Thermal Conductivity and Melting Point Measurements on Paraffin-Zeolite Mixtures[1]

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This paper presents measurements of the thermal conductivity of paraffins mixtured with zeolites of the type 5A and 13X. Because of their high enthalpy change at the phase transition paraffins are able to store more thermal energy at nearly isothermal conditions than sensible heat materials. The poor thermal conductivity of paraffins is a disadvantage, however. The zeolite provides a structure to support the solid and liquid paraffin and to enhance the thermal conductivity. The thermal conductivity of the mixture is increased by a factor of about 1.8 in dependence on the paraffin zeolite ratio. The determination of the thermal conductivity was performed with a heat flow meter apparatus on sample disks with a diameter of 85 mm. Also the laser flash method combined with the measurements of the mass density and the specific heat capacity was used to gain comparative data.

KEY WORDS: paraffin, zeolite mixture, thermal conductivity, melting point.

1. INTRODUCTION

Thermal energy storage is a basic technique for the efficient use of solar energy. In the case of low temperature heat storage in buildings sensible heat storage media such as water are commonly used. In the recent years phase change materials (PCMs) are also in the focus of interest. The high phase change enthalpy released with solidification or absorbed with melting is the key feature of those materials. The PCMs have some advantages compared with sensible heat storage media. They store more heat per unit mass and the latent heat can be used with small temperature gradients at approximately constant temperature. The latter property is typically desirable for efficient operation of most thermal systems, because every heat exchange at a finite temperature difference causes an increase in the systems entropy.

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Potential candidates for PCMs are paraffins and salt hydrates such as calcium chloride hexahydrate. Paraffins exhibit a lower phase change enthalpy than salt hydrates but they are advantageous in some other respects. They are ecologically harmless, non-toxic, chemically inert and compatible with construction materials. The handicap of the paraffin is however the poor thermal conductivity of less than 0.2 W/(m·K) in the solid and also in the liquid state. Furthermore a containment of the paraffin is often desirable for technical applications. For this purposes the paraffin can be microencapsulated or incorporated into a carrier matrix such as silica or alumina compounds.

The latter technique provides both a structure to support the solid and liquid paraffin and to enhance the thermal conductivity. Also zeolites, especially the zeolite 5A, are reported to exhibit a strong adsorption capability for longer chain paraffins of C_{13} and higher [1]. Due to this property these materials might also be promising candidates for a support matrix of paraffines. A paraffin blend with a mean melting point of about 28°C was chosen for the experiments.

The aim of the present paper is to determine the increase of the thermal conductivity of the paraffin-zeolite mixture. Furthermore the transition temperature is measured for the paraffin and the paraffin-zeolite composite.

2. EXPERIMENTAL TECHNIQUE

For the measurements of the thermal conductivity a heat flow meter apparatus with two heat flux transducers was used. The relative measurement error of this device was proven to be less than 4 % [2]. The temperature difference was 10 K and the mean sample temperature 10°C. A ring from MACOR-plastics with an inner diameter of 85 mm, an outer diameter of 95 mm and a height of 20 mm was applied for the measurements of the zeolite 13X in powder form and the zeolite 5A in granular form with a mean grain size of about 1.5 mm. To prevent a contamination of the heat flow meter apparatus with paraffin, the samples made of zeolite and paraffin were sealed with an aluminium coated polymer foil. These envelope was tested by a comparative measurement to have no significant influence on the measured thermal conductivity. The zeolite paraffin samples had also a diameter of 85 mm and a height of about 20 mm. Both the plastic ring and the polymer foil envelope were applied for the paraffin sample.

As a comparative method for the determination of the thermal conductivity the laser flash method for the thermal diffusivity has been used in combination with the measurements of the mass density and the specific heat capacity. The laser flash device Netzsch LFA 427 with a laser wavelength of 1064 nm and a MCT detector is especially designed for the lower temperature range of –40 to 230°C. Due to the structure and stability of the material only the sample of paraffin with zeolite 13X was suited for the laser flash method. A sample with a diameter of 10 mm and a height of 2.1 mm has been made and coated on both sides with a thin graphite film. This preparation is necessary because the paraffin has been found to have a transmission of about 90 % at the wavelength of the laser of 1064 nm and also the paraffin zeolite mixture is expected to have a notable transmission at this wavelength. To avoid a contamination of the laser flash device only sample temperatures sufficient below the mean melting point of 30°C of the paraffin blend have been used.

The determinations of the melting point and the specific heat capacity have been performed with a Calve type Setaram Micro DSC II calorimeter at a temperature range from 0°C to 50°C in general. Each sample has been measured at three heating rates of 0.2 K/min, 0.3 K/min and 0.5 K/min. The first heating rate has been performed two times, whereas the data of the first melting haven't been accounted for.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Table I shows the measurement results for the thermal conductivity of the pure substances and the mixtures. The paraffin content was 35 mass% (27.4 vol%) for the zeolite 13X and 24 mass% (21.7 vol%) for the zeolite 5A. With these paraffin contents the mixtures feature a rather stable structure both at temperatures below and above the melting temperature of the paraffin. Due to the melting point of around 28°C the paraffin blend appear to consist mainly of octadecane. For the solid phase of this substance in [2] a survey of thermal conductivity measurements from several authors is given. Values from $\lambda = 0.15$ to $\lambda = 0.56\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ are cited. We found $\lambda = 0.162\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ in fair agreement with these data. In the case of the paraffin zeolite 13X mixture an increase of the thermal conductivity of about 76% was reached in comparison to the pure paraffin blend.

Table I. Results of the thermal conductivity measurements with the heat flow meter apparatus

Sample	Mass density ρ at 23°C in $\mathrm{kg \cdot m^{-3}}$	Thermal conductivity λ at a mean sample temperature of 10°C in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$
Paraffin blend	880	0.162
Zeolite 13X, powder	690	0.070
Zeolite 5A, granulate	797	0.104
Paraffin zeolite 13X mixture	1283	0.286 0.330[a]
Paraffin zeolite 5A mixture	957	0.200

[a]Derived from laser flash thermal diffusivity measurement

The laser flash measurement of the paraffin zeolite 13 X sample yielded a thermal diffusivity of $a = 0.0011$ cm²/s. With $\lambda = a \cdot \rho \cdot c_p$ one get a thermal conductivity of $\lambda = 0.330\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The overall relative error of this measurement is 10%. Therefore the value is in reasonably coincidence with the data from the heat flow meter apparatus.

The results from the calorimetric measurements are shown in Table II. The extrapolated onset temperature T_{onset} and the peak temperature T_{peak} have been derived from the melting peak of the DSC-curve. There is an obvious increase of the onset temperature T_{onset} and the peak temperature T_{peak} in the case of the paraffin zeolite mixtures. The corresponding DSC-curves at a heating rate of 0.3 K/min are depicted in Fig. 1. Further on there is a sharper onset visible for the paraffin zeolite mixtures in comparison to the paraffin alone.

Table II. Results of the calorimeter measurements

Sample	T_{onset} in °C	T_{peak} in °C	Mean specific heat capacity c_p in $J\cdot g^{-1}\cdot K^{-1}$		Energy density (19 - 34°C) in $kJ\cdot dm^{-3}$
			Solid paraffin (10 - 20°C)	Liquid paraffin (30 - 40°C)	
Paraffin blend	24.9	26.9	3.78	2.34	172.9
Paraffin zeolite 13X mixture	26.6	28.5	2.28	2.14	115.7
Paraffin zeolite 5A mixture	25.6	27.4	1.87	1.77	61.6

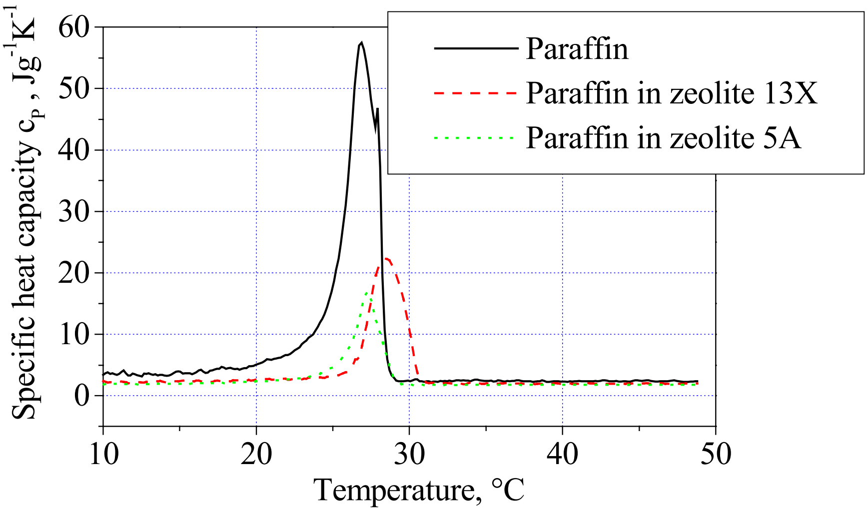

Fig. 1. DSC-curves at 0.3 K/min

To make sure, that this increase is neither an effect of the heating rate nor of the sample mass, the experiments have been repeated with modified test parameters. Fig. 2 and 3 show the DSC-curves of the paraffin and the paraffin zeolite 13A mixture with different heating rates. There is no significant change of T_{onset} and T_{peak} in dependence on this parameter for both samples.

Also no dependencies of T_{onset} and T_{peak} on the sample masses were found. Exemplarily the DSC-curves for different sample masses of the paraffin zeolite 13X mixture are shown in Fig. 4.

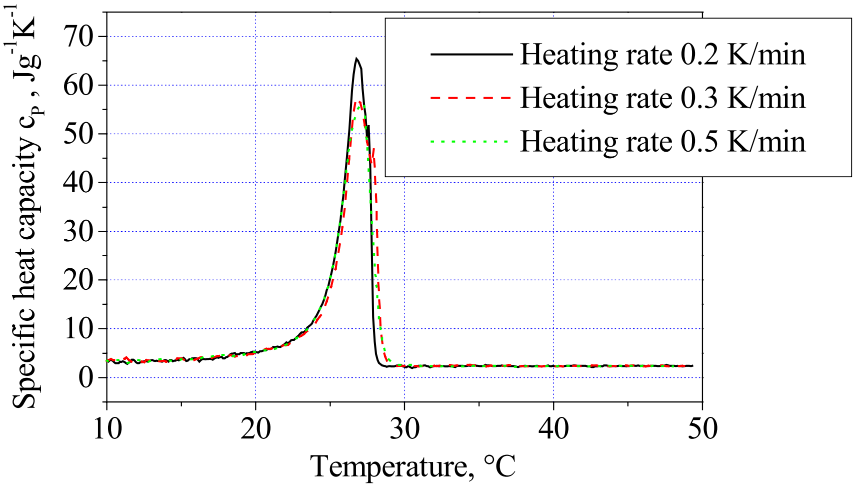

Fig. 2. Specific heat capacity of paraffin at different heating rates

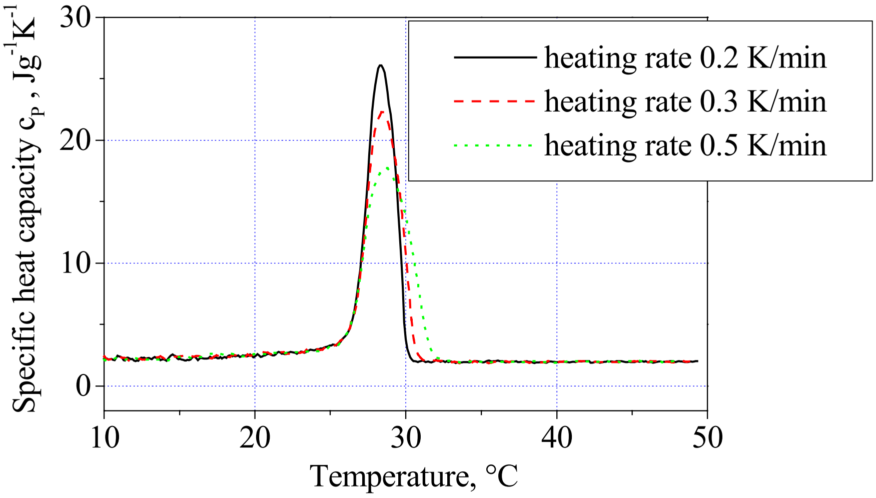

Fig. 3. Specific heat capacity of paraffin in zeolite 13X at different heating rates

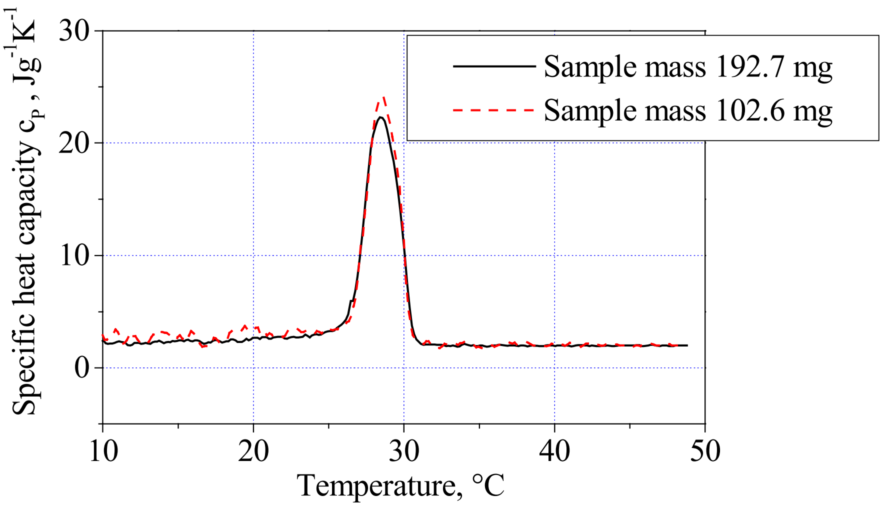

Fig. 4. Specific heat capacity of paraffin in zeolite 13X with different sample masses

The effect of increasing the melting point of the paraffin embedded into a zeolite is quite different from the well known decrease of the freezing and melting point of pure substances in mesoporous substances according to the Gibbs-Thomson equation.

As shown in Table II all substances have a lower specific heat capacity for temperatures above the melting temperature of the paraffin.

The overall energy density (sensible heat and enthalpy of fusion) of a small temperature interval of 15 K around the peak temperature is also presented in Table II. The paraffin zeolite 13X mixture exhibits an energy density one third less than the paraffin but with a 76 % higher thermal conductivity.

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