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Effect of Glass Transition on Thermal Conductivity of Rough Rice

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The behaviour of the bulk thermal conductivity of rough rice above and below glass transition temperature was examined. The thermal conductivity values were measured using the line heat source method at initial temperatures of 3 to 69°C and moisture contents of 9·2–17·0% wet basis. The thermal conductivity values were determined using the maximum slope method. It was found that the thermal conductivity of rough rice increased with increasing moisture content. A multiple regression equation relating thermal conductivity to temperature and moisture content was developed through stepwise regression analysis. It was found that the thermal conductivity changed little below and increased considerably above the glass transition temperature.

1. Introduction

The objective of rice drying is to maximise dryer throughput while minimising quality loss. To achieve this objective, mathematical modelling offers an effective tool to better understand the drying process. Heat and mass transfer properties are of fundamental importance to mathematical modelling of a drying process. Thermal conductivity, specific heat and thermal diffusivity are three important thermal properties to the quantitative analysis of a drying process.

In mathematical terms, thermal conductivity, denoted by k, is the proportional factor in Fourier's law describing steady-state conduction of heat (Mohsenin, 1980):

$$q = -kA\frac{\mathrm{d}T}{\mathrm{d}x} \tag{1}$$

where: q is the thermal energy flow per unit time, A is the cross-sectional area, T is temperature and x is the distance in the direction of heat flow.

The value of k for a food material is related to the thermal diffusivity α in $m^2 s^{-1}$ by

$$\alpha = \frac{k}{(\rho C_p)} \tag{2}$$

where: ρ and C_p are, respectively, the density in $\mathrm{kg\,m^{-3}}$ and the specific heat in $\mathrm{J\,kg^{-1}\,K^{-1}}$ of the material. Since the value k can be determined experimentally with a higher degree of accuracy, the thermal diffusivity is usually estimated from the corresponding k value and the thermophysical properties of a food material (Drouzas & Saravacos, 1988).

Methods of measurement of k can be divided into two broad categories: those using the steady-state condition of heat transfer and those using the unsteady state. The latter have been found more suitable for biological materials, which are generally heterogeneous and have a high moisture content (MC) (all moisture contents are expressed on a wet basis), whereas, the steady-state method requires a long time to reach a steady state and moisture migration may introduce significant measurement errors. The unsteady-state methods of thermal conductivity measurements make use of either a line source of heat or one or more plane sources of heat. In both categories the procedure is to apply a steady heat flux to the medium that must be in thermal equilibrium initially, and to measure the temperature rise resulting from the applied flux at a certain point in the medium. The line heat source method is one of the most commonly used unsteady-state methods, particularly with granular materials (Mohsenin, 1980).

The line heat source method uses either a bare-wire type apparatus or a thermal conductivity probe (Mohsenin, 1980; Yang, 1998). A line heat source (no mass and no volume) is placed in an infinite conduction-heating, homogeneous medium of a uniform initial temperature distribution with constant thermal conductivity. Heat is generated along the line source at a constant rate (Wang & Hayakawa, 1993). The heat transfer equation applicable for the line heat source method is the Fourier equation. The solution to the Fourier equation for the line heat source method has been given by several researchers, including Hooper and Lepper (1950). This solution for the change in temperature at a point close to the line heat source as a function of time can be written as:

$$k = \frac{I^2 R}{4\pi} \frac{\mathrm{d}\ln(t)}{\mathrm{d}T} \tag{3}$$

where: k is in W m^{-1} K^{-1}, I is the electric current in A, R is the electric resistance per unit length in Ω m^{-1}, t is time in s, and T is the temperature in °C (Mohsenin, 1980). The term $\mathrm{d}T/\mathrm{d}\ln(t)$ is the slope when the temperature rise is plotted again $\ln(t)$.

An initial curvilinearity occurs in a temperature–time data curve due to the fact that any real line heat source has a finite radius and there is resistance to heat transfer between the source and sample. The linear part of the curve was identified by either a time correction factor method (Van der Held & Van Drunen, 1949) or the maximum slope method (Wang & Hayakawa, 1993). Through close examination of response curves, Asher *et al.* (1986) observed that the local slope of the temperature-ln(time) curve increased gradually to a maximum plateau and then decreased as time increased. They attributed the initial increase and later decrease to non-ideal experimental conditions. They found that the maximum slope value determined the thermal conductivity of the sample without calibration. Wang and Hayakawa (1993) verified the maximum slope method theoretically and experimentally.

The change of state of starch, as it goes through a glass transition temperature T_g, has been reported to play an important role in rice drying in terms of kernel fissuring potential (Perdon *et al.*, 2000; Cnossen & Siebenmorgen, 2000; Yang *et al.*, 2000a, 2000b), drying rate (Cnossen *et al.*, 2002) and tempering rate (Cnossen & Siebenmorgen, 2000). For a given MC, when the temperature is below the value for T_g, starch exists as a glassy material, with low expansion coefficients, specific volume, specific heat and diffusivity. Above the value for T_g, starch exists as a rubbery material with higher expansion coefficients, specific volume, specific heat and diffusivity. The molecules are mobile in this region (Slade & Levine, 1991, 1995; White & Cakebread, 1966). The glass transition temperatures of rice kernels that can be found in literature include those measured with a differential scanning calorimeter by Perdon *et al.* (2000) and those measured with a thermomechanical analyser by Sun *et al.* (2001). Their results for T_g led to slightly different glass transition state diagrams due to the difference in measurement methods, but the values for T_g were comparable and of a similar magnitude. The data for T_g from both reports are used in this study for the analysis of transitional change in the thermal conductivity data.

Pronounced transitional changes in physical and thermal properties of grains such as the thermal expansion coefficient, volumetric shrinkage, or head rice yield during the drying process have been reported by Arora *et al.* (1973) and Ekstrom *et al.* (1966). Arora *et al.* (1973) found that, at temperatures around 53°C, the rice variety Calora incurred a rapid increase in the percentage of broken kernels, and it kernels exhibited a marked increase in the rate of thermal expansion. Ekstrom *et al.* (1966) reported that maize went through a transitional change in property at around 43°C. Yang *et al.* (2000a) pointed out that transitions observed by Arora *et al.* (1973) and Ekstrom *et al.* (1966) might very well be related to the glass transition of rice or maize.

As the transitional changes were observed on physical and thermal properties of rice and maize as mentioned above and the fact that other properties of rice such as the thermal expansion coefficient (Perdon *et al.*, 2000) are affected by T_g, it is expected that thermal conductivity k would also be significantly affected by T_g. Although the thermal conductivity was reported (Morita & Singh, 1979; Chuma *et al.*, 1981), no research has been done to examine the effect of the T_g on k. Therefore, the objective of this study was to: (1) examine the behaviour of k of rice above and below T_g using the line heat source method, and (2) develop a regression equation relating k to temperature and MC that reflects the effect of T_g for use in the modelling of the rice drying process when the glass transition effect is considered.

2. Materials and methods

2.1. *Sample preparation*

Medium-grain rice (*cv.* Bengal) at about 17·0% initial MC was used in this study. The rice was stored in a walk-in cooler at 8°C before it was used for this study. Three target MCs, *i.e.*, 10, 13 and 17% were prepared (the resultant MCs were 9·2, 12·1 and 17·0%). To obtain the target MCs, samples were gently dried in a thin-layer drying chamber at 40°C air temperature for pre-set durations and then equilibrated in a sealed plastic bag in a refrigerator for at least 24 h before using. To determine the MC of each sample, approximately 10 g of rough

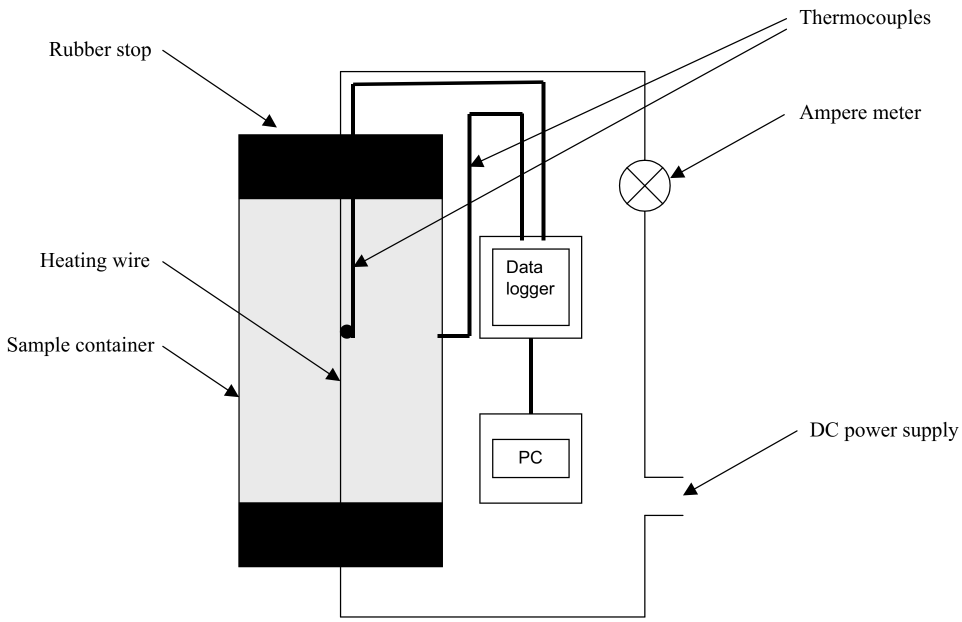

Fig. 1. Schematic of the device for measuring bulk thermal conductivity of rice; PC, personal computer; DC, direct current

rice were dried in an air oven at 130°C for 24 h in triplicate (Jindal & Siebenmorgen, 1987).

2.2. *Thermal conductivity apparatus*

The experimental apparatus for measuring k by the line heat source method is shown in *Fig. 1*. The apparatus consisted of an aluminium cylinder 29·1 cm in height and 8·3 cm in inner diameter, with a removable rubber top and bottom cover. A nickel–chromium resistance heating wire with a diameter of 0·32 mm (13·95 $\Omega\,m^{-1}$) threaded through the rubber covers and connected to a DC power source. Temperature rise was measured by a 0·813 mm diameter thermocouple (K-type) (Omega Engineering Inc., Stamford, CT), glued approximately 1 mm from the heating wire at the middle of the heating cylinder (*i.e.* the heating wire and the thermocouple was held together and separated apart for around 1 mm by the glue). The assumption of an infinite medium required that the surface temperature of the sample holder was constant during the experiments. To validate this assumption, a second thermocouple was attached to the surface of the cylinder to monitor its temperature. A 21X Campbell Scientific data logger (Logan, UT) was used to collect the temperature data.

2.3. *Experimental procedures*

Tests were conducted at initial rice temperatures between 3 and 69°C (see Table 1 for the actual initial temperatures) for the MCs of 9·2, 12·1, and 17·0%. The samples filled in the sample container were placed in an oven (for generating a high temperature environment), refrigerator (for a low temperature) or an environment-controlled chamber (for an intermediate temperature), which were all maintained at a pre-set initial temperature (Table 1), for at least 2 h, in order for the samples and the container to equilibrate to the desired initial temperature. As soon as a constant temperature of the thermocouples was reached, a constant DC voltage was applied from the power supplier, resulting in a constant electric current through the heating wire. A digital multi-meter was used to monitor the current. Power levels of 3–7 $W\,m^{-1}$ were used, which resulted in a temperature rise of the sample of 6 to 15°C at the thermocouple tip. The thermocouple temperatures were recorded by the data logger every second for 4 min. At least two replications were taken for each sample; after one replication, the sample was cooled to the initial temperature before the next replication began. The MC of the used samples was also checked by the oven method to ensure no significant moisture loss occurred during the experiments.

2.4. *Data analysis*

Thermal conductivity was calculated using the maximum slope method (Asher *et al.*, 1986; Wang & Hayakawa, 1993). Matlab software (The MathWorks, Inc., Natick, MA) was used to calculate the local slopes

Table 1
Experimental values for the thermal conductivity *k* of Bengal rice

Moisture content, % w.b.					
9·2		*12·1*		*17·0*	
Temp, °C	*k, $Wm^{-1}K^{-1}$*	*Temp, °C*	*k, $Wm^{-1}K^{-1}$*	*Temp, °C*	*k, $Wm^{-1}K^{-1}$*
6	0·080	3	0·085	6	0·093
6	0·087	10	0·102	17	0·104
17	0·087	24	0·096	17	0·110
17	0·109	24	0·111	24	0·107
24	0·103	24	0·099	24	0·099
24	0·103	38	0·113	24	0·099
24	0·099	38	0·111	38	0·108
38	0·108	38	0·105	38	0·121
38	0·100	46	0·099	38	0·118
38	0·101	46	0·106	46	0·099
46	0·102	46	0·113	46	0·082
46	0·093	57	0·113	46	0·119
61	0·111	57	0·099	57	0·108
61	0·106	57	0·108	57	0·102
61	0·120	61	0·115	61	0·123
66	0·110	61	0·115	61	0·129
66	0·116	61	0·104	66	0·127
69	0·128	66	0·12	66	0·134
69	0·119	66	0·116	69	0·138
69	0·131			69	0·122

from the temperature-ln(time) data at each of the four time steps: 5, 6, 7 and 8 s for the first 60 s (sometimes 63 or 64 s depending on the size of the time step) for each measurement. The local slopes were plotted as a function of time, and the maximum slope was determined from the set of local slopes corresponding to one of the four time steps that could generate the clearest peak. Only the first 60 s were used, because this was the section of the curve where temperature rise *versus* time relationship was linear. Thermal conductivity of the rice was calculated from the following equation derived from the unsteady-state heat conduction from a line heat source to an infinite medium (Mohsenin, 1980):

$$k = \frac{I^2 R}{4\pi S} \tag{4}$$

where S is the maximum value of the slope $dT/d\ln(t)$.

The general linear model (GLM) procedure of SAS (Version 7, SAS, Cary, NC) was used to determine the significance ($\alpha = 0{\cdot}05$) of the effects of the independent variables MC and temperature on k and to construct a multiple regression model to predict k of rough rice.

3. Results and discussion

Table 1 shows the experimentally determined values of k for rough rice. The values for k ranged from 0·080 to 0·138 $W\,m^{-1}\,K^{-1}$ in the temperature range of 3 to 69°C and MC range of 9·2–17·0%. The resultant multiple regression model for k as a function of temperature, MC and their interactions by the GLM procedure of SAS was:

$$k = 6{\cdot}5335 + 2{\cdot}3835 \times 10^{-2} T + 9{\cdot}9736 \times 10^{-4} M - 6{\cdot}8155 \times 10^{-5} T^2 + 6{\cdot}3510 \times 10^{-7} T^3 \tag{5}$$

where: k is thermal conductivity in $W\,m^{-1}\,K^{-1}$, T is temperature in °C, M is moisture content as a %, and the value for the coefficient of determination R^2 was 0·87 at a confidence level of 0·05.

In order to show the trend of thermal conductivity data in the temperature and MC ranges tested in this study, Eqn (5) is plotted in *Fig. 2* together with the measured data in Table 1. Shown in *Fig. 2* are also the statistical trend lines of the T_g data measured with a thermal mechanical analyser (TMA) (Sun *et al.*, 2001) and a differential scanning calorimeter (DSC) (Perdon, 1999). As evident from *Fig. 2*, thermal conductivity of rice underwent a clear transitional change around where glass transition line lay (relative to either the T_g line by TMA or the T_g line by DSC).

To elaborate more clearly on this regard, 95% confidence limits of the T_g data by TMA were taken into account and Eqn (5) was plotted as a function of

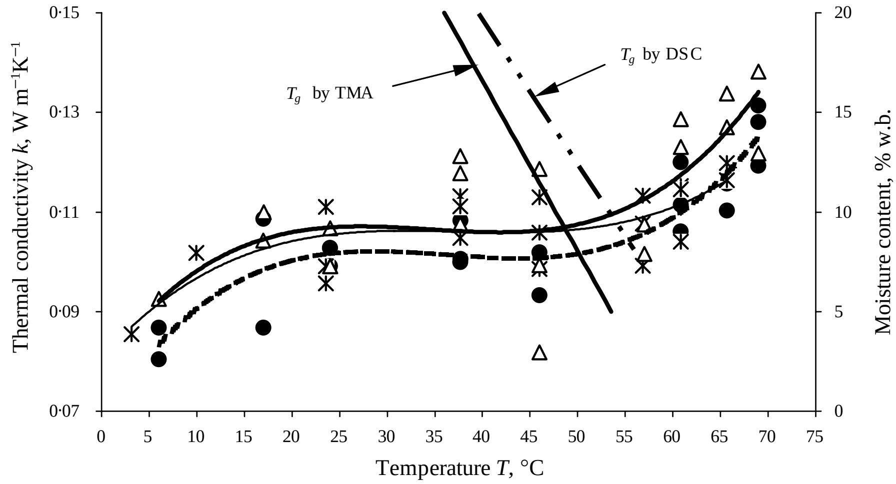

Fig. 2. A combined plot of the rice glass transition state diagrams measured with a thermal mechanical analyser (TMA) (Sun et al., 2001) and a differential scanning calorimeter (DSC) (Perdon, 1999) and the thermal conductivity versus temperature relationships at three moisture contents: 9·2% (● measured, - - - estimated), 12·1% (measured, —— estimated) and 17·0% (Δ measured, ━━ estimated)*

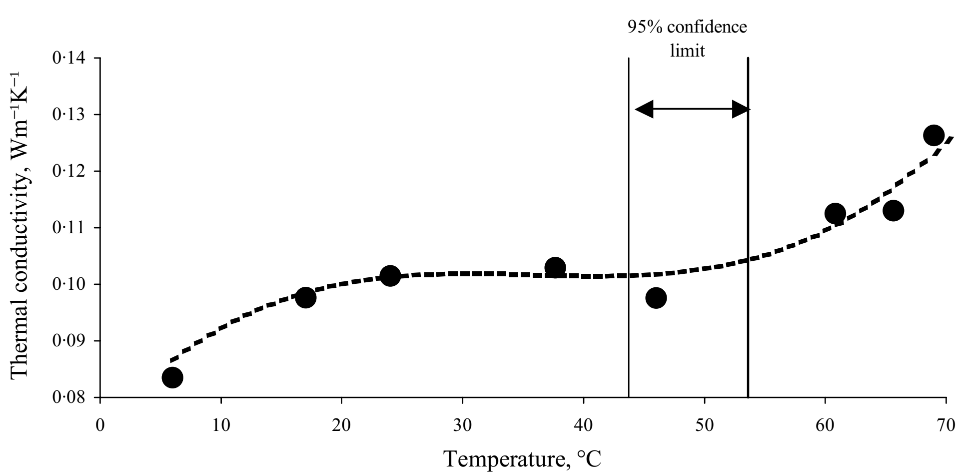

Fig. 3. Mean (●) and Eqn (5) estimated (- - -) thermal conductivity of Bengal rice at 9·2% initial moisture content (MC) and different initial temperatures; also shown is the 95% confidence limit of the glass transition temperature T_g for rice by a thermal mechanical analyser at 9·2% MC

temperature in *Figs 3–5* along with the mean of the measured k values at each of the three MCs.

As shown in *Figs 3–5*, two distinctive k regions were observed below and above the T_g range—the 95% confidence limit for T_g. Below the T_g range, k remained relatively constant from approximately 25°C (room temperature) to the lower limit of the T_g. However, below 25°C, k decreased with decreasing temperature. In the constant-k region, the average k values were approximately 0·102, 0·106 and 0·109 W m^{-1} K^{-1} for 9·2, 12·1 and 17·0% MC, respectively. Although in this region k did not change with temperature, k increased as MC increased. This finding agrees with the k data reported by Morita & Singh (1979) and Chuma *et al.* (1981). The decrease of k with decreasing temperature at temperatures lower than room temperature could be explained by reduced water mobility at lower temperatures.

Above the upper limit of the T_g, k values exhibited a significant increase with increased temperature for each of the three MC levels. In other words, k of rice increased considerably as rice kernels changed their state from glassy to rubbery. This result verified the theoretical prediction that thermal properties, such as

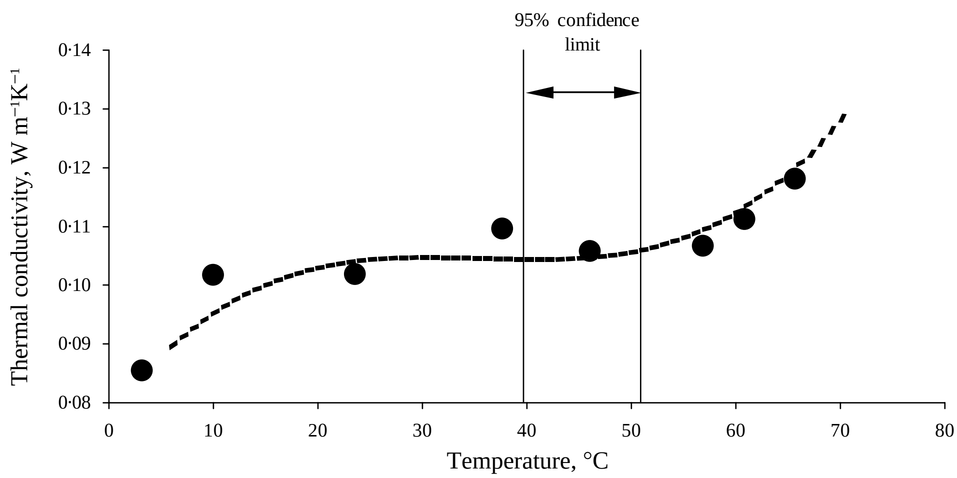

Fig. 4. Mean (●) and Eqn (5) estimated (---) thermal conductivity of Bengal rice at 12·1% initial moisture content (MC) and different initial temperatures; also shown is the 95% confidence limit of the glass transition temperature T_g for rice by a thermal mechanical analyser at 12·1% MC

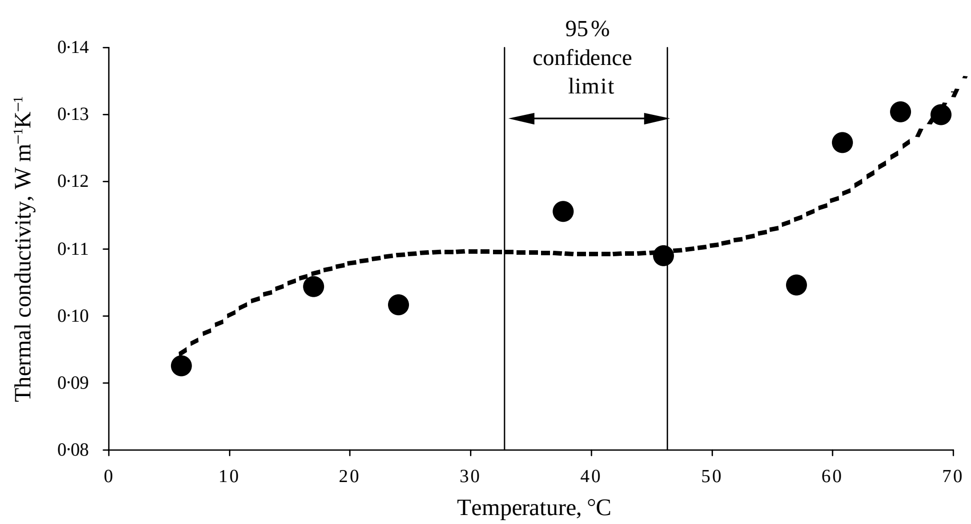

Fig. 5. Mean (●) and Eqn (5) estimated (---) thermal conductivity of Bengal rice at 17·0% initial moisture content (MC) and different initial temperatures; also shown is the 95% confidence limit of the glass transition temperature T_g for rice by a thermal mechanical analyser at 17·0% MC

k, would change substantially as the kernel transitioned from a glassy to a rubbery state.

In the Section 1, it was mentioned that around 53°C, Arora *et al*. (1973) noticed a pronounced increase in the rate of thermal expansion for rice variety Calora. A close examination of *Fig. 2*, as well as *Figs 3–5*, led to a finding that the characteristic temperature, 53°C, reported by Arora *et al*. (1973) fell into the temperature range in which the thermal conductivity of Bengal rice underwent a significant transitional change.

As mentioned in Section 2.2, thermal conductivity measurement based on the line heat source method that assumes an infinite medium necessitates the surface temperature of the sample holder to be constant during the experiments. In this study, the surface temperature of the sample holder did not change significantly with time within 65 s—the duration for the experiment, as shown in *Fig. 6* that gives, as an example, the surface temperature history of the sample holder during one of the experiments at around 39°C initial temperature. This indicates that the sample container could be considered

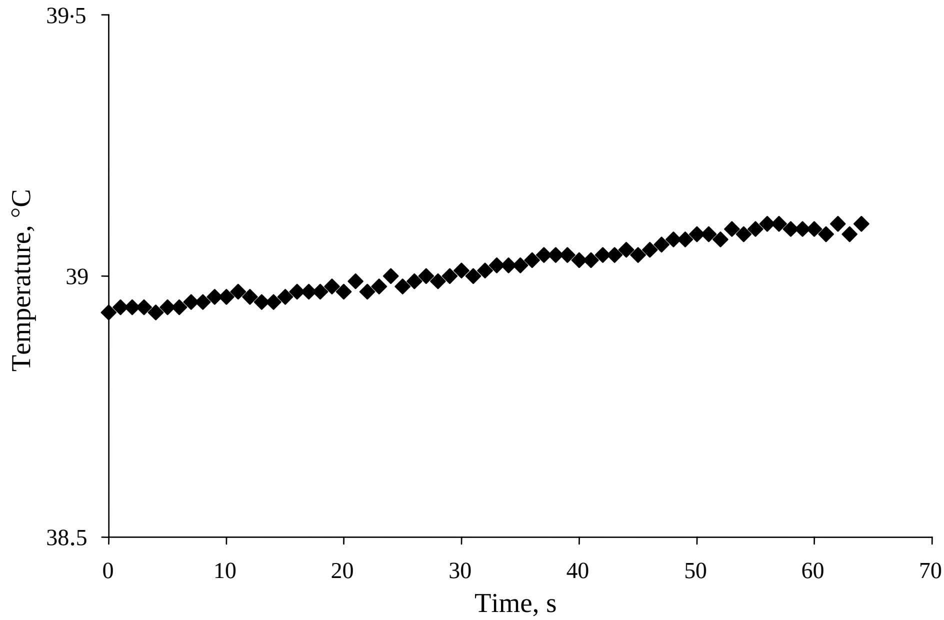

Fig. 6. The surface temperature of the sample holder as a function of time during one measurement at an initial temperature around 39°C

as holding an infinite sample size, which is one of the underlying assumptions to reach Eqn (4).

4. Conclusions

The thermal conductivity of rough rice ranged from 0·080 to 0·138 $\mathrm{W\,m^{-1}\,K^{-1}}$ in the temperature range of 3 to 69°C and moisture content range of 9·2 to 17·0%, as measured by a line heat source method and processed using the maximum slope method. Thermal conductivity increased dramatically after the rice temperature increased above the glass transition temperature T_g. The thermal conductivity was relatively constant from around 25°C to the T_g, and decreased with decreasing temperature below 25°C. A multiple regression model was developed to relate thermal conductivity to temperature and moisture content.

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