

Carbonaceous materials for adsorptive refrigerators

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Carbon monoliths prepared from hard coal precursors were obtained. The porous structure of the monoliths was evaluated on the basis of nitrogen adsorption – desorption equilibrium data. The investigated monoliths have a well-developed microporous structure with significant specific surface area (S_{BET}). Equilibrium studies of methanol vapour adsorption were used to characterize the methanol adsorptive capacity that was determined using a volumetric method. The heat of wetting by methanol was determined in order to estimate the energetic effects of the adsorption process. The results of the investigations show that all monoliths exhibit high adsorption capacity and high heat of wetting with methanol.

Keywords: carbon monoliths, heat of wetting, adsorptive cooling systems

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1. Introduction

The processes of mass and energy storage with the application of a microporous adsorbent may outline prospective directions in the adsorption technology development. Carbon adsorbents can be employed for heat storage in adsorptive refrigerators utilizing closed thermodynamic cycles [1]. The most interesting pair is methyl alcohol and microporous carbon material [2]. Active carbon is a good adsorbent for the storage of mass and energy because of its ability to adsorb selectively vapours and gases, its extended internal porosity as well as large specific surface area [3]. Methanol is more easily desorbed and its working pressure is always lower than atmospheric pressure, which allows rapid identification of any faults in the cooling system. The temperature of desorption of methanol from adsorbent is considerably lower than that of water vapour. For all these reasons the methanol-active carbon pair can be used for mass and energy storage.

The widely developed techniques for solar heating with the use of various types of solar collectors also found application in adsorption

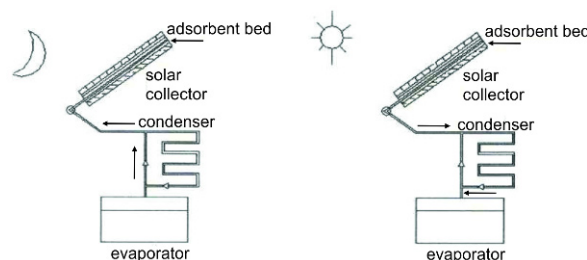


Fig. 1: Scheme of an adsorption solar refrigerator [4].

cooling systems. The greatest advantage of the application of solar systems in cooling is that they work most effectively during the day, when the temperature, and in consequence the demand for cooling power, are at its highest. Solar energy is used for regeneration of the adsorption bed. The adsorptive cooling system with a solar collector is presented in Fig. 1.

The adsorbent performance in a thermodynamic system depends on the properties such as specific area, type and number of pores, adsorbent form and adsorption enthalpy of the adsorbate, and its thermal conductivity. Therefore, any method of the modification of active carbon has to improve carbon structural features and increase heat and mass transfer [5].

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A good adsorbent should have not only a well-developed microporous structure but also large bulk density, features that improve packing properties and heat conductivity of the adsorbent bed [6]. These features depend on the form of the adsorbent, either powder, granular or monolith [7, 8]. Packing might be increased by using microporous materials in the monolithic form, which contributes to the increase in the heat conductivity of the adsorbent bed.

The active carbon-methanol pair appears to be suitable for various adsorptive cooling systems. This pair can be successfully used in the fridges for food and medicines storage, ice manufacture, in air conditioning devices and heat pumps [4].

The aim of this study was to characterize carbon monoliths in terms of their application in adsorptive cooling systems.

2. Experimental and results

The investigations were carried out on four carbonaceous monoliths. The aim of this study was to evaluate the properties of monoliths used for adsorptive cooling systems. The carbon monoliths made from hard coal precursors were obtained from Wrocław University of Technology, Faculty of Chemistry [9].

First, hard coal precursors were prepared by pyrolysis at 793 K. Afterwards, the product of carbonization (char/coke) was mixed with solid KOH, in a mass ratio of 1:3 (precursor/KOH). The activation process was carried out at 1073 K for 1 hour. The powdered product of KOH activation was mixed with a polymer binder and then the tablets were formed. The monolith tablets were 18 mm in diameter and 7-10 mm in height. The technological characteristics and the designation of the monoliths are presented in Table 1.

2.1. Analysis of the porous structure

The porous structure of the monoliths was evaluated on the basis of nitrogen adsorption-desorption data. The isotherms were determined by a volumetric method using Sorptomatic 1900 apparatus. The measurements were taken at a

Table 1: Characteristics of raw materials used for preparation of carbon monoliths.

Monoliths	Hard coal precursors	Type of binder
PS25MA	Semi-coke from coal-tar pitch	10% polyvinyl alcohol (PVA)
PS25MF	produced by coking plant Makoszowa	10% polyvinylidene fluoride (PVDF)
CS25MA	Semi-coke from hard coal produced by coking plant	7.5% PVA
CS25MF	Szczygłowie	8.5% PVDF

Table 2: Structural properties of the monoliths.

Monolith	W_0 cm ³ /g	E_0 kJ/mol	S_{BET} m ² /g	V_p cm ³ /g
PS25MA	0.714	18.3	1910	0.925
PS25MF	0.672	18.1	1830	0.887
CS25MA	0.709	18.4	1880	0.876
CS25MF	0.689	18.4	1805	0.854

temperature of 77.5 K, the pressure range was $p/p_0 = 0.00001 - 0.999$.

From the equilibrium data, the volume of micropores (W_0) and the characteristic energy of adsorption (E_0) were determined using the Dubinin-Radushkevich equation [10]. The specific surface area (S_{BET}) was obtained from BET equation [11]. The total volume of pores (V_p) was calculated from nitrogen isotherms using the value $p/p_0 = 0.99$. The results of all calculations are shown in Table 2.

The carbonaceous monoliths are characterized by a well-developed microporous structure. The monoliths show a large volume of micropores (0.672–0.714 cm³/g) and a very extensive specific surface area (1805–1910 m²/g). The values of the characteristic energy of adsorption are similar for all the studied materials. The monoliths formed with polyvinyl alcohol (PS25MA and CS25MA) have significantly better structural properties than the monoliths formed with polyvinylidene fluoride.

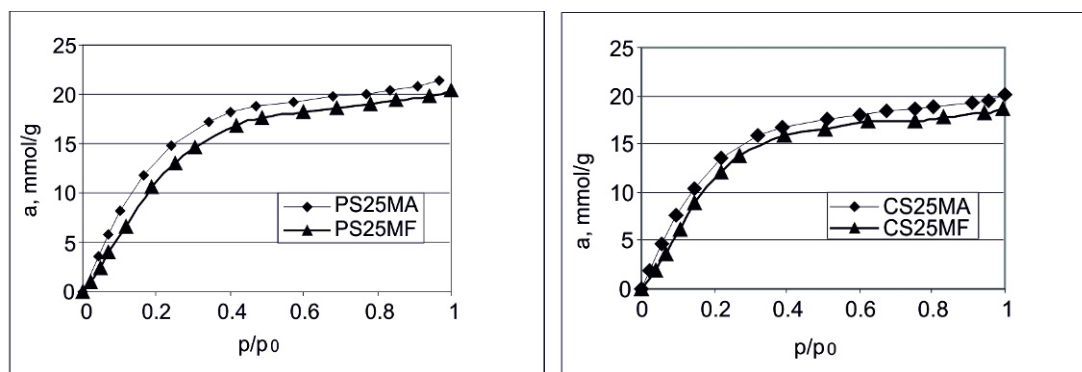


Fig. 2: Methanol adsorption isotherms for the monoliths obtained from the same coal precursors.

2.2. Adsorption of methyl alcohol

In the design of the adsorption cooling equipment, the characteristics of both constituents of the adsorbent–adsorbate (refrigerant) pair play an important role. Many suggestions for the appropriate adsorbate, which meets the operating requirements in such a system can be found in the literature [12, 13]. Nowadays, active carbon–methanol prevails in all the refrigeration systems.

The equilibrium studies data of methanol vapour adsorption were used to characterize the methanol adsorptive capacity. Methyl alcohol sorption isotherms on monoliths were determined by a volumetric method. The measurements were carried out at 298 K.

The methanol vapour adsorption isotherms for the studied monoliths are presented in Fig. 2.

All the samples readily adsorb methanol giving reversible type I isotherms according to IUPAC classification [14]. The investigated carbon monoliths have very high methanol adsorption capacity. The monoliths have structural proprieties, which are reflected in the shape of isotherms. The shapes of the isotherms are very similar in the whole range of pressures for all the monoliths. The monolith PS25MA is characterized by a significantly large adsorptive capacity. The monoliths with PVA as a binder demonstrate noticeably higher methanol adsorptive capacities.

2.3. Heat effects

The factors important for designing systems of adsorptive refrigeration are thermal effects of the process which are decisive for their performance. Energetic effects of adsorption can be directly determined by calorimetric measurements. They can also be estimated using computing methods on the basis of adsorption isotherms measured at various temperatures (the isosteric heat of adsorption).

The heat of wetting by methanol has been determined for the monoliths in order to estimate the energetic effects. The heat of wetting, evolved as a result of mutual interactions between the molecules of the wetting liquid and the adsorbent surface, is a valuable source of information. The measurements of the heat of wetting were carried out in the original apparatus, which is presented in Fig. 3 [15].

During the measurement, temperature variation in time was determined for the monoliths. The course of temperature variation is presented in Fig. 4.

The curves of temperature variation as a function of time are characterized by a rapid rise in the temperature after a contact of the monolith with methanol (on average, the maximum temperature was achieved in 40 s). The increase in the temperature is very high and ranges from 5.3 to 7.9 °C. The most rapid rise (maximum temperature was achieved after only 10 s) was recorded for the monolith CS25MA.

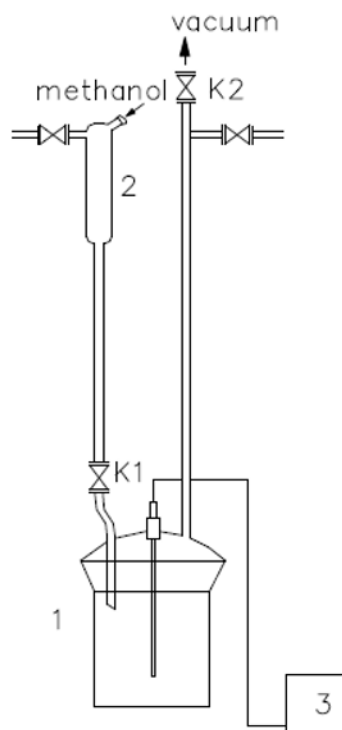


Fig. 3: Scheme of the device for measuring the heat of wetting: 1 – calorimetric cell, 2 – methanol container, 3 – electronic temperature measuring system.

The rates of temperature rise were calculated from dT/dt . The calculation was carried out starting from the moment of methanol injection until achieving maximum temperature.

The heat of wetting the monolith by methanol has been determined in order to estimate the energetic effects. The values of the heat of wetting, Q , and the values of the temperature increase, ΔT , dT/dt and $\frac{1}{Q} \frac{dT}{dt}$ are collected in Table 3.

Other authors have published data on thermal effects for various adsorbents. For example, active carbons obtained from renewable precursors and their modification by potassium hydroxide were evaluated based on thermal effects of adsorption [5]. For the investigated adsorbents, the thermal effects of wetting yielded temperature rises in the range of 2.0–6.5 °C. Carbon monoliths

Table 3: Heat effect and heat of wetting the monoliths under investigation.

Monoliths	ΔT	Q , J/g	dT/dt	$\frac{1}{Q} \frac{dT}{dt}$
PS25MA	7.6	159.83	177.0	1.1
PS25MF	5.3	111.03	331.2	2.98
CS25MA	7.9	165.14	35.9	0.22
CS25MF	7.6	160.43	119.8	0.75

were characterized by significantly great energetic effects related to the heat of wetting with methanol. The large values of heat evolved during the wetting process are the indication of a well-developed microporous structure and denser packing.

The heat effects and the calculated heat of wetting for all the investigated monoliths are very high. The largest thermal effect (165.14 J/g) as well as the most rapid rise of temperature ($dT/dt = 35.9$) was observed for the monolith CS25MA.

The energetic effects of wetting depend both on the microporous structure and on the nature of adsorbent. It seems reasonable to compare the values of the heat of wetting taking into consideration the raw materials used for the preparation of the carbon monoliths. So, drawing a comparison between both monoliths PS25MA and PS25MF, it can be noticed that the monolith formed with PVA (PS25MA), with a larger value of heat effect, also exhibits larger volume of micropores and specific surface area. The same relationship was observed in the case of the monoliths CS25MA and CS25MF - larger values of heat effects were observed for the monolith with better structural parameters and with PVA as a binder.

For the monoliths with polyvinyl alcohol as a binder (PS25MA, CS25MA), larger heat of wetting was observed than for the monoliths with polyvinylidene fluoride (PS25MF, CS25MF). The rate of temperature increase was also high.

3. Conclusions

The porous structure of monoliths was analysed in this study by means of adsorption equilibrium and heat effects of wetting by methyl alcohol. We

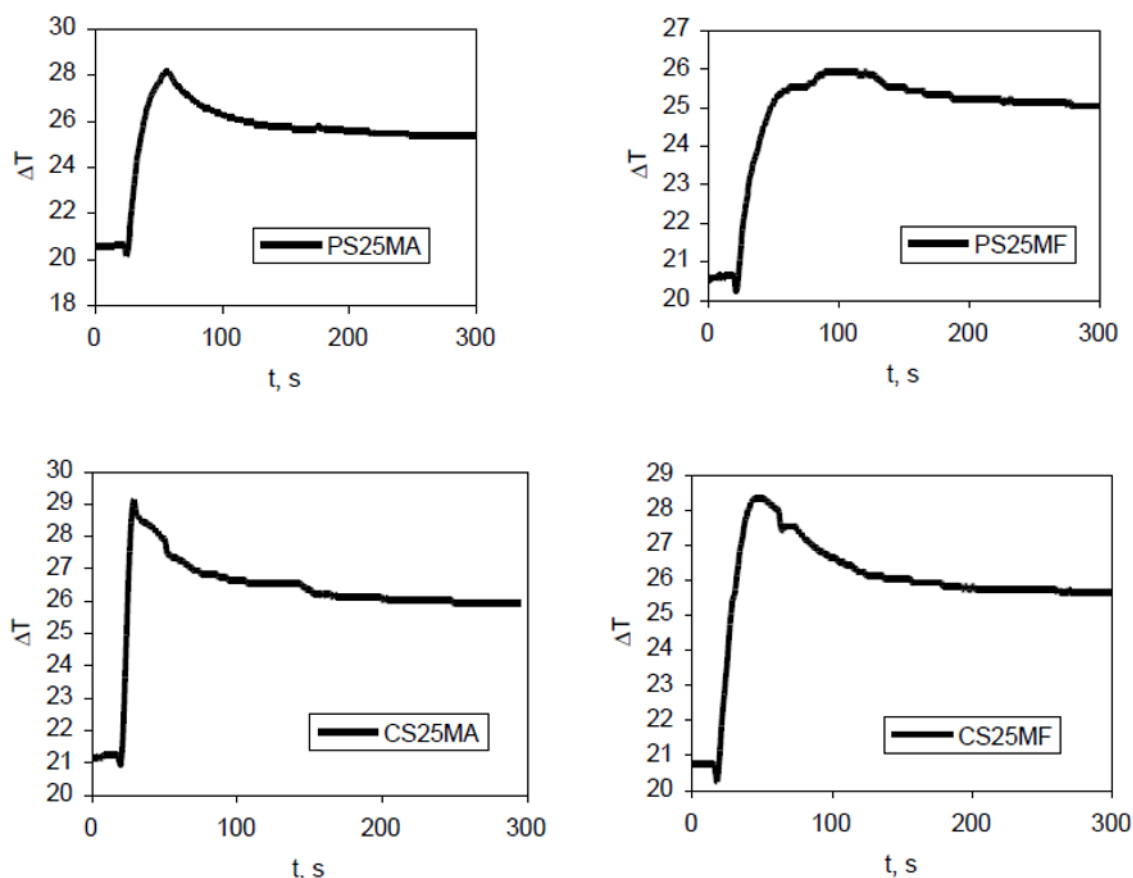


Fig. 4: Temperature variation in time.

were able to evaluate the carbon monoliths used for adsorptive cooling systems.

Pyrolysis of raw materials, e.g. hard coal precursors, activation with potassium hydroxide and monolith formation gives very attractive materials to be used as adsorbent for energy storage systems. The porous structure of the monoliths was evaluated on the basis of nitrogen adsorption - desorption data. The investigated monoliths have well developed microporous structures. Large specific surface areas (1805–1910 m²/g) and volumes of micropores (0.672–0.714 cm³/g) were observed for the studied carbonaceous monoliths. The methanol adsorptive capacity of all monoliths is also impressive (about 20 mmol/g).

Experimental results show that carbon monolith materials have very high methanol adsorption capacity and the heat of wetting, which can

improve the heat exchange and efficiency of the processes of cooling and air conditioning.

The carbon monoliths were also characterized by large energetic effects compared to the heat of wetting with methanol. All these advantages might improve the performance and efficiency of the system in adsorptive refrigeration.

Acknowledgments

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