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Resorption system for cold storage and long-distance refrigeration

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1. Introduction

More and more households are equipped with some form of air conditioning systems, and these systems have increased the primary energy demand, causing electricity grid congestion and considerable green house gas (GHG) emission. The increasing use of electricity-powered devices to provide comfort triggered the development of technology to harness either renewable energy or waste heat as energy source for such devices. Industrial waste heat resources exist in various industrial sectors, and it has been claimed as one of the five major conventional energy sources, following coal, petroleum, natural gas and waterpower [1]; however, the majority of industrial waste heat goes unutilized [2]. China has 18 large-scale oil refineries with 225 million tons of annual refining capacity, and they reject between 40% and 50% of its total energy consumption as thermal waste. According to Lai [2], there is a huge recovering potential of this waste heat as more than 50% of this energy has temperature in the range of 90–200 °C. Although the energy to be recovered is available, the majority of the oil refineries and power plants are located several kilometers away from large urban areas, which brings difficulty to this heat recovery for residential purposes, as the transmission of thermal energy for distances over 10 km may imply in unacceptable large thermal losses. Hence, two solutions have been proposed [3-12] to address this challenge: one of them is energy storage; whereas the other is the long-distance transmission of a reactive fluid, instead of the

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ABSTRACT

A thermochemical resorption refrigeration system was designed and two types of application were investigated: (1) cold storage and (2) long-distance refrigeration. Manganese chloride and ammonium chloride were used as high-temperature salt (HTS) and low-temperature salt (LTS), respectively, and ammonia was utilized as reacting gas. The working performance in terms of coefficient of performance (COP) and specific cooling power (SCP) was assessed at different heat source temperature (140–170 °C) and refrigeration temperature (-15 to 5 °C). The COP obtained at these conditions varied between 0.20 and 0.31, whereas the SCP was from 87 to 125 W per kg of MnCl₂ composite sorbent, depending on the working condition and on the type of utilization.

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long-distance transmission of thermal energy, to avoid thermal losses. These approaches to use waste heat are important for a better and sustainable management of energy resources, and they can be realized by thermally driven chemisorption systems with reversible reaction between a gas and a salt.

Several studies [13–15] concluded that thermochemical adsorption processes can be utilized for energy conversion and storage process, particularly on deep-freezing, because of its relative higher-energy density, negligible heat loss, stability for long-term storage, and also due to the great number of working pairs that are capable of heat pumping at different temperature levels. On the other hand, since the 1990s [12] long-distance transmission of waste heat has been considered for district heating, and two studies which employed LiBr/H₂O⁹ and NH₃/H₂O [11] absorption system dealt with the use of this heat for cooling purposes. Nevertheless, thermochemical solid sorption systems involving the transmission of ammonia are more preferable than absorption systems based on sensible heat when the transmission distance is longer than 10 km [12]. Moreover, thermochemical adsorption systems avoids the need for separating the exhaust and coolant heat exchange processes, which is normally found in absorption systems, and also avoid the use of radiators in summer.

The objective of this paper is to evaluate the performance of a thermochemical resorption machine employed for cold storage and for long-distance heat pumping for distributed cooling effect production. Resorption cycle, which has been reported in the liter-ature [13–16] has two advantages over the conventional adsorption cycle: the first one is the higher enthalpy of the solid/gas reaction when compared to the enthalpy of vaporization, and the second advantage is the absence of liquid inside the system operating





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Nomenclature						
C S COP m m pinst-cooling Ouseful-cold	specific heat capacity, kJ/(kg K) coefficient of performance mass, kg mass flow rate, kg/s instantaneous cooling power, W useful cold production, kJ	$egin{array}{l} ho_f \ \Delta H_r \ \Delta P_{equ} \ \Delta T_{in-out} \end{array}$	density of the alcohol solution, kg/m ³ reaction enthalpy, kJ/kg the thermodynamic equilibrium pressure drop, bar temperature difference between the inlet and the outlet of heat exchange fluid, °C			
Q _{total-cold}	total cold production, kJ	Other su	bscripts			
$\begin{array}{c} Q_{lose-cold} \\ Q_{elec} \\ SCP \\ T \\ \overline{T} \\ V_{f} \\ x \\ \rho_{B} \end{array}$	loss of cold production to the ambient, kJ input electric energy, kJ specific cooling power, W/kg temperature, °C average temperature difference, °C volume flow rate of the alcohol solution, m ³ /s conversion degree of refrigerant density of the composite sorbent, kg/m ³	c equ EG f l m	constrain equilibrium expanded graphite alcohol solution fluid low middle			

under this cycle, which make it less sensitive to shocks, vibration, and to environment with microgravity, as that inside spacecrafts.

Since the single effect resorption cycle requires at least two different adsorbents, a comparative work between different working pairs was previously conducted [17]. The latter study determined the best combination of the reactant salts among three well-known candidates for sub-zero refrigeration; and afterwards, a small refrigerator with the preferable working pair was designed, manufactured, and its performance was evaluated. The results demonstrated the feasibility of the cold storage, but also exposed some problems that need to be corrected [18]. Therefore, based on the experience gained with these previous studies, the current experimental investigation was carried out on another prototype, which was manufactured with reduced thermal capacity and improved heat exchange design. The prototype tested in this study was larger than the prototypes previously tested [17,18] by this research group, to allow us the evaluation of its performance in a scale closer to that necessary for a commercial application. Then, the specific cooling power and the coefficient of performance of the machine was assessed when it operated under cold storage and long-distance refrigeration conditions with cooling production occurring between -15 and 5 °C. To our best knowledge, there has never been reported in the literature a resorption system producing cooling effect below $-10 \,^{\circ}$ C.

2. Fundamentals, experimental rig and materials

2.1. Working principle of a resorption cycle

A single-effect resorption system comprises two reactors, and each one contains a different inorganic salt. The salts have different equilibrium temperature when they react with refrigerant gas at the same pressure. Therefore, they are named as high temperature salt (HTS) and low temperature salt (LTS). Those two reactors interact through mass transfer in gaseous phase as shown in Fig. 1a and b, and they interact cyclically throughout two periods of the cycle. The process is analogous to the conventional adsorption: high pressure period (HPP) and low pressure period (LPP), as can be seen in Fig. 1c, where the lines marked by NH₄Cl and MnCl₂ correspond to the thermodynamic equilibrium condition for the reaction in each salt complex. The LTS reactor substitutes the evaporator and the condenser in the role of heat extraction for cold production and heat release for the thermal machine represented by the reactor with the HTS.

In the high pressure period of an ideal cycle (at P_h), the HTS reactor is subjected to the temperature constraint T_h , and the LTS

reactor is subjected to the temperature constraint T_m . They undergo, respectively, decomposition consuming heat $Q_{de,HTS}$ and synthesis releasing heat $Q_{sy,LTS}$. In the low pressure period (at P_1), the direction of the reaction is reversed, and the HTS and LTS reactors are subjected to the temperature constraints at T_m and T_1 , respectively. During this period, the cold effect can be obtained due to the endothermic decomposition occurring in LTS reactor. The following reactions occur between ammonia and the salts used in this work:

$$\begin{aligned} \mathsf{MnCl}_2 \cdot 2\mathsf{NH}_3 + 4\mathsf{NH}_3 &\leftrightarrow \mathsf{MnCl}_2 \cdot 6\mathsf{NH}_3 + 4\Delta H_{\mathsf{MnCl}_2} \end{aligned} \tag{1} \\ \mathsf{NH}_4\mathsf{Cl} + 3\mathsf{NH}_3 &\leftrightarrow \mathsf{NH}_4\mathsf{Cl} \cdot 3\mathsf{NH}_3 + 3\Delta H_{\mathsf{NH}_4\mathsf{Cl}} \end{aligned}$$

2.2. Experimental setup

Fig. 2 shows the photos of the thermochemical resorption refrigeration machine and the auxiliary devices required for the experimental investigation. The machine had small mass ratio between the metallic components and the sorbent (about 6:1), to achieve reduced thermal capacity and improved thermal efficiency. The components of the system are described below, and numbered according to Fig. 2.

- (1) 9 HTS reactors. Each one had an electric heater installed in its axial center. They were equipped peripherally by a water jacket heat exchanger, whose outwards was thermally insulated, as shown in Fig. 2b.
- (2) 8 LTS reactors. They are equipped with peripheral jackets filled with alcohol solution (chilled medium), which during the experiments, circulated through a thermostatic bath. Fig. 2a shows a box numbered (2) which contained all LTS reactors and their jackets isolated from the surroundings by a 50 mm thick plastic foam.
- (3) Pressure gauge.
- (4) Pressure transducer.
- (5) Blocking valve in the gas connection between the HTS and LTS reactors.
- (6) Components to emulate the operation of long-distance heat pumping for distributed cold production. This part used small diameter coiling tubes that created an analogous condition of pressure drop during long-distance transmission of the reactive fluid. The tube with 4 mm inner diameter was 10 m long, and was coiled into 20 circles with diameter between 160 and 165 mm.
- (7) Valve for refrigerant filling.



Fig. 1. Scheme of two consecutive periods in a single-effect cycle of a resorption system, (a) high pressure period; (b) low pressure period; (c) Clausius–Clapeyron diagram of NH₄Cl–NH₃ and MnCl₂–NH₃.



Fig. 2. (a) The resorption refrigeration machine; (b) the experimental rig including auxiliary equipments.

Fig. 3a and b show a scheme of the heat exchange system outside the HTS and LTS reactors, respectively. Fig. 3b shows that there is an extra fluid channel in the axial center of each LTS reactor. Consequently, the heat exchange surface was enlarged and the heat transfer resistance decreased. Fig. 3c depicts the vertical view of the LTS reactor, where the hatched area represents the space for chilled alcohol fluid; the blank area represents the LTS composite sorbent with five gas channels distributing evenly; T1, T2 and T3 denote temperature measurement by thermoresistances at three different positions in the radial direction.

2.3. Material

The sorbent material was as a composite of expanded graphite and inorganic salts with the mass ratio of 7:13. The use of an inert porous graphite matrix aimed to avoid salt agglomeration and to enhance the heat transfer properties of the sorbent blocks [19,20]. The procedure of material preparation consisted of a thermal treatment of the expandable graphite at 800 °C for 2 min, followed by impregnation of the expanded graphite into a salt solution. Afterwards, the mixture was dried and compressed inside the reactors.

The mass ratio of the composite sorbents to the metallic materials of the reactors was approximately 1:6. Other information of the sorbents used in the system is summarized in Table 1.

3. Experimental procedures and analysis method

3.1. Experimental procedures

The experimental investigation was divided in three sets of experiments:

EXP 1: Operation of the resorption refrigerator under different conditions of heat source temperatures (from 140 to 170 °C); and then, identification of the preferable operation condition to achieve higher coefficient of performance (COP) and higher specific cooling power (SCP).

EXP 2: Operation of the refrigerator under the condition identified in EXP 1 to assess its feasibility for cooling effect production



Fig. 3. (a) Water heat exchange loops for HTS reactors; (b) alcohol heat exchange loops for LTS reactors; (c) the vertical view of the LTS reactor structure and the measurement arrangement.

Table 1

Characteristics of the experimental materials.

	NH ₄ Cl	MnCl ₂
Mass of salt (kg)	1.38	2.44
Mass of expanded graphite (kg)	0.71	1.29
Height of sorbents (mm)	550	400
Bulk density of the sorbent (kg/m ³)	310	310
Thickness of sorbents layer (mm)	19.5	19
$\Delta H_r (\mathrm{kJ/kg})$	1628 [21]	2924 [22,23]
$C_f (kJ/(kg K))$	3.38-3.43 ^a	
C_{salt} (kJ/(kg K))	1.514–1.555ª	0.591 ^a
C_{EG} (kJ/(kg K))	0.598-0.640 ^a	0.722-0.724 ^a
$C_{\rm NH3}$ (kJ/(kg K))	2.227-2.346ª	2.227-2.346 ^a
C _{metal} (kJ/(kg K))	0.46 ^b	0.46

^a These figures varied with the operation condition [24].

^b Stainless steel 304 [25].

from -15 to 5 °C, under cold storage (CS) and long-distance refrigeration (LDR) applications.

EXP 3: Operation of the system at the heat source temperature of 170 °C during the high-pressure period to ensure that the reaction is completed in its largest degree. Thereafter, operating the refrigerator for CS application during 3 h, to assess the maximum degree of conversion that can be achieved during cold production.

Table 2 shows the operating conditions of all experiments. The heat sink temperature was always 20 $^\circ C.$

The experimental sets EXP 1 and EXP 2 were conducted sequentially in three steps:

Step 1: HTS reactors were heated for 60 min, while an electricity power meter measured the input energy. The gas desorbed by the HTS reactor was adsorbed in the LTS reactors, which released heat to a heat sink at 20 $^{\circ}$ C.

Step 2: HTS and LTS reactors were, respectively, cooled to ambient temperature and refrigeration temperature, while the connecting valve between the reactors was closed. The length of this period was between 5 and 10 min.

Table 2
Operating conditions of the experiments in three sets of experiments.

	Utilization	Heat source temperature T_c (°C)	Refrigeration temperature <i>T</i> ₁ (°C)
EXP 1	CS, LDR	140, 150, 155, 160,170	0 and -5
EXP 2	CS	Preferable condition	-15 to 5
	LDR	Preferable condition	-10 to 5
EXP 3	CS	170	–15 to 5

Step 3: Chilled alcohol solution flowed through the heat exchange jackets of the LTS reactors, with constant inlet temperature, while the LTS sorbents desorbed at low temperature for 60 min. Meanwhile, the HTS reactors adsorbed the gas desorbed by the LTS reactors, and released heat to cooling water at ambient temperature.

The experimental set EXP 3 also passed through Step 1 and 2, as described above; however the Step 3 was longer, and lasted 3 h instead of 60 min.

The temperature measurements were accomplished by Pt 1000 sensors with uncertainty of ± 0.1 °C. A turbine flow meter with the full scale of 1 m³/h and 0.5% uncertainty was utilized to measure flow rate of the chilled alcohol solution. A piezoelectric pressure transducer with uncertainty of ± 2.5 kPa was installed in the HTS reactor, and another one in the LTS reactor. The above measured data was recorded every 6 s by an Agilent HP34970A data logger.

3.2. Analysis method

The performance of the system was calculated with Eqs. (3)-(9) and the data measured as described in Section 3.1.

$$p_{inst-cooling} = V_f \cdot \rho_f \cdot C_{p,f} \cdot \Delta T_{in-out} \tag{3}$$

$$Q_{useful-cold} = \int p_{inst-cooling} \cdot dt \tag{4}$$

7)

$$COP_{max} = \frac{\Delta H_{r,LTS}}{\Delta H_{r,HTS}}$$
(5)

$$COP = \frac{Q_{useful-cold}}{Q_{elec}} d\overline{T}_{sorbent} + (mc) d\overline{T}_{metal} \wedge u^{d} dm$$
(6)

$$\frac{(me)_{(salt+EG+NH_3)}}{(salt+EG+NH_3)} dt + (me)_{(metal)} dt = \frac{1}{dt} dt$$

$$+\dot{m}c(T_{in} - T_{out})$$

$$\frac{dm}{dt} = m_{max} \cdot \frac{dx}{dt} \tag{8}$$

$$SCP = \frac{Q_{useful-cold}}{t \cdot m_{HTS}}$$
(9)

where m_{max} is the maximum amount of the refrigerant that can reacted, *x* is the conversion degree of the reaction.

4. Results

4.1. Identification of the preferable working condition

4.1.1. Temperature and pressure

In the high-pressure period, the variation of temperature or the pressure with the time presented similar pattern regardless the heat source temperatures. The setup temperature (T_c) is shown as $T_{2,HTS}$ in Fig. 4, and it was measured in the sensor position T2, as shown in Fig. 3c.

The heating period of the HTS comprised three sub-periods as shown in Fig. 4. In the first sub-period (Part I), the thermal energy was consumed as sensible heat and no decomposition was observed; thus $T_{\rm HTS}$ gradually rose while both the system pressure and $T_{\rm LTS}$ remained practically constant. $T_{1, \rm HTS}$ indicated the temperature inside the HTS sorbents that was near to the heater (see Fig. 3c), and it was about 10 °C higher than $T_{2, \rm HTS}$, and about 20 °C higher than $T_{3, \rm HTS}$, due to the heat transfer resistance within the sorbent.

When $T_{\rm HTS}$ reached around 120–130 °C, the pressure suddenly boosted, and $T_{\rm LTS}$ began to increase. Such variation in the pressure implied that the process went to the second sub-period (Part II) where the reaction started and consumed large amount of the input thermal energy. As the input power was constant, the rate of increment of $T_{\rm HTS}$ decreased. In the third sub-period (Part III), which started at different time in different parts of the sorbent, the rate of variation of $T_{\rm HTS}$ increased again, which was an indication that the input thermal energy was mainly consumed by the sensible load of the sorbent beds, and the reaction could be considered almost completed.



Fig. 4. Variation of temperature and pressure in high period phase when heat source setup temperature was $160 \,^{\circ}$ C.

4.1.2. Performance under different heat source temperature

The equivalent degree of reaction conversion during the low pressure period of the cycle was calculated with Eqs. (7), (8), and it was plotted versus the setup heat source temperature (T_c), as shown in Fig. 5a.

Once T_c exceeded 160 °C, the equivalent degree of reaction conversion remained practically constant. Such a result indicated that increasing T_c above this value did not lead to a larger desorbed mass, and hence, to a larger adsorbed mass and higher cooling capacity. This fact is corroborated by the data presented in Fig. 5b which shows that the COP starts to decrease once T_c exceeded 150 °C, regardless of the refrigeration temperature.

When the setup T_c was lower than 150 °C, an increment of T_c increased the equivalent degree of reaction conversion and consequently, increased the amount of cold production more than the amount of total heat consumed, which enhanced the COP. However, when the setup T_c was higher than 150 °C, the effect that the increment of T_c had on the increment of the equivalente degree of reaction conversion was smaller than the effect that the former variable had in the increment of the consumed sensible heat load, and thus, the COP started to decrease.

The maximum theoretical COP (Eq. (5)) of the MnCl₂/NH₄Cl resorption system is 0.55. However, experiments that were conducted to evaluate the energy consumption by the sensible heat load of HTS sorbents and metallic reactors indicated that this heat accounted for about 29–32% of the total thermal energy input; hence, reducing the maximum possible COP to about 0.37–0.39 even if the reaction is completed. The experimental COP was between 0.28 and 0.31 when T_1 was 0 °C, whereas it was 0.19–0.25 when T_1 was –5 °C.



Fig. 5. Performance of the cold storage system under different heat source temperature, (a) equivalent degree of reaction conversion; (b) COP.

From the results of obtained in this part of the work, the preferable heat source temperature (T_c) to achieve the highest COP is 150 °C when the heat sink temperature (T_m) is 20 °C.

4.2. Performance under preferable operating condition

4.2.1. Temperature and pressure patterns

Fig. 6 shows the variations of temperature and pressure inside the LTS sorbents during the low-pressure period for cold storage utilization. As soon as the valve that connected the reactive gas between the reactors was open, the temperature of the LTS dropped sharply in the first moments of the reaction; then, it increased again, before it starts to decrease again.

It is possible to see in Fig. 6 that the temperature of the LTS dropped more when the salt was initially at -5 °C or -10 °C than when it was at 0 °C or 5 °C. A possible reason for this larger temperature decrease that occurred when the LTS was initially held at -5 and -10 °C, is due to the fact that the equilibrium conditions for the fully charged salt and the partially charged salt that delimits the pseudo-equilibrium zone, as shown in Fig. 7, become more distant at lower pressures. The suddenly reaction at the very beginning of the process caused the temperature of the LTS to drop, respectively 12 °C and 16 °C, when the initial temperature of the LTS was -5 °C and -10 °C.

The evolution of the pressure with the temperature of the LTS and HTS, together with the equilibrium curves for the reaction between these salts and NH_3 can be seen in the Clapeyron diagram of Fig. 7. The equilibrium curves for the reaction between NH_3 and NH_4Cl and between NH_3 and $MnCl_2$ were plotted according to



Fig. 6. (a) Variation of the temperature of the LTS during the low pressure period for cold storage use; (b) variation of the pressure of the LTS during the low pressure period for cold storage use.

previously presented results [21,22], and the arrows shows the direction of the pressure evolution with the time.

It is possible to see in Fig. 7 that at the beginning of the lowpressure period of the cycle, the pressure of the LTS was close to the equilibrium condition of the fully charged salt (line "1" in Fig. 7). Once the valve that connected the gas phase of the LTS reactor and HTS reactor was opened, the pressure inside the LTS reactor decreased, and the temperature of the LTS was forced to become closer to its equilibrium temperature of fully charged salt. Once the salt desorbed some ammonia, its equilibrium condition was shifted to another value (line "2" in Fig. 7). Between these two equilibrium conditions, there is a zone of low reaction rate, or pseudo-equilibrium zone, as described by other authors [13], where the reaction occurs slowly.

In all experiments, the initial temperature of the HTS was the same, and hence, its initial equilibrium pressure. When the gas phase of the reactors was put in contact, the pressure initially tended to a mean value. Because the driving force for the reaction is the difference between the actual pressure and the equilibrium pressure, in the experiments where the initial temperature of the LTS was higher, the amount of ammonia desorbed by this salt at the first moments of reaction was higher than that at lower temperatures. At the first moments of the reaction, the rate of desorption of one salt may be very different from the rate of adsorption of the other salt, and the variation in the pressure inside the system occurs mainly due to this unbalance between the amount of gas that is desorbed and the amount of gas that is adsorbed. Afterwards, the pressure reaches a condition where both the desorption rate and the adsorption rate are the same, and the variation of the working pressure is caused by a change in the equilibrium pressure of both salts.

Similar pattern of temperature and pressure were observed in the experiments for the long-distance refrigeration application (LDR). The main difference was that the pressure inside each reactor took between 35 and 60 min to reach a common value due to the mass transfer resistance caused by the narrow spiral pipe. The pressure drop of the reactive gas in the long coiled pipe was about 15–25 kPa, which is about 9% of the working pressure at the refrigeration temperature of 5 °C, and reached 46% when the refrigeration temperature was -10 °C. The mass transfer resistance had a negative effect on system performance because it brought the working pressure closer to the equilibrium pressure; hence, decreasing the rate of reaction.

4.2.2. Performance analysis: cooling power, COP and SCP

Fig. 8a and b display the instantaneous cooling powers ($p_{inst-cooling}$ in Eq. (3)), for the applications of CS and LDR respectively.

The cooling power had a sharp increase at the first 10–15 min of reaction, except when the initial temperature of the LTS was 5 °C, and the systems was used for LDR application. It is worth noting that when the initial LTS temperature was higher, there was a stronger driving force at the beginning of the reaction, which resulted in faster reaction rate and sharper peak value, whereas when the initial LTS temperature was lower, the reaction driving force was weaker and caused a flatter cooling power output. Such a behavior was more evident for the LDR utilization as shown in Fig. 8b. The stable cooling output lasted longer when the cooling effect occurred at lower temperatures. A continuous cooling output of least 330 W, occurred for 40 min when at the cooling effect occurred at -10 °C, whereas it was reduced to 24 min when the cooling effect occurred at 0 °C.

In order to achieve a more constant cooling power output, Lepinasse et al. [14] proposed a mechanical relief device to control the system pressure, and consequently, the reaction rate and cooling power output. In our study, the narrow spiral tube located between the HTS reactors and the LTS reactors during the LDR application acted



Fig. 7. Clapeyron diagram of the LTS during the low pressure phase for cold storage use, when the T_1 at: (a) 5 °C; (b) 0 °C; (c) -5 °C; (d) -10 °C. 1 = pseudo-equilibrium of NH₄Cl in synthesis, 2 = pseudo-equilibrium of NH₄Cl in decomposition, 3 = pseudo-equilibrium of MnCl₂ in synthesis, 4 = pseudo-equilibrium of MnCl₂ in decomposition. The maximum equilibrium pressure represents the decomposition equilibrium pressure of the LTS corresponding to the refrigeration temperature. The minimum equilibrium pressure is referred to the equilibrium pressure of the HTS at the heat sink temperature. The maximum mean equilibrium pressure is the average value of the leading pressure and the minimum equilibrium pressure.



Fig. 8. The instantaneous cooling power, (a) for cold storage; (b) for long-distance refrigeration.



Fig. 9. COP and SCP of cold storage and long-distance refrigeration operating under preferable condition.

similar to the mechanical relief device; hence, at this type of application, the cooling power could be kept constant for a longer time. Although the cooling power can be more stable when the pressure of the systems is controlled, the total cooling power decreases, and cooling power obtained under LDR utilization was much smaller than that obtained under CS condition. For instance, it is possible to see in Fig. 9 that the specific cooling power in the LDR application was 68% and 85% smaller than that obtained with CS application , when the cooling output occurred, respectively at 0 °C, and -10 °C. This figure also shows the COP and SCP at different refrigeration temperatures. The error in the calculated COP and SCP is lim-

Table 3 The values of performance obtained by different single-effect cooling systems.

ited to 5.4% and 2.6%, respectively. For the CS application, the COP was 0.24 and the SCP was 95 W per kg of HTS composite sorbent when the refrigeration temperature was below -5 °C, and these figures rose, respectively, to beyond 0.31 and 125 W per kg of HTS composite sorbent, when the refrigeration temperature increased to 0 °C. The existence of these two levels of performance is explained in the next section. For the LDR application, the variation of the COP and SCP with the refrigeration temperature was less pronounced, and between the extreme temperatures, these figures rose less than 8%. The pressure drop through the narrow spiral pipe can explain such a behavior, because the working pressure is relevant to the reaction rate.

Table 3 presents the operation conditions, the sorbent characteristics and the SCP achieved with previous resorption refrigeration systems and those of the system studied in the current work. Prototypes of smaller size presented higher SCP than larger prototypes, and the highest value was obtained with a machine using NiCl₂ as HTS and BaCl₂ as LTS [13]. The size of the prototype studied in this work is larger than that of any other prototype presented in the literature, and its SCP had similar magnitude than that of a medium size refrigerator presented by Lépinasse et al. [14]. On the other hand, the operating time impacts significantly the SCP, and machines operating under shorter cycles may have higher SCP, because the reaction rate decreases as the reaction proceeds. The machine presents a peak mean SCP, and it decreases with the prolonging of the reaction time and the evolution of the reaction degree. For instance, when refrigeration temperature was at 0 °C, the SCP of the machine studied in this work began to decrease after 15 min of reaction when the mean SCP was around 240 W/kg. The latter value is twice as that presented in Table 3,

No.	Reference	Working pairs	m(g) salt	m(g) EG	$\rho_B (\mathrm{kg}/\mathrm{m}^3)$	T_l (°C)	T_m (°C)	T_h (°C)	SCP (W/kg)	Cooling period (min)
1	Lépinasse et al. [14]	PbCl ₂	401	216	520	-3-5	20	150	99	20
		MnCl ₂	217	117	400					
2	Goetz et al. [13]	BaCl ₂	66	35	300	0	40	240	318	15
		NiCl ₂	82	44	300					
3	Bao et al. [26]	BaCl ₂	46	25	303	0 to 10	30	155	25 to 150	50
		MnCl ₂	56	30	306					
4	Bao et al. [26]	NaBr	35	19	299	0	30	155	156	50
		MnCl ₂	56	30	306					
5	Bao et al. [26]	NH4Cl	31	17	299	0	30	155	148	50
		MnCl ₂	56	30	306					
6	This work	NH ₄ Cl	1380	710	310	-15-0	20	150	95-125	60
		MnCl ₂	2440	1290						



Fig. 10. Performance variation in 3 h cold producing process for cold storage: (a) equivalent conversion degree; (b) SCP.

which indicated the mean SCP over a period of 60 min. To our best knowledge, among the resorption systems presented in the literature, the machine studied in this work is the only one that produced cooling effect at temperatures below -10 °C. Besides the possibility to achieve lower cooling production temperature, the use of the working pair studied in this work allowed the utilization of lower regeneration temperature, when compared to the system that use NiCl₂ and BaCl₂ as working pair [13].

4.2.3. Performance in 3 h' cooling producing phase

Fig. 10 depicts the equivalent degree of conversion and the SCP of the machine for CS application when the length of the low pressure period was prolonged to 3 h to guarantee that the reaction had higher degree of conversion.

From Fig. 10a it is possible to see that the reaction was almost halted at any working condition, after 70 min of reaction, and that at the first 60 min, 88–91% of reaction was completed.

Hence, although the increase of the cooling period can increase the total cooling capacity, the cooling power was greatly reduced, and if one intends to achieve higher values of SCP, the refrigeration period should not be longer than 20–30 min.

It is also possible to observe that there is a large difference between the degree of conversion at the higher refrigeration temperatures (0 °C and 5 °C) and the lower refrigeration temperature (-15 °C, -10 °C, -5 °C), and this difference explain the two level steps for the SCP and COP, which are observed at Fig. 9. The final working pressure at the refrigeration temperature of -5 °C was below 80 kPa, whereas at the refrigeration temperature of 0 °C, it was above 120 kPa. The mass transfer resistance inside the sorbent block may be at reason why at refrigeration temperatures of -5and below, the reaction was halted when the conversion degree reached 60–70%.

5. Conclusion

A bench-scale thermochemical resorption system with the working pair $MnCl_2/NH_3$ and NH_4Cl/NH_3 was built and investigated under different operation conditions to demonstrate the feasibility of two kinds of utilization: cold storage and long-distance refrigeration.

In order to achieve higher COP, the preferable condition for the heat source was 150 °C, when the heat sink was 20 °C. For cold storage application, the refrigeration temperature should be kept at 0 °C or above, because it was observed a great decrease in the COP and cooling power when the refrigeration temperature was below this level. The COP and SCP can be, respectively, 0.31 and 125 W per kg of MnCl₂ composite sorbent in the machine if the refrigeration temperature is kept at the recommended level. For the long distance cooling production, the refrigeration temperature had less influence in the performance, and the COP was 0.21 and the SCP reached 87 W per kg of MnCl₂ composite sorbent, when the refrigeration temperature was 0 °C.

The experimental results also indicated that if one intends to maximize the cooling power instead of the COP, the cooling period should be no longer than 20–30 min.

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