SPECIFIC HEAT CAPACITY OF LENTIL SEEDS BY DIFFERENTIAL SCANNING CALORIMETRY

J. Tang, STUDENT MEMBER ASAE
S. Sokhansanj, MEMBER ASAE
S. Yannacopoulos,
S. O. Kasap

ABSTRACT

Differential scanning calorimetry (DSC) was used to determine the specific heat of lentil seed. Accurate measurement with this method requires a good seal condition of the sample pan and relatively thin sample specimen. The value of specific heat of lentil seeds ranged from 0.81 to 2.2 kJ/kgK. Specific heat increased quadratically with moisture content over the range from 2.1% to 25.8% (w.b.) and linearly with temperature varying from 10° C to 80° C. The classical compartment model was modified to accommodate the variation of specific heat with temperature and moisture content.

KEYWORDS. Specific heat, Physical properties, Differential scanning calorimetry, Lentils.

INTRODUCTION

Grain lentil (*Lens culinaris, Medik*) is a legume crop with a protein content of 28%. Laird lentil, the most popular lentil variety in Canada, is lens-shaped about 7 mm in diameter and 3 mm in thickness. Lentil seed is a dicotyledon consisting of three major components: cotyledons 90%, seed coat 8%, and embryo 2%, of the total weight (Singh et al., 1968).

Mechanized production of lentil in North America and the inherent indeterminate growth habit of the plant require the seeds to be dried artificially during the harvest season. Rigorous research toward a better understanding of drying and storage of the crop demands a knowledge of thermal properties including the specific heat of the grain. Values of specific heat have been determined for many grains. Only one value of specific heat (1.84 kJ/kgK) was listed for lentil seed at 12% moisture content (Ordinanz, 1946).

The objective of the present study was to determine the specific heat of Laird lentil seed as affected by moisture content and temperature, using differential scanning calorimetry.

LITERATURE REVIEW

Moisture content in agricultural products has profound effect on the specific heat due to relatively high specific heat of water and heat of sorption. Specific heat is often expressed as a function of moisture content using linear relations (Mohsenin, 1980).

Temperature also has an effect on the specific heat of organic material though this has been generally ignored in the early work with grains. Muir and Viravanichai (1972) observed that specific heat of wheat increased almost linearly with temperatures of - 30° C to 20° C for a seed moisture content up to 20% (w.b.). Suter (1972) related the specific heat of peanuts to temperature in linear and second order polynomial relations. Similar relationships were observed by Dutta et al. (1988).

The method of mixture has been the most common method reported in the literature for the measurement of specific heat of biological materials (Mohsenin, 1980). Although this technique is direct, the accuracy of the measurement is questionable. The heat of hydration released when the material absorbs moisture from the calorimeter water can introduce errors in the measurements (Sharma and Thompson, 1973). Babbit (1945) found the heat of hydration evolved during the measurement was inversely related to the initial grain moisture content. Heat loss from mixture during calorimetry has been another concern (Mohsenin, 1980). The effect of temperature on specific heat is also difficult to observe with the method of mixture.

The dynamic feature of differential scanning calorimetry (DSC) allows the determination of specific heat as a function of temperature. McMillin (1969) and Koch (1969) employed DSC to determine the specific heat of wood and dry tree bark, respectively. In both cases, the specific heat were observed to increase with temperature. Chakrabarti and Johnson (1972) used DSC and observed an increase in specific heat of tobacco up to 16% with an increase in temperature from 40° C to 70° C. Using DSC, Murata et al. (1987) determined the specific heat of eight cereal grains over a temperature range of 10° C to 70° C and a moisture content range of 0% to 35% (w.b.). The specific heats were related linearly to moisture content and quadratically to temperature.

MATERIAL AND METHOD

Specific heat of Laird lentil seeds at seven moisture contents 2.1%, 7.3%, 10.8%, 15.7%, 18.0%, 19.5%, and 25.8% (w.b.) were determined using differential scanning calorimetry (DSC) over a temperature range from 10° C to 80° C. The tests were carried out in a randomized order with six replicates at each moisture content.

SAMPLE PREPARATION

Lentil samples at 10.8%, 15.7%, 18.0%, and 19.5% moisture contents (w.b.) were obtained from a field in the

Article was submitted for publication in July 1990; reviewed and approved for publication by the Food and Process Engineering Div. of ASAE in November 1990.

The authors are **J. Tang**, Graduate Student, and **S. Sokhansanj**, Professor, Dept. of Agricultural Engineering, **S. Yannacopoulos**, Associate Professor, Dept. of Mechanical Engineering, and **S. O. Kasap**, Associate Professor, Dept. of Electrical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

vicinity of Saskatoon during the 1989 harvest season. The hand-harvested samples were stored in air-tight containers at 4° C for six months prior to the tests. A sample with moisture content of 25.8% was prepared by spraying a predetermined amount of distilled water on 100 g of seeds from the sample lot of 19.5% moisture content. About 100 g of seeds from the 10.8% moisture content lot was dried in a thin layer dryer at 40° C and 10% relative humidity to obtain a sample with 7.3% moisture content. Another 100 g of seeds from the same lot was dried in an air-oven at 70° C to a moisture content of 2.1%. These samples were kept in air-tight containers at 4° C for two weeks before measurements.

To determine the moisture content of the samples, eight seeds from each moisture content were dried in a convection oven at 130° C for 20 h. Moisture content was determined from the moisture loss in individual seeds using an analytical balance (± 0.01 mg). The standard deviation of the moisture content of the individual seeds varied from 0.26 to 0.35% moisture content.

DSC Measurement Technique

The measurement of specific heat was carried out using a Mettler TA 3000 (Mettler Instrumente AG, Switzerland) which consisted of Model TC10 thermal analyzer and DSC30 cell. Before tests, the equipment was calibrated according to the manufacturer's specification.

For specific heat measurements, the instrument raises the temperature of the sample in the DSC cell at a constant heating rate. The heat flow rate into the sample of a known mass is measured and the specific heat of the sample is determined according to the following equation (Widmann and Riesen, 1987):

$$C = \frac{dQ / dt}{m\, dT / dt} \qquad (1)$$

where C is specific heat (J/gK), dQ/dt is the heat flow rate (J/s), dT/dt is the heating rate (K/s), and m is the mass of the sample (g). To obtain high precision, the measured values of heat flux were referred to a baseline determined with an empty standard sample pan covered with pierced lid.

Prior to tests, about 40 seeds were picked randomly from each lot at the seven moisture contents and conditioned in sealed 10 mL vials at room temperature for 24 h. To prepare the seed for test, a kernel was cut into a thin disk along the major axis and weighed with a micro balance to 0.001 mg. This disk was placed in an aluminium sample crucible (5.5 mm diam × 1.4 mm deep) which was covered with an aluminium lid and sealed. The lid was then pressed down to ensure contact between the sample and the container.

Determination of Sample Size and Heating Rate

The measurement of specific heat with DSC is based on the assumption that during test the temperature is uniform in the sample and the sample container. However, due to low thermal diffusivity of biological materials, thermal lag within the sample may introduce error in the measured value of specific heat. Theoretical estimation of the temperature distribution in the sample during measurement with DSC could provide an insight into the physical process and help to reduce errors in measurements.

The temperature distribution in a thin disk sample with a thickness 2L may be simplified as one dimensional problem and the governing equation can be expressed by:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} . \qquad (2)$$

where α is the thermal diffusivity of the sample. The initial condition is:

$$T = T_i \qquad \text{at} \quad t = 0 \quad \text{for} \quad -L < x < L \qquad (3)$$

Assuming a perfect contact between the sample and container, the boundary conditions are:

$$T = \beta t + T_i \qquad \text{for} \quad t > 0$$
$$\text{at} \quad x = -L \quad \text{and} \quad x = L \qquad (4)$$

where β is the heating rate. A series solution to the above equations is given by Carslaw and Jaeger (1959):

$$T = \frac{\beta (x^2 - L^2)}{2\alpha} + \frac{16\beta L^2}{\alpha \pi^3} \sum_0^{\infty} \frac{(-1)^n}{(2n+1)^3} \exp\left[\frac{-\alpha (2n+1)^2 \pi^2 t}{4L^2}\right] \cos\frac{(2n+1)\pi x}{2L} + \beta t + T_i$$

The temperature distribution in a thin sample of 18% moisture content was obtained from the above equation for the six combinations of the following two variables:

sample thickness : 2L = 2.4 mm, 1.6 mm, and 0.8 mm

heating rate : β = 5 K/min, 10 K/min, and 15 K/min.

The other thermal and physical property values used in equation 5 were: k = 0.125 W/mK (Zuritz et al., 1989 for kidney bean), ρ = 1360 kg/m^3 (Tang et al., 1990), C = 1.84 kJ/kgK (Ordinanz, 1946). The series solution of equation 5 was truncated at n = 100, and temperature was raised from 10° C to 90° C. The computed temperature as shown by a typical example in figure 1 revealed that at the beginning of the heating the temperature at the sample center started to lag behind the temperature rise at the surface. within less than 20 s, the value of this difference approached constant value which varied from 0.13° C to 3.53° C for the conditions listed in Table 1. The differences increased linearly with heating rate, and quadratically with the sample thickness as has been further proven analytically in the appendix.

The effect of sample thickness on the measurement of specific heat was also investigated experimentally. The results obtained for sample thicknesses of 0.8 mm and 2.4 mm and with heating rate of 5 K/min are presented in figure 2. The values for specific heat of the 2.4 mm thick samples were about 0.25 kJ/kgK less than that of 0.8 mm

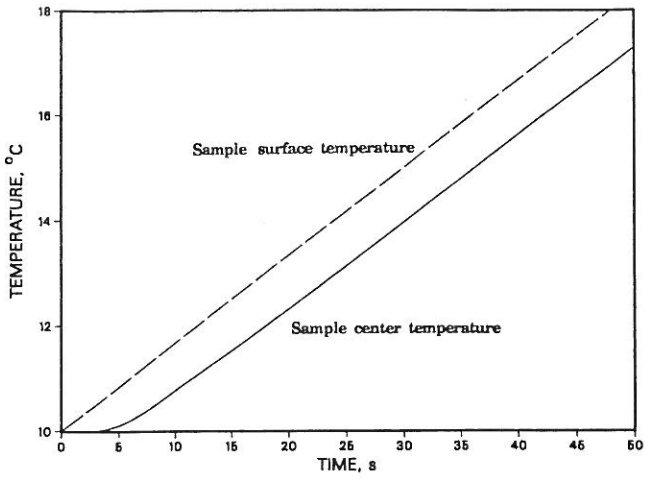

Figure 1–The variation of temperatures at the sample surface and at the sample center for the heating rate of 10 K/min and sample thickness of 1.6 mm. Dashed line stands for surface temperature and solid curve for centre temperature.

samples. Assuming a linear relationship between specific heat and temperature, the error in specific heat measurement also increased linearly with temperature difference between the surface and center temperature of the sample. Therefore, from the difference in the specific heat results for 0.8 mm and 2.4 mm thick samples and the temperature differences listed in Table 1, the measurement error of specific heat of the 0.8 mm sample at 5 K/min heating rate is about 0.03 kJ/kgK.

Thus, to reduce the measurement error and at the same time maintain a reasonable signal to noise ratio, the scanning speed and sample thickness for the specific heat determination were chosen to be 5 K/min and less than 0.8 mm, respectively.

Effect of Sample Seal Condition

Moisture in biological materials is in the form of free and bound water within cell walls and in intercellular spaces. Temperature rise during a DSC test increases vapour pressure within the sample and, as a result, moisture may escape from the material in the form of water vapour. The latent heat absorbed in the process may introduce error in the measurement.

Trial tests were carried out to investigate the effect of

TABLE 1. Theoretical temperature difference between the surface and the center of a sample

Sample thickness (mm)	Heating rate (K/min)	Temperature difference (° C)
0.8	10	0.26
	15	0.39
1.6	5	0.52
	10	1.05
	15	1.57
2.4	5	1.18
	10	2.36
	15	3.53

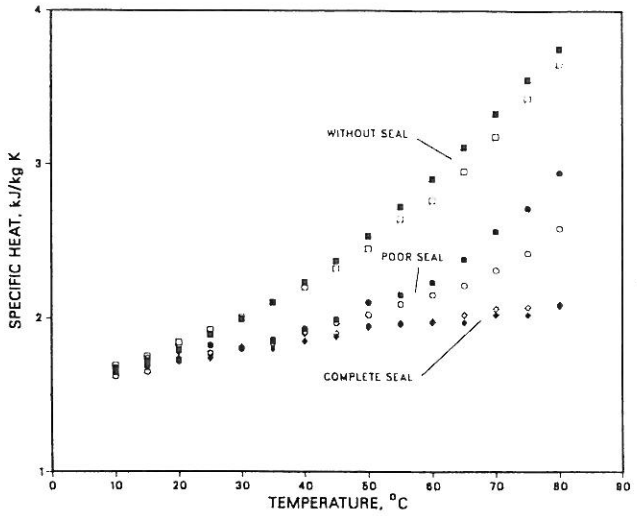

Figure 2–Effect of sample thickness on the measurement of specific heat.

seal condition of sample pan on the measured specific heat. Three types of seal conditions were prepared: complete seal where there was no moisture escape from the sample pan; poor seal where sample pan was not properly sealed but with no visible openings; and no seal where the lid of the sample pan was pierced with three holes. Tests were conducted on the 18.0% moisture content sample (0.8 mm thick) with a heating rate of 5 K/min.

The measured values of specific heat as presented in figure 3 revealed that seal condition had a significant effect on the results. Poor seal resulted in high values of specific heat, especially at elevated temperatures. The magnitude of the deviations from that of completely sealed samples depended on the degree of the seal of the sample pan and the amount of moisture escaped from the sample. The weight check of the samples after each run indicated that the moisture loss from the improperly sealed samples were up to 30% of the total initial moisture content of the samples. In these cases, 20% to 40% of the heat flow into the sample was used for moisture evaporation. Therefore,

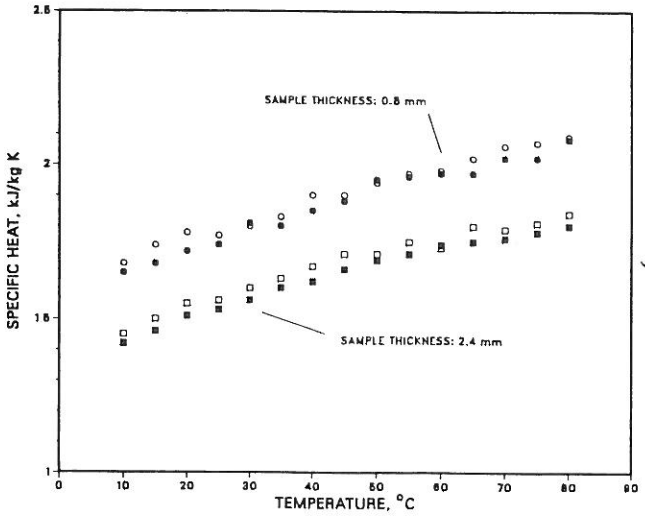

Figure 3–Effect of seal conditions on the measurement of specific heat of lentil seeds.

care was taken in completely sealing the sample pans for the following tests, and the weight of samples was checked after each run. Measurement results were discarded whenever a weight loss was detected.

Results and Discussion

Table 2 lists the measured specific heat of Laird lentil seeds at seven moisture content levels, together with the values of specific heat of distilled water obtained with the same procedure. The standard deviation among the six replicates for all the moisture levels was less than 0.05 kJ/kgK, a part of which has been due to the variation of moisture content of individual seeds (from 0.26% to 0.35% w.b.). The measured values of distilled water were almost constant over the test temperature range, and the values were within 3% of those in literature.

Effect of Temperature and Moisture Content

The value of specific heat of lentil varied from 0.80 to 2.19 kJ/kgK in the ranges of moisture content and temperature used in this study. In general, the specific heat increased with temperature almost linearly as shown in figure 4. An unusual broad peak in the specific heat vs temperature was observed with the lentil seeds at 10.8% moisture content. This peak appeared consistently in all six replicates at this moisture content and when temperature reached about 60° C. Similar peaks were also observed with samples from another lot of lentil at 10.3% moisture content. Further investigation is needed to explain this peak.

The specific heat of lentil seeds also increased with moisture content but not linearly as was observed by other researchers (Dutta et al., 1988; Murata et al., 1987, Mohsenin, 1980). The increase at low moisture content was more rapid than that at higher moisture content. A similar trend was also observed by Chakrabarti and Johnson (1972) with tobacco. Analysis of variances indicated that the interaction between the temperature and moisture content was not significant at the 5% level.

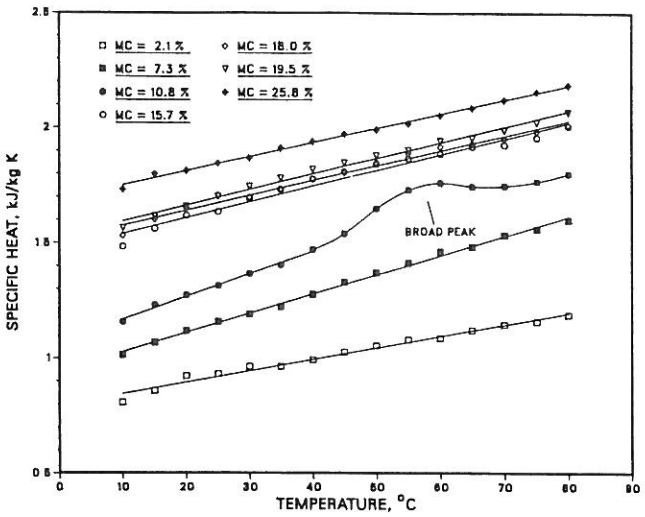

Figure 4–Effect of temperature on specific heat of lentil seeds at seven moisture contents, average of six replicates.

Data Reduction

As early as 1892, Siebel (Mohsenin, 1980) estimated the specific heat of products from the specific heat of the dry matter, C_d, and that of water, C_m, using:

$$C = (C_m - C_d)\, M_w + C_d \quad (6)$$

TABLE 2. Measurement values of specific heat of Laird lentil and distilled water

Temp. (° C)	Specific heat of lentil* (kJ/kgK) Moisture content, w.b. (%) 2.1	7.3	10.8	15.7	18.0	19.5	25.8	Distilled water†
10	0.807	1.013	1.157	1.483	1.530	1.560	1.730	4.19
15	0.857	1.067	1.230	1.560	1.602	1.615	1.798	4.15
20	0.922	1.117	1.272	1.617	1.650	1.657	1.812	4.13
25	0.930	1.157	1.312	1.633	1.697	1.700	1.844	4.18
30	0.963	1.190	1.365	1.692	1.710	1.743	1.868	4.15
35	0.963	1.222	1.403	1.730	1.733	1.780	1.912	4.17
40	0.992	1.275	1.470	1.775	1.775	1.818	1.940	4.15
45	1.025	1.328	1.538	1.803	1.807	1.847	1.972	4.15
50	1.053	1.370	1.648	1.840	1.848	1.880	1.992	4.13
55	1.080	1.413	1.728	1.865	1.890	1.903	2.018	4.15
60	1.087	1.462	1.758	1.885	1.917	1.943	2.054	4.14
65	1.120	1.482	1.742	1.921	1.930	1.955	2.086	4.12
70	1.145	1.532	1.745	1.925	1.952	1.990	2.122	4.18
75	1.158	1.558	1.763	1.957	1.983	2.023	2.156	4.12
80	1.187	1.597	1.797	2.007	2.012	2.068	2.186	4.13

* Average of six replicates; standard deviation less than 0.05.
† Average of three replicates; overall standard deviation less than 0.04; sample weight from 3 to 7 mg.

C_m (kJ/kgK) and C_d (kJ/kgK) in the above equation were considered to be constant (Mohsenin, 1980). M_w (decimal) in equation 6 is moisture content on wet basis.

GLM procedure in Statistic Analysis System (SAS, Barr et al., 1979) was employed to relate measured values of specific heat to moisture content using the following expression:

$$C = 1.03 + 4.08 \quad M_w$$
$$(r^2 = 0.71, \ C.V. = 11.8\%) \qquad (7)$$

Equation 7 can be rearranged to form equation 6 with the results that C_m = 5.11 kJ/kgK and C_d = 1.03 kJ/kgK. It is interesting to note that C_m had a higher value than that of pure water. This may indicate that more energy is needed to raise the temperature of bound water than of pure water. Nevertheless, relatively low r^2 and high C.V. indicate that equation 6 does not represent the values of specific heat adequately. Mohsenin (1980) pointed out that although equation 6 provided a reasonable estimate of specific heat for materials of high moisture content, it failed to provide sufficient accuracy for specific heat of low moisture content materials. One of the drawbacks of equation 6 may lie in the assumption that C_m does not depend on moisture content in grain.

Equation 6 can be rearranged into the following expression:

$$C(1 + M) = C_d + C_m M \qquad (8)$$

Where M is moisture content in decimal on dry basis. Equation 8 was fit to the experimental data using GLM procedure in SAS. The parameters C_m and C_d were estimated as functions of temperature and moisture content:

$$C_d = 0.493 + 0.0083 T \qquad (9)$$
$$C_m = 8.165 - 10.24 \ln (M + 1) \qquad (10)$$

where 10° C ≤ T ≤ 80° C, and 0.02 ≤ M 0.35.

With the above expressions, equation 6 explains 98% (r^2 = 0.98) of the variation in the experimental data with a C.V. value of 3.4%. As indicated in equation 10, the specific heat of moisture in the seed C_m increases with decrease in the moisture content. This may result from the presence of bound water, the percentage of which increases with a decrease in the total moisture in the seed.

While equation 6 together with equations 9 and 10 bear some physical significance, a more straight forward relationship was developed in form of a second order polynomial equation:

$$C = 0.5773 + 0.00709 T + (6.22 - 9.14 M) M$$
$$(r^2 = 0.98, C.V. = 3.0\%) \qquad (11)$$

where 10° C ≤ T ≤ 80° C, and 0.02 ≤ M ≤ 0.35.

The low C.V. value indicates that equation 11 provides a better presentation of the experimental data than equation 7.

CONCLUSIONS

Accurate measurement with DSC requires a good seal condition of the sample pan and relatively thin sample specimen. Specific heat of lentil seeds ranged from 0.8 to 2.2 kJ/kgK, varying linearly with temperature and quadratically with moisture content. An empirical model representing the variation due to temperature and moisture content was developed with a r^2 value of 0.98.

SYMBOLS

- C = sample specific heat, kJ/kg K
- k = sample thermal conductivity, W/m K
- L = half of the sample thickness, mm
- m = mass of the sample, g
- M = moisture content on dry basis, decimal
- M_w = moisture content on wet basis, decimal
- t = time, s
- T = temperature, ° C
- T_i = initial scanning temperature, ° C
- α = k/ρC, thermal diffusivity, m^2/s
- β = heating rate, K/min
- ρ = sample density, kg/m^3
- C.V. = coefficient of variation

APPENDIX

From equation 5, the temperature at the sample center, T_c is:

$$T_c = T_{x=0} = \frac{\beta(-L^2)}{2\alpha} + \frac{16\beta L^2}{\alpha\pi^3} \sum_0^\infty \frac{(-1)^n}{(2n+1)^3} \exp\left[\frac{-\alpha(2n+1)^2\pi^2 t}{4L^2}\right] + \beta t + T_i \qquad (12)$$

Thus, the difference between the temperature at the sample surface and that in the sample center is:

$$\Delta T = T_s - T_c = \frac{\beta(L^2)}{2\alpha}\left\{1 - \frac{32}{\pi^3} \sum_0^\infty \frac{(-1)^n}{(2n+1)^3} \exp\left[\frac{-\alpha(2n+1)^2\pi^2 t}{4L^2}\right]\right\} \qquad (13)$$

where T_s represents sample surface temperature and is given by equation 4. From equation 13 the temperature difference between the center and surface temperatures increases linearly with the heating rate, β, and quadratically with the sample thickness L.

ACKNOWLEDGMENT. This research was supported by grants to S. Sokhansanj in part by the Saskatchewan Pulse Crop Development Board and by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

Babbit, J.D. 1945. The thermal properties of wheat in bulk. *Canadian Journal of Research* F23:388-401.

Barr, J., J.H. Goodnight, J.P. Sall and J.T. Helwig. 1979. A user's guide to SAS, SAS Institute Inc., Raleigh, NC.

Carslaw, H.S. and J.C. Jaeger. 1959. *Conduction of Heat in Solids*. Oxford: Oxford University Press.

Chakrabarti, S.M. and W.H. Johnson. 1972. Specific heat of flue-cured tobacco by differential scanning calorimetry. *Transactions of the ASAE* 15(5):928-931.

Dutta, S.K., V.K. Nema and R.K. Bhardwaj. 1988. Thermal properties of gram. *J. Agric. Engng. Res.* 39:269-275.

Koch, P. 1969. Specific heat of oven dry spruce, pine wood and bark. *Wood Science* 1(4):203-214.

McMillin, C.W. 1969. Specific heat of oven dry loblolly pine wood. *Wood Science* 2(2):107-111.

Mohsenin, N.N. 1980. *Thermal Properties of Foods and Agricultural Materials*. New York: Gordon and Breach, Scientific Publishers, Inc.

Muir, W.E. and S. Viravanichai. 1972. Specific heat of wheat. *J. Agric. Engng. Res.* 1:338-342.

Murata, S., A. Tagawa and S. Ishibashi. 1987. The effect of moisture content and temperature on specific heat of cereal grains measured by DSC. *J. of the Japanese Society of Agricultural Machinery* 46(6):547-554.

Ordinanz, W.O. 1946. Specific heat of food in cooking. *Food Industries* 18(2):101.

Sharma, D.K. and T.L. Thompson. 1973. Specific heat and thermal conductivity of sorghum. *Transactions of the ASAE* 16(1):114-117.

Singh, S., H.D. Singh and K.C. Sikka. 1968. Distribution of nutrients in the anatomical parts of common indian pulses. *Cereal Chem.* 45:13.

Suter, D. 1972. Heat of respiration and specific heat of peanuts. Ph.D. thesis, Oklahoma State University, Stillwater.

Tang, J., S. Sokhansanj and F. Sosulski. 1990. Effect of swathing and moisture content on seed properties of lentils. *Can. J. Plant Science* 70:1173-1178.

Widmann, G., and R. Riesen. 1987. *Thermal Analysis: Terms, Methods, and Applications*. Heidelberg, Germany: Dr. Alfred Huthig, Verlag GmbH.

Zuritz, C.A., S.K. Sastry, S.C. McCoy, E.G. Murakami and J.L. Blaisdell. 1989. A modified Fitch device for measuring the thermal conductivity of small food particles. *Transactions of the ASAE* 32(2):711-718.