Effect of moisture and temperature on thermal conductivity of pigeon pea seeds

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Abstract: The thermal conductivity of agricultural seeds has been used as engineering parameter in the design of process and machines for drying, storing, aeration and refrigeration. The thermal conductivity of white and red pigeon pea seeds with changes in moisture content and temperature was investigated using the transient heat transfer method. The thermal conductivity of white and red pigeon pea seeds increased from 0.2387 to 0.3497 $Wm^{-1}K^{-1}$, and 0.2375 to 0.3425 $Wm^{-1}K^{-1}$ respectively, as the moisture content increased from 5% to 35% w.b. Thermal conductivity of white and red pigeon pea seeds increased significantly ($p<0.05$) from 0.2643 to 0.3543 $Wm^{-1}K^{-1}$, and from 0.2711 to 0.3311 $Wm^{-1}K^{-1}$ respectively, as temperature increased from 10℃ to 70 ℃. The Arrhenius type equation was used to study the temperature dependence with an activation energy of 3.93 and 2.68 KJ mol^{-1} for white and red pigeon pea seeds respectively. The relationship between the thermal conductivity and temperature was analyzed and found to be linear.

Keywords: thermal conductivity, pigeon pea seeds, moisture content, temperature, activation energy.

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1 Introduction

Food legumes have been well recognized as valuable source of dietary proteins in many parts of the world. A major portion of the world population relies on legumes as staple food particularly in combination with cereals (Sreerama et al., 2009).

Pigeon pea (*Cajanus cajan*) is an underutilized legume known as “*fio-fio*” and “*waken*” in South Eastern Nigeria and Northern Nigeria respectively (Enwere, 1998). It can grow and reproduce in a poor soil and with little or no rain for a long period of time (Adjei-Nsiah, 2012). Pigeon pea serves as an economical source of protein for the rural and urban poor people who cannot afford animal protein. Pigeon pea is rich in protein “19.63%” (Okpala and Mama, 2001), also it is an important source of all dietary essential minerals (Torres et al., 2007).

Dried mature seed of pigeon pea is cooked and eaten with yam and stew. Cooking of pigeon pea produces a tender edible food with aroma, which is mostly preferred by consumers. It also inactivates antinutritional factors present in the grain. There are two main types of pigeon pea namely, the white and the red, but the most preferred type for cooking is the white.

Legume grains require a relatively long cooking time ranging from 1 to 4 h due to its hard to cook phenomenon as a result of hard shell that develops during storage. Cooking process involves the combined effect of heat and mass transport phenomena, physical and chemical reactions

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such as starch gelatinization and protein denaturation. Absorption of water by the pigeon pea during soaking and boiling at relatively low temperatures below 100°C promotes a

soft and moist product texture, with minimal mass loss. Cooking time of legumes primarily depends on some processing methods such as soaking applied prior to cooking softens the seeds, and significantly reducing cooking time. In order to find the optimum cooking time, information on the thermal properties and the heat and mass transfer characteristics should be known. Therefore, the knowledge of the thermal properties is important for design and evaluation of the process control and devices (Aviara et al., 2008). Also the rate of addition and removal of heat is determined by the thermal properties of the products. Measurement of thermal conductivity is therefore important owing to its applications for processing and storage. Thermal conductivity is required to design and properly control the thermal processes. The thermal conductivity of food and agricultural materials are affected by temperature, proximate composition, and state of the materials during processing (Becker and Fricke, 1999; Tansakul and Lumyong, 2008). Information on thermal conductivity is also important for understanding the thermogenic processing stored high–moisture seeds and grains that develop “heat pockets” (Irtwange and Igbeka, 2002). Since individual material have their own specific compositions, thermal properties of materials will also vary.

Since temperature is a major factor in grain deterioration during storage, predicting the temperature of grain in bulk is important if a sound temperature control system is to be designed. To make such a prediction, information on thermal conductivity of the grain is required. The Arrhenius equation could be used to describe the temperature dependence of the thermal conductivity of white and red pigeon pea seeds.

The linear relationship of thermal conductivity with moisture content and density of food and biological materials have been reported by many researchers (Opoku et al., 2006; Muramatsu et al., 2006; Aviara et al., 2008; Perussello et al., 2010). The importance of thermal conductivity data for thermal food processing equipment design and maximum evaluation have been reported in the literature (Polley et al., 1980). It controls the heat flux in food during processing such as cooking, frying, freezing, sterilization, drying or pasteurization. The steady and transient state heat transfers are the major methods for thermal conductivity measurement (Mohsenin, 1980). Thermal conductivity, specific heat and thermal diffusivity are important food engineering properties that influences the organoleptic properties of processed and preserved foods and their energy consumption (Opoku et al., 2006). Thermal conductivity depends mainly on moisture content, temperature, porosity, and distribution of component phases (Mohsenin, 1980). For improved quality and value addition of some processed food, information on their thermal conductivity values is very important. Krokida et al. (2001) selected and presented data in the literature for thermal conductivity of foodstuffs obtained from various scientific sources, and Maroulis et al. (2002) also studied on improving a mathematical model to estimate the thermal conductivity of some foodstuffs as a function of moisture content and temperature, and to fit the model simultaneously to a data available in the literature. Data on thermal conductivities of various food products have been widely reported in the literature, however, data of pigeon pea seeds were scanty. Therefore, the objective of this study was to determine the effects of moisture content and temperature on thermal conductivity of white and red pigeon pea seeds.

2 Materials and methods

2.1 Sample preparation

Two pigeon pea seed cultivars, white and red used in this study were purchased from a local market in Abakaliki, Ebonyi State, Nigeria. The seeds were cleaned manually by removing foreign materials and damaged seeds. The thermal conductivity measurements of both cultivars were conducted at seven moisture content levels, of 5.0%, 10.0%, 15.0%, 20.0%, 25.0%, 30.0% and 35.0% wet basis.

The initial moisture content accepted as low moisture level of the seeds and was determined by oven drying the sample at 105 ℃ ± 1℃ for 24 h (AOAC, 2002). The desired moisture contents for higher levels were obtained by adding distilled water to the seeds. The amount of distilled water added was calculated using Equation 1 (Balasubramanian, 2001).

$$M_w = \frac{M_i(m_f - m_i)}{100 - m_f} \qquad (1)$$

where: M_w is the mass of distilled water (g), M_i is the initial mass of sample (g), m_f is the final moisture content of sample (% w.b.) and m_i is the initial moisture content of sample (% w.b.).

The prepared samples were sealed in separate polythene bags and kept in a refrigerator at 5°C for five days to ensure uniform moisture distribution throughout the samples. Just before starting a test, the required amount of seed was taken out of the refrigerator and allowed to equilibrate at room temperature for at least 24 h (Dutta et al., 1988; Alagusundaram et al., 1991).

2.2 Thermal conductivity determination

Thermal conductivity of white and red pigeon pea seeds was determined by thermal conductivity probe method using line heat source principle (Singh and Goswami, 2000). The experimental apparatus for determination of thermal conductivity was shown in Figure 1.

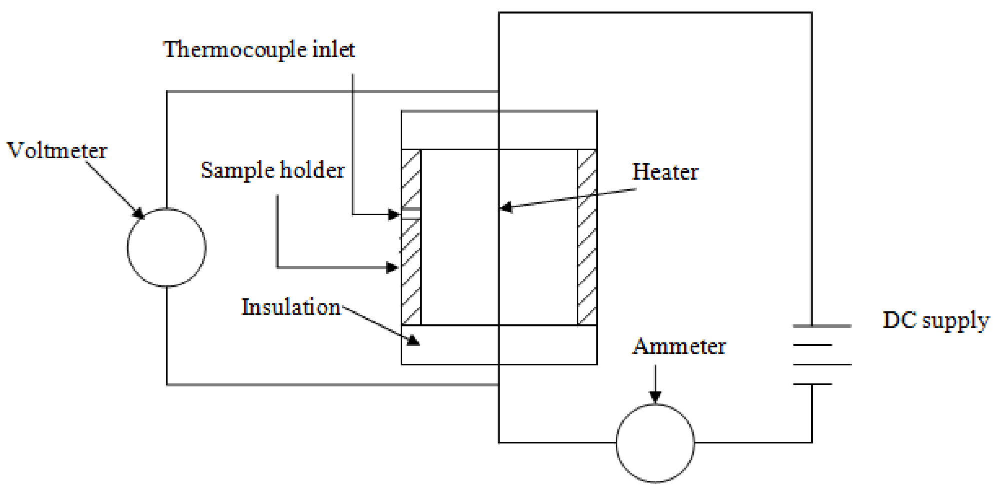

Figure 1 Schematic diagram of the thermal conductivity measuring apparatus

The thermal conductivity probe, which was built in the laboratory conditions in this study, was constructed from glass material and had a diameter of 3.84 mm, a length of 130.0 mm with a thickness of 0.27 mm. The heating wire used for heating apparatus had a diameter of 0.4 mm and a length of 130.0 mm (10.74 Ω m^{-1}). Temperature rise was measured using K-type thermocouple of 0.5 mm diameter. The white and red pigeon pea seeds were respectively filled in cylindrical container then, the container was closed by a lid with a hole right in the center and later, the thermal conductivity probe was inserted into the bulk of pigeon pea seed through the hole. A 3 V voltage and 1 A current were applied to thermal conductivity probe which was inserted into the center of the sample. The temperature (*T*) increases were recorded for 90 seconds with one-second intervals when the power was on. Then the power was switched off and the decreases were recorded for 90 seconds with one-second intervals. The maximum slope method was used to calculate the thermal conductivity of white and red pigeon pea seeds and thermal conductivity (*k*) of a sample was calculated using the following equation (Singh and Goswami, 2000);

$$k = \frac{Q}{4\pi} \frac{d\ln(t)}{d\,(\Delta T)} \qquad (2)$$

where: k is bulk thermal conductivity (W $m^{-1}K^{-1}$); Q is the heat input per unit length of hotwire (W m^{-1}); t is time (s); T is temperature (K). Local slope (S) and the coefficient of determination (R^2) of temperature versus the ln (t) were determined for each 7 data point using linear regression analysis. Local slope was calculated using the following equation.

$$\frac{d\ \ln(t)}{d\ (\Delta T)} = \frac{1}{S} \tag{3}$$

The maximum slope obtained from the curve of local slopes versus time was deter-mined based on the highest slope value and the highest R^2 for the thermal conductivity calculation (Yang et al., 2002). The heat in Equation 2 was generated in a hot wire at a rate Q:

$$Q = I^2 R \tag{4}$$

Where: I is electric current (A) and R is the electric resistance per unit length hot wire ($\Omega\ m^{-1}$).

When Equation 2 was reorganized, the thermal conductivity of white and red pigeon pea seeds was calculated using the Equation 5;

$$k = \frac{I^2 R}{4\pi}\frac{1}{S} \tag{5}$$

Experiments were repeated three times for each moisture level to determine the effect of moisture content of white and red pigeon pea seeds on thermal conductivity. Temperature readings were taken at regular time interval of one minute for 40 minutes for each sample experimented. Thermal conductivity was determined at seven sample temperatures of 10°C, 20°C, 30°C, 40°C, 50°C, 60°C and 70°C.

2.3 Activation energy determination

The Arrhenius equation was used to describe the temperature dependence of the thermal conductivity of white and red pigeon pea seeds k_{wps} and k_{rps} respectively in the following manner:

$$k_{ps} = k_o\, exp\left(-\frac{Ea}{RT}\right) \tag{6}$$

where: k_0 is the pre-exponential factor of the Arrhenius equation ($m^2\ s^{-1}$), Ea is the activation energy for the seed conduction ($KJmol^{-1}$), R is the ideal gas constant (= 8.314 KJ mol^{-1} K^{-1}), and T is the temperature in (K). On linearization, Equation 6 becomes

$$InK = InK_o + \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \tag{7}$$

When lnK is plotted against, $\left(\frac{1}{T}\right)$, a straight line with slope $\left(\frac{E_a}{R}\right)$ is obtained from which the activation energy can be calculated and sensitivity of the constant to temperature can be assessed.

The goodness of fit of the models was evaluated by means of the coefficient of determination (R^2) (Equation 8) and root mean square error ($RMSE$) (Equation 9) between the experimental data sets and predicted data.

$$R^2 = 1 - \frac{\sum(Xeq_{exp} - Xeq_{pre})^2}{\sum Xeq_{exp}{}^2 .\ \sum Xeq_{pre}{}^2} \tag{8}$$

$$RMSE = \sqrt{\sum \frac{(Xeq_{exp} - Xeq_{pre})^2}{n}} \tag{9}$$

where: Xeq_{exp} and Xeq_{pre} are the experimental and predicted thermal conductivity values, respectively, and n is the number of experimental data. The model with the lowest value of $RMSE$ and the highest coefficient of determination was considered to be the best fit (Wang and Brennan, 1991).

2.4 Statistical analysis

An analysis of variance (ANOVA) procedure of Minitab 14.0 Software (Minitab Inc., State Park, PA) was used to determine the significance ($p < 0.05$) of the effects of the moisture content on the thermal conductivity of the white and red pigeon pea seeds and to construct linear regression equations to predict thermal conductivity of the white and red pigeon pea seeds.

3 Results and discussion

3.1 Effect of moisture content on thermal conductivity of pigeon pea seed

The effect of moisture content on the thermal conductivity of white and red pigeon pea seeds presented in Figure 2, showed that the thermal conductivity of the white and red pigeon pea seeds increased linearly from 0.2387 to 0.3497 $Wm^{-1}K^{-1}$, and 0.2375 to 0.3425 $Wm^{-1}K^{-1}$ respectively with increasing moisture content, with white pigeon pea seed having higher thermal conductivity values than that of red pigeon pea seeds. This finding is consistent with reported literature that thermal conductivity increased with moisture content for soybean (Deshpande et al., 1996), cumin seed (Singh and Goswami, 2000), sheanut kernel (Aviara and Haque, 2001), guna seed (Aviara et al., 2008), rough rice (Yang et al., 2003), borage seeds (Yang et al., 2002), millet grains (Subramanian and Viswanathan, 2003), brown rice (Muramatsu et al., 2006), maize and cowpea (Bart-Plange et al., 2009) and ground cocoa beans and ground sheanut kernels (Bart-Plange et al., 2012).

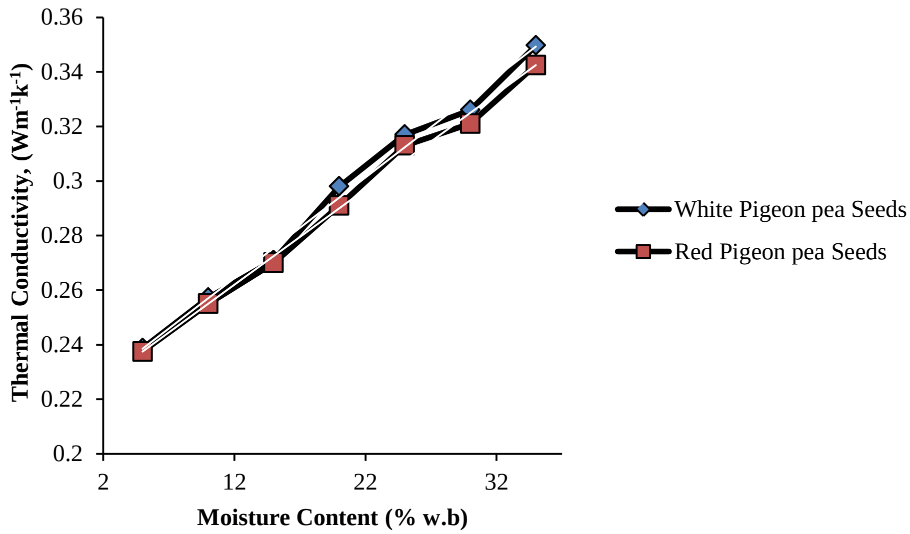

Figure 2 Thermal conductivity as a function of moisture content

The variation in thermal conductivity of the seeds with moisture content might be due to the ability of the seeds to absorb water into the intercellular spaces, which will lead to conductive heat transfer (Bart-Plange et al., 2012).

The relationship existing between thermal conductivity (k, $Wm^{-1}K^{-1}$) and moisture content (M, % d.b) of pigeon pea seed was found to be linear and can be represented with the following equation:

$$k_{wps} = 0.0037M + 0.2201 \qquad (R^2 = 0.9915) \qquad (10)$$

$$k_{rps} = 0.0035M + 0.220 \qquad (R^2 = 0.9938) \qquad (11)$$

3.2 Effect of temperature on thermal conductivity of pigeon pea seed

The thermal conductivity of white and red pigeon pea seeds was found between 0.2643 and 0.3543 $Wm^{-1}K^{-1}$, and 0.2711 and 0.3311 $Wm^{-1}K^{-1}$ respectively with varying temperature in the range of 10 ^{o}C to 70 ^{o}C (Figure 3). The temperature affected significantly the thermal conductivity which increased linearly with the increase in the temperature. Similar observation was reported in the thermal conductivity of sheanut kernel (Aviara and Haque, 2001), guna seed (Aviara et al., 2008), maize and cowpea (Bart-Plange et al., 2009) ground cocoa beans and ground sheanut kernels (Bart-Plange et al., 2012), cashew apple (Kurozawa et al., 2008) and pomegranates (Mahmood and Hosein, 2008).

The values of thermal conductivity are, in real terms, the heat flow through unit thickness of material over a unit area per unit time for unit temperature difference. While specific heat dictates the quantity of heat to be absorbed by a material, thermal conductivity sets the rate of this addition. Since biological materials are not homogenous, numerical values of the thermal conductivity vary with chemical composition, physical structure, the state of the substance, and temperature. For practical purposes, however, the thermal conductivity values of pigeon pea seeds generated in this work are useful and can be applied to the design and analysis of the numerous machines and processes that involve heat treatment.

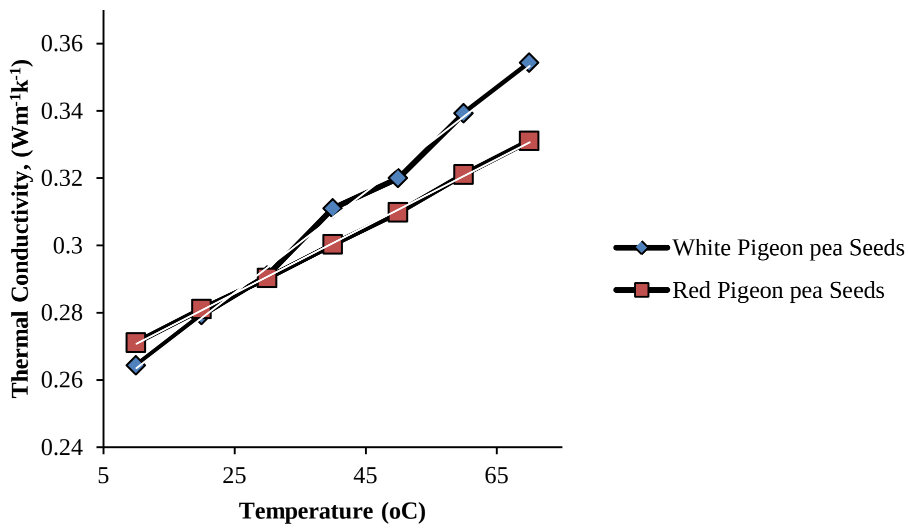

Figure 3 Thermal conductivity as a function of temperature

The linear relationship existing between thermal conductivity and white and red pigeon pea seeds and temperature (^oC) can be expressed using Equations 12 and 13 respectively.

$$k_{wps} = 0.0015T + 0.2486 \qquad (R^2 = 0.9957) \qquad (12)$$

$$k_{rps} = 0.0010T + 0.2608 \qquad (R^2 = 0.9994) \qquad (13)$$

where: k_{wps} and k_{rps} are thermal conductivity of white and red pigeon pea seeds, respectively (W $m^{-1}K^{-1}$), and T is temperature (K). The thermal conductivity of white pigeon pea seeds was found to be higher than that of the red pigeon pea seeds.

3.3 Activation energy

The minimum energy provided to the system to start a chemical reaction is called activation energy. The effect of thermal conductivity on activation energy was calculated by Arrhenius-type (Equation 6). By plotting the thermal conductivity data as ln(k) versus 1/T, (Figure 4) the slope of the resulting line for each temperature value multiplied by R was determined to equal the activation energy (E_a).

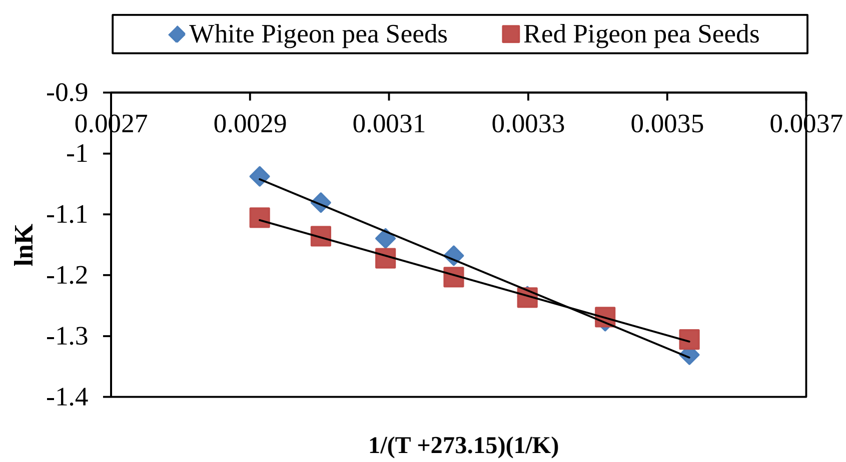

Figure 4 Effect of temperature on the thermal conductivity for white and red pigeon pea seeds

The sensitivity of the white and red pigeon pea seeds as influenced by temperature can be understood through activation energy. The activation energy value (Figure 4) was found to be 3.93 KJ mol^{-1} for the white pigeon pea seeds which is higher than the activation energy of 2.68 (KJ mol^{-1}) for red pigeon pea seeds. This reported result indicates that the white pigeon pea seed was more sensitive to the temperature changes.

In view of the temperature sensitivity of the thermal conductivity for these pigeon pea seeds, Equations 14 and 15 shows the effect of temperature on thermal conductivities of white and red pigeon pea seeds respectively, with following coefficient:

$$k_{wps} = 1.4000\exp\left(-\frac{473.21}{R(T+273.15)}\right)$$

$$R^2 = 0.9952;\ RMSE = 0.0674 \qquad (14)$$

$$k_{\mathrm{rps}} = 0.8448\exp\left(-\frac{322.88}{R(T+273.15)}\right)$$

$$R^2 = 0.9998;\ RMSE = 0.0633 \qquad (15)$$

The predictive equation revealed high R^2 values (0.9952 – 0.9998) indicating that the incorporation of the thermal conductivity into the Arrhenius model is appropriate for describing the activation energy of white and red pigeon pea seeds. Using the percentage root mean square of error (percent RMS), which was found to be generally low (< 10 percent), the suitability of Equation 6 for predictive purposes was checked. Low percentages of RMS values indicate a good fit and suitability of a model for practical purposes, according to Wang and Brennan (1991).

4 Conclusions

Investigations on the thermal conductivity of white and red pigeon pea seeds revealed the following:

1. Thermal conductivity of pigeon pea seeds was significantly affected by moisture content, and temperature. Thermal conductivity of white and red pigeon pea seeds increased significantly ($p<0.05$) from 0.2387 to 0.3497 $Wm^{-1}K^{-1}$, and from 0.2375 to 0.3425 $Wm^{-1}K^{-1}$ respectively with increasing moisture content from 5% to 35% w.b. A linear relationship was found to exist between thermal conductivity and moisture content.

2. The thermal conductivity of white and red pigeon pea seeds increased significantly ($p<0.05$) from 0.2643 to 0.3543 $Wm^{-1}K^{-1}$, and from 0.2711 to 0.3311 $Wm^{-1}K^{-1}$ respectively as temperature increased from 10 ^{o}C - 70 ^{o}C. A linear regression best describes the relationship between thermal conductivity and temperature.

3. The thermal conductivity of white pigeon pea seeds was higher than that of red pigeon pea seeds. The thermal conductivity of pigeon pea seeds was not significantly ($p>0.05$) affected by cultivar.

4. The Arrhenius type equation was used to study the temperature dependence with an activation energy of 3.93 and 2.68 KJ mol^{-1} for white and red pigeon pea seeds respectively.

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