Application of Sensitive Adiabatic Calorimetry to Beet Industry Problems

W. O. Bernhardt[1] and R. A. McGinnis[2]

Introduction

Over the years, the beet industry has experienced a number of costly fires in bulk storage of dried beet pulp. While some fires were the result of burning embers from the driers which were carried into storage, other fires were the result of spontaneous heating. Spontaneous heating may also degrade stored pulp and ultimately render it unfit for consumption, even when no ignition occurs.

Spontaneous heating occurs in many materials other than beet pulp and may be caused by the metabolism of microorganisms and by chemical reactions in the material [1,3,4,5][3]. Since microorganisms are not biologically active at the moisture levels and relative humidities encountered in normal pulp storage, spontaneous heating of dried pulp is largely due to oxidative reactions. It is reasonable to assume that oxidation of pulp constituents occurs at all practical storage temperatures. Since oxidation is an exothermic process, spontaneous heating of pulp cannot be prevented. The oxidative processes in beet pulp are not particularly harmful if the pulp temperature is kept reasonably low during storage. Elevated temperatures lead to accelerated heating rates and pulp degradation.

Spontaneous heating, degradation and ignition of dried pulp can be controlled through suitable storage practices which prevent harmful temperature increases. It is necessary to cool the dried pulp to a reasonable temperature before storage and to provide, during storage, for the removal of the heat generated through the spontaneous processes. Since dried pulp has a relatively low bulk density and 80% of its volume is air, it is a very efficient thermal insulator. It may thus be necessary to remove heat from a storage pile by artificial means. The design of facilities for heat removal requires a prior knowledge of the rates of spontaneous heat generation as a function of storage temperature and pulp composition. This knowledge may be acquired only through sensitive methods of calorimetry.

Calorimetric Techniques

Figure 1 illustrates an elementary calorimeter.
Here, the sample is contained in the inner calorimeter, C, which is enclosed in the calorimeter jacket, J. The inner calorimeter is separated from the jacket by an air space, A, which acts as a thermal insulator. The jacket is submersed in a water bath, B, which is stirred by stirrer, S, to maintain a uniform temperature throughout the bath. T_C and T_J are temperature sensors.

When heat is generated in the inner calorimeter, its temperature rises above that of the jacket and heat flows through the air gap from the inner calorimeter to the jacket and bath. When the temperature of the jacket and water bath is held constant and heat is generated in the calorimeter at a constant rate, the temperature difference between the calorimeter and jacket, $T_C - T_J$, is also constant. The temperature difference is a function of the rate of heat evolution, dQ/dt, and the leakage modulus of the calorimeter, k. It is expressed by the equation: $dQ/dt = k(T_C - T_J)$. The leakage modulus k may be determined by electrical means, i.e., by passing a precisely known current through a resistor of precisely known value, located inside the inner calorimeter.
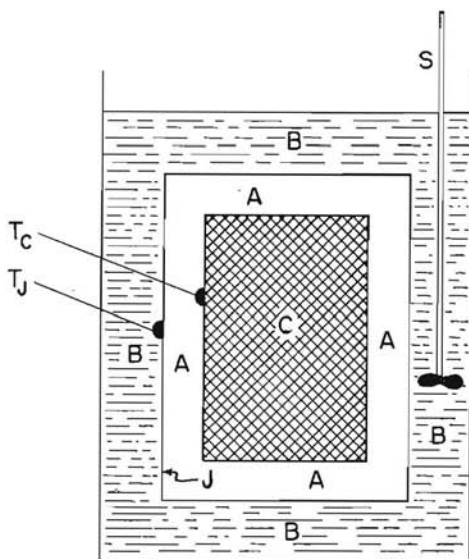

Figure 1.—Calorimeter.

The above procedure is generally referred to as the ordinary method of calorimetry. It is capable of high accuracy, subject to the ability of measuring extremely low temperature differences.

When calorimeter and jacket temperatures are exactly equal, no heat flows through the air gap. When heat is generated in the inner calorimeter while no heat flows through the air gap, the temperature of inner calorimeter and contents will rise. Obviously, it is necessary to raise the temperature of the jacket and bath at the rate of temperature increase occurring in the inner calorimeter in order to maintain the equality of temperatures necessary for zero heat flow through the air gap. This method of calorimetry, wherein all heat generated within the inner calorimeter is retained, is known as the adiabatic method. Here the rate of heat evolution, dQ/dt, is a function of the rate of temperature increase, dT/dt, and the heat capacity, C, of the inner calorimeter and its contents. This is expressed by the equation: $dQ/dt = C(dT/dt)$. As in the ordinary method, electrical means are employed for the determination of the heat capacities of the inner calorimeter and its contents.

Calorimeter Design

A comprehensive study of spontaneous heating in beet pulp must encompass a wide range of heating rates. At the lower rates of heating, the ordinary method of calorimetry may suffer from inaccuracies in the measurement of extremely small temperature differences. In the adiabatic method, where increases of temperature are measured, it is possible to extend the duration of the experiment until a precisely measurable temperature increase has occurred. In this method, the major problem is the continued maintenance of the adiabatic state, i.e., temperature equality of inner calorimeter and jacket.

In either method, the temperature of the bath ·cannot be held constant; at best, it oscillates about the control point by small deviations. In the ordinary method, the determination of the low temperature difference between calorimeter and jacket is obviously made difficult by the temperature oscillations of the bath. In the adiabatic method, the temperature of the inner calorimeter is unaffected by the temperature oscillations of the bath, and the temperature increase during the test can be made larger by extension of the test duration. The temperature oscillations of the bath do not preclude adiabatic operation; it is necessary, however, to maintain equality between the temperature of the inner calorimeter and the mean temperature of the bath. The adiabatic method is therefore preferable for the determination of spontaneous heating of beet pulp.

The Spreckels research group chose the adiabatic method for its investigations of spontaneous heating of beet pulp. Two calorimeters, of identical design, were constructed and placed into service in 1956. Details of calorimeter design, associated automatic controls, and operational procedures follow.

The inner calorimeter is fabricated from a section of copper tubing, 4" in diameter and 10½" long, with 1/16" wall thickness. Six copper fins extend from the wall inward and thereby provide for heat transfer between pulp and calorimeter wall. Figure 2 shows the construction of the inner calorimeter. The fins are soldered to the wall, together with twelve small copper tubes. These tubes contain twelve thermocouples for temperature control, three thermocouples for temperature measurement, a precision resistor for electrical calibration, and an additional resistance element used to bring the calorimeter to the desired starting temperatures for tests. The inner calorimeter is suspended from the lid of the calorimeter jacket by a structure of low thermal conductivity. Connections to bath thermocouples, reference thermocouples, controller and recorder leads, and for the resistance heaters are brought out through copper tubing attached to the lid.

Figure 2.—Inner calorimeter.

The calorimeter jacket is fabricated from 6" diameter copper tubing. A Neoprene gasket and twelve machine screws provide for watertight attachment of the jacket lid. A one-inch air gap separates the inner calorimeter from the jacket. The assembled calorimeter is shown in Figure 3.

It is desirable to draw atmospheric air through the pulp sample during the tests. The air must be adjusted to the temperature and to the equilibrium relative humidity of the pulp sample. This is accomplished by passing the air through the tubing coil at the base of the jacket and then over a suitable mixture of
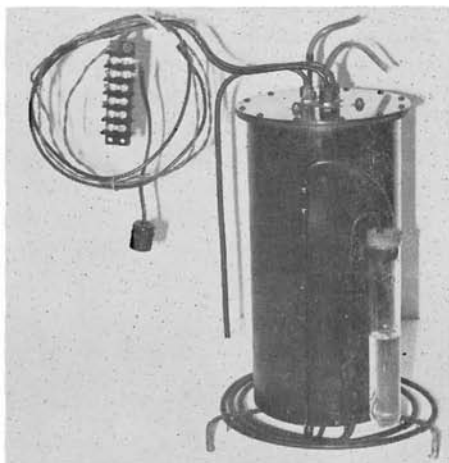
Figure 3.—Assembled calorimeter.

sulfuric acid and water in a test tube attached to the calorimeter. After passage through the pulp sample, the air is drawn through spiral absorbers [2] for subsequent analyses for the amount of CO_2 produced by the spontaneous reactions. The air pumps consist of hypodermic syringes driven through a scotch yoke by a constant-speed motor. The absorbers and pump mechanism are shown in Figure 4.
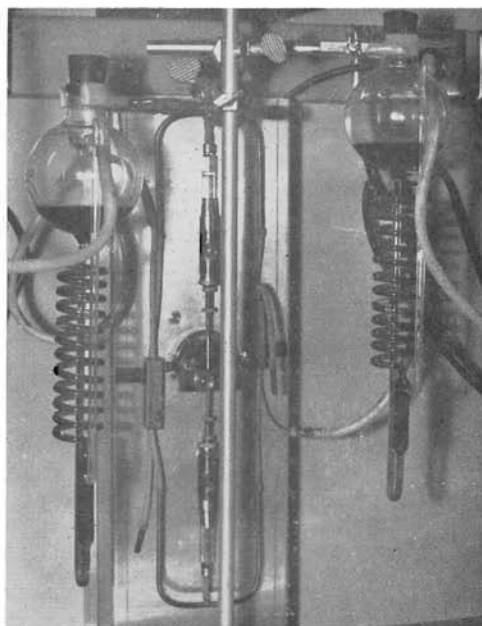

Figure 4.—Absorbers and air pumps.

During operation, the assembled calorimeter is submerged in a water bath, which serves as a temperature controlled environment. The two calorimeters employed in our tests are shown in Figure 5 with their associated recorders, controllers, and auxiliaries. The calorimetric equipment operates from the 115 volt laboratory lines; an auxiliary generator, located outside the laboratory, provides standby power in the event of power outages. The air temperature in the calorimetric laboratory is maintained at 75 ± 1°F.
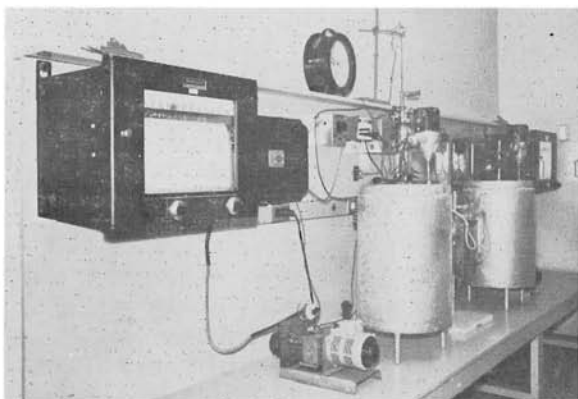

Figure 5.—Adiabatic calorimeters and controls.

The two large tanks are the calorimeter water baths, which are heated electrically by the output from variable-voltage transformers, one of which is shown in the foreground on the bench. Pulp temperatures are recorded on two stripchart recorders located at the extreme ends of the bench. The black enclosures adjacent to the recorders contain temperature control amplifiers which operate the variable-voltage transformers through servo motors and gear trains.

For adiabatic operation it is necessary that the temperatures of the inner calorimeter and the jacket be exactly equal. Since the jacket is in intimate contact with the water in the calorimeter bath, the required condition of temperature equality is achieved when the inner calorimeter and the bath are in thermal equilibrium. A string of 24 copper-constantan thermocouples senses any temperature differences and, through a Honeywell servo amplifier and motor, controls the electric input to the heaters in the shell of the bath. The thermocouple junctions are alternately located in the inner calorimeter and in the temperature probe in the bath. In this manner a temperature difference of 1°C produces an electric output of about 0.5 millivolts from

the string. Since the amplifier initiates motor action with inputs of 0.003 millivolts, a temperature difference of 0.006°C results in correction of the heat input to the bath. Sensing lags and the capacity of the bath produce a state of steady hunting of the bath temperature about the temperature of the inner calorimeter, with a period of about two minutes and a maximum deviation of less than ±0.01°C from the mean. Without this steady hunting, the jacket temperature could remain about 0.01°C above or below that of the inner calorimeter, due to the dead-zone of the servo amplifier. This would lead to significant heat transfer to or from the inner calorimeter. With steady hunting, the mean temperature difference is effectively zero and the calorimeter operates in the adiabatic mode.

The temperature of the water bath is controlled by the voltage applied to the heater windings. This voltage is adjusted by a variable transformer which is driven by a servo motor through a gear reducer with a ratio of 150:1. The control is shown in Figure 6. A resistor, placed in series with the heater, is bridged by
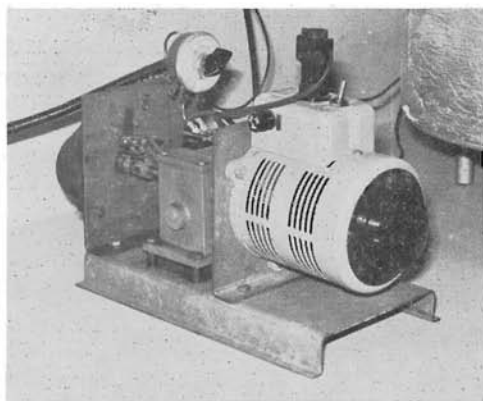

Figure 6.—Voltage control unit.

a mercury switch which is actuated by rotation of the servo motor shaft. When additional heat is required, initial rotation of the shaft in one direction causes the closing of the mercury switch and thereby increases instantly the heat input to the bath by a discrete amount without change of the voltage setting of the variable transformer. When less heat is required, the motor shaft begins to turn in the opposite direction and causes the mercury switch to open, thereby instantly reducing the heat input to the bath. With a heater resistance of 100 ohms and a series resistor of 50 ohms, the heat input to the bath varies between +40% and −40% of the mean, due to the action of

the switch. When the temperature of the inner calorimeter is constant, the output voltage of the variable transformer also remains constant. As the calorimeter temperature increases, due to spontaneous heating of the sample, the sorvo motor adjusts the output voltage gradually upward to maintain adiabatic operation of the calorimeter.

All servo amplifiers display a small amount of offset, i.e., an output signal is produced in the absence of any input signal. For adiabatic operation of the calorimeters, it is necessary to compensate for this offset. In our calorimeter controls, compensation is provided by insertion of an opposing voltage in the thermocouple leads. The magnitude and polarity of the compensating voltage is determined through calorimetric tests on the empty calorimeter. Aging of components causes a gradual change of the amplifier offset voltage. It is thus necessary to redetermine this offset at regular intervals.

The temperature of the inner calorimeter is sensed by three thermocouples and recorded on a strip chart recorder having a span of 1 millivolt, full scale. The recorder has provisions for variable suppression. It is thus possible to zero the recorder at any calorimeter temperature. The thermocouple reference junctions are maintained at $50 \pm 0.005°C$ in a reference oil bath, shown in Figure 7.
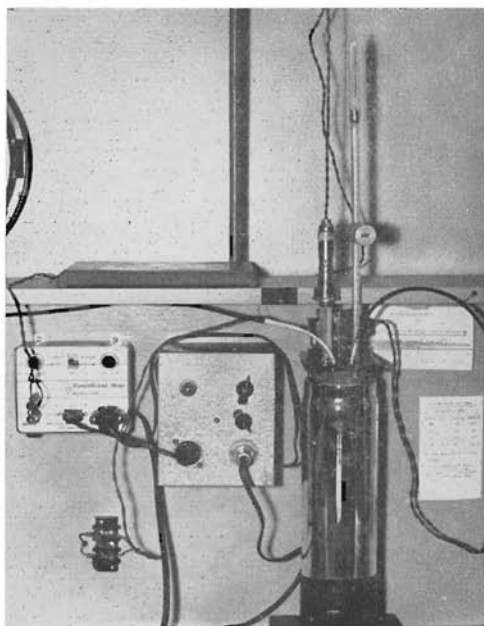

Figure 7.—Reference oil bath.

The oil bath consists of a 1-liter Dewar flask with an internal electric heater and a stirrer. The temperature is controlled by an adjustable mercury-in-glass contacting thermometer and a transistorized relay. Instead of the customary on-off control, we employ a two-position control wherein the electrical heat input is alternately slightly above and below that required to maintain the desired temperature. Bath temperature is maintained within $\pm$ 0.005°C as indicated on a Beckman differential thermometer.

The quantity recorded on the strip chart recorders is the voltage produced by the thermocouples due to the temperature difference between the inner calorimeter and the reference bath. This quantity is converted to temperature, in °C, with the aid of conversion tables, calculated for three pairs of copper-constantan junctions and a reference temperature of 50°C. Recorder output may be read within $\pm$ 0.001 millivolt and the temperature may be determined within $\pm$ 0.008°C. Thus, a temperature increase of 1°C may be measured with a maximum error of $\pm$ 1.6%. Duplicate tests with pulp samples of very low spontaneous heating rates and resultant temperature increases of about 0.5°C in a 27 day period have shown agreement within 3%. It is thus seen that calorimetric accuracy is limited mainly by the accuracy of temperature determinations.

Test Procedure

The pulp to be tested is mixed thoroughly and a sample is taken for moisture analysis by oven drying. While awaiting the results of the moisture analysis, the pulp is stored in a plastic bag to prevent changes in moisture content. From the moisture analyses and applicable equations, the specific heat of the pulp is calculated. With the aid of graphs, which relate pulp moisture to equilibrium relative humidity, the concentration of the dilute sulfuric acid charge for the air humidifying test tube in the calorimeter is determined. The inner calorimeter is charged with the sample, packing it firmly, and the weight of the pulp charge is determined.

The calorimeter is then assembled, placed into the water bath, and the electrical connections are made to the control and recording units. The air pump is connected to the calorimeter and is started. The suppression of the temperature recorder is adjusted to record zero on the scale, and the bath agitator is turned on. Next, the electrical heater in the inner calorimeter is energized, and the calorimeter temperature begins to increase. The resulting temperature difference between inner calorimeter and bath is sensed by the thermocouples, and corrective action is initiated by the amplifier and servo motor to

increase the heat input to the calorimeter bath. While the inner calorimeter temperature approaches the desired starting temperature of the test, the bath temperature follows within a small fraction of a degree.

When the starting temperature is reached, the heater in the inner calorimeter is de-energized and the suppression of the recorder is adjusted to match the starting temperature. The calorimeter is left on automatic control for about 20 hours during which the pulp charge and the inner calorimeter reach thermal equilibrium. This is followed by the calorimetric test run. During the test run, calorimeter temperatures are determined at intervals of 24 hours and recorded. Ventilating air flow through the pulp sample is maintained at constant rate. The incoming air is passed through a soda lime tube for the removal of atmospheric CO_2. The exhaust air passes through spiral absorbers filled with a solution of barium hydroxide for the determination, by titration, of the quantity of CO_2 generated by the spontaneous processes[5].

The duration of each test is governed by the rate of spontaneous heating of the sample. For accuracy, a minimum temperature increase of 0.5°C should occur during the test; an increase of about 1°C is generally employed in our tests.

Test Evaluation

Spontaneous heating rates determined in our calorimeters are expressed in units of gram-calories developed in 1 kg of pulp during a 24 hour period, i.e., g-cals/(kg) (day). This is calculated from the temperature increase, the test duration and the heat capacity of inner calorimeter and pulp sample. The following example may illustrate the procedure:

Data: Heat capacity of empty calorimeter, C_e = 408 g-cals/°C
       Heat capacity of pulp sample, C_p = 166 g-cals/°C
                                       Total C = 574 g-cals/°C

       Starting temperature   40.02°C
       Final temperature   41.20°C
       Temperature increase, ΔT = 1.18°C
       Test duration, Δt = 7 days
       Sample weight,   W   =   .439 kg

Calculations

The spontaneous heating rate, R, in g-cals/(kg (day), is calculated from the equation: $R = \dfrac{C \, \Delta T / \Delta t}{W}$. For the above data: R = (574 × 1.18) / (7.00 × .439) = 220 g-cals/(kg) (day). Stated in

more familiar terms, a ton of the pulp tested will generate spontaneously about 793 BTU per day when stored at 40-41°C. Under these conditions, a storage pile of 10,000 tons of this pulp will generate spontaneously nearly 8 million BTU/day. It is thus necessary to remove heat from the storage pile at a rate of 8 million BTU/day, through radiation, conduction, convection, and other means. If the rate of heat generation exceeds the rate of removal, the temperature of the pile will rise continuously, and it may eventually ignite spontaneously.

Factors in Spontaneous Heating

Since 1956 the research group of Spreckels Sugar Company has directed its attention to the determination of factors which govern spontaneous heating in dried pulp storage through adiabatic calorimetry and chemical analyses. Special emphasis was placed on the effects of factors which can be controlled in manufacture and storage. The data indicate clearly that spontaneous heating rates increase exponentially with temperature, moisture content and levels of additives. It was also determined that the type of additive dried onto the pulp has a significant bearing on spontaneous heating rates.

Adiabatic tests over a span of twelve years have shown that spontaneous heating rates of beet pulp are governed not only by the type and level of additives, moisture content and storage temperature, but also by seasonal factors. The heating rate of pulp produced one year differed from that produced in another year by a factor of 2.5 at comparable levels of molasses addition, moisture, and storage temperature. To insure storage safety, it is thus necessary to determine periodically the heating rates of production pulp and to adjust pulp composition or storage practices accordingly.

Literature Cited   ·

(1) CARLYLE, R. E. 1940. Iowa State Coll. J. Sci. 15: 60.
(2) MARTIN, WM. and McK. and JESSE R. GREEN. 1933. Ind. & Eng. Chem. Anal. Ed. 5 (2) : 114.
(3) MILNER, M. and W. F. GEDDES. 1945. Cereal Chem. 22: 477.
(4) MILNER, M. and J. B. THOMPSON. 1954. J. Agr. & Food Chem. 2: 303.
(5) PAAR, W. DEUT. ZUCKERIND. 1940. 65: 658.