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Performance of an integrated thermochemical heat pump/energy store

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Abstract

The thermal performance of a thermochemical heat pump, when employed as an energy store, has been investigated experimentally. The working pair of activated alumina and water has been used. A general relationship relating the equilibrium pressure and temperature of the system is deduced. The coefficients of performance of the heat pump, in the heating and the cooling modes, are calculated.

Keywords: Adsorbate; Desiccant; ESM; Heat pump; Heat storage

1. Thermochemical heat pump

A thermochemical heat pump (TCHP) can be used for either (instantaneous or delayed) cooling or heating. It has the ability to upgrade the exergetic potential of heat as in thermal-comfort applications and water heating. In addition, a TCHP system operates with less electrical power than conventional heat pumps, but can be integrated into an energy-store system [1].

A TCHP usually consists of two storage vessels (see Fig. 1). The first encloses the desiccant (e.g. activated alumina), whereas the second contains the adsorbate (e.g. water) [1]. The basic principle of the process, occurring under vacuum conditions, is shown in Fig. 2. Owing to the pressure difference $(p_1 - p_2)$ between the two vessels and the high adsorption affinity of the desiccant, the vapour of the adsorbate will

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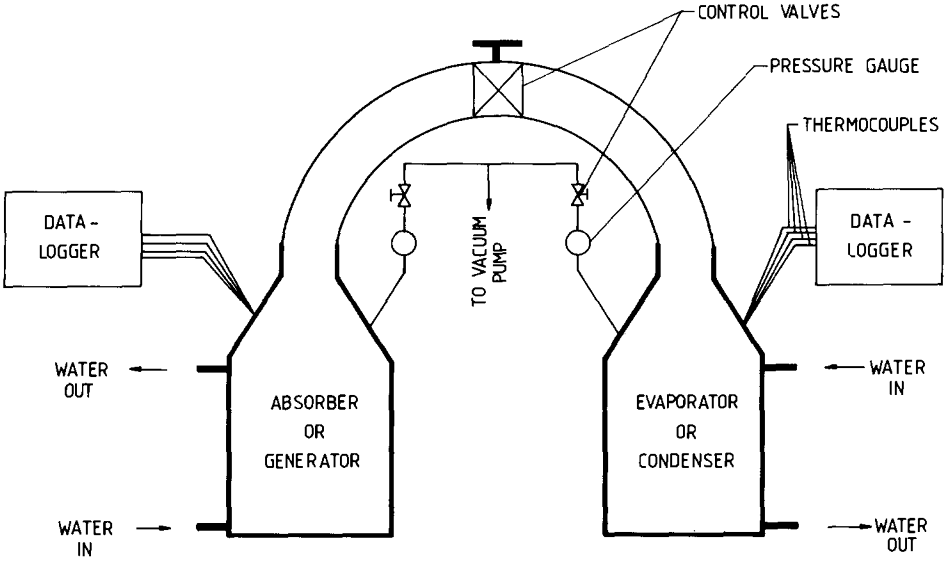

Fig. 1. Schematic representation of the experimental TCHP rig.

be transferred to the second vessel and be absorbed (i.e. point b), thus releasing the heat of absorption. This will proceed until a state of equilibrium ensues (i.e. point b′). For the process to continue, heat is supplied to dry the desiccant, i.e.

$$\text{Heat} + \text{Wet adsorbent} \rightleftharpoons \text{Dry adsorbent} + \text{Vapour} \qquad (1)$$

The high-pressure (p_3) vapour generated at point c flows to the second vessel and condenses (i.e. point d of Fig. 2). This will proceed until a state of equilibrium results (i.e. point c′), after which the adsorbate and the desiccant are cooled to temperatures, T, corresponding to points a and b respectively. As a result, the respective pressures in both vessels will drop to p_1 and p_2.

If the mass transfer is to be sustained (i.e. points a to b), heat must be supplied continuously to the high-pressure end (point a) and removed from the low-pressure end (point b). The existence of temperature and pressure differences leads to irreversibilities in the process and hence energy losses. It is important to minimise such losses in any TCHP system. The pressure drop between the evaporator and the absorber can easily be regulated, whereas it is more difficult to control the internal pressure within the desiccant bed.

The evaporation/condensatoin of the adsorbate is the process for storing heat in a TCHP. Therefore, the latent heat of vaporisation of the adsorbent will play an important role in dictating the energy density of a TCHP. Equally important factors are the mass of the vapour that can be absorbed per unit mass (or per unit volume) of the adsorbate and the effect of the chemical energy of absorption or desorption [2].

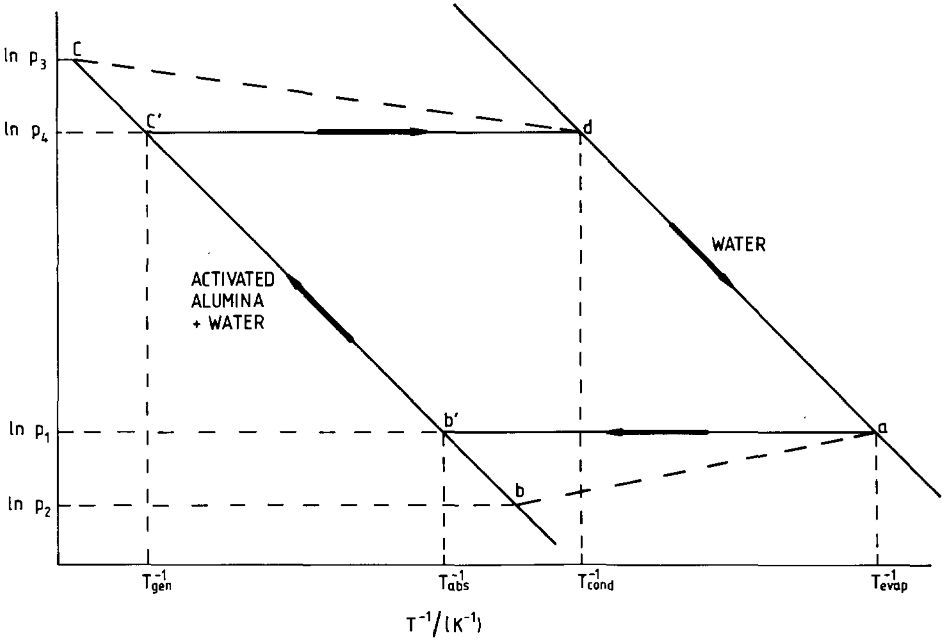

Fig. 2. The working principle of a TCHP system.

2. Desiccants and adsorbates

Solid-core desiccants, or block forms, consist of desiccant granules held together by a binder. This binder is usually a non-desiccant material. Desiccants must remove water and not react unfavourably with any other materials in the system. In addition, desiccants that take up water by chemical reaction are not recommended. For instance, activated alumina, silica gel and molecular sieves are the most widely used desiccants acceptable for refrigerant drying. These materials remove moisture by physical adsorption. Also, a combination of desiccants can be used and may have certain advantages over a single desiccant because they can adsorb a greater variety of contaminants [3].

Several factors need to be considered when selecting the working pair (i.e. the desiccant and the adsorbate) for a TCHP. A highly-porous desiccant will increase the exposed surface area, and so higher rates of absorption ensue. In addition, the appropriate concentration of the vapour local to the desiccant and the diffusion through the desiccant are essential to ensure the absorption below the desiccant-bed's surface (i.e. the subsequent layers). Raising the thermal conductivity of the desiccant will enhance the rate of heat transfer, resulting in a greater driving potential (e.g. pressure and temperature differences) between the adsorbate and the desiccant.

3. Theoretical considerations

For solid–gas equilibrium, the Clausius–Clapeyron equation applies [1], i.e.

$$\frac{\mathrm{d}(\ln p)}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{2}$$

where H is the enthalpy per unit mass of the desiccant and R is the specific gas constant.

The isoteric heat of adsorption is given by

$$\Delta H = R\frac{(T_{\mathrm{abs}}T_{\mathrm{gen}})}{(T_{\mathrm{gen}} - T_{\mathrm{abs}})}\ln\left(\frac{p_{\mathrm{gen}}}{p_{\mathrm{abs}}}\right) \tag{3}$$

The maximum coefficient of performance (COP) of a TCHP is given by the well known Carnot formula, derived for a cyclic reversible process. In general, the TCHP process involves, (i) a high-temperature heat-engine, and (ii) a low-temperature heat-pump. These two modes are generally coupled to each other and run simultaneously (see Fig. 3).

The COP of the heat-engine (HE) mode operating between the condenser and the generator is [4]

$$(\mathrm{COP})_{\mathrm{HE}} = \frac{\text{Total heat provided for heating}}{\text{Energy supplied to the generator}} \tag{4}$$

$$(\mathrm{COP})_{\mathrm{HE}} = \frac{Q_{\mathrm{cond}} + Q_{\mathrm{abs}}}{Q_{\mathrm{gen}}} = \frac{T_{\mathrm{cond}}(T_{\mathrm{abs}} - T_{\mathrm{evap}}) - T_{\mathrm{evap}}(T_{\mathrm{gen}} - T_{\mathrm{abs}})}{T_{\mathrm{gen}}(T_{\mathrm{abs}} - T_{\mathrm{evap}})} \tag{5}$$

The COP of the heat-pump (HP) mode operating between the absorber and the evaporator is [4]

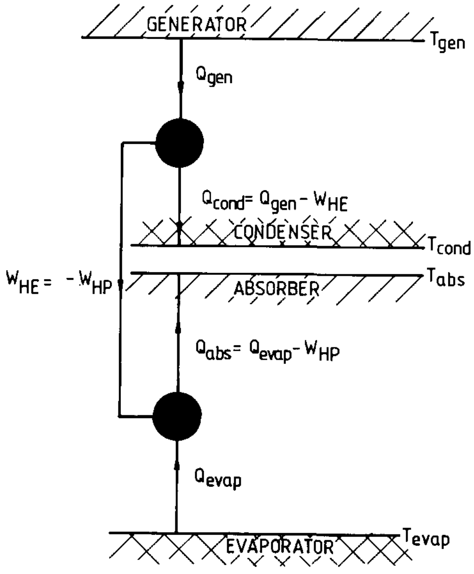

Fig. 3. Heat analysis of the TCHP system, where Q is the heat flow and W is the mechanical work.

$$(\mathrm{COP})_{\mathrm{HP}} = \frac{\text{Useful thermal energy}}{\text{Thermal energy used}} \tag{6}$$

$$(\mathrm{COP})_{\mathrm{HP}} = \frac{Q_{\mathrm{evap}}}{Q_{\mathrm{gen}}} = \frac{T_{\mathrm{evap}}(T_{\mathrm{gen}} - T_{\mathrm{cond}})}{T_{\mathrm{gen}}(T_{\mathrm{abs}} - T_{\mathrm{evap}})} \tag{7}$$

4. Scope of the present investigation

The aims are, (i) to investigate experimentally the thermal performance of a thermochemical heat pump when employed as an energy store, (ii) to establish the relationship governing the vapour pressure of the adsorbate and the temperature of the desiccant, and (iii) to determine the COPs of the TCHP in the heating and cooling modes. Activated alumina (Al_2O_3) (desiccant) and water (adsorbate) are chosen as the working pair.

5. Experimental rig

A dynamic TCHP closed system was designed and constructed to test the performance of an activated alumina/water working pair for storing energy. It consists of two 120 mm high and 120 mm diameter thermally-insulated stainless-steel cylindrical vessels (i.e. the absorber or generator and the condenser or evaporator). Both storage vessels are connected via a 40 mm diameter thermally-insulated aluminium conduit, fitted with a control valve. This conduit was short in order to reduce the resistance to the flow between the vessels during the process (see Fig. 1). The system operated under vacuum.

When designing the TCHP system, the following points were considered. (i) In order to reduce the likelihood of leakage, the number of lead-through and entry ports for the pipe connections is a minimum. (ii) The effective heating/cooling surfaces per kilogram of the solid desiccant are a maximum (iii) It is essential to obtain maximum thermal contact between the inner surface of the absorber or generator vessel and the desiccant. (iv) The size of each vessel is large enough to enable its contents to be replaced or increased easily.

Small spheres of activated alumina, each with a diameter of about 2 mm, were used as the desiccant. These were dried under vacuum conditions in an electric oven for at least 72 h at a temperature of 120°C and were allowed to cool to room temperature overnight in a tightly-sealed permanently-evacuated container.

Both vessels, during the adsorption/desorption process, were either heated and/or cooled via incorporated water circuits, connected to the water heaters/chillers. An electrical spiral-shaped heater with an 800 W power output was placed inside the absorber or generator vessel for use during the desorption process. (This electrical power to the heater was adjusted via a variac, and measured by an electronic wattmeter.) Each vessel contained 13 thermojunctions to measure the temperature rise of its contents. They were evenly placed at different depths to demonstrate the temperature distribution. Each of the measured temperatures was accurate to ±0.2°C and the pressures were accurate to ±200 Pa.

6. Thermal performance

The reaction of the aluminium oxide with water vapour in the present experimental investigation is an adsorption and also a desorption association which occur as described in the equation [1]

$$Al_2O_3 + nH_2O \rightleftharpoons Al_2O_3 \cdot nH_2O \tag{8}$$

where the number of moles $n = 3$. Therefore, one mole of Al_2O_3 (with molecular weight $M = 102$) can absorb 3 moles of water vapour ($M = 18$). The mass of the desiccant, m, required to absorb a given mass of water vapour can be deduced from

$$\frac{m_{Al_2O_3}}{m_{H_2O}} = \frac{M_{Al_2O_3}}{nM_{H_2O}} \tag{9}$$

Therefore

$$1.7\ \text{kg}\ Al_2O_3 + 1.0\ \text{kg}\ H_2O \rightleftharpoons 2.7\ \text{kg}\ Al_2O_3 \cdot 3H_2O \tag{10}$$

The specific heat C_p of water vapour in the absorbed state at 25°C can be evaluated from

$$C_{p_{H_2O}} = \frac{M_{Al_2O_3 \cdot 2H_2O} C_{p_{Al_2O_3 \cdot 2H_2O}} - M_{Al_2O_3} C_{p_{Al_2O_3}}}{M_{H_2O}} \tag{11}$$

i.e.

$$C_{p_{H_2O}} = \frac{(156 \times 1.66 - 102 \times 0.76)}{(3 \times 18)} = 3.4\ \text{kJ kg}^{-1}\ \text{K}^{-1} \tag{12}$$

For all the calorimetric tests undertaken, activated alumina absorbed water vapour up to 45 ± 1% of its mass. This agrees within experimental error with the prediction from Eq. (10), that under ideal conditions, it can absorb water vapour up to 53% of its mass.

A series of experimental tests was carried out, with activated alumina and water as the working pair, in a closed TCHP system. The mass of the adsorbed water vapour in the first vessel and that being evaporated from the second vessel were measured at 15 min intervals. Also determined are the rates of heat being released (i.e. heat of adsorption) and adsorbed (i.e. heat of evaporation). The evolved heat of adsorption for the activated alumina was 2.92 ± 0.1 MJ per kg of water. This agrees within experimental error with the measured heat of adsorption of 3.15 ± 0.1 MJ per kg of water.

For each experiment, the pressures in both vessels were measured. The relationships between the equilibrium pressures and temperatures obtained for the TCHP system with different water-vapour contents are shown in Fig. 4. At a specific water-vapour content, the water-vapour pressure decreased by increasing the gener-

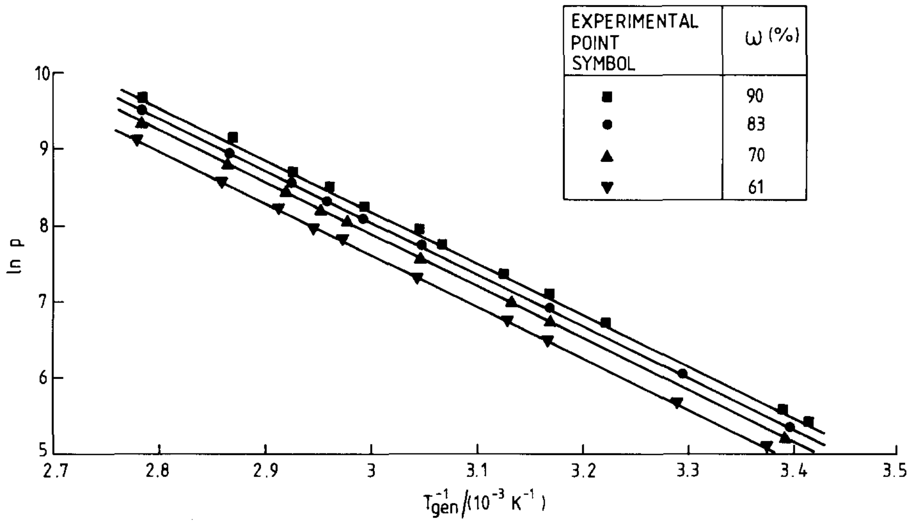

Fig. 4. Pressure–temperature relationship for activated alumina as function of the water–vapour content.

ator's temperature. The relationship can be expressed as

$$\ln p = -\frac{A}{T_{\text{gen}}} + B \tag{13}$$

where p is pressure in pascals. Experimentally determined values of A and B are displayed in Table 1. Hence, the general relationship governing the equilibrium pressure and temperature of the working pair (i.e. activated alumina and water) in the TCHP system with the water-vapour content is

$$\ln p = -\frac{6253 + 83.84\mathrm{e}^{2.27\omega}}{T_{\text{gen}}} + 5.33\omega + 24.15 \tag{14}$$

By applying Eqs. (5) and (6), the COPs for the TCHP system at given ranges of absorber and the evaporator temperatures in the heating and the cooling modes were found and are shown in Figs. 5 and 6, respectively. For both modes, the COPs

Table 1
Experimentally determined values of A and B in Eq. (13)

$\omega/\%$ [a]	A/K	B
90	6905 (±1.7%)	28.97 (±1.2%)
83	6795 (±1.7%)	28.46 (±1.2%)
70	6686 (±1.8%)	27.95 (±1.2%)
61	6583 (±1.7%)	27.37 (±1.2%)

[a] Water-vapour content.

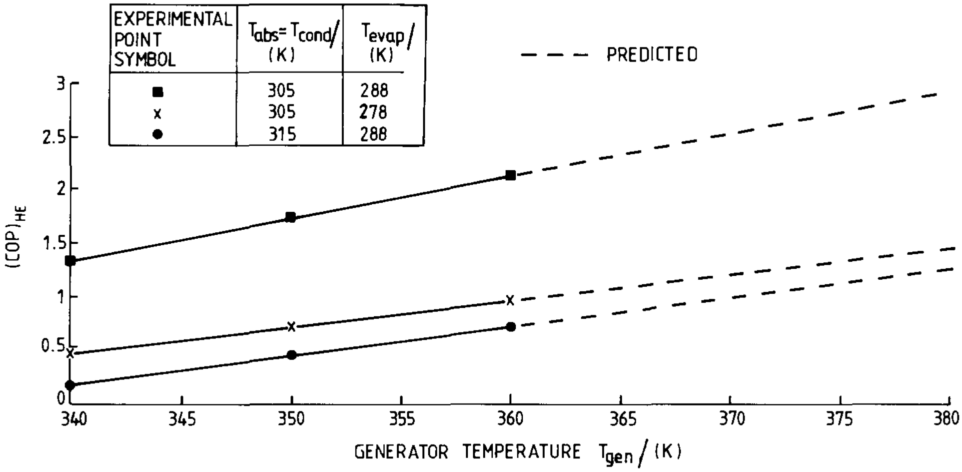

Fig. 5. The expected coefficient of performance of the TCHP system in the heating mode.

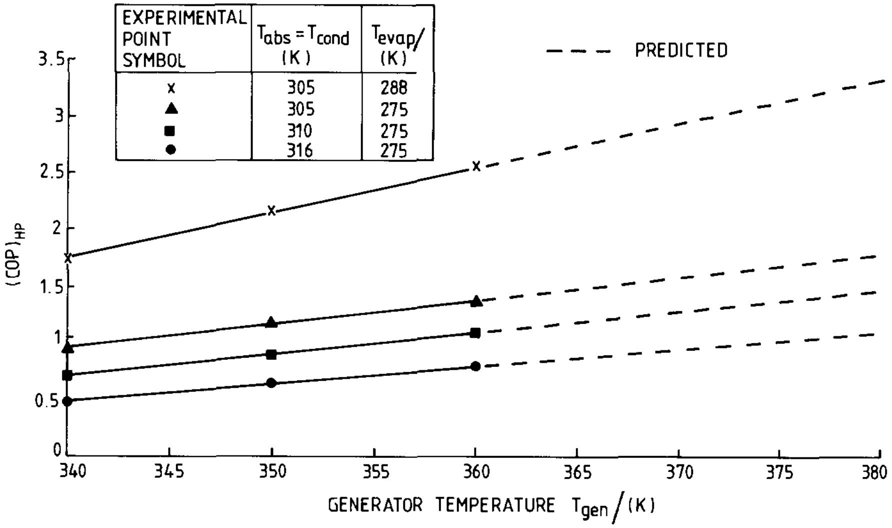

Fig. 6. The expected coefficient of performance of the TCHP system in the cooling mode.

increased as the generator and evaporator temperatures were increased, whereas they decreased as the absorber temperature was increased.

7. Conclusions

Below 100°C the working pair of activated alumina and water provided a suitable medium for a TCHP system to be employed as an energy store. The evolved heat of adsorption for activated alumina compared favourably with other pairs [4].

However, at a higher temperature, activated alumina demonstrated a lower capability of absorbing water vapour, all other conditions remaining invariant.

A general expression for the equilibrium pressure and temperature of the TCHP system has been deduced. This easy-to-use first-approximation relationship will enable designers of such TCHP systems to predict the equilibrium pressure and temperature at different water-vapour contents.

The coefficients of performance of the TCHP system, in the heating and cooling modes, improved more rapidly with decreasing condenser and absorber temperatures than with increasing evaporator or generator temperature.

Such a TCHP system can incorporate a solar panel that can charge the desiccant during the adsorption process. Thus, the system can utilise that energy of adsorption at a later time when it is needed. Hence, less fuel will be consumed, and consequently, emission rates of pollutants will be reduced.

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