



Thermal Conductivity of Chickpea Flour and Isolated Starch and Protein

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Abstract

Thermal conductivity of chickpea flour, isolated starch, and protein extracted from chickpea flour was measured at four temperatures and three levels of bulk density at constant moisture content for each sample. The line heat source method was employed; thermal conductivity value was calculated using the maximum slope method. In all three samples, the thermal conductivity was found to increase linearly with increase of temperature and bulk density. The thermal conductivity of chickpea flour, isolated starch and isolated protein ranged from 0.0739 to 0.1058, from 0.0688 to 0.0919, and from 0.0643 to 0.0787 $W m^{-1} K^{-1}$, respectively. The first order polynomial model was fitted to measured data well with high R^2 and low standard error of estimate.

Keywords: Thermal conductivity, maximum slope method, line heat source, chickpea flour, starch, protein.

INTRODUCTION

Thermal properties including specific heat, thermal conductivity, and thermal diffusivity of foodstuffs are necessary in the design, calculations, modeling, and optimization of food processing operations involving heat transfer such as freezing, thawing, cooking, drying, pasteurization, and sterilization (Nesvadba 1982; Drouzas and Saravacos 1988; Drouzas et al. 1991). This information can also be used in study of packaging and shelf-life of the products. Thermal properties of some food materials are available in the literature; however, those of processed materials with different compositions and porosities in a non-homogenous structure are more difficult to predict or find in the literature and need to be measured using experimental methods (Drouzas et al. 1991). Thermal properties of biomaterials are influenced by different parameters. For example, thermal properties of starch can be affected by its crystalline structure.

Thermal conductivity is affected by sample moisture, temperature, and bulk density. Studies on starch granules and cumin seeds have shown that as moisture content and temperature increase, thermal conductivity increases (Drouzas et al. 1991; Singh and Goswami 2000). Drouzas and Saravacos (1988) showed that thermal conductivity increased linearly with bulk density. Increasing the temperature resulted in an increase of thermal conductivity; this effect was greater in moisture content of 6.5% and higher. Similar results were obtained by Fang et al. (2000) on granular rice starch and Lan et al. (2000) on tapioca starch. In biomaterials, the effect of bulk density and moisture content on thermal conductivity is greater than temperature (Mohsenin 1980).

Since the line heat source method, also called probe method, is simple, quick, accurate, low cost, and usable for any geometry of sample, it is used in thermal conductivity measurement of most food materials (Wang and Hayakawa 1993; Rahman 1995). This method has been used for measuring thermal conductivity of corn starch granules (Drouzas et al. 1991), barley, lentil, and pea (Alagusundaram et al. 1991), cumin seed (Singh and Goswami 2000) and apple, banana, carrot, cheese, chicken breast, and beef muscle (Fontana et al. 2001). The use of line heat source method started when Van der Held and Van Drunen (1949) developed a probe using a high thermal conductivity cylinder. Inside the cylinder is a heater wire throughout its length and a thermocouple in the middle of its length (Mohsenin 1980). The remaining space in the probe tube is filled with high thermal conductivity paste. The probe is inserted into a sample with a uniform temperature and heated at a constant rate. The temperature adjoining the line heat source is measured using the thermocouple. After a brief period, the slope resulting from the natural logarithm of time versus temperature is determined. The slope equals $q/(4\pi k)$ (Rao and Rizvi 1995).

The heat flow from the probe in an infinite sample is given by the Fourier equation (Singh and Goswami 2000; Fontana et al. 2001):

$$\frac{\partial \theta}{\partial t} = \alpha \left[\frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} \right] \quad (1)$$

This equation has been solved by several researchers including Hooper and Lepper (1950) and Nix (1967) and they discussed the basic theory behind the use of line heat source. The solution of equation 1 is as follows:

$$k = \frac{q'}{4\pi(T_2 - T_1)} \ln \frac{t_2}{t_1} \quad (2)$$

where: k = thermal conductivity of the sample infinite in size surrounding the heat source ($\text{W m}^{-1} \text{K}^{-1}$)

$q' = I^2 R$ = heat input per meter of line source (W m^{-1});

T = temperature ($^{\circ}\text{C}$); and

t = time (s) (Mohsenin 1980; Iwabuchi 1999).

Heating of the sample starts at constant rate along the probe; the temperature and time are recorded. Thermal conductivity value is calculated using the maximum slope method. The slope of the straight line graph of temperature differences versus $\ln t$ is calculated (Wang and Hayakawa 1993):

$$S = \frac{T_2 - T_1}{\ln \frac{t_2}{t_1}} \quad (3)$$

where S is slope. Substitution of S into equation (2) gives the thermal conductivity:

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

The objectives of this study were: 1) to determine thermal conductivity of chickpea flour, isolated starch and protein resulting from chickpea flour; and 2) to determine the effect of bulk density and temperature changes on thermal conductivity of the above mentioned materials.

MATERIALS AND METHODS

Sample Preparation

Commercial dehulled split desi chickpea (dhal) from the crop harvested in the fall of 2003 were obtained from Canadian Select Grains of Eston, Saskatchewan, Canada. The split chickpea grain was stored in a walk-in cooler maintained at a temperature of $2 \pm 2^{\circ}\text{C}$. It was then milled using pin mill (GM 280/S-D, Condux werk, Hannau, Wolfgang, Germany) to obtain chickpea flour. The pin mill had two discs: the first one had 86 pins rotating at 8034 rpm; and the second one had 108 pins and was stationary.

A hydrocyclone was employed (Figure 1) for producing isolated starch and isolated protein from chickpea flour using isoelectric precipitation method. This procedure was modified from the method reported by Sumner and co-workers (1981). After freeze drying, the isolated starch and isolated protein were ground using a Wiley mill (Model 4, Thomas Wiley Mill, Thomas Scientific, Swedesboro, NJ) with a 2 mm screen opening.

Instrumentation and Measurement

Thermal conductivity was measured using the line heat source method. A thermal conductivity probe was made using a brass cylinder with 1.57 mm in diameter and 89.82 mm in length. The schematic of probe assembled in this study is shown in Figure 2. A single insulated constantan wire with diameter of 0.13 mm was inserted through whole length of cylinder until it appeared at the tip; this wire acted as a heater. The tip was plugged and the bare constantan wire was

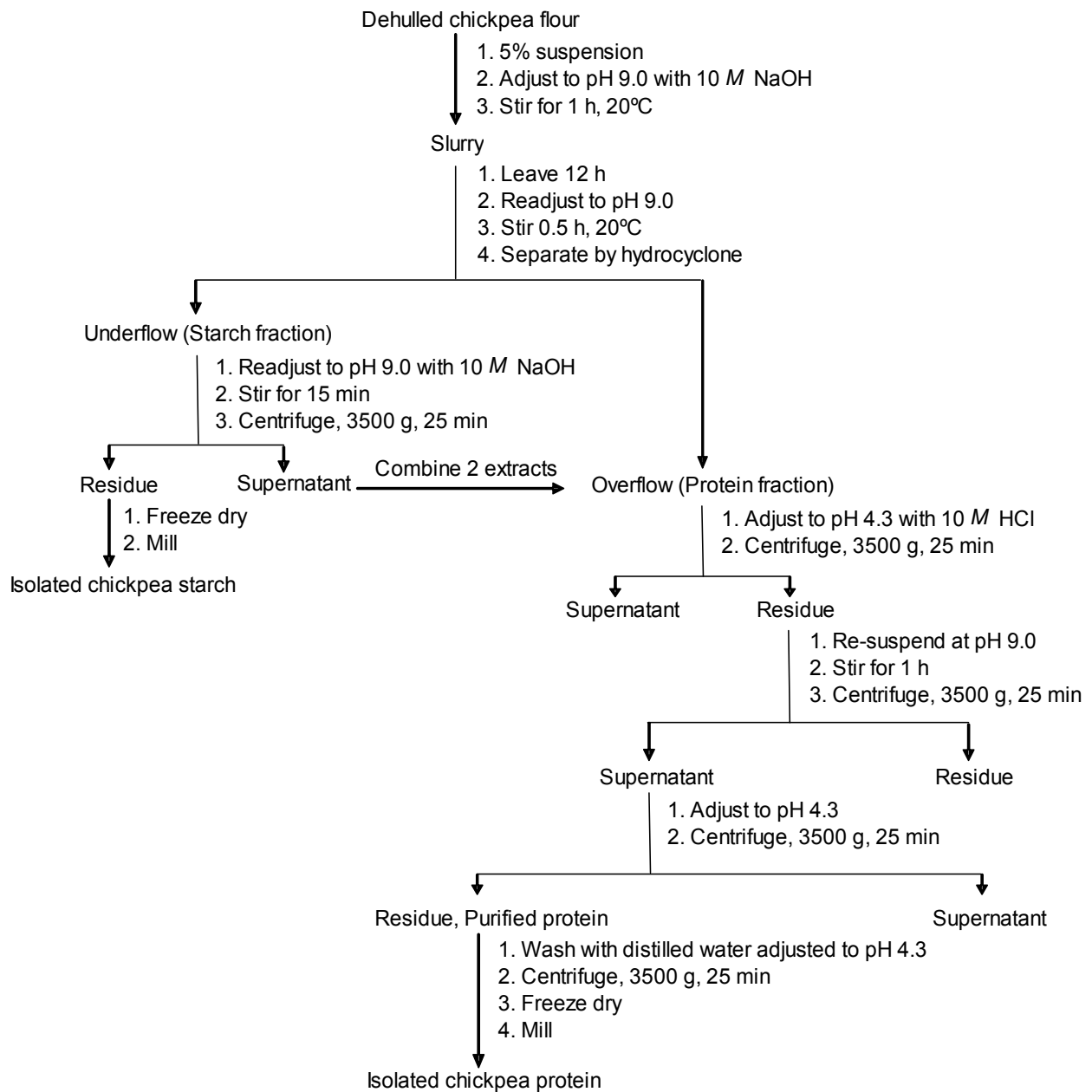


Figure 1. Schematic diagram of isolating of starch and protein using a hydrocyclone

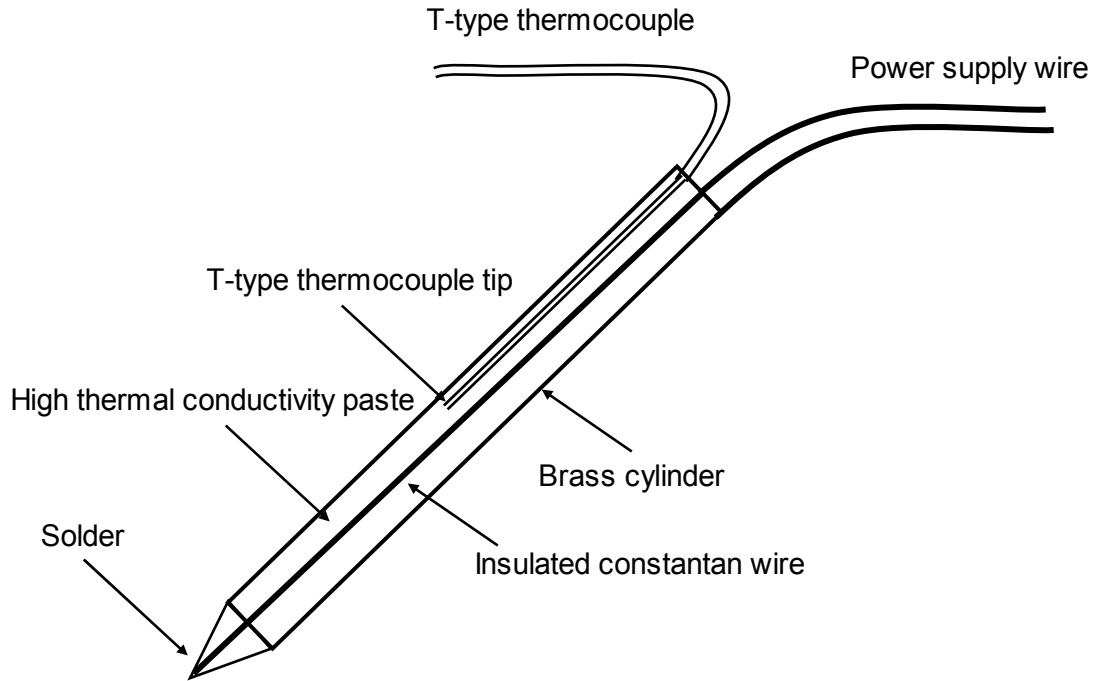


Figure 2. Schematic of thermal conductivity probe.

soldered to the tip. The other end of this wire was attached to the positive wire of the power source. Another power wire (negative polarity) was soldered to the outer layer of cylinder. A T-type (constantan and copper) thermocouple with diameter of 0.13 mm was inserted halfway into the cylinder. The remaining space in the cylinder was filled with high thermal conductivity paste (Wakefield Thermal Solutions, Inc., Pelham, NH). A 2-cm heat shrink was connected to the end of cylinder to keep the heater wire and thermocouple secure and in place.

Thermal conductivity of distilled water containing agar (1% w/v) (Iwabuchi et al. 1999) was measured at temperatures of -18, 4, 22, and 40°C and compared with values reported in references to calculate for error percentage as explained by Fontana et al. (2001). Agar forms a gel in water medium and it was used to minimize natural heat convection in water (Iwabuchi et al. 1999). Thermal properties of agar gel and water are almost the same.

The schematic of the set up used for thermal conductivity measurement is presented in Figure 3. The specimen's thermal conductivity was measured for about 1 min using the probe; time and temperature were recorded in 0.25 s intervals using Campbell data logger (Model CR10X, Campbell Scientific, INC. Logan, UT). Data was transferred to a laptop computer. Power supply provided a constant current of 0.600 A. The heating-wire resistance was $51.21 \Omega m^{-1}$ as measured. The thermal conductivity value was calculated using maximum slope method (Wang and Hayakawa 1993). Local slope was calculated between each 20-sequence of $\ln t$ and probe temperature differences using linear regression analysis. The maximum slope was determined and substituted in equation (4) to calculate the thermal conductivity value.

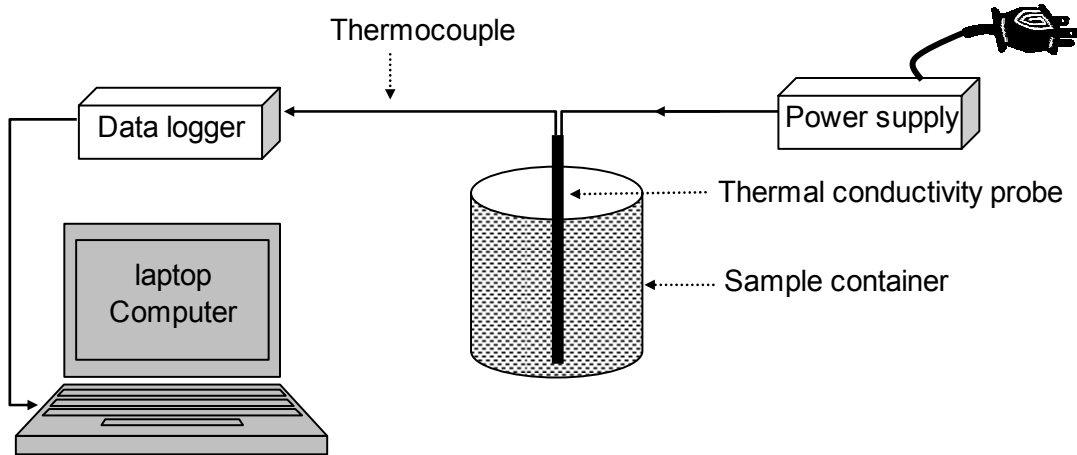


Figure 3. Schematic set up for thermal conductivity measurement.

Bulk Density, Particle Density, and Porosity Determination

Bulk density was measured in five replicates using $0.5 \times 10^{-3} \text{ m}^3$ cylindrical container filled by a funnel, with its discharge opening located 55 mm above the top edge of the container. Since the powder in the funnel bridged, it was stirred with a thin glass bar to provide continuous flow of the sample to the container. The funnel was removed from top of the container and the powder on the container was leveled by rolling a steel bar across the container in two perpendicular directions. Then, the container was weighed. The bulk density was calculated using the following equation:

$$\rho_b = \frac{M}{V} \quad (5)$$

where: ρ_b = bulk density (kg m^{-3});
 M = mass sample in the cylinder (kg); and
 V = volume of cylinder (m^3).

A gas pycnometer (Multi Pycnometer Model MVP-2, Quantachrome Corp., Boynton Beach, FL, USA) was employed to measure the solid volume of sample followed by measuring the corresponding mass. Particle density was measured in five replicates and calculated using the following equation:

$$\rho_t = \frac{M}{V_s} \quad (6)$$

where: ρ_t = particle density (kg m^{-3});
 M = mass sample in the cylinder (kg); and
 V_s = volume of solid (m^3).

As proposed by Fang et al. (2000) and Mohsenin (1986) the porosity was determined by calculated bulk density and particle density using the following equation:

$$\varepsilon = \left(1 - \frac{\rho_b}{\rho_t} \right) \times 100 \quad (7)$$

where: ε = porosity (%);

ρ_b = bulk density (kg m⁻³); and
 ρ_t = particle density (kg m⁻³).

Since porosity was calculated using bulk density and particle density values resulting from measurement, the error of porosity in the calculated function is the root of the individual errors (equation 8). This kind of error calculation was discussed by Ma et al. (1998) for determination of error of secondary quantities.

$$\Delta\varepsilon = 100 \times \sqrt{\left(\frac{\partial\varepsilon}{\partial\rho_b} \Delta\rho_b\right)^2 + \left(\frac{\partial\varepsilon}{\partial\rho_t} \Delta\rho_t\right)^2} \quad (8)$$

where: $\Delta\varepsilon$ = error of porosity;
 $\Delta\rho_b$ = error of bulk density; and
 $\Delta\rho_t$ = error of particle density.

In the current study, each value in equation (8) is given by:

$$\frac{\partial\varepsilon}{\partial\rho_b} \Delta\rho_b = -\frac{1}{\rho_t} \Delta\rho_b \quad (9)$$

$$\frac{\partial\varepsilon}{\partial\rho_t} \Delta\rho_t = \frac{\rho_b}{\rho_t^2} \Delta\rho_t \quad (10)$$

Therefore, the error of porosity is obtained by substituting equations (9) and (10) into equation (7):

$$\Delta\varepsilon = \sqrt{\left(-\frac{1}{\rho_t} \Delta\rho_b\right)^2 + \left(\frac{\rho_b}{\rho_t^2} \Delta\rho_b\right)^2} \quad (11)$$

Moisture Content Determination

The moisture content of samples was determined in three replicates using oven method according to the AOAC method 925.10 (AOAC, 2002).

Experimental Design and Data Analysis

This study was conducted in a combination of four temperatures (-18, 4, 22, and 40°C) and three levels of bulk density (from 346.68 to 504.12 kg m⁻³) in duplicates. Therefore, a completely randomized experimental design with factorial treatment resulted in 12 treatments. A 10-min interval was permitted between tests so that the probe reached a stable temperature. To provide three bulk density levels of a sample, a 0.5-L cylindrical container was used and filled by three methods: 1) by spoon; 2) by funnel with its discharge opening located 55 mm above the top edge of the container; and 3) by tapping of container which has been filled by funnel. To prevent change in moisture content of samples at different treatments, the cylinder container was covered with air-tight plastic bag. The Statistical Analysis System (SAS 2003) was used for statistical analysis of the experimental data, such as analysis of variance (ANOVA) and regression analysis.

RESULTS AND DISCUSSION

Sample Physical Characteristics

Table 1 shows the physical characteristics of chickpea flour, isolated starch, and isolated protein. The bulk density increased as the porosity decreased for all samples as the air spaces between particles diminished. Chickpea flour had the lowest porosity at bulk density of 504.12 kg m⁻³; isolated starch had the highest porosity at bulk density of 346.68 kg m⁻³. Isolated protein had the lowest moisture content among samples. Isolated protein was obtained by the isoelectric precipitation method where proteins are denatured at isoelectric point. Therefore, its water solubility is diminished and its ability to adsorb water is reduced.

Table 2 shows the thermal conductivity of distilled water containing agar (1% w/v) and error of measurements. In the temperature range of 4 to 40°C, both measured and reference thermal conductivity increased as the temperature increased. At temperature below freezing, such as -18°C, the semi-liquid phase changes to solid phase with thermal conductivity approximately 4 times higher than samples above freezing. Regression analysis between the measured thermal conductivity and reference values of distilled water showed a linear relationship with $R^2 = 1.0$ (Figure 4). The slope of linear regression was 0.9792 which was very close to 1.0. Thus, the probe was suitable for the measurement of thermal conductivity. Since the regression equation resulted in a slope very close to 1.0 and high R^2 , the measured thermal conductivity values were used in this study.

Table 1. Bulk density, particle density and porosity of chickpea flour, isolated starch and isolated protein.

Sample	Moisture content ^a (% w.b.)	Particle density ^b (kg m ⁻³)	Bulk density ^b (kg m ⁻³)	Porosity ^b (%)
Chickpea flour	9.6	1457.60 ± 0.01 ^c	416.49 ± 0.01	71.43 ± 0.00 ^d
			456.02 ± 0.01	68.71 ± 0.00
			504.12 ± 0.01	65.41 ± 0.00
Isolated starch	7.8	1508.24 ± 0.01	346.68 ± 0.00	77.01 ± 0.00
			387.05 ± 0.00	74.34 ± 0.00
			427.10 ± 0.00	71.68 ± 0.00
Isolated protein	2.2	1289.65 ± 0.00	335.06 ± 0.00	74.02 ± 0.00
			375.12 ± 0.00	70.91 ± 0.00
			414.98 ± 0.00	67.82 ± 0.00

^a Values are an average of three determinations.

^b Values are an average of five determinations.

^c Values in front of means are standard error.

^d Standard error for porosity was calculated using equation (11).

Table 2. Thermal conductivity of distilled water containing agar (1% w/v) at different temperatures.

Temperature (°C)	Measured k (W m ⁻¹ K ⁻¹)	Reference k (W m ⁻¹ K ⁻¹)	Reference	Error (%)
-18	2.4803 (0.38) [†]	2.440	Mohsenin 1980	1.65
4	0.5756 (0.01)	0.568	Singh and Heldman 2001	1.34
22	0.6079 (0.01)	0.597	Singh and Heldman 2001	1.83
40	0.6176 (0.01)	0.633	Singh and Heldman 2001	2.43

k: Thermal conductivity

[†] Values in the parentheses are standard deviation of the means.

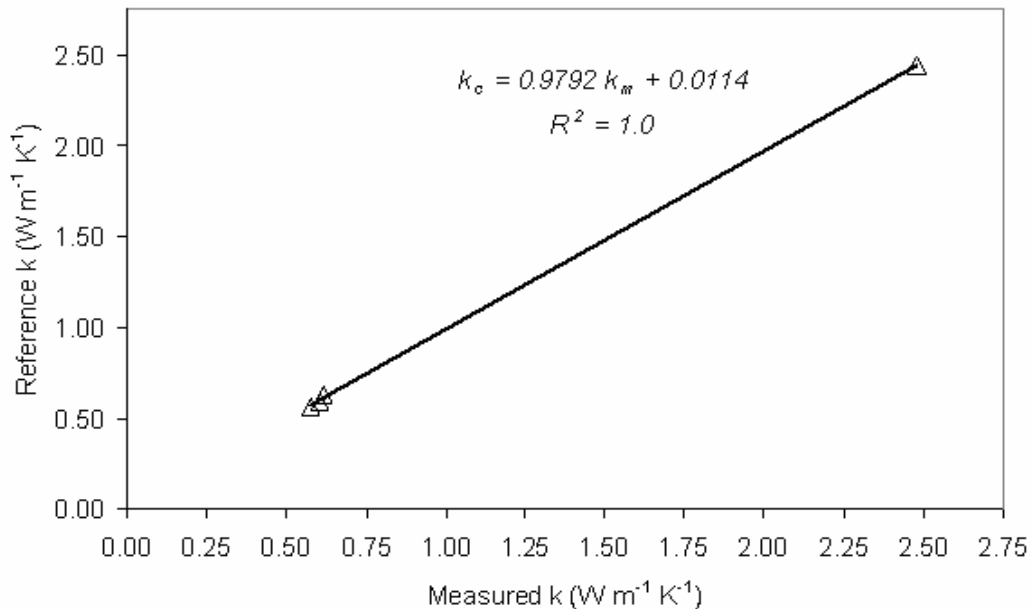


Figure 4. Relationship between measured thermal conductivity and reference thermal conductivity (k_c = corrected thermal conductivity; and k_m = measured thermal conductivity).

Table 3 shows the thermal conductivity of chickpea flour, isolated starch, and isolated protein at moisture content of 9.6, 7.8, and 2.2% w.b., respectively, which were the sample moisture in equilibrium with laboratory environment. The thermal conductivity of each sample was determined at four temperatures and three bulk densities. Thermal conductivity of samples increased with temperature at a given bulk density and increased with bulk density at a given temperature. For chickpea flour, the highest thermal conductivity (0.1058 W m⁻¹ K⁻¹) was measured at the highest temperature (40°C) and bulk density (504.12 kg m⁻³). Conversely, the lowest thermal conductivity (0.0739 W m⁻¹ K⁻¹) was measured at the lowest temperature (-18°C) and bulk density (416.49 kg m⁻³). Similar trends were obtained for isolated starch and isolated protein. For chickpea flour, ANOVA results (Table 4) showed that the effects of temperature and bulk density on thermal conductivity were significant; whereas, their interaction did not show significant difference. For isolated starch, ANOVA results demonstrated that the effect of

Table 3. Thermal conductivity of chickpea flour and isolated starch and protein in different temperatures and bulk densities.

Temperature (°C)	Chickpea flour		Isolated starch		Isolated protein	
	ρ_b (kg m ⁻³)	Mean* (W m ⁻¹ K ⁻¹)	ρ_b (kg m ⁻³)	Mean (W m ⁻¹ K ⁻¹)	ρ_b (kg m ⁻³)	Mean (W m ⁻¹ K ⁻¹)
-18	416.49	0.0739 ± 0.0007 [†]	346.68	0.0688 ± 0.0018	335.06	0.0643 ± 0.0021
-18	456.02	0.0807 ± 0.0011	387.05	0.0717 ± 0.0005	375.12	0.0701 ± 0.0012
-18	504.12	0.0843 ± 0.0025	427.10	0.0720 ± 0.0016	414.98	0.0716 ± 0.0037
4	416.49	0.0839 ± 0.0016	346.68	0.0733 ± 0.0002	335.06	0.0682 ± 0.0030
4	456.02	0.0896 ± 0.0023	387.05	0.0780 ± 0.0022	375.12	0.0715 ± 0.0014
4	504.12	0.0978 ± 0.0120	427.10	0.0789 ± 0.0031	414.98	0.0716 ± 0.0012
22	416.49	0.0846 ± 0.0013	346.68	0.0751 ± 0.0046	335.06	0.0707 ± 0.0005
22	456.02	0.0933 ± 0.0034	387.05	0.0810 ± 0.0022	375.12	0.0722 ± 0.0010
22	504.12	0.0986 ± 0.0041	427.10	0.0837 ± 0.0049	414.98	0.0755 ± 0.0012
40	416.49	0.0921 ± 0.0007	346.68	0.0896 ± 0.0094	335.06	0.0752 ± 0.0040
40	456.02	0.0998 ± 0.0054	387.05	0.0915 ± 0.0031	375.12	0.0767 ± 0.0009
40	504.12	0.1058 ± 0.0009	427.10	0.0919 ± 0.0053	414.98	0.0787 ± 0.0020

ρ_b : bulk density

* Mean thermal conductivity of three determinations.

[†] Values in front of means are standard error.

Table 4. ANOVA results of thermal conductivity of chickpea flour, isolated starch, and isolated protein.

Source of variation	Chickpea flour		Isolated starch		Isolated protein	
	df †	Probability	df	Probability	df	Probability
Temperature	3	0.00	3	0.00	3	0.00
Bulk density	2	0.00	2	0.23	2	0.03
Interaction	6	1.00	6	0.99	6	0.91
Error	12		12		12	
Total	23		23		23	

† Degree of freedom

temperature on thermal conductivity was significant, although the effect of bulk density and interaction effect of temperature and bulk density were not significant. In the case of isolated protein, the effects of temperature and bulk density ($P=0.03$) were significant, while their interaction was not significant.

The influence of temperature on thermal conductivity is due to high atomic activity at high temperatures. At higher atomic activity, the material has greater ability to transfer heat energy; thus, the material has higher thermal conductivity. The direct relationship between bulk density and thermal conductivity can be attributed to the presence of pores and air pockets among powder particles. Since air has low thermal conductivity, higher porosity (low bulk density) would result to lower thermal conductivity. Since chickpea flour has lower porosity than isolated starch and isolated protein (table 1), its thermal conductivity was higher. The effect of temperature on thermal conductivity of the samples in this study was similar to the results reported by Drouzas and Saravacos (1988) and Lan and co-workers (2000) for granular starch. Lan and co-workers (2000) reported increase in thermal conductivity of 0.077 to $0.090 \text{ W m}^{-1} \text{ K}^{-1}$ when temperature increased from 25 to 75°C . Moreover, the trend on the effect of bulk density on thermal conductivity was similar to the results of studies reported by Drouzas and Saravacos (1988) and Fang and co-workers (2000) for granular starch. Drouzas and Saravacos (1988) reported a linear increase of thermal conductivity with bulk density for granular starch materials.

Prediction Models

In practical applications, prediction models are very helpful. SAS REG procedure was employed to determine the prediction models of thermal conductivity. Table 5 shows relationship between thermal conductivity values of each sample and its bulk density and temperature as well as statistical parameters of each predicted model. All equations had low standard error of estimate and high R^2 showing good fit to the experimental data. The models obtained for all samples had positive coefficients for temperature and bulk density showing that thermal conductivity increases with bulk density and temperature.

Table 5. Relationship between thermal conductivity value and bulk density and temperature values.

Sample	Thermal conductivity equation [†]	R^2	SEE*
Chickpea flour	$k = 3.18 \times 10^{-4} T + 1.47 \times 10^{-4} \rho_b + 0.019414$	0.95	0.002
Isolated starch	$k = 3.29 \times 10^{-4} T + 6.16 \times 10^{-5} \rho_b + 0.051857$	0.91	0.003
Isolated protein	$k = 1.39 \times 10^{-4} T + 5.89 \times 10^{-5} \rho_b + 0.048437$	0.90	0.001

[†] k = thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), ρ_b = bulk density (kg m^{-3}), T = temperature ($^{\circ}\text{C}$).

*SEE: standard error of estimate.

CONCLUSION

Thermal conductivity values were obtained by the line heat source method. The thermal conductivity of chickpea flour, isolated starch, and isolated protein increased linearly with temperature and bulk density. The thermal conductivity of chickpea flour and isolated starch and protein was found to range from 0.0739 to 0.1058, from 0.0688 to 0.0919, and from 0.0643 to 0.0787 $\text{W m}^{-1} \text{K}^{-1}$, respectively. For all three samples, thermal conductivity was not significantly affected by the interaction of temperature and bulk density.

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