Energy Research (ZAE Bayern).

In this study, a detailed investigation based on energy and exergy is carried out of an open thermochemical TES. The objective is to improve understanding of the technology,

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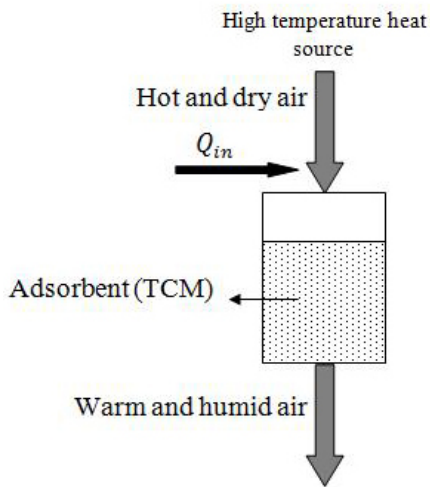
Fig. (1). Desorption process in open thermochemical TES. Adapted from [11].

so as to facilitate its development. An illustrative example is included based on experimental data from the open literature.

2. ENERGY AND EXERGY ANALYSES

A general open thermochemical TES is considered and energy and exergy analyses are performed. The system considered, consists of a working fluid (air) and a thermochemical material. Thermal energy from an energy supply (e.g. a district heating system) is transferred to air and provides the energy necessary for desorption of the thermochemical material. After a storing period, energy released from adsorption of the thermochemical material warms air to be used for heating purposes.

This analysis is limited to open TES systems where internal substances are not separate from the heat transport fluid. The following assumptions are made in this investigation:

- Chemical reactions within the reactor occur at constant pressure.

- Work interactions into and out of the control volume are neglected, as are kinetic and potential energy. The former assumption implies that pump, compressor and fan work are neglected.

- The physical exergy change of the components is neglected relative to their chemical exergy changes.
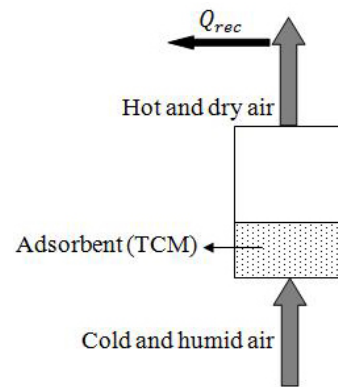
2.1. Charging (Desorption) Process

A general charging process for an open thermochemical TES is illustrated in Fig. (**1**). A hot air stream is heated by a high temperature heat source, and flows through the storage. There, the hot air stream desorbs the water from the adsorbent (thermochemical material) and dries it, after which it exits the packed bed a lower temperature and a higher humidity. The process is endothermic and the net energy input to the packed bed Q_{in} is supplied by the input air.

2.1.1. Energy Analysis for Charging

A general energy balance for the charging process of a TES can be written as [12]:

Energy input – Energy output = Energy accumulation   (2)

Fig. (2). Adsorption process in open thermochemical TES. Adapted from [11].

The net input energy is supplied by the air flow for this system. An energy balance for the charging process can be written as follows:

Net energy input – Heat loss = Energy accumulation in TES   (3)

or

$$Q_{in} - Q_i = \Delta H_{ds} \tag{4}$$

where Q_{in} is the net energy input to the system during the charging process and Q_i denotes the total heat loss. The term ΔH_{ds} is the enthalpy change of the desorption process.

The energy efficiency of the charging process can be expressed as follows:

$$\eta_c = \frac{\text{Energy gained by adsorbent}}{\text{Energy input}} = \frac{\Delta H_{ds}}{\Delta Q_{in}} \tag{5}$$

2.1.2. Exergy Analysis for Charging

A general exergy balance for this system can be written as

Exergy input – Exergy loss – Exergy destruction = Exergy accumulation   (6)

or

$$\in_{in} - \in_l - \in_D = \Delta \in_{ds} \tag{7}$$

Here,

$\varepsilon_{in} =$ Energy input = Net energy delivered by air   (8)

Also, $\in_D$ denotes the exergy destruction, $\in_l$ the exergy loss, and $\Delta \in_{ds}$ the exergy accumulation in the charging process.

We can evaluate the exergy efficiency of the charging process as follows:

$$\Psi_c = \frac{\text{Exergy stored in desorption}}{\text{Exergy input}} = \frac{\Delta \in_{ds}}{\in_{in}} \tag{9}$$

2.1.3. Storing Process

According to the assumptions made for the storing process, energy and exergy efficiencies of the storing process are equal to unity.

2.2. Discharging (Adsorption) Process

A general discharging process for an open thermochemical TES is illustrated in Fig. (**2**). The previously humidified, cool indoor air enters the desorbed packed bed. Then, the adsorbent adsorbs water vapor from the air flow and releases the heat of adsorption (Qrec). The process is exothermic.

2.2.1. Energy Analysis for Discharging

We can write an energy balance for the discharging period for a TES as follows [12]:

$$-[\text{Energy recovered} + \text{Heat Loss}] = \text{Energy accumulation} \quad (10)$$

The recovered energy is gained by the air flow for this process. We can evaluate the energy efficiency of this process as follows:

$$\eta_d = \frac{\text{Energy recovered}}{\text{Energy relaesed in adsorption}} = \frac{Q_{rec}}{\Delta H_{ad}} \quad (11)$$

2.2.2. Exergy Analysis for Discharging

We can write an exergy balance for the discharging process as follows:

$$-(\text{Exergy recovered} + \text{Exergy loss}) - \text{Exergy destruction} = \text{Exergy accumulation} \quad (12)$$

or

$$-(\in_{rec} - \in_i) - \in_D = \Delta\in_{ad} \quad (13)$$

Here,

$$\varepsilon_{rec} = \text{Exergy recovered} = \text{Net Exergy recovered by air} \quad (14)$$

where $\Delta\in_{ad}$ denotes the exergy accumulation in the discharging process. We can evaluate the exergy efficiency of this process as

$$\psi_d = \frac{\text{Exergy recovered by air}}{\text{Exergy released in adsorption}} = \frac{\Delta\in_{rec}}{\Delta\in_{ad}} \quad (15)$$

2.3. Overall Process

The energy and exergy analyses of the overall processes are considered in this section.

2.3.1. Energy Analysis and Efficiency for Overall Process

An energy balance for the overall open thermochemical storage process can be written as

$$Q_{in} - Q_{rec} - Q_{i,tot} = \Delta E \quad (16)$$

For the case of a complete cycle with identical initial and final states, $\Delta E = 0$. The energy efficiency for the overall storage process can be written as follows:

$$\eta_o = \frac{\text{Energy recovered from TES during adsorption}}{\text{Energy output to TES during desorption}} = \frac{Q_{rec}}{Q_{in}} \quad (17)$$

2.3.2. Exergy Analysis and Efficiency for Overall Process

An exergy balance for the overall storage process can be written as

$$\in_{in} - \in_{rec} - \in_{i,tot} - \in_{D,tot} = \Delta\in \quad (18)$$

For the case of a complete cycle with identical initial and final states, $\Delta\in = 0$. The exergy efficiency for the overall storage process can be expressed as follows:

$$\Psi_O = \frac{\text{Exergy recovered from TES during adsorption}}{\text{Exergy output to TES during desorption}} = \frac{\in_{rec}}{\in_{in}} \quad (19)$$

3. ILLUSTRATIVE EXAMPLE

To illustrate the analysis of an open thermochemical TES system, we consider an existing system for which experimental data have been reported.

3.1. System Description

An open sorption system has been utilized in a school in Munich, Germany since 1996. This system is connected to the district heating net. This thermochemical storage uses zeolite 13X as the adsorbent and can provide heating in winter as well as an air conditioning possibility in summer. This system is used to heat a school building in winter and cool a jazz club in summer. Both the school building and jazz club are connected to the Munich district heating system. The storage system is connected to a combined air, radiator and floor heating system [11]. The storage contains 7000 kg of zeolite 13X beads. Zeolite 13X is non-toxic and non-flammable and can be handled easily. The maximum air flow through the zeolite storage is 6000 m^3/h [8]. The heating mode of the system (applicable during winter) is investigated in this study. An energy storage density of 135 kWh/m^3 (0.5 GJ/m^3) can be obtained in the heating mode of the storage [13].

The following assumptions are made in this investigation:

- The maximum storage capacity is utilizable in the charging process.
- The formula for zeolite 13X is $Na_2O.Al_2O_3.3SiO_2.6H_2O$.
- Zeolite 13X has a maximum water uptake during the charging process and dried zeolite 13X hydrates have the maximum number of water molecules.
- The maximum volumetric air flow rate (6000 m^3/h) occurs during charging and discharging.
- The energy changes during adsorption and desorption are equal in magnitude, i.e. $\Delta H_{ad} = -\Delta H_{ds}$.
- The exergy changes during adsorption and desorption are equal in magnitude, i.e. $\Delta\in_{ad} = -\Delta\in_{ds}$.
- Properties of dry air are considered for the air as the working fluid.

The effect of the assumptions made in this study can be investigated on the efficiency results. It is particularly important to note that in this investigation the maximum storage capacity is considered and the volumetric air flow rate during charging and discharging processes is assumed to have its maximum value. With additional practical data, these values may vary and efficiencies and other results will change correspondingly.

3.2. Charging Process

The thermochemical storage is charged when energy is available from the district heating system in off-peak hours.
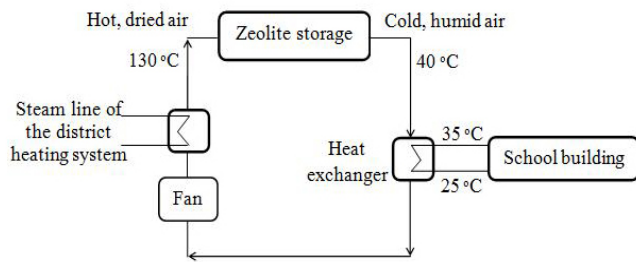
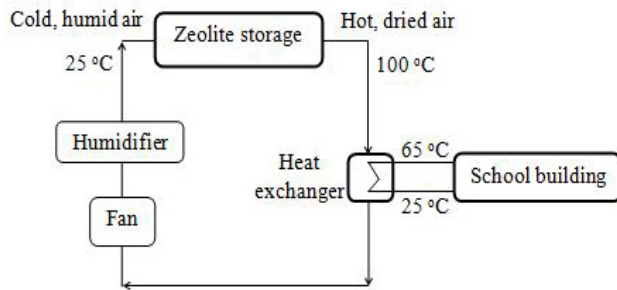**Fig. (3).** Charging (desorption) process at night. Adapted from [11].

Fig. (4). Discharging (adsorption) process during the day. Adapted from [11].

Charging is performed during 10 hours nightly (from 9 p.m. to 7 a.m.) each day.

The charging process is illustrated in Fig. (3). At first the air is heated from 25 °C to 130 °C by the district heating system. At night, the zeolite is charged using the air. Under these conditions zeolite is dried and the waste heat of the charging process at a temperature level of 35 to 40 °C supplies the heating system of the school. The maximum storage capacity of the charging process is 1400 kWh at a charging temperature of 130 °C [11]. As noted earlier, it is assumed that the maximum storage capacity can be obtained during charging. Temperatures and the maximum storage capacity are optimistic according to the design conditions.

3.3. Discharging Process

The thermochemical storage is discharged during daytime (the peak period). The discharging process is illustrated in Fig. (4). Air is heated to 25 °C and saturated with water vapor by a humidifier. Then, the saturated air is blown through the storage of dried zeolite. The air temperature rises to 100 °C. Discharging occurs over 14 hours (from 7 a.m. to 9 p.m.) each day and can provide a maximum heating power of 95 kW at an outdoor temperature of -16 °C [11].

3.4. Energy Analysis of TES Processes

Energy efficiencies are determined for the charging and discharging processes for the considered thermochemical TES, as well as for the overall process. Note that the energy efficiency for the storing period is not discussed extensively, as it is 100%.

3.4.1. Charging

The charging energy efficiency can be calculated using Equation (5). We calculate the energy efficiency of each process as the ratio of the useful energy output to the energy input as follows:
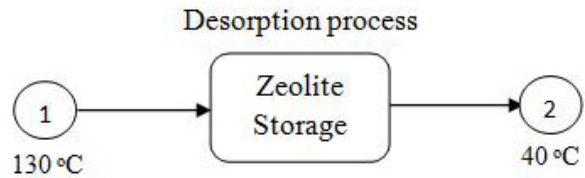

Fig. (5). Desorption process with inlet and outlet conditions of the air stream.
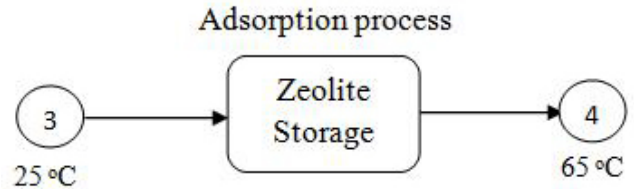

Fig. (6). Adsorption process with inlet and outlet conditions of the air stream.

$$\eta_c = \frac{useful\ output\ energy}{input\ energy} \qquad (20)$$

In this analysis, the zeolite storage is taken to be the control volume (see Fig. 5). In the charging process, the useful output energy is equal to the storage capacity of the charging process, which is 1400 kWh (or 5,040,000 kJ).

The input energy is supplied by the air flow and can be calculated as

$$Q_{in} = m_c C_p (T_1 - T_2) \qquad (21)$$

Here, m_c is the mass of air which blows through the storage during the charging period and can be calculated as

$$m_c = q_c t_c \rho_c \qquad (22)$$

where q_c denotes the volumetric air flow rate, and t_c and ρ_c are charging time and air density, respectively. The density and specific heat at constant pressure C_p of the air are evaluated at the mean temperature of the inlet and outlet air (85 °C). Thus,

$$m_c = 6000\ m^3/h \times 10\ h \times 0.99\ kg/m^3 = 59,400\ kg \qquad (23)$$

So, the input energy is

$$Q_{in} = 59,400 \times 1.009 \times (130 - 40) = 5,394,114\ kj \qquad (24)$$

The useful output energy is 5,040,000 kJ and the charging energy efficiency is:

$$\eta_c = \frac{useful\ output\ energy}{input\ energy} = \frac{5,040,000}{5,394,114} = 0.93 \qquad (25)$$

Comparing Equations (5) and (20), it is observed that the energy gained in the desorption process is equal to the numerator of the efficiency equation (5,040,000 kJ). Since the reaction is reversible, the energy released during the adsorption process is 5,040,000 kJ as well.

3.4.2. Discharging

The discharging energy efficiency is calculated using Equation (11). In this analysis, the zeolite storage is taken to be the control volume (see Fig. 6).

The recovered energy can be calculated as

Table 1. Evaluating Standard Chemical Exergy of Selected Components for Normal Reference-Environment Conditions (T_0 = 298.15 K; P_0 = 101.325 kPa)

Compound	ΔG_f kJ/mol	n_e		ε_{chne} (kJ/mol)		ε_{chne} (kJ/mol)
Na_2O	-262.05	2 (Na)	0.5 (O_2)	336.6 Na	3.97 (O_2)	413.14
Al_2O_2	-1582.19	2 (Al)	1.5 (O_2)	988.2 Al	3.97 (O_2)	400.17
SiO_2	-851.18	1 (Si)	1 (O_2)	854.9 Si	3.97 (O_2)	7.69
H_2O (gas)	-228.75	1 (H_2)	0.5 (O_2)	236.09 (H_2)	3.97 (O_2)	9.32
H_2O (liquid)	-237.32	1 (H_2)	0.5 (O_2)	236.09 (H_2)	3.97 (O_2)	0.76

Taken from [16].

$$Q_{rec} = m_d C_p (T_4 - T_3) \qquad (26)$$

The quantity m_d is the mass of air which passes through the storage during the discharging period and can be calculated as

$$m_d = q_d t_d \rho_d \qquad (27)$$

Here, q_d denotes the volumetric air flow rate. t_d and ρ_d are discharging time and density of air, respectively. The density and C_p of the air are evaluated at the mean temperature of the inlet and outlet air (45 ^{o}C), thus

$$m_d = 600 m^2/h \times 1.106\ kg/m^2 = 92.904\ kg \qquad (28)$$

Thus,

$$Q_{res} = 92,9904 \times 1.006 \times 40 = 3{,}738{,}457\ kJ \qquad (29)$$

The discharging energy efficiency is

$$\eta_d = \frac{3{,}738{,}457}{4{,}040{,}000} = 0.74 \qquad (30)$$

3.4.3. Overall TES Process

The energy efficiency of the overall TES process can be calculated using Equation (17):

$$\eta_0 = \frac{Q_{rec}}{Q_{in}} = \frac{3{,}738{,}457}{5{,}394{,}114} = 0.69 \qquad (31)$$

3.5. Exergy Analysis of TES Processes

Charging, discharging and overall exergy efficiencies are determined for the considered thermochemical TES. As before, the exergy efficiency for the storing period (100%) is not discussed extensively.

3.5.1. Charging

The exergy efficiency of the charging process can be evaluated using Equation (9). During charging, air is heated from 40 ^{o}C to 130 ^{o}C. The exergy input for the charging process can be evaluated as

$$\in_{in} = Net\ exergy\ delivered\ by\ air = m_c\ [h_2 - h_1 - T_0(s_2 - s_1)] \qquad (32)$$

where h_1 and h_2 denote the specific enthalpy of the air at the input and output conditions, S_1 and S_2 denote the specific entropy of the air at the input and output conditions. The relevant properties of the air are as follows:

- $h_1 = 338.8 kJ/kg$ (at $T_1 = 65^\circ C, P_4 = 101 kPa$)

- $S_1 = 5.746 kJ/kg$ (at $T_1 = 4^\circ C, P_1 = 101 kPa$)

- $h_2 = 6 kJ/kg\ K$ (at $T_2 = 130^\circ C, P_2 = 101 kPa$)

- $S_2 = 6 kJ/kg\ K$ (at $T_2 = 130^\circ C, P_2 = 101 kPa$)

The exergy input in the charging process can be calculated using Equation (32):

$$\in_{in} = 60{,}240 \times [404.5 - 313.16 - 298 \times (6 - 5.746)] = 942{,}635k \qquad (33)$$

To determine the exergy change during a thermochemical reaction, we calculate the exergy of reactants before the reaction as well as the exergy of products after the reaction. The difference between these two quantities is the exergy change within the control volume over the period of the reaction. The exergy of the control volume before the reaction is the sum of the exergies of the reactants. This exergy includes the physical, potential, kinetic and chemical exergy components of the reactants. As pointed out earlier, potential and kinetic exergy are neglected and also the physical exergy change of the components can often be neglected relative to their chemical exergy changes. This assumption is applied in this analysis. Consequently, we need only focus on the chemical exergy of the reactants.

The chemical exergy of compounds can be determined following the treatment [14, 15]. The standard chemical exergy of a chemical compound h_1 can be calculated by means of the exergy balance for a reversible reaction:

$$\in_{chn} = \Delta G_f + \sum_e n_e \in_{chne} \qquad (34)$$

Here, ΔG_f denotes the Gibbs energy of formation, n_e the amount of element e (in kmol), and $\in_{chne}$ the standard chemical exergy of the element.

A typical chemical formula for zeolite 13X composition is $Na_2O.Al_2O_3.(2.8\pm0.2(SiO_2.(6\sim7)H_2O$. We assume the formula for zeolite 13X in this study as $Na_2O.Al_2O_3.3SiO_2.6H_2O$. The molecular weight for zeolite 13X is 452.3 grams. There are 7000 kg of zeolite in the storage system, so the numbers of moles of zeolite 13X is 15,476. The charging reaction can be expressed as
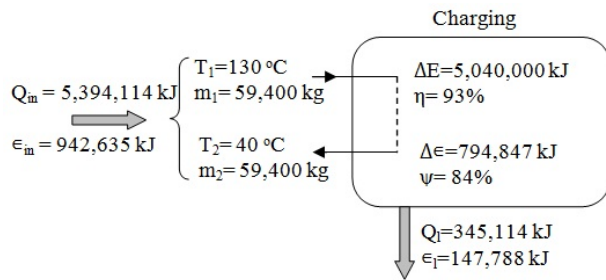
$$Na_2O.Al_2O_3.3SiO_2.6H_2O + heat \rightarrow Na_2O.Al_2O_3.3SiO_2 + 6H_2O \qquad (35)$$
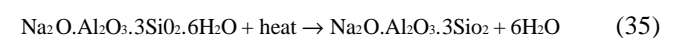
Fig. (7). The charging process, showing energy and exergy parameter values.
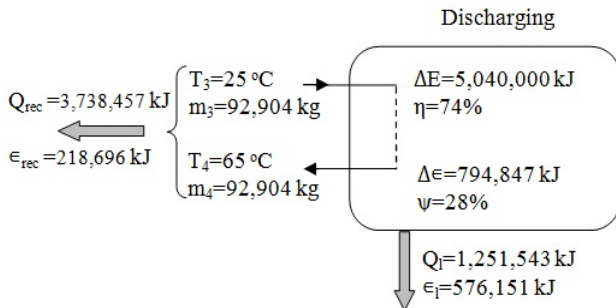

Fig. (8). The discharging process, showing energy and exergy parameter values.
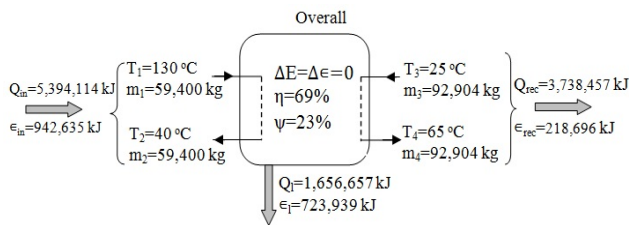

Fig. (9). The overall storage process, showing energy and exergy parameter values.

In order to calculate the exergy stored in this reaction, we need to evaluate the standard chemical exergy of each component (see Table **1**). The standard chemical exergy of a chemical compound $\in_{chn}$ can be calculated by means of the exergy balance for a reversible reaction.

Using calculated data from Table **1**, the standard chemical exergy of zeolite 13X (before and after desorption) can be calculated as follows. For $Na_2 O.Al_2O_3. 3SiO_2. 6H_2O$:

$$\in_{chn} = 413.14 + 400.17 + (3 \times 7.69) + (6 \times 0.76) = 840.94 \, kJ/mol \qquad (36)$$

For: $Na_2 O.Al_2O_3. 3Sio_2$

$$\in_{chn} = 413.14 + 400.17 + (3 \times 7.69) = 836.38 \, kj/mol \qquad (37)$$

The exergy accumulation during the charging period can be expressed as

$$\text{Exergy stored in desorption} = \in_{tot, products} - \in_{tot, reactants} \qquad (38)$$

Here, $Na_2O.Al_2O_3.3SiO_2$ and H_2O are products and $Na_2O.Al_2O_3.3SiO_2.6H_2O$ is the reactant, and the corresponding standard chemical exergies of the products and the reactant have been calculated:

Exergy stored in desorption = 15,476 moles x {[836.38kJ/mol + (6x9.32) kj/mol]-840.94kj/mol} $\qquad (39)$

Thus, the exergy efficiency of the charging process can be calculated as

$$\Psi_C = \frac{Exergy\ stored\ in\ desorption}{Exergy\ input} = \frac{794,847}{942,635} = 0.84 \qquad (40)$$

3.5.2. Discharging

The exergy efficiency of the discharging process can be evaluated using Equation (15). During discharging, air is heated from 25 ^{o}C to 65 ^{o}C. The exergy recovered in this process can be evaluated as

Net exergy recovered by air $= m_d[h_4 - h_3 - T_0(S_4 - S_2)] \qquad (41)$

where h_3 and h_4 denote respectively the specific enthalpy of the air at the input and output conditions, and S_3 and S_4 respectively denote the specific entropy of the air at the input and output conditions. Thus, the relevant properties of the air are as follows:

- $h_3 = 298.6 \, kJ/kg$ (at $T_3 = 25°C$, $P_3 = 101 kPa$)

- $S_3 = 5.696 \, kJ/kg \ K$ (at $T_3 = 4°C$, $P_3 = 101 kPa$)

- $h_1 = 338.8 \, kJ/kg$ (at $T_1 = 65°C$, $P_4 = 101 kPa$)

- $S_4 = 5.823 \, kJ/kg \ K$ (at $T_4 = 65°C$, $P_4 = 101 kPa$)

From Equation (41):

$$\in_{rec} = 92,904 \times [338.8 - 298.6 - 298 \times (5.823 - 5.696] = 218,696 \, kJ \qquad (42)$$

So,

$$\psi_d = \frac{Exergy\ recoverd\ by\ air}{Exergy\ released\ in\ adsorption} = \frac{218,696}{794,847} = 0.28 \qquad (43)$$

3.5.3. Overall TES Process

The exergy efficiency of the overall TES process can be calculated using Equation (19):

$$\psi_0 = \frac{\in_{rec}}{\in_{in}} = \frac{218,696}{794,847} = 0.23 \qquad (44)$$

4. SUMMARY

The energy and exergy analyses for the charging and discharging processes are summarized illustratively in Fig. (**7**), (**8**) and (**9**). Note that $\in_l$ in these diagrams is the summation of the exergy loss and the exergy destruction.

5. DISCUSSION

The energy- and exergy-based methodology applied here is similar to that employed for analyses of other types of TES systems. General efficiency expressions are determined for the charging, storing and discharging processes, as well as the overall TES process. These efficiencies are calculated for an illustrative example, based on an actual system.

Exergy analysis is seen to be useful, when applied with or in place of energy analysis, for assessing efficiencies of the various processes occurring in open thermochemical TES systems as well as other aspects of their thermodynamic performances. Exergy analysis is more useful than energy analysis for identifying the locations and reasons of thermodynamic losses in a TES system and can assist efforts to improve or optimize designs. The energy loss of the overall process is 1,656,657 kJ and the exergy loss of the overall

Table 2. Comparison of Efficiencies for Various Types of TES

TES Type		η_o	ψ_o	Remarks
Sensible		70%	40%	Aquifer TES [18]
Latent		45%	2.2%	$CaCl_2.6H_2O$ as PCM [19]
Thermochemical	Closed-loop	50%	9%	$SrBr_2.6H_2O$ as TCM [20]
	Open-loop	69%	23%	Zeolite 13X as TCM [11]

storage system is 723,939 kJ. It is seen in Figs. (**7-9**) that 76% of the total energy loss and 79% of the total exergy loss occur during discharging. So, optimizing the discharging process can help to improve the overall efficiency of the storage process.

Efficiencies of the storing process have been taken to be 100%, based on the assumption that there is no energy loss during storing period. This assumption is likely reasonable, in that the materials stored are at ambient conditions so no heat losses are expected. Nonetheless, the storing-period efficiencies could be lower than 100%, depending on the characteristics of the thermochemical material, the working fluid, the storing temperature, the storing duration, etc.

In this study, a single cycle of an open TES system operation is considered. Therefore, degradation of the thermochemical materials over time, as they undergo repeated cycles, is not considered. However, the effects of degradation are potentially significant, especially if repeated thermochemical cycles affect performance and the properties of the thermochemical material degrade notably over time. Little information on the degradation of thermochemical storage materials is available, but it is noted that phase change materials (PCMs) are also degraded with cycling in latent TES systems. Sari and Karaipekli investigated the characterization and thermal properties of palmitic acid/expanded graphite as a PCM in latent TES systems and showed that, after 3000 melting/freezing cycles, the melting latent heat decreased from 148.36 kJ/kg to 140.38 kJ/kg and freezing latent heat decreased from 149.66 kJ/kg to 139.97 kJ/kg [17].

A TES system for heating capacity only is investigated here. The system considered in the illustrative example supplies heat to a school building during winter or mid-season periods. The storage of cooling capacity is not considered.

For the illustrative example, the energy and exergy efficiencies respectively are determined to be 93% and 84% for the charging process and 74% and 28% for the discharging process. The results demonstrate that the energy efficiency of the discharging process is higher than the corresponding efficiency for the charging process and that the exergy efficiency of the charging process is higher than the corresponding efficiency for the discharging process. The overall energy and exergy efficiencies are found to be 69% and 23%, respectively. The results demonstrate that the exergy efficiencies of the charging, discharging, and overall processes are higher than the corresponding energy efficiencies. Exergy analysis takes into account the loss of availability of energy in storage operations and it reflects the thermodynamic and economic value of the storage operation. In the analyses, the maximum flow rate has been considered for the air and also it has been assumed that zeolite 13X is dried during desorption process to the maximum extent possible.

Therefore, the energy gained by the adsorbent attains a maximum value. The same assumption has been made for the adsorption process.

Exergy analysis takes into account the loss of availability of energy in a thermochemical TES system and indicates the thermodynamic and economic value of the system. The differences between energy and exergy efficiencies for the thermochemical TES and its processes are dependent on various factors, including the thermodynamic properties of the working fluid (air) and the thermochemical material, the nature of the desorption or adsorption process, the maximum output temperature of the heat source (a district heating system in the case study). The TES energy or exergy losses likely vary with all of these factors and others.

The factors discussed above suggest that the performance attained with other types of TES (sensible and latent) may be attained with open thermochemical TES, but with more compact storage systems. Efficiencies of various types of TES systems are compared in Table **2**.

CONCLUSIONS

The thermodynamic analysis presented here of an open thermochemical TES allows energy and exergy efficiencies for the overall TES and its processes, as well as other performance measures, to be determined and better understood. Exergy analysis is particularly useful for specifying the locations and reasons of thermodynamic losses in TES systems. Energy and exergy analyses help understand and contrast efficiencies for the various processes occurring in TES systems and thereby assist efficiency improvement efforts. The results presented here suggest that further research is needed to improve understanding of open thermochemical TES. The results suggest that open thermochemical TES may be as efficient other types of TES but more compact. For decision making regarding the selection of thermochemical TES for a particular application, other factors beyond the thermodynamic ones considered here need to be assessed, including the environmental effects of the TES system, economics, the degradation of the thermochemical material over time as well as its cycling behavior, the reliability of the overall system and required maintenance. Feasibility studies that consider these factors for specific applications appear to be merited.

NOMENCLATURE

Cp	=	specific heat at constant pressure (kJ/kgK)
E	=	energy (kJ)
h	=	specific enthalpy (kj/kg)
m	=	mass of working fluid (kg)

n	=	number of moles (-)
P	=	pressure (kPa)
Q	=	heat (kJ)
s	=	specific entropy (kJ/kgK)
T	=	temperature ($^\circ$C or K)
V	=	volume (m^3)

SUBSCRIPTS

0	=	reference environment
ad	=	adsorption
ds	=	desorption
D	=	destruction
e	=	element
in	=	input
l	=	loss
o	=	overall
rec	=	recovered
tot	=	total

GREEK LETTERS

ΔG_f	=	Gibbs energy of formation (kJ/mol)
ΔE	=	energy accumulation (kJ)
$\Delta \in$	=	exergy accumulation (kJ)
$\in$	=	exergy (kJ)
$\in_{chn}$	=	standard chemical exergy of a compound (kJ/mol)
$\in_{chne}$	=	standard chemical exergy of an element (kJ/mol)
η	=	energy efficiency (-)
ρ	=	density (kg/m^3)
Ψ	=	exergy efficiency (-)

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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