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Adsorption cycle "heat from cold" for upgrading the ambient heat: The testing a lab-scale prototype with the composite sorbent CaClBr/silica

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HIGHLIGHTS

- A new adsorption cycle HeCol for upgrading the ambient heat is studied.
- Heat source with low temperature of 2–30 °C is used to get the useful heat at 35–50 °C.
- The HeCol feasibility is demonstrated for the first time on a lab-scale prototype.
- The composite methanol sorbents exchanging up to 0.46 g/g are prepared for HeCol cycle.
- The maximum specific heating power in HeCol cycle equals 1.4–3.6 kW/kg of the sorbent.

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ABSTRACT

Adsorptive transformation of heat is an emerging technology that is especially promising for low-temperature heat sources. Recently, an adsorption cycle (the so-called "Heat from Cold" or HeCol) has been suggested for upgrading the ambient heat in cold countries. This paper addresses the selection of composite sorbents of methanol specialized for this cycle and the study of their sorption properties. First, we analyzed which adsorbent is optimal for the HeCol cycle and how its properties depend on the HeCol cycle boundary temperatures. Then, three composite sorbents, based on $CaCl_2$, $CaBr_2$ and their mixture confined inside the silica gel mesopores, were prepared and their sorption equilibrium with methanol was analyzed keeping in mind the HeCol cycles with various boundary temperatures. It was shown, that these composite sorbents exchange up to 0.48 g of methanol per 1 g of the composite that far exceeds this value for common activated carbons. Finally, a first lab-scale HeCol prototype was built and tested with one of the studied sorbents, namely $CaClBr/SiO_2$, to evaluate the feasibility of the cycle.

1. Introduction

Heating and cooling demands are currently accounted for about 50% of the primary energy consumption. Only 18% of this energy is produced from renewable sources and 75% – from fossil fuels that causes severe ecological problems over the last decades [1]. For this reason, there is an urgent need for the development of heating/cooling systems driven by renewable sources, the thermal energy of which is directly released to the ambient at enormous amount [2,3]. The temperature level of renewable heat sources (the Sun, heat wastes, ambient heat, etc.) is significantly lower than that achieved by burning fossil fuels. Moreover, this low-grade heat even has no commercial value until it is upgraded to acceptable temperature level [4]. However, technologies available to recover low-grade heat below 100 °C are currently extremely limited [5,6]. Adsorptive heat transformation, AHT, (cooling, heat pumping, heat amplification) is an energy saving and environmentally benign technology, which holds a great promise for utilization of these low-temperature heat sources [7,8]. The adsorption cooling has attracted a lot of researches during last decades, a number of pilot units have been investigated for air conditioning and refrigeration [8–12], ice-making [13], desiccant cooling [14,15], climate control [16,17], tri-generation systems for combined cooling, heating, and power supply [18,19], combined cooling – desalination [20], etc. and nowadays several chillers are commercially available [21]. On the contrary, to the best of our knowledge, the adsorption heat amplification or the upgrading the temperature level is still being at the very initial stage [4,22].

Recently, an adsorptive cycle for amplification of the ambient heat

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Nomenclature

α	heat transfer coefficient (W/m^2 K)
Cp	heat capacity (J/g K), (J/K)
d_{av}	average pore size (nm)
δ	relative error (%)
f	flow rate (L/h), (m^3/s)
Δ*F*	adsorption potential (kJ/mol)
ε	absolute error (K)
Δ*H*°	standard enthalpy (kJ/mol)
Δ*S*°	standard entropy (J/(mol K))
L	salt content (mmol/g)
m	mass (g)
M	molar mass (g/mol)
n	methanol sorption (mole/mole)
P	pressure (mbar)
ρ	density (kg/m^3)
R	universal gas constant (J/(mol K))
S	surface area (m^2)
S_{sp}	specific surface (m^2/g)
T	temperature (°C), (K)
Q	heat (kJ/g)
V_p	specific pore volume (cm^3/g)
W	power (kW)
W_{sp}	specific power (kW/kg)
w	uptake (g/g)

Subscripts

1	adsorption stage
2	desorption stage
ad	adsorption
av	average
in	inlet
L	low
con	condensation
des	desorption
ev	evaporation
H	high
HEx	heat exchanger
M	medium
max	maximal
out	outlet
ex	experimental
t	theoretical
fm	fluid-metal

has been suggested [23]. The originality of the HeCol cycle is that the regeneration of the adsorbent occurs owing to the drop of the vapor pressure over the adsorbent, not by heating the adsorbent up to high temperature (60–120 °C) as in the common adsorption heat pumps. The desorption proceeds at low temperature of 2–25 °C and the heat for desorption is used for free from the natural heat source. The HeCol cycle uses the temperature difference between two natural thermostats, both being at low temperature (near 0 °C and below). They can be, for instance, the ambient air with low-temperature level (T_L) and a natural non-freezing water basin, like ocean, sea, river, lake, underground water, etc, at medium temperature (T_M) that is somewhat above 0 °C. In addition to the natural water basins, the waste heat of domestic sector with a higher temperature T_M of 15–25 °C can be used in this cycle. Heat from both sources is available for free. In cold countries during winter time, the temperature difference between them can reach 30 °C and more. This difference can be used to upgrade the temperature of the heat taken from the water reservoir up to a higher level T_H sufficient for heating [23], thus gaining commercial value. Since the useful heat is deemed to be produced by means of a low ambient temperature, the cycle was called “Heat from Cold” (HeCol). It can be interesting for countries with cold climate, and especially for the Arctic zone.

Among common adsorbates (water, methanol, ethanol, and ammonia) for AHT, water has the largest heat of evaporation (2.24 kJ/g), but it cannot be used in the HeCol cycle because of its high freezing temperature (0 °C) and very low saturation vapor pressure (0.5–10 mbar) at the cycle temperatures. Ethanol possesses the lowest evaporation heat (0.84 kJ/g). Therefore, the best adsorbates for the HeCol cycle are methanol and ammonia, which latent heat equals 1.10 and 1.37 kJ/g, respectively. The former one is considered in this paper because it is less toxic.

This paper presents experimental results on the first lab-scale realization of the HeCol cycle. Quite specific adsorbent is necessary for the suggested HeCol cycle. On the one hand, it has to adsorb methanol at high temperature T_H sufficient for the heating purposes. On the other hand, it has to be regenerated at low temperature T_M of the heat source. It has been shown previously, that activated carbons, which are the common methanol adsorbents, can hardly be employed for the HeCol cycle because they exchange too small amount of methanol under conditions of the cycle [24]. To select the appropriate sorbent, we, first, considered the thermodynamic requirements to an ideal (imaginary) adsorbent that is optimal for a given HeCol cycle. Then, we chose several sorbents of methanol, which were expected to be suitable for appropriate HeCol cycles. For these sorbents, the methanol sorption isobars and isosters were measured, and the isosteric sorption enthalpy and entropy were calculated. These data are used to evaluate the amount of methanol exchanged in several HeCol cycles with different operating conditions to assess the potential of the tested sorbents. Finally, the first lab-scale HeCol prototype was designed, built, and tested with one of the studied composite sorbents. The feasibility of the HeCol cycle was clearly demonstrated and the effect of the operating temperature T_M on the cycle performance was studied.

2. The cycle description

Herein, we only briefly introduce the HeCol cycle, which is described in more detail in [23]. In the simplest, three temperature (3T) version, the cycle operates between three thermostats with temperatures T_L, T_M and T_H, and consists of two isosters and two isotherms (Fig. 1a). The condenser temperature corresponds to the lowest temperature T_L. It is the temperature of ambient air, which in cold territories during winter time can be as low as (−10 °C) − (−60 °C). The thermostat at intermediate temperature T_M, which is used as a source of heat for desorption, is also a part of the environment. It can be a non-freezing natural water basin (ocean, sea, river, lake, underground water), or a soil. Its temperature may change in a wide range, commonly, between 0 and 30 °C. The third thermostat at high temperature T_H is connected to the heating circuit at consumer side, where the useful heat is released.

The initial adsorbent state (point 1 in Fig. 1a) corresponds to temperature T_M and pressure of the adsorbate vapor $P_L = P_0(T_L)$, where $P_0(T_L)$ is the saturation adsorbate pressure at temperature T_L. Under these conditions, the equilibrium adsorbate content $w_1 = w(T_M, P_L)$ is low due to the low adsorbate pressure P_L. Then, the adsorbent is heated up to temperature T_H (stage 1–2) at constant uptake w_1. At point 2, the adsorber is connected to an evaporator maintained at T_M which generates the constant pressure $P_M = P_0(T_M)$ of adsorbate. This pressure jump causes the vapor adsorption that leads to an increase in the equilibrium uptake to $w_2 = w(T_H, P_M)$ (point 3 in Fig. 1 a). The evaporation heat Q_{ev} is absorbed in the evaporator at T_M and the useful adsorption heat Q_{ads} is released at constant temperature T_H (isotherm