Int. Agrophysics, 2005, 19, 187-192

INTERNATIONAL
Agrophysics
www.ipan.lublin.pl/int-agrophysics

Thermophysical properties of granular food materials[1,2]

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Received June 7, 2004; accepted December 1, 2004

A b s t r a c t. The present work deals with thermophysical properties of granular food materials – grains and seeds. The results of measurement of the specific heat at the constant pressure and results of the thermal conductivity measurement of corn grains and colza are presented as a function of temperature. Measurements of the specific heat are performed by differential scanning calorimetry and the thermal conductivity is measured using the hot-wire method. Description of measurement methods and measuring equipment is presented. Differential scanning calorimeter is used for measuring the temperature dependence of the specific heat. The probe modification of the standard hot wire method is utilized as the measuring technique and computer-controlled experimental apparatus for measuring the thermal conductivity is used. The moisture content of the samples was determined by electronic (conduction) moisture meter.

Dependence of thermophysical properties, *ie* the specific heat and the thermal conductivity on the temperature are presented.

K e y w o r d s: food properties, specific heat, thermal conductivity

INTRODUCTION

Food materials are very complicated biological materials – they have complex chemical composition (proteins, lipids, saccharides, additive components), structure, phase (food or their components are dispersed systems), conformation, *etc*. Granular food material exactly the grains or seeds set of a certain botanic variety, is in the macroscopic as well as in the microscopic scale a considerably inhomogeneous, capillary-porous, wet dispersed medium. It is well known that the water influence dominates among the other effects that have impact on the properties of food materials. An important factor is also the material's temperature, but the most significant is the influence of the presence of free or bound water, different binding energy in each water bond (chemical, physical-chemical and physical) in the material and sorptive properties of the materials. The binding energy of water per unit amount of substance E (J mol^{-1}) is:

$$E = -RT \ln \varphi \qquad (1)$$

where: R (J mol^{-1}K^{-1}) is the universal gas constant, T (K) is the thermodynamic temperature and φ (%) is the relative moisture content of the air. Influence of physical properties on the time and on the history of the external conditions is a characteristic feature of biological materials. Moisture content and temperature are the most important physical properties that influence physical and physiological processes running in the food materials.

Temperature is one of the main controlling factors used in food processing. Typical thermal food processes (pasteurization, sterilization, baking, boiling, drying, cooling, and freezing) induce some physical and chemical processes in the material such as vaporisation, melting, freezing, crystallization, crystal modification, denaturation, chemical reaction (oxidation), *etc*. In addition, temperature is the value which influences nearly each property of the material. Knowledge of thermophysical properties is the basic condition for describing food material's behaviour during a food processing.

Heat being absorbed by a system under specified conditions, *eg* at the constant pressure, changes the heat energy of that system (Haines, 1995). Under the constant

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[1]This work was supported by Slovak Science Grant Agency under the contracts Nos 1/90/79/02 and 1/0609/03.

[2]The paper is published in the frame of activity of the Centre of Excellence AGROPHYSICS - Contract No. QLAM-2001-00428 sponsored by EU within the 5FP.

pressure, this represents a change in the enthalpy H (J). Specific heat at the constant pressure c_p (J kg^{-1}K^{-1}) is defined by equation:

$$c_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p, \qquad (2)$$

where: m (kg) is the mass and T (K) the temperature. Here c_p expresses the heat required per unit mass to change the temperature of a substance by one degree at the constant pressure.

The thermal conductivity k (W m^{-1}K^{-1}) basically characterizes the process of heat transfer in the material (Krempaský, 1969). It is defined by the Fourier law:

$$\vec{q} = -k\, gradT, \qquad (3)$$

where: $\vec{q}$ (W m^{-2}) is the heat flux. The thermal diffusivity, a (m^{2}s^{-1}) is connected with the thermal conductivity k by the formula:

$$k = a\rho c_p, \qquad (4)$$

where ρ (kg m^{-3}) is the density.

Chemical composition, structure, moisture content and binding of water, temperature and thermal history of the material, are the key factors affecting the thermophysical properties of food materials.

Temperature dependence of the specific heat gives information about the endothermic or exothermic processes in material and about phase transition. Temperature dependence of the thermal conductivity provides information about heat transport running in the material.

Problems of moisture and thermal properties of agricultural materials (soil) are well-developed by authors (Walczak and Usowicz, 1994) and problems of heat and mass transport are described in details in (Usowicz, 2002).

MATERIAL AND METHODS

Measurements of thermophysical properties – the specific heat and the thermal conductivity as a function of the temperature – are realized. Experimental methods of thermal analysis – differential scanning calorimetry and hot-wire method – are used for an estimation of thermophysical behaviour of granular food materials. Measurements are performed on the samples of corn grain *Zea mays* variety LG 2306, with 15.5 % moisture content wet basis (w.b.), with bulk density of 730 kg m^{-3}, and on the samples of colza *Brassica napus* (mixture of cultivars) with 7.78 % moisture content (w.b.) and with bulk density of 635 kg m^{-3}.

Differential scanning calorimetry (DSC) is a technique in which difference in heat flow (power) to a sample and to a reference is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. In practice, the heat is supplied to the sample contained in the pan, and similarly, to the reference in its pan (Haines, 1995).

Measurement of the specific heat by differential scanning calorimetry is based on definition (Eq. (2)), which can be rewritten as:

$$c_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right) = \frac{1}{m}\left(\frac{\frac{\partial H}{\partial t}}{\frac{\partial T}{\partial t}}\right) = \frac{1}{m}\frac{\Delta P}{\beta}, \qquad (5)$$

where: ΔP (W) is difference between power supplied to the sample and to the reference and β (K s^{-1}) is heating rate (Šimon, 2000).

Differential scanning calorimeter DSC 822 (METTLER TOLEDO) is used for measurement of the specific heat of corn grains and colza as a function of the temperature. The apparatus (METTLER TOLEDO, 1998) consists of a silver furnace with a flat heating element and a FRS5 ceramic sensor. The sensor contains two small spots for placing the sample and reference pans. The sensor contains 56 Au-AuPd thermocouples. Thermocouples do measure the difference between temperatures of both pans. Furnace temperature is measured with the platinum Pt100 thermocouple with uncertainty of less then ±0.2°C. Measurement range is limited from -65 to 700°C. The lower limit depends on the use of an intracooler that is connected to the heat sink of the furnace. The higher limit depends on the use of 400 W power amplifier. Measurements are based on the Boersma or heat flux principle. Heat flow resolution is better than 0.04 μW. The heat capacity measurement accuracy is better than ±3% of the measured value. For the measurement of the sample mass microbalance, the METTLER TOLEDO AX26 Delta Range is used with the resolution of 10^{-6} g. The temperature scale is calibrated using the In and Zn standards, the enthalpy calibration is carried out for melting enthalpy of In. Measurements are performed on samples of corn grains and colza under nitrogen atmosphere (flow rate 80 ml min^{-1}) in the temperature range from -50 to 40°C with heating rate 5 K min^{-1}. The sample of corn has been ground before measurement; colza was measured as a whole. Weight of the samples was 3-4 mg. The samples are embedded in standard aluminium pans where an empty pan is used as a reference.

The hot-wire method is a standard non-destructive experimental method of measuring the thermal conductivity. It is a transient dynamic technique based on measurement of the temperature rise in a defined distance from a linear heat source embedded in the test material. If the heat source is assumed to have a constant and uniform output along the length of test piece, the thermal conductivity can be derived directly from the resulting change in the temperature over a known time interval (Davis, 1984). If the hot wire is heated since the time $t = 0$ with constant heat flux q per unit wire length, the radial heat flow around the wire occurs. The temperature rise ΔT (r,t) in any distance r from the wire as a function of time describes with the simplified equation:

$$\Delta T(r,t) = \frac{q}{4\pi k} \ln \frac{4at}{r^2 C}, \quad (6)$$

where: k is the thermal conductivity, a the thermal diffusivity and $C = \exp(\gamma)$, with γ the Euler's constant (Carslaw and Jaeger, 1960). The thermal conductivity is calculated from the slope S of the temperature rise $\Delta T(r,t)$ vs. natural logarithm of the time ln$t$ evolution using the formula:

$$k = \frac{q}{4\pi S}. \quad (7)$$

Several corrections have been introduced to account for the heat capacity of the wire, the thermal contact resistance between the wire and the test material, finite dimension of the sample and finite dimension of the wire embedded in the sample as reviewed in (Labudová and Vozárová, 2002).

The computer-controlled experimental apparatus, which allows the determination of the thermal conductivity of solids, powders and granular materials is used (Vozár, 1996). It allows to utilize one of three measurement techniques: standard cross wire technique, resistance potential lead method and the probe modification of hot wire method. In the study, the results of measurement obtained using the cross technique are presented. A wire cross is embedded in ground grooves between two equally sized samples. The cross consists of a linear heat source - the kanthal wire 0.4 mm in diameter (Bulten Kanthal AB), and of a spot welded thermocouple, K type, made from Ni-NiCr wires (Heraeus) 0.1 mm in diameter which acts as the temperature sensor. The hot spot of the thermocouple is in the direct contact with the heating wire and it is placed in the centre of the sample. The cold junction is put on the reference place in Dewar's cup at 0°C.

The current flowing through the heating wire is produced by the stabilized regulated direct current supply Z-YE-2T-X (Mesit) operated by PC via remote control unit JDR-1 (Mesit). The setting of the optimal current generally depends mainly on sample thermal properties and dimensions and is chosen to have the hot wire temperature rise of 5-10°C. High resolution data acquisition board PCL-818HG (Advantech) with lock in pre-amplifier Z-35 (Metra) is used for serial measurements of transient *emf* of the thermocouple, and the transient voltage corresponding to temperature rise. A proportional feedback temperature controller provides the temperature regulation of the electro-resistive furnace. The apparatus allows measurement on air or in a controlled environment, under atmospheric pressure, in the temperature range from 20°C up to 1200°C (for technical materials).

Measurements of the thermal conductivity as a function of temperature are performed on the air at the atmospheric pressure in the temperature range from room temperature up to 100°C on the samples of corn kernels and colza with volume of 1 dm^3. Measurement for the given sample was repeated 15 times with the temperature stabilization in the meantime (2 h) to achieve the needed accuracy. The moisture content of the samples was determined by electronic (conduction) moisture meter HE 50 (Pfeuffer) and according to standard test procedure (Vozárová, 2001).

RESULTS

Figure 1 presents DSC curve – the temperature evolution of the specific heat of corn grains in the temperature range from -50 to 40°C. The dependence is

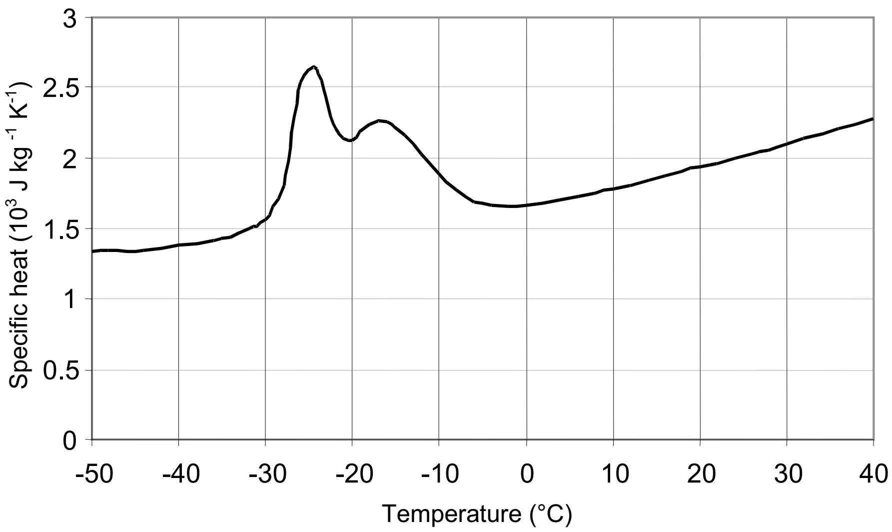

Fig. 1. Specific heat of corn grains as a function of the temperature.

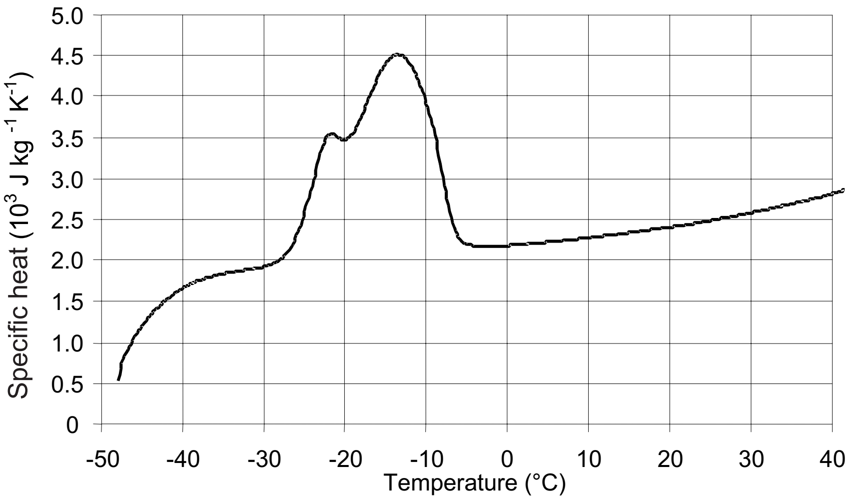

Fig. 2. Specific heat of colza as a function of the temperature.

almost linear except for two peaks at the temperature of -24 and -16°C, which probably corresponds to the phase transition of the water bound to the starch. Figure 2 presents DSC curve of colza obtained in the same temperature range. There are also two marked peaks at the temperature: -13 and -21°C. Specific heat of the both samples at the temperature above 0°C linearly increases up to the temperature of 40°C.

Values of the specific heat of materials are significantly influenced by the chemical composition and by presence of the water. Values of c_p of the air, proteins and saccharides are low, between 1.1-1.2 kJ kg^{-1}K^{-1}. Lipids have almost double value of the specific heat in the comparison with proteins and saccharides (Blahovec, 1993), which influenced the obtained values of colza.

Figures 3 and 4 present the thermal conductivity as a function of temperature. Thermal conductivity of the granular food materials (grains and seeds) is relatively low; it is influenced by the chemical composition of the material, by the moisture content and by the presence of the air between individual elements. Thermal conductivity of saccharides and lipids is between 0.05-0.2 W m^{-1}K^{-1}, thermal conductivity of proteins is lower – values are between 0.02-0.05 W m^{-1}K^{-1} (Blahovec, 1993). The dependence of the thermal conductivity of corn grains (Fig. 3) is linear up to the temperature of 80°C, which appears to be nonlinear. The thermal conductivity at higher temperatures is influenced by two factors: releasing of the water from the material and saturation of the air by the vapour. Presence of

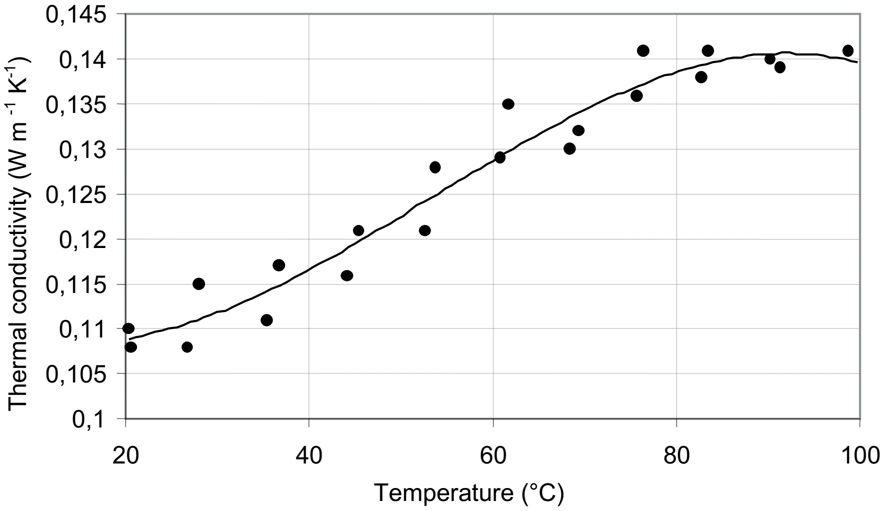

Fig. 3. Thermal conductivity of corn grains as a function of the temperature.

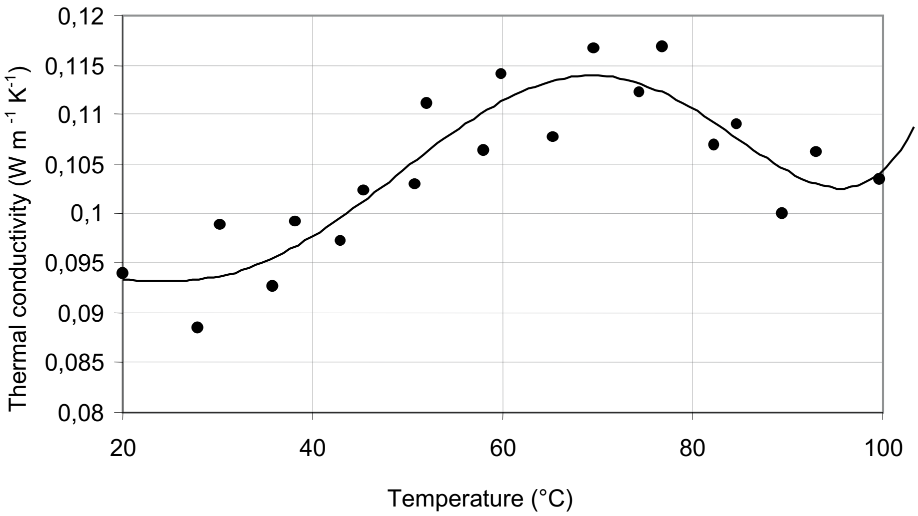

Fig. 4. Thermal conductivity of colza as a function of the temperature.

the water in the sample of colza slightly affects the temperature dependence of the thermal conductivity. Decreasing of thermal conductivity of colza (Fig. 4) in the temperature from 70 up to 90°C can be caused by releasing of the water and other unstable ingredients of seeds (oil).

CONCLUSIONS

The paper presents preliminary results of the specific heat measurement at the constant pressure and the thermal conductivity measurement of the corn grains and colza as a function of the temperature which indicate:

1. Obtained values of the specific heat of corn grains are between 1.337-2.275 kJ kg^{-1}K^{-1} (approx. 1.9 kJ kg^{-1}K^{-1} for the temperature 20°C), it corresponds to the chemical composition of corn (approximately 71-75% of saccharides, 6-21% of proteins, 3.5-7% of lipids) and to the moisture content (15.5%, w.b.). Measured values of the specific heat of colza are between 0.527-2.815 kJ kg^{-1}K^{-1} (approx. 2.4 kJ kg^{-1}K^{-1} for the temperature 20°C), it corresponds to the chemical composition of colza (approximately 30-36% of proteins, 15-25% of lipids and 15-25% of saccharides) and to the moisture content (7.78%, w.b.). The influence of the moisture content is dominant for both samples.

2. Increasing of the specific heat of both samples with the temeperature (except for two peaks corresponding to endothermal processes) is in accordance with the published knowledge (Blahovec, 1993).

3. Obtained values of the thermal conductivity of corn are between 0.108-0.141 W m^{-1}K^{-1} and values of the thermal conductivity of colza are between 0.088-0.117 W m^{-1}K^{-1}. Higher values of the thermal conductivity of corn are caused by higher moisture content.

4. Temperature evolutions of the thermal conductivity of both samples are in accordance with the published information for stable materials. Progress in the dependencies is more complicated namely for the temperature above 70-80°C. Accurate interpretation of results requires DSC study of samples in this temperature range.

The obtained data are the important information for the analysis of the material's behaviour during processing. The main objective is the following detailed analyses of the optimal food storage and the thermal processing regime proposal.

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