SPECIFIC HEAT OF CITRUS JUICE AND CONCENTRATE

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Abstract. The principles and published work of specific heat of citrus juice and concentrate were reviewed. Prediction equations for specific heat above freezing point are presented. Applications of Riedel's Mollier Chart to derive the enthalpy or total heat content, as well as effective specific heat of 11°, 45° and 65° Brix concentrate in the freezing temperature ranges, are presented.

The specific heat or heat capacity is a fundamental physical property that is often needed in calculating the amount of heat to be added or removed for heating or cooling processes.

The specific heat of citrus juices and concentrates is normally estimated from the sucrose solution for which data is available for a wide range of concentrations above freezing. The specific heat is known to vary greatly with temperatures in the freezing region, and the estimation becomes more difficult and less accurate. Attempts to measure specific heat of frozen concentrate have been complicated by the fact that partial freezing occurs, so that the latent heat of fusion is removed over a wide temperature range. Shadr and Johnson (8) reported that orange juice is not completely solidified at —139°F. Because of this, Dickerson (3) points out that the generally accepted criterion of latent heat (change of phase at constant temperature) cannot be applied to the process of freezing foods. Neither can the concept of specific heat be applied because there is no way to separate the specific heat component from latent heat in the food freezing process. Therefore, the total heat content, or enthalpy, rather than specific heat is generally employed in freezing calculations.

Heat contents for only 42° and 65° Brix orange concentrate are available in the citrus concentrate industry as shown in Fig. 1 (4). The original source is not known. The chart was found satisfactory for the prediction of cooling load. It appeared that the data are in good agreement with the results derived from Riedel's Mollier Chart (5) for fruit juices which includes orange juice.

Over the years, some process requirements and technologies have changed. Concentrate is now stored in large containers or tank farms at approximately 65° Brix for later processing or blending with concentrates from other orange varieties to utilize the best characteristics of each. The blended products are packed at 45° Brix. Because of the increasing volume involved, the accuracy of specific heat as well as other thermal properties is becoming a practical concern.

This paper presents prediction equations for specific heat and an extension of the use of Riedel's Mollier Chart to predict the heat content for various concentrates and to derive effective specific heat for the freezing region.

Specific heat, latent heat and enthalpy

Heat is generally defined as the flow of thermal energy by virtue of a temperature difference (2). Heat is measured in terms of the energy changes it causes. Since these changes are most easily described in terms of temperature changes, the unit of heat is defined in terms of the capacity to raise the temperature of a unit mass of standard substance such as pure water a unit degree, under specified conditions of state. By definition, the quantity of heat can be written as

\[ Q = MC_p \Delta T \] for constant pressure

or

\[ Q = MCV \Delta T \] for constant volume

Where

\[ Q = \text{quantity of heat added}, \]
\[ M = \text{mass}, \]
\[ C_p (\text{or } C_v) = \text{heat capacity or specific heat}, \]
\[ \Delta T = \text{temperature change}. \]

Equations (1) and (2) also defined the heat capacities. For noncompressible liquids and solids, the difference between heat capacity at constant pressure and heat capacity at constant volume is insignificant.

Heat capacities are usually measured directly in an instrument known as a calorimeter. In calorimeter measurement, a known amount of heat is supplied to a known mass of substance at constant pressure and the temperature change is measured. The average heat capacity over the temperature range is then given by solving equation (1), i.e.
\[
C_p = \frac{Q}{M \Delta T}
\]  

The specific heat is defined as the ratio of the heat capacity of a given mass of substance to the heat capacity of the same mass of water. When the heat capacity of the water is unity, then the specific heat of the substance is numerically equal to its heat capacity per unit mass, and is also denoted by \(C_p\).

The energy required to transform unit mass of substance from the solid to the liquid state, at constant temperature, is termed latent heat of fusion.

Foodstuffs experience a phase change over a wide temperature range rather than a specific temperature observed in pure substance (e.g. water freezes at 32°F). In the phase-change range, the specific heat includes latent heat as well as sensible heat (heat to cause a change of temperature). Since there is no way to separate the latent heat and sensible heat, the specific heat determined by equation (3) is termed effective specific heat or apparent specific heat. The effective specific heat for freezing foods in the phase-change temperature range is found to increase dramatically at a certain temperature. Therefore, the total heat content or enthalpy is the preferred parameter under these conditions.

Enthalpy is a property of a substance and is defined as

\[
H = U + PV
\]

Where
- \(H\) = enthalpy,
- \(U\) = internal energy,
- \(P\) = absolute pressure,
- \(V\) = volume.

Or, dividing by the total mass, \(M\), the specific enthalpy \((h)\) is

\[
h = \frac{H}{M}
\]

The specific enthalpy is related to the heat input to the substance as follows:

\[
Q = M (h_2 - h_1) = M \Delta h
\]

Where
- \(h_2\) = specific enthalpy at the final state
- \(h_1\) = specific enthalpy at the initial state

Combining equations (1) and (6), we obtain

\[
C_p = \frac{(\Delta h / \Delta T)_p}{h_2 - h_1}
\]

Where subscript \(p\) denotes constant pressure.

Since internal energy is a function of temperature so is the enthalpy. A base temperature at which enthalpy is arbitrarily designed as zero needs to be identified. This does not imply that the heat content of a substance is zero. Instead it means that this is a reference point (datum) which permits the use of enthalpy differences as indicated in equation (6).

The enthalpy is determined in the same manner as the specific heat, with the distinction that there be a datum point (i.e. zero enthalpy at a reference temperature). The enthalpy (or total heat content) of a substance at a temperature above the datum point is the heat energy required to raise the temperature of a substance from the reference temperature to the temperature of interest. Zero enthalpy is arbitrarily taken at —40°F for all data presented in this paper.

The specific heat above freezing

The first study of the specific heat of food products was conducted by Siebel (6) in 1892. He assumed that the specific heat of food is equal to the weighted sum of the specific heat of the water content and of the solid portions. He suggested the following equation for predicting specific heat above freezing:

\[
C_p = 0.20 + 0.008 X_w
\]

Where \(X_w\) = percent moisture content, %

Based on the same concept, Riedel (5) has validated Siebel’s method and presented a generalized correlation for juices of fruits and vegetables including oranges.

\[
C_p = 0.43 + 0.0057 X_w
\]

Turrell and Perry (9) reported an empirical equation for whole Washington navel oranges.

\[
C_p = 0.347 + 0.006 X_w
\]

Both equation (9) and (10) are applicable at room temperature.

For nearly all liquids, specific heats rise with temperature increase; only a very few exceptions (e.g. mercury) are known. Predictions of specific heat for wide range conditions can be approximated by using data of sucrose solutions, the following empirical equation was found satisfactory.

\[
C_p = (1 - 0.00633 X_s) (1 + (4.34 X 10^{-6} X_s^{1.53}) T)
\]

Where \(T\) is between 32 and 212°F, and \(X_s\) is percent solids content, %.

Enthalpy and effective specific heat

Freezing citrus juice concentrate differs radically from freezing water. When the freezing point is attained and ice begins to form, the thermal capacity increases abruptly and becomes a temperature dependent variable until complete solidification occurs. In 1892, Siebel (6) proposed a simplified method for calculating the refrigeration effect for freezing food products. It was assumed that all water contained in the food became solidified at the freezing point and that the thermal capacity below this temperature was constant, but smaller in magnitude than in the unfrozen state. By this method the refrigeration effect is assumed to be the latent heat of the water content and the sensible heat below freezing (7). He proposed the thermal capacity below freezing be evaluated by

\[
C_p = 0.20 + 0.008 X_w
\]

Siebel’s method and equations (8) and (12) have been used in calculating values of specific heat and latent heat of frozen foods and presented in handbook form (1).

Short and Bartlett (7) have determined specific heats for many food products. Riedel has also investigated many fruits and vegetables, and presented a generalized Mollier chart for fruit juices. A plot of heat content vs. concentrate temperature derived from Riedel’s Mollier chart is shown in Fig. 2. 11° Brix line in Fig. 2 agrees very well with the data reported by Short and Bartlett (7) for oranges in the freezing region 29.3 to —40°F. There appears no irregularity in the entire range for all the products being investigated. When the values are plotted on the same scale, good agreement is shown between Fig. 1 and Fig. 2, except 65° Brix line in Fig. 1 has a small irregularity. Such irregularity is questionable and needs further verification.

By adopting Fig. 2, it is possible to derive the effective specific heat, \(C\), which is defined as including the latent heat. The average effective specific heat as a function of temperature was obtained from Eq. (7) by dividing small differences in enthalpy by the corresponding intervals of temperature, \(\Delta T\). The range of temperature, \(\Delta T\), was kept small. Values

for the effective specific heat so obtained are shown in Fig. 3. Insoluble material, or pulp, was neglected in these calculations, because refractive index was used in constructing Fig. 2.

It should be pointed out that the accuracy of the data in Figs. 2 and 3 is limited by the interpolation of values from the original chart and the use of enthalpy is preferred, because it is less prone to errors.

**EFFECT OF PH ON CLARIFICATION OF CITRUS JUICES BY LOW METHOXYL PECTINS**

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Abstract. Low methoxyl (LM) pectins were tested for clarifying activity in fresh orange juice adjusted to varying pH values. Two series of LM pectins ranging from 0.33 to 5.72% methoxyl (MeO) content were derived by enzymic or chemical demethylation of citrus pectin. The MeO content required to induce optimal clarification was not fixed, but depended on method of demethylation and pH of juice.

Cloud removal in juice was maximum under the following conditions: chemically derived LM pectins—2.4% MeO at pH 2.6-3.2 and 0.33% MeO at pH 3.4-4.2; enzymically derived LM pectins—4.5% MeO at pH 2.6-3.2, 2.9% MeO at pH 3.4, and 0.85% MeO at pH 3.6-4.2. Such pectins can be effective clarifying agents for products that require clear juices.

Low methoxyl (LM) pectins, if properly prepared, can be effective clarifying agents for citrus juices. Their effectiveness is dependent both on preparation method and methoxyl (MeO) content (2). Methoxyl content can be reduced either chemically (alkaline saponification) or enzymically (pectinesterase). Alkaline saponification removes methoxyl groups randomly, leaving a statistical distribution of methylated and demethylated sites along the pectin molecule. Pectinesterase (PE) tends to remove methoxyl groups in a linear fashion on the molecule, creating a blockwise arrangement of demethylated sites (4). These sites have a higher linear