Specific Heats of Cottonseed and Its Co-products

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ABSTRACT: Most of the annual crop of cotton is harvested and stored for the entire crushing season until the new crop year begins. It is desirable to have specific heat data of agricultural materials so the engineer can manage the heat transfer problem associated with each crop during storage. Thermal properties of agricultural products, such as cottonseed and its oil mill co-products, are not commonly available. Partially because these materials are bulky and lack uniformity, their thermal properties are difficult to assess precisely. The highly sensitive and large-sample volume differential scanning calorimeter has made the precise determination of specific heat of agricultural material possible. This report describes a procedure used to obtain the specific heat of white cottonseed and its co-products as a function of temperature. The materials tested included cotton fiber, whole cottonseed, linters, hulls, meats, and meal. Specific heat values of these materials ranged from 0.32 to 0.6 cal/g/°C at 30°C and 0.42 to 0.72 cal/g/°C at 90°C. When these materials were dried, the values converged to 0.24 to 0.33 cal/g/°C at 30°C.

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KEY WORDS: Cotton, delinted cottonseed or black seed, DSC, hulls, kernels, linters, meal, specific heat, white cottonseed.

Cottonseed, a by-product of cotton fiber production, had an average annual production of 33 million metric tons (MMT) worldwide and 6.8 MMT in the United States for the 2000/2001 season (1). After harvesting, the seed is separated from the cotton fiber at a cotton gin. Most of the seed is stored after the cotton fiber is ginned. Owing to its unique seed structure, with a layer of linters (fuzzy fibers <0.33 mm long) that remain on the seed surface after ginning, seed quality is difficult to maintain (2–4). The seed temperature tends to rise with storage time, and its crucial quality marker, FFA content in the seed, also rises with the storage temperature and time. To allow the engineer to estimate the proper air flow to keep the seed dry and cool or to develop innovative means to cool the seed, a precise value of specific heat (C_p, cal/g/°C) is very helpful. Heat capacities of fuzzy and starch-coated cottonseed have been measured with a bulk heat exchange principle (5). In this report, an experimental procedure was designed to measure the specific heats of white cottonseed (seed still containing linters) and cottonseed co-products derived from oil mills using a large-scale differential scanning calorimeter (DSC) over a wide range of temperatures. The materials tested include cotton fiber, whole white cottonseed (white seed), linters, delinted seed (black seed), hulls, meats, crude oil, and meal.

MATERIALS AND METHODS

Samples of whole white cottonseed, delinted seed, meats or kernels, hulls (containing broken kernels), and linters were obtained from a screw press cottonseed mill in Elgin, Texas. Glandless cottonseed was supplied by a company in California and processed into meal and oil by the pilot plant at the Food Protein R&D Center, Texas A&M University (College Station, TX). Cotton fibers, both long and short, were provided by the cotton research group in the Southern Regional Research Center (SRRC), ARS, USDA (New Orleans, LA). Moisture contents of these materials were determined with a forced-air oven (Gallenkamp Oven 300 Plus Series, Loughborough, England) at 110°C by drying to a constant weight.

The specific heats of mill-run cottonseed components were determined with a Hart Scientific model 4100 DSC (Hart Scientific, Provo, UT). The calorimeter was equipped with four cylindrical 1-mL Hasteloy screw-top ampoules lined with gaskets that provided a hermetic seal. Only two of the ampoules were used for the specific heat determinations.

Each sample was first scanned in cell #1, with ampoule #4 in the reference cell being empty. The sample was then scanned in ampoule #4 in the reference cell, with ampoule #1 in sample cell #1 being empty. The absolute values of the two runs were calculated to obtain specific heat in cal/g/°C. The absolute values of the two thermograms obtained from the two scans were then added and divided by two to obtain the final curve of C_p vs. temperature. This method corrected for any difference between the sample cell and the reference cell.

Specific heats were determined for cottonseed component samples obtained from the mill that were stored at ambient conditions and for dried samples that were brought to constant weight by drying them in an oven set at 110°C. The samples were weighed directly into the ampoule; the sample weights varied from 0.3 to 0.85 g, depending on the compressibility of the component. The cottonseed linters and fibers were the most difficult to pack owing to their resilience.

The samples were heated from 0 to 100°C, cooled to 0°C, and then reheated and cooled two more times in the same manner. The heating and cooling rate was 60°C/h or 1°C/min with a heat flow measurement every 10 s. A few samples exhibited small melting peaks around 60°C during the first heating, probably due to melting of trace amounts of solidified fats in seed materials or waxes on the cotton fibers; therefore, the

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second heating was always used for the specific heat calculation. The second and third heating curves were always superimposible. This verified that no sample loss had occurred during the repeated heatings and coolings. In most cases all three heating curves were superimposible. It takes the instrument about 20°C from the starting temperature to acquire a steady baseline and reproducible thermograms. The equations for C_p as a function of temperature for all materials tested were calculated from the final heating curves. Calibration of the DSC was checked with pure water for melting temperature and enthalpy of ice melting.

RESULTS AND DISCUSSION

All samples were analyzed with the DSC on both an as-is and a dry basis. The moisture contents of the samples were 7.72, 8.04, 6.36, 10.53, 5.90, 8.19, 6.51, and 10.18% (by weight) for the white seed, black seed, kernels, hulls, linters, long and short cotton fibers, and glandless cottonseed meal, respectively. The values of C_p for the cotton fibers and mill-run materials are presented in Figure 1. As with most materials, C_p values of all the samples increased slightly with temperature. For comparison, the C_p of deionized water was also measured with DSC and is displayed along with values for the cotton and samples of cottonseed and its co-products. C_p vs. temperature lines for all samples were generally parallel to one another, with kernels having the highest C_p between 30 and 95°C, followed by white seed, black seed, hulls, short cotton, linters, and long cotton. C_p vs. temperature lines for hulls, short cotton, linters, and long cotton were closely packed but still distinctly differentiated from each other. The C_p of crude cottonseed oil has a smaller slope with increasing temperature than most of the solid samples tested.

When all the materials were dried, the separation of the C_p vs. temperature lines was drastically reduced, as shown in Figure 2. Apparently, the presence of moisture had a more pronounced influence on the C_p values of kernels, white cottonseed, and delinted seed than on the other materials being examined. Except for long and short cotton fiber and mill-run linters, drying also reduced the slopes of the C_p vs. temperature curves. However, the calculated C_p at a given temperature derived from C_p of the dry material at the same temperature plus the C_p contributed by the amount of moisture present in the original material did not match those values determined directly by DSC. The calculated C_p values were consistently lower than those measured directly. This difference may be explained by the hydrogen bonding between water and cellulose or protein and other seed materials (6).

The initial heating curve of a sample generally exhibits several endothermic peaks that are related to either melting of fats or waxes or protein denaturation by heat. None of these endothermic peaks was reversible under the test condition, making the assessment of C_p difficult. Therefore, the initial heating thermograms of the samples were ignored and not characterized for this work. Only the second-round heating curve was used to assess the heat capacity. With the recommended procedure for C_p measurement, one has to assume that the initial heating will not drastically alter the heat capacity properties of the cottonseed materials. However, one should remember that during heating or cooling of an agricultural material, there is always the possibility of fat melting or protein denaturation during the heating cycle and fat crystallization during the cooling cycle. These latent heats should not be neglected in any heat exchange computation.

In general, the values of C_p for cottonseed (5), cotton fiber (6), and cottonseed oil (7,8) determined by this work checked
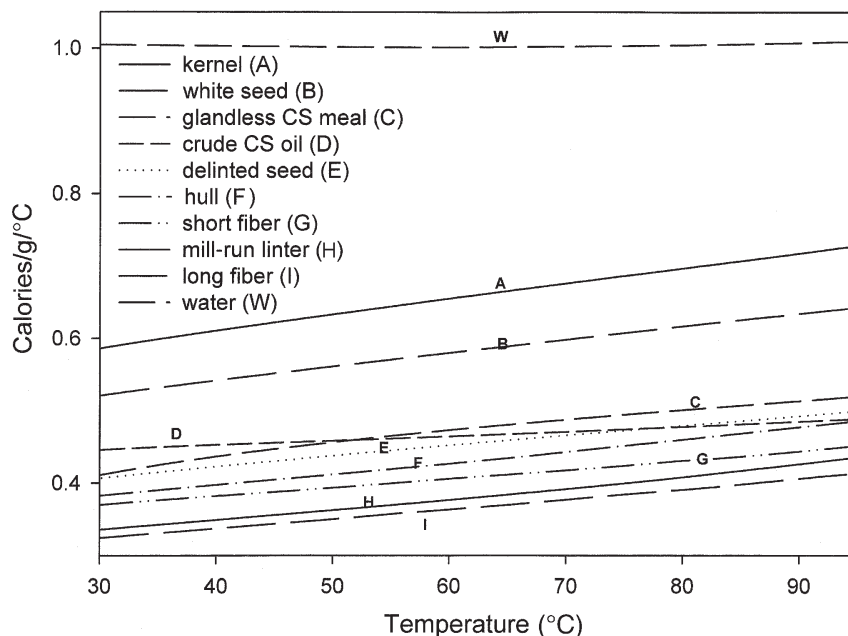

FIG. 1. Specific heats vs. temperature for water, cotton fiber, cottonseed (CS), and its co-products.
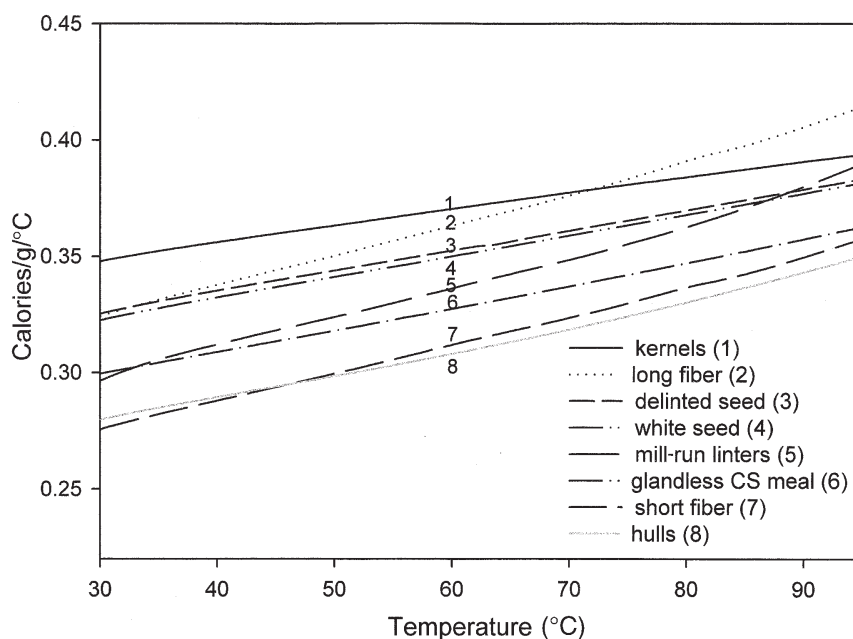
FIG. 2. Specific heats vs. temperature for oven-dried cotton fiber, cottonseed, and its co-products.

TABLE 1
Intercepts and Slopes of C_p vs. Temperature Between 30 and 95°C
Determined by Using a Large-Scale Differential Scanning Calorimeter
for Cottonseed and Its Co-products, Both As-is and Dry Basis

Material	Moisture (wt%)	As-is moisture basis		Dry basis	
		Intercept (cal/g/°C)	Slope × 10^3 (cal/g/°C²)	Intercept (cal/g/°C)	Slope × 10^3 (cal/g/°C²)
Deionized water	100	1.005	0.002		
Kernels	6.36	0.520	2.215	0.326	0.727
White seed	7.72	0.463	1.921	0.295	0.911
Delinted seed	8.04	0.363	1.456	0.299	0.892
Hulls	10.53	0.336	1.550	0.250	1.009
Short cotton	6.51	0.333	1.223	0.239	1.223
Mill-run linters	5.90	0.292	1.448	0.257	1.325
Long cotton	8.19	0.284	1.333	0.284	1.341
Cottonseed oil (crude from expeller mill)	0.25	0.427	0.640	—	
Glandless cottonseed meal	10.18	0.357	1.798	0.271	0.954

well with published data. With the large-scale, high-sensitivity DSC, the C_p values under a wide range of temperatures for various agricultural materials can be effectively measured following the procedure described in this report. For an easy reference, the C_p values vs. temperature for all cotton and for cottonseed and its co-products tested are given in the following linear equation:

$$C_p \text{ (cal/g/°C)} = \text{intercept at 0°C} + \text{slope} \times \text{temperature (°C)}$$

between 30 and 80°C   [1]

The values of intercept and slope for each of the C_p vs. temperature lines displayed in Figures 1 and 2 were calculated and listed in Table 1. Calculated values from these equations may deviate from the actual measured values beyond the temperature range of 30 to 80°C where an obvious curvature is observed. The calculated values of C_p according to the linear equations in Table 1 are within 0.5% of the actual values measured by DSC.

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