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Characterization of diethyl ether adsorption on activated carbon using a novel adsorption refrigerator

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ABSTRACT

In order to remove the limitations originating from inefficient heat and mass transfer in adsorption refrigeration/heat pump, an innovative arrangement design was proposed. It was equipped with meshed multi-tubular involving activated carbon in a sealed cylindrical adsorber. Related aspects of adsorption refrigeration key parameters were addressed. Working pair, activated carbon–diethyl ether, is used in the above system in order to determine the *optimum* adsorption refrigeration parameters.

In order to estimate the adsorption characteristics and the adsorption capacity of the adsorbent, the adsorption isotherms of that adsorbent, with a specific adsorbate, are carried out. The measured adsorption data were adequately described by the Langmuir equation. The adsorption capacity of the diethyl ether on activated carbon at 26, 35, and 50 °C were 0.0159, 0.0220, and 0.0188 mmol/g, respectively.

Two kinetic adsorption models namely pseudo-first and second order kinetic models were investigated. The thermodynamic parameters, ΔH°, entropy, ΔS°, and Gibbs free energy, ΔG°, of the adsorption process were also obtained from the gas adsorption experiments at various temperatures. These values were −45.84 kJ/mol, −88.87 J/(mol K), and −19.27 kJ/mol, respectively.

The pseudo-first order model was not applicable in this adsorption system, suggesting that the adsorption process and the rate-limiting step was the pseudo-second order reaction. Therefore, the dominant mechanism might be a chemisorption process between the diethyl ether molecules and the activated carbon surface. The k_2, however, decreased as the initial diethyl ether pressure increased.

1. Introduction

Most of the refrigeration and heat pump technologies are dominated by vapour compressor system [1]. However, the vapour compressor system is highly concerned with the environmental regulations, as most of the vapour compressor technologies are using refrigerant gases which are known as ozone depleting and global warming gases. Therefore, there is great demand to originate or to develop an alternative to vapour compressor refrigeration devices. Thermally driven, adsorption technology is one of the possible alternatives. In recent years, solid sorption systems driven by low temperature waste heat or solar energy have received increasing attention [1]. In comparison with the existing absorption systems and vapour compression refrigeration systems, the advantages of adsorption systems are less vibration, simple control, low initial investment and expenditure, and less noise [2].

Adsorption is a surface phenomenon occurring at the interface of two phases, in which cohesive forces including Van der Waals forces and hydrogen bonding, act between the molecules of all substances irrespective of their state of aggregation [3]. Surface forces or unbalanced forces at the phase boundary cause changes in the concentration of molecules at the solid/fluid interface. Solid and the fluid adsorbed on the solid surface are referred to as adsorbent and adsorbate, respectively. Adsorption may be due to a physical process generally referred to as physical adsorption, or physisorption, caused by Van der Waals forces, or a chemical process referred to as chemical adsorption or chemisorption, involving valence forces.

However, regardless of the type of adsorption involved, all involve evolution of heat of adsorption. The heat of adsorption is usually small in physisorption processes and large in chemisorption. Adsorbent substances can be restored to original conditions by a desorption process usually involving the application of heat, except in some cases chemisorption processes may be irreversible. Depending upon adsorbent and adsorbate phases, adsorption systems may be classified as solid/gas, solid/liquid, liquid/gas and liquid/liquid [4].

Adsorption characteristics of adsorbents are determined by the adsorption isotherms, for the amount a substance adsorbed [4]. Adsorption is always accompanied by evolution of heat, the quantity of which depends upon the magnitude of the Van der Waals

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forces involved, phase change, electrostatic energies and chemical bonds. Heats of adsorption are either derived from adsorption isotherms, generally referred to as the isosteric heat of adsorption or determined experimentally using the calorimetric method, referred to as differential heat of adsorption [4–6].

Adsorption refrigeration/heat pump systems works as following: the refrigerant is vapourized by the heat from cooling space and the generator (absorbent tank) is cooled by ambient air. The vapour from the cooling space is leaded to the generator tank and absorbed by adsorbent. The rest of the refrigerant is cooled. In the regeneration process, the adsorbent is heated at a high temperature until the refrigerant vapour in the adsorbent is desorbed out, goes back and condenses in the refrigerant tank (condenser).

This process relies on adsorption capacity of a particular solid for particular gas between two temperatures. Targeted gases are adsorbed by a solid material at low temperature, approaching a state of gas phase/adsorbed phase equilibrium. The latent heat of adsorption is rejected to a cryogenic bath or to the environment. In the case of a vacuum pump, the pressure of the vacuum chamber is reduced; in the case of the compressor, fresh gases from the environment further feed the compressor. Next, when the temperature of the adsorbent is raised, the adsorption capacity of the solid is reduced and the gas is releases either to the environment or to a closed volume that becomes pressurized (desorption (generation) process). The heat necessary for the generation process can be supplied by a low-grade heat source, such as solar energy. There are several factors for design of an adsorber (adsorption compressor), including adsorbent material selection, heat and mass transfer, and material properties.

Research has shown that solid adsorption technology has a promising potential for competing with conventional absorption and vapour compression technologies. The commercial solid/vapour adsorption systems are still non-existent [7]. There are two types of adsorbates used with the activated carbon, ammonia and methanol. Many investigations focus on the activated carbon–ammonia system during the current decades [7]. Wang et al. (2005) demonstrated a heat pipe type adsorption ice-maker designed for fishing boats with specific cooling power and coefficient of performance about 731 W/kg and 0.41, respectively, at the evaporating temperature $-15\,^{\circ}C$ [8]. A multifunction heat pipe adsorption refrigerator, using compound adsorbent-ammonia working pair, was studied by Wang et al. (2004) [9]. The chemical adsorbent $CaCl_2$ has the problems of expansion and agglomeration [10]. Kumita et al. (2002) studied the adsorption equilibria of ethanol and methanol vapours on activated carbon fibre (ACF) and granular one (GAC) at 30 and $50\,^{\circ}C$. The cooling effect in an ideal cycle of adsorption refrigerators was estimated under the typical operating temperature conditions from the predicted isotherms. The results obtained showed that the ACF with large surface area has high adsorptive capacity for both ethanol and methanol vapours. El-Sharkawy et al. (2006) also improved the performance of thermally powered adsorption/cooling systems by selecting a new adsorbent/refrigerant pair. Adsorption equilibrium data of ethanol onto Unitika activated carbon fibre (ACF) of types (A-20) and (A-15) were measured. It was found that ACF (A-20)/ethanol pair has considerably higher adsorption capacity than ACF (A-15)/ethanol pair. Zisheng et al. (2006) [11] overcome these problems by appropriate technology. The compound adsorbent was mixed with $CaCl_2$ and activated carbon by a mass ratio of 4:1, can improve the adsorption performance greatly. In this paper, new adsorbent–adsorbate combination, the activated carbon and the diethyl ether, will be investigated.

Activated carbons have been used as adsorbents in various industrial fields, such as solvent recovery, gas separation, catalysts, wastewater treatment and deodorization [3]. The activated carbons are characterized by a strong adsorption capacity that is attributed to their large internal surface area, high porosity, and high degree of surface reactivity [3]. Activated carbon contains heteroatoms on its surface and the main heteroatom is oxygen. Different functional groups can be derived from these chemical heteroatoms. The most common are: carboxyl, lactonic, carbonyl and phenolic. Moreover, activated carbons can show acidic and basic pH values in aqueous solution. The basic properties are ascribed to the presence of basic surface oxides. Carbons with low oxygen content show basic properties and anion exchange behaviour. The acidic surface properties are due to the presence of acidic surface groups. Carbons with high oxygen content, on the other hand, show acidic surface properties and cation exchange behaviour [12].

Diethyl ether with the chemical formula $(C_2H_5)_2O$ is a polar molecule that can interact with the carbon surface via dispersive interactions of its hydrocarbon moiety, two ethyl groups. It can also be hydrogen bonded to oxygen containing surface functional groups such as carboxylic and phenolic compounds. In addition, ether is capable of donating a pair of electrons from the oxygen lone pairs and thus interacts with the electron pair receptors on the surface as a Lewis base [13]. The heat of diethyl ether adsorption on carbon black was reported to be about 36 kJ/mol [14].

The performance of this system is largely determined by heat transfer process. Good heat transfer can significantly improve the efficiency of the heat pump and enhancement of bed thermal conductivity. Mass transfer resistance is due to gas flow through the bed consisting of a porous medium and to gas diffusion inside adsorbent particles [15].

The heat and mass transfer limitations result in extended durations of the adsorption heat pump cycles [16]. An innovative arrangement design equipped with a multi-tubular involving adsorbent in meshed tubes in a sealed cylindrical adsorber is proposed to eliminate the limitations originating from inefficient heat transfer in adsorption heat pumps. Such an arrangement, which allows a good contact between the metal and the adsorbent and within the adsorbent layer itself, would provide the opportunity of shortening the cycles to a great extent. One working pair, activated carbon–diethyl ether, is proposed in the system to determine the *optimum* adsorption refrigeration parameters.

It is of importance to precisely analyse the performance of an adsorption refrigeration cycle, based on an accurate determination of the adsorbent–adsorbate (refrigerant) behaviour and on an exact understanding of the influence of operating conditions and the working pair characteristics on the performance [17]. This includes evaluation of the adsorption capacity, rate of adsorption and the effect of various adsorption refrigeration parameters.

Therefore, the aim of this paper is to design of an innovative adsorber by taking into account the heat and mass transfer effect, study the equilibrium adsorption isotherms, adsorption kinetic rate and investigate the effect of a number of key parameters on the adsorption process and develop a complete, precise and clear understanding of the adsorption refrigeration using the activated carbon. Thermodynamic parameters are also calculated for the system.

2. Experimental

2.1. Materials

Activated carbon, NORIT PK 1-3 was obtained from NORIT, Holland in a granular bead form. It was produced by steam activation. Some of the physical and chemical properties for NORIT PK 1-3 are presented in Table 1.

The carbon was sieved by using a Sieve Shaker, HAVER & BOECKER EML, the range collected was 850–1000 μm. The carbon particles were sealed in plastic bags for further use in the adsorption experiments without any further treatment.