CALORIMETRIC DETERMINATION OF THE SPECIFIC HEAT OF SOYBEANS

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Soybeans have the potential of being an important livestock feed. They give high yields and have a high protein content. However, inherent in raw soybeans is a chemical compound called a trypsin inhibitor (1) which causes indigestion and has other adverse effects on simple-stomach animals. The usual commercial method of breaking down this compound uses super-heated steam in special processing plants, although a new process using L.P. gas has been patented. However, a process that could be implemented right on the farm would save livestock producers both time and money.

One of these methods involves the use of a microwave oven. It is necessary to heat the beans to some specific internal temperature, dependent on the animal being fed. However, temperature determination is very difficult in a microwave field; thermocouples and mercury thermometers are subject to corona discharge, alcohol thermometers burst, and waxes (although they are not affected by microwaves) first go through a plastic stage and then liquify due to the heat from the beans with which they are in contact. Other solutions included switching off the microwaves and then inserting a temperature-measuring device into the beans, or, secondly, removing a number of beans and determining their bulk temperature by a calorimetric method. The first alternative required an assumption concerning the thermal resistance between the temperature-measuring device and the beans. Due to the ellipsoidal shape of the beans, it was decided that the error due to the virtually point contact between the beans and a temperature-measuring device could not be determined to any degree of precision. Hence, this alternative was set aside in preference to the second, which assumed a knowledge of the specific heat of soybeans for the particular moisture content and temperature range.

The moisture content obviously affects the specific heat because the specific heat of water is higher than that of the other materials involved. The temperature, too, has a sometimes unpredictable effect on specific heat values. For instance, the specific heat of water (2) drops from 1.00738 calories/gram/°C at 0°C to 0.99795 at 35°C and then increases to 1.00697 at 100°C. Even though these changes are small, they indicate that one can not always extrapolate specific heat values from one temperature range to another with absolute certainty. Because the authors could not find any literature pertaining to the specific heat of soybeans in the moisture content and temperature range with which they were concerned, it was decided to determine the specific heat of soybeans at the approximate moisture content at which they are commercially stored, and for a temperature range which would enable further work to be carried out in thermally treating soybeans.

EQUIPMENT AND METHOD

A Parr Bomb Calorimeter (Figure 1) was modified to take a polished aluminum can with a slip-on cover. Aluminum stirrer blades were made to fit around the aluminum can in order to mix the water in the chrome-plated water jacket of the calorimeter. Soybeans were weighed, placed in the can, and covered with a known weight of Stanolax, a paraffin-base

Figure 1. Disassembled Calorimeter

oil with a known specific heat and good thermal conductivity. The can and contents were heated in a Fisher Scientific isotemp forced-air oven for two hours or until an equilibrium temperature was reached. Due to the oil impregnating the beans to some extent, it was not possible to determine their moisture content after a test. Therefore, it was assumed that the moisture content of the beans was not affected by the two-hour heating period. Because the oil surrounded the beans throughout the heating, it was felt that this assumption was somewhat valid.

Water of known volume (1750 cubic centimeters) and temperature was placed in the calorimeter's water jacket. The heated can and contents were put into the water, the calorimeter was assembled, and the calorimeter stirrer motor started. Temperature measurements of the water in the calorimeter jacket were taken every minute until no change was observed for a period of three minutes. The temeparture rise of the water gave an indication of the heat in the beans from which their specific heat could be calculated.

In preliminary tests, attempts were made to seal the can with silicon rubber so that no water could enter the can when it was placed in the calorimeter. However, it was difficult to find a compound that would dry quickly, not deteriorate due to the heating period in the oven, withstand the pressure involved in the expansion of the air under heating and the suction produced upon cooling, and still be easy to remove. Also, no theoretical reason why the entrance of water should affect the specific heat of the soybeans could be found. Furthermore, the calibration of the calorimeter was run without sealant, so any errors induced would be largely compensated for in the calibration.

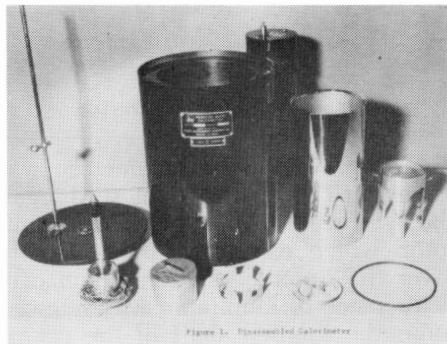The value of the specific heat was dependent on three temperatures: 1)

the temperature to which the can, Stanolax and beans were raised, 2) the initial temperature of the water in the calorimeter jacket, and 3) the ambient temperature. An error of ± one degree Centigrade in the first temperature gave an error of ±1 per cent in the specific heat. An error of ±0.1°C in the second temperature yielded an error of ±6 per cent in the specific heat, and an error of ±1°C in the third temperature resulted in an error of ±0.5 per cent in the specific heat reading. To calibrate the calorimeter, the known amount of heat was added using only Stanolax in the aluminum can. The results of the specific heat determinations will be discussed briefly along with the assumptions on which they are based.

Temperature of Can, Stanolax and Beans

It was necessary to know the temperature to which the can, Stanolax, and beans were raised in order to obtain their temperature drop and the amount of heat added by the can and the Stanolax. Temperature gradients in the oven prevented the use of the oven temperature as the true temperature.

It was necessary, therefore, to insert a thermocouple inside the can and have leads from it which were readily detachable. In short, the thermocouple leads were brought through the press-on cover. The following is a detailed description of the actual placing of the wires.

Small sockets and plugs were used at first, but the technical problems involved in securing the sockets to the can and yet insulated from it proved too difficult. A terminal bar made from pieces of tin plate was fastened onto the snap-on lid. The copper and constantan wires from the thermocouple inside the can were soldered onto separate sides of the terminal bar, insulated both from each other and from a third supporting piece of tin plate. An alligator clip was secured to the leads from the potentiometer, the copper and constantan wires being secured to and insulated from the inside of the alligator clip, one on one side and one on the other side of the clip. This was then clipped onto the terminal bar, the appropriate wires being matched.

The thermocouple was always set in the same point in the can which always contained the same depth of oil. In this way, the error due to any steady state temperature gradients that might exist in the can would be absorbed by the water equivalent, assuming that the gradients were the same in all tests. The alligator clip was left attached to the can throughout the heating period. The temperature was measured using a Honeywell potentiometer and an ice-water reference bath; thus, it was possible to read the temperature to ±0.1° Centigrade at 135° Centigrade.

The temperature of the can and contents decreased as they were moved from the oven to the calorimeter. This loss of heat has been accounted for by calibration; however, to make the time as short as possible from the oven to the calorimeter, a means had to be found of quickly attaching the rotating shaft of the calorimeter to the can. Permanent magnets gradually lost their strength due to the heat in the oven. There was insufficient space in the calorimeter shaft to put the coil for an electromagnet. A press fit tended to be too unreliable and slow. Therefore, a mechanical means (Fig. 2)
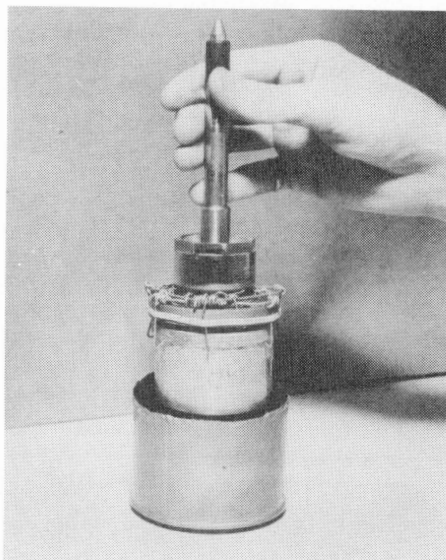

Figure 2. Quick Catch Top

which proved to be satisfactory was devised. This consisted of six hinged hooks fastened to a piece of aluminum which was made to fit loosely over the cover of the aluminum can. This piece of aluminum was screwed onto the rotating shaft of the calorimeter. The hooks were forced inward toward the center of the can by means

of an elastic band. The quick-catch top was simply pressed down over the aluminum can forcing the hooks outward so that they engaged the cover of the can as it was lifted.

Initial Water Temperature

In order to bring the water and the calorimeter to an equilibrium temperature before a test, a Fisher Laboratory stirrer was used to rapidly mix the water for at least five minutes prior to each test. The water was cooled initially 1 to 1½ degrees Centigrade below ambient. All water temperatures were measured using a Parr Calorimeter thermometer with gradations to 1/40 degree Centigrade.

Ambient Temperature

When the temperature of the water in the calorimeter was different from ambient, there was a certain loss or gain of heat due to radiation. The calorimeter bath was sealed to cut down any convection losses to the outside air. To determine the amount of heat lost or gained, three radiation loss experiments were performed, and the data was collected to yield a single radiation loss curve. To do this, water was heated above ambient and put in the calorimeter water jacket. Measurements of the temperature drop per unit time were recorded and plotted against temperature above ambient during the entire cooling time.

Since the ambient temperature in the room varied up to eight degrees Centigrade in the half-hour duration of a test, it was felt that the temperature which most affected the radiation loss of the calorimeter occurred at the point when the calorimeter was assembled. This was the last point at which the ambient air was in contact with the water bath. Thus, this was the value of ambient temperature used when evaluating the radiation loss.

Investigation of Errors

Even though the Stanolax was heated for two hours in the oven before every test, the loss of Stanolax due to evaporation was found to be negligible when the top was on the polished aluminum can. The heat input to the calorimeter by the continuous stirring in the duration of a test was found to be of no consequential magnitude. This was investigated

with the aid of a Yew wattmeter and a General Radio Strobotac. Measurements were taken of the power and speed of the stirrer motor with and without water in the calorimeter.

Not all heat from the beans and Stanolax was conducted out of the can in the half-hour test period. A plateau was reached in the calorimeter-water temperature rise; then there was a small increase of a few hundredths to a few tenths of a degree. At this point, however, the temperature of the calorimeter was 4°C above ambient, and the radiation loss was about 0.004°C per minute. Had the time period been extended, there would have been greater dependence on the radiation loss curves and less on the heat removed from the can. Hence, the tests were terminated at the first plateau on the assumption that most of the error induced in the specific heat tests was compensated for in the water equivalent determinations.

Calibration

The calibration of the equipment was accomplished using the water equivalent. The water equivalent is the amount of heat required to raise the water and calorimeter a unit temperature. In this study it is given in calories per degree Centigrade. Transition time is the term used to define the time taken to open oven doors, lift the can out of the oven, put on the stirrer blades, and place the can into the water. Several tests were made to determine the variation of water equivalent for various transition times (Fig. 3). Fifteen tests were run at the ten and fifteen second tran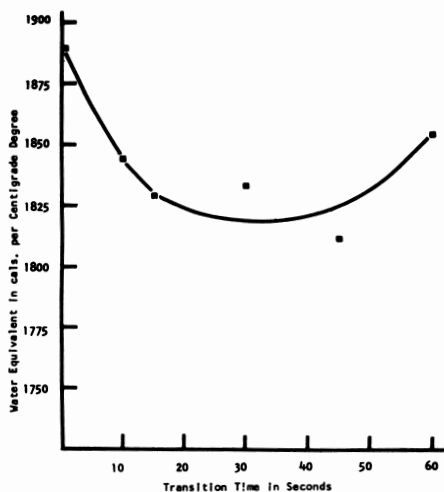sition times, and five tests at the thirty, forty-five, and sixty second transition times. The value at zero transition time is the theoretical water equivalent, calculated from the specific heats of the calorimeter's components. The curve apparently assumes a parabolic shape. This may be due to the large scatter at the short transition times. One possible explanation for the rise in the curve at low transition times is as follows.

With increasing transition time, the quantity of heat lost due to radiation is decreasing per unit time due to decreasing temperature of the can; but, as a total summed quantity, it increases. Also, it would be expected for laminar flow that the film coefficient would increase as the square root of the velocity; but the transitory time would decrease as the inverse of the velocity. Thus, more heat should be lost at lower velocities (longer transition times). This, however, assumes that the motion has no effect on the internal conduction of heat out to the surface. It can be hypothesized that at the shorter transition times the liquid contents of the can are agitated more vigorously, thus aiding in heat transfer to the outer surface of the can. Therefore, although the film coefficient does not increase in equal proportion to the transition time decrease, the vigorous motion of the can at short transition times maintains the can surface at a higher temperature than if the can were moved slowly and the contents not agitated. Hence, the heat lost at shorter transition times would be greater than at longer transition times.

ard deviation of 24.6 calories per degree Centigrade (1.4 per cent deviation).

RESULTS AND CALCULATIONS

All calculations were made on an I.B.M. digital computer. The potentiometer output was converted to temperatures using a straight line approximation for the temperature range of 110 to 120 degrees Centigrade. The specific heat of the Stanolax changed linearly with respect to temperature. Hence, the average specific heat for the temperature range used was calculated separately for each test and was employed in determining the heat input by the Stanolax. The specific heat of the polished aluminum can, terminal bars, and the Epoxy glue used to secure the terminal bars to the can were all assumed to have the specific heat of pure aluminum.

The total heat was obtained as the product of the water equivalent and the calorimeter water temperature rise which had been corrected for the radiation heat loss.

The heat input by the can and the Stanolax was obtained by the product of their specific heats, weights, and temperature drops. The heat of the beans were calculated by subtracting the heat inputs by the can and Stanolax from the total heat input. The specific heat of the soybeans was then found knowing their weight and temperature drop.

The results of the soybean determinations are shown in Table 1. The

TABLE I. SPECIFIC HEAT OF SOYBEANS

Specific Heat Oil cals./gm.-C°	Corrected Temp. Rise C°	Heat Oil cals.	Heat Can cals.	Total Heat cals.	Heat Bean cals.	Specific Heat Bean cals./gm.-C°	Temp. Range C°
.511	2.88	2193	741	5263	2330	.47	30.7 - 126.5
.512	2.79	2137	767	5111	2207	.46	31.2 - 127.6
.512	2.76	2360	731	5050	1960	.46	31.8 - 126.2
.513	2.68	2248	724	4898	1926	.48	34.4 - 125.5
.513	2.78	2252	723	5091	2116	.47	34.4 - 127.6
.512	2.94	2524	813	5387	2050	.42	27.0 - 131.7
.511	2.98	2360	803	5457	2293	.45	27.4 - 128.2
.511	2.93	2245	766	5365	2354	.43	29.8 - 127.7
.510	2.88	2146	796	5263	2322	.43	27.5 - 127.7
.512	2.75	2254	762	5030	2013	.45	31.0 - 127.0
.514	2.83	2328	769	5172	2075	.42	32.2 - 131.3
.510	2.97	2154	761	5426	2511	.50	27.6 - 125.9
.511	2.78	2366	788	5091	1937	.39	27.1 - 128.9

Average Moisture Content is 7.4 Percent (w.b.)

Figure 3. Calibration Curve of the Calorimeter

The scatter in the data was less at fifteen seconds than at ten seconds; hence, the transition time used was fifteen seconds. Consequently, the water equivalent was 1829 calories per degree Centigrade with a stand-

TABLE II. MOISTURE CONTENT vrs. SPECIFIC HEAT

Specific Heat cals./gm.-C	Moisture Content percent (w.b.)	Reference Source
0.45	7.4	This paper
0.47	17.72	(3)
0.49	21.72	(3)