Effects of temperature and concentration on thermal properties of cassava starch solutions

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Abstract

The thermal properties and densities of cassava starch solutions (CSS) were studied as functions of temperature (30-50°C) and concentration (20-50%w/w). Thermal conductivity (k) and specific heat (Cₚ) were determined by line heat source and mixture calorimetry methods, respectively, while density (ρ) was determined by the pycnometer. The k value was in the range of 0.307-0.333 W/m°C, which decreased as temperature and concentration increased. The Cₚ value was in the range of 3.354-4.004 kJ/kg°C, which also decreased as temperature and concentration increased. The ρ value was in the range of 1044-1120 kg/m³, which decreased with increasing temperature but increased with concentration. A multiple regression equation of thermal conductivity, specific heat and density was developed as a function of temperature and concentration.

Keywords: cassava starch, thermal properties, assembled colorimeter, density

1. Introduction

Cassava starch obtained from cassava roots is widely used in the food industry because of its high viscosity, clear appearance, and low production cost (Pongsawatmanit et al., 2006). Thailand produced 27.62 million tons of cassava roots in 2007 (The Thai Tapioca Trade Association, 2008) and has been the only country where modified starch from cassava has been produced in large quantity (Sriroth et al., 2002). Normally, modified starch is used in industrial applications for both food and non-food sectors as a wet-end additive, binder of coating pastes, etc. giving added value to raw cassava starch powder. To obtain the modified cassava starch, raw cassava starch is used as a starting substrate and is dissolved in the form of a colloid solution, referred as cassava starch solution (CSS). Knowledge of the various physical properties of CSS is important for the design of various processing machines, especially for the modified cassava starch reactor, and to assist the design process for commercial production in relation to fluid flow and heat transfer. For example, a low heating rate in the reactor is required in the first step to initiate the CSS paste. In addition, during the filling period of chemical reagents, the quality of product significantly depends on the thermal properties of CSS. Therefore, thermal properties of CSS are useful for the prediction of the chemical reagent mixing period.

Generally, the variation in temperature and concentration of CSS during modified starch processing greatly affects its thermal properties. Some important thermal proper-
ties of CSS include thermal conductivity (k), specific heat (C\text{p}) and thermal diffusivity (\alpha). Thermal properties for several foods and agricultural materials have been reported by Rahman (1995), Mohsenin (1980) and Sweat (1995). By definition, the k value is an intensive property of material indicating its ability to conduct heat. It is used primarily in Fourier’s Law for heat conduction. Measurement techniques of k values can be divided into two categories; steady state and transient techniques. Among the transient techniques, the line heat source method is rapid and applicable to non-convective food and biological materials because moisture loss from food is minimal. Therefore, it is more popular using researchers in determining the thermal conductivity of food and biological materials compared to the steady state methods. An example of the transient measurement of k on some food materials has been recently reported by Opoku et al. (2006). C\text{p} is defined as the amount of heat necessary to increase the temperature of a unit mass of a material by a unit degree. Rahman has reviewed four methods of measuring C\text{p}; the method of mixture, the comparison method, the adiabatic method and the differential scanning colorimeter (DSC). DSC is a very accurate method to determine the C\text{p} of agricultural materials, but it has the drawback of high equipment and operating costs (Sweat, 1995). The comparison method employs two cups in the calorimeter of the same size, same material, same exterior finish and of identical mass (Mohsenin, 1980), thus, the equipment is difficult to manufacture. The adiabatic method is appropriate for measuring the specific heat of frozen foods. It is simple and requires a short duration time (Rahman, 1995). The method of mixture is more popular for measuring C\text{p} (Rahman, 1995) than the DSC method because it is simpler and less expensive.

Earlier studies on thermal properties of starches focused on gelatinized starch gels. Wang and Hayakawa (1993) determined the k value of starch gels using the line heat source technique, and found values ranging from 0.4770 to 0.5667 W/m\(\cdot\)K at 80 to 120°C with varied moisture content from 39.6 to 75% wet basis. Morley and Miles (1997) determined the k value of starch using line heat source technique in the range of water content from 51 to 97% by mass. The k values of hydrated starch (mass fraction of water 0.22) and dry starch were found to be 0.364, 0.386 and 0.388 W/m\(\cdot\)K, and 0.293, 0.305 and 0.301 W/m\(\cdot\)K at 10, 50 and 80°C, respectively. Additionally, data on the thermal properties of tomato juice concentrates (Choi and Okos, 1983), passion fruit juice (Gratão et al., 2005) and coconut milk (Tansakul and Chaisawang, 2006) have been reported. To date, however, there have been no reports on the k value of CSS.

Many studies have been conducted to determine the thermal properties of different agricultural starches such as Amioca starch (Wang and Hayakawa, 1993), potato starch, waxy maize starch (Morley and Miles, 1997) and high amylose corn starch (Hsu and Heldman, 2004). However, we have found no such literature relating to the effect of temperature and concentration on the thermal properties of CSS. Therefore the objective of this study is to determine the thermal properties e.g., k, C\text{p} and density (\rho) of CSS to provide data for the design of a mixing reactor, which is one of the important unit operations in the chemical and biochemical reaction processes.

2. Materials and Methods

2.1 Material preparation

Cassava starch powder obtained from Sanguan Wongse Industries Co., Ltd., Thailand was used in this study. The basic physical properties of starch reported by the company are a whiteness of 93.7%, a pH of 6.0, a sulphur dioxide concentration of 27.6 ppm, a viscosity of 720 BU and a pulp content of 0.02%.

The CSS was prepared in a 500 mL beaker with distilled water by mixing cassava starch powder in specific ratio by weight. The k, C\text{p} and \rho values were measured at temperatures of 30, 40 and 50°C, and concentrations of 20, 30, 40 and 50% by weight. These temperatures and concentrations were selected according to industry practice to process modified cassava starch. During heating, the mixing beaker was covered with aluminum foil to prevent moisture loss due to evaporating. The CSS sample was continuously stirred until ready for all analyses. The temperature samples were measured using pre-calibrated mercury and digital thermo-meters with a temperature accuracy within ±1°C.

2.2 Thermal conductivity measurement

The k of CSS was measured using the line heat source method. A k-probe model number TC-18 (Thermologic Inc., Pullman, WA, USA) was used in this study. The k-probe consisted of a fine gauge heating wire and a type E thermocouple embedded in a stainless steel needle of 36.87 mm in length and 1.27 mm in diameter. The heating wire retained a resistance of 1041.5 ohm/m. The probe was calibrated in 99.5% glycerol (0.286 W/m\(\cdot\)C; Rahman, 1995), dry starch (0.216 W/m\(\cdot\)C; Roth and Tsao, 1970) and saturated starch granule (0.3486 W/m\(\cdot\)C; Mattea et al., 1986). The thermal conductivity measurements of CSS were conducted using the protocol proposed by Holeschovsky et al. (1996). The CSS sample was immediately taken from the beaker in water bath and a portion of 60 mL was placed in a plastic bottle covered with styrofoam to prevent heat loss for each treatment. The heating wire was connected to a power supply providing a current of 58.9 mA, resulting in a power rating of 4.25 W/m. The thermocouple wires were connected to a datalogger (Model 350-454, Testo AG, Lenzkirch, Germany) with a resolution of 0.01°C. The temperature was recorded at every 0.5 s for a total duration of 30 s. The temperature rises were plotted against the logarithm of time. The thermal conductivity value was calculated from a straight line section after a lag period using equation (1) (Yang et al., 2002; Opoku et al., 2006) as follows:

\[
q = \frac{k}{\alpha} \ln \left(\frac{T_{\text{final}} - T_{\text{initial}}}{t_0}\right)
\]
2.3 Specific heat measurement

The specific heat was determined using the method of modified mixtures following the protocol proposed by Jindal and Murakami (1984). The specific heat calorimeter consisted of a vacuum flask with a styrofoam insulation cover to prevent heat loss. A rubber O-ring was attached to the edge of the flask to provide additional sealant for heat loss. Thermocouples of type K and size of 0.65 mm in diameter were inserted through the center of the lid into the calorimeter. The heat capacity of the vacuum flask calorimeter with a polyethylene bag was calibrated using distilled water and found to be 0.124 kJ/°C, which was within the range of reported values by Sabapthy and Tabil (2004) of 0.457 kJ/°C and Jindal and Murakami (1984) of 0.055 kJ/°C.

A 500 mL sample of water with a temperature 20°C lower than the CSS sample was used for each measurement. The CSS samples were mechanically stirred and maintained at constant temperatures of 30, 40 and 50°C in the water bath. The starch solution sample was quickly weighed and put inside a polyethylene bag of size 127x203.2x0.025 mm to prevent mixing. The temperature changes of water and the CSS sample in the vacuum flask calorimeter were recorded every 1 min with a resolution of 0.1°C by a datalogger model DW-40BT T/C-V (ECD, Dataworker 10/40, Milwaukie, OR, USA). The vacuum flask calorimeter was continuously shaken to prevent sedimentation in order to reach peak temperature in about 10 min of treatment and then shaken every 5 min to reach equilibrium temperature in 120 min. A heat loss correction curve was determined. The specific heat of the CSS was calculated following the heat balance equation (2) as follows:

\[ C_w (\Delta T_w) = C_s W_s (\Delta T_s) + H_s (\Delta T_s) \]  

(2)

where \( C \) is the specific heat (kJ/kg°C), \( W \) is the weight (kg), \( \Delta T \) is the difference between the initial temperature and the equilibrium temperature (°C), \( H \) is the heat capacity of the calorimeter (kJ°C), and the subscripts refer to the starch solution, water, and calorimeter, respectively.

2.4 Density measurement

The density of CSS was determined with pycnometers. Each pycnometer was calibrated with distilled water at 30-70°C in 10°C increments to compensate for the change in pycnometer volume due to thermal expansion. The error in the density measurement due to thermal expansion was found to be 0.48% for this temperature range. For the CSS density measurement, each measurement was conducted at a constant temperature using a water bath model WB/OB7-45 (Memmert, Germany) with a resolution of 0.1°C. To measure the density of CSS, the pycnometer was placed in a water bath without its lid to equilibrate the temperature distribution. When the CSS sample reached the specified temperature, it was immediately put into the pycnometer and covered with the lid to avoid external air interference. The pycnometer was removed from the water bath, excessive water was blotted with tissue paper and the pycnometer was then quickly weighed using a model AFP-720 balance with 0.001 g resolution. The density was calculated from the ratio of mass to volume of CSS.

2.5 Thermal diffusivity determination

The thermal diffusivity (\( \alpha \)) of CSS was calculated using the measured values of \( k \), \( C_p \) and \( \rho \), and the following equation (3) as:

\[ \alpha = \frac{k}{\rho C_p} \]  

(3)

where \( k \) is the thermal conductivity (W/m°C), \( \alpha \) is the thermal diffusivity (m²/s), \( \rho \) is the density of CSS (kg/m³) and \( C_p \) is the specific heat (kJ/kg°C).

2.6 Statistical analysis

The thermal properties and density of CSS was studied at temperatures of 30, 40 and 50 °C and at concentrations of 20, 30, 40 and 50% w/w. A full factorial complete randomized design (CRD) was applied. Four replications of the \( C_p \) and \( \rho \) measurements were obtained for each treatment. The replications of the \( k \) measurements were in the range of 4.9 due to consideration from the coefficient of determination (r²). All statistical analyses were performed using SPSS version 10.0.1 (SPSS Inc., Chicago, IL, USA) for Windows. Analysis of variance (ANOVA) was performed and the average mean was analyzed by Duncan’s test at a \( p \)-value of 0.05.

3. Results and Discussion

3.1 Thermal conductivity (\( k \))

For the \( k \) measurements, the typical heating curves were obtained as shown in Figure 1. During the lag phase (initial heating), the temperature rise was less than 1.5°C. The temperature rise increased non-linearly in the lag phase for the first 5 s and increased linearly afterward. The temperature rise varied from 1 to 3°C during the linear phase for another 15 s. The temperature rise after 20 s became non-linear again, possibly due to the effect of reflecting heat from container wall. Therefore, the experimental measurement of \( k \) on CSS was performed for the time interval of 5-20 s to avoid the effect of reflecting heat, as recommended by...
Zhang et al. (2005).

Table 1 shows that the k value of CSS are in the range of 0.307 - 0.333 W/m°C with a standard deviation varying from 0.003 to 0.012 W/m°C. The k value significantly decreased (p<0.05) with increasing temperatures and concentrations. The k value reached a maximum value of 0.333 W/m°C at a temperature of 30°C with a concentration of 20% w/w, then it slightly decreased until reaching a minimum value of 0.307 W/m°C at a temperature of 50°C with a concentration of 50% w/w. Compared to other fluid foods, Choi and Okos (1983) found that the k of tomato juice increased with increasing temperature in the range of 20-150°C but decreased with increasing solid content in the range of 4.8-80%. Similarly, Tansakul and Chaisawang (2006) found that the thermal conductivity of coconut milk increased linearly with temperature but decreased linearly with fat content. They suggested that the influence of fat content on thermal conductivity was stronger than that of temperature. Correspondingly, Zainal et al. (2001) found that the thermal conductivity of pink guava juices decreased with increasing temperature and total soluble solids. Since most agricultural materials are dominated by water compositions which also dominates the k value, the moisture content tended to have a greater influence on the k of CSS than the temperature. However, granules of cassava starch might change the bulk properties of CSS at increased temperature. Njie et al. (1998) reported that as sucrose content increased, the free water decreased, which probably caused a decrease in the thermal conductivity. In our work, CSS exhibited similar behavior, as the thermal conductivity of CSS decreased with increasing temperatures and concentrations. It is possible that as the concentration of CSS increases, the ratio of dry starch mass to water quantity increases. This limits the mobility of the starch solution and water, thus the material’s ability to conduct heat between molecules decreases. As a result, the k value decreases at increased concentrations.

3.2 Specific heat ($C_p$)

The $C_p$ values of CSS at various temperatures and concentrations as shown in Table 2 are in the range of 3.354-

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**Table 1. Thermal conductivity of CSS at different temperatures and concentrations.**

<table>
<thead>
<tr>
<th>Concentration (%w/w)</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.333±0.006a,A</td>
<td>0.322±0.009b,A</td>
<td>0.318±0.012c,A</td>
</tr>
<tr>
<td>30</td>
<td>0.330±0.009a,A</td>
<td>0.318±0.005b,A</td>
<td>0.315±0.007c,A</td>
</tr>
<tr>
<td>40</td>
<td>0.328±0.003a,B</td>
<td>0.317±0.010b,B</td>
<td>0.311±0.004c,B</td>
</tr>
<tr>
<td>50</td>
<td>0.327±0.004a,B</td>
<td>0.316±0.007b,B</td>
<td>0.307±0.009c,B</td>
</tr>
</tbody>
</table>

*Means within a column (capital letter) or row (small letter) with different letters are significantly different (p<0.05).

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**Table 2. Specific heat of CSS at different temperatures and concentrations.**

<table>
<thead>
<tr>
<th>Concentration (%w/w)</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.004±0.195a,A</td>
<td>3.956±0.121a,A</td>
<td>3.716±0.166b,A</td>
</tr>
<tr>
<td>30</td>
<td>3.886±0.166a,B</td>
<td>3.686±0.138a,B</td>
<td>3.531±0.083b,B</td>
</tr>
<tr>
<td>40</td>
<td>3.607±0.046a,C</td>
<td>3.522±0.062a,C</td>
<td>3.461±0.070b,C</td>
</tr>
<tr>
<td>50</td>
<td>3.571±0.059a,C</td>
<td>3.481±0.033a,C</td>
<td>3.354±0.136b,C</td>
</tr>
</tbody>
</table>

*Means within a column (capital letter) or row (small letter) with different letters are significantly different (p<0.05).
4.004 kJ/kg°C with standard deviations varying from 0.033 to 0.195 kJ/kg°C. Compared to the previously reported values of \( C_p \) for cassava root of 3.07-3.27 kJ/kg°C (Njie et al., 1998) and for pink guava juice of 3.49-4.12 kJ/kg°C (Zainal et al., 2001), our \( C_p \) values for CSS are reasonable. The \( C_p \) of CSS decreased with increasing temperature and concentration with a maximum value of 4.004 kJ/kg°C at a temperature of 30°C and a concentration of 20% w/w. The \( C_p \) was not significantly different \((p \geq 0.05)\) at temperatures of 30 and 40°C but was significantly different \((p < 0.05)\) at a temperature of 50°C. The specific heats at concentrations of 20 and 30% w/w are significantly different \((p < 0.05)\), whereas there is no significant difference between the values of \( C_p \) at concentrations of 40 and 50% w/w. Sweat (1986) proposed that \( C_p \) depended mostly on the proximate composition of the crop. Siebel (1892) reasoned that the \( C_p \) of food materials was equal to the sum of \( C_p \) values of the solid and water components. The disparity was ascribed to the fact that water in food exhibited distinct properties in the free state more than when it was in the state of solid component (Mohsenin, 1980). A decrease in \( C_p \) affected by temperature and concentration might possibly be due to the increase in volume occupied by cassava starch granules, thus decreasing free water movement around the granules.

### 3.3 Density (\( \rho \))

The \( \rho \) value of CSS is in the range of 1044.0-1119.8 kg/m\(^3\), as presented in Table 3. The standard deviation is in the range of 1.7-10.9 kg/m\(^3\). The \( \rho \) value linearly increases with increasing concentration but decreases with increasing temperature. The minimum value for \( \rho \) was 1044.0 kg/m\(^3\) at 50°C with a concentration of 20% w/w, whereas the maximum value for \( \rho \) was 1119.8 kg/m\(^3\) at 30°C with a concentration of 50% w/w. The \( \rho \) of CSS affected by concentration and temperature corresponded with values reported by Romos and Ibarz (1998) who studied the density of juice and fruit puree as a function of soluble solids content and temperature. The \( \rho \) of peach juice was in the range of 1042.37-1274.36 kg/m\(^3\) at concentrations between 10 and 60 °Brix and for temperatures between 5 and 80°C. The principal solids content of CSS is carbohydrate starch granule and its concentration directly affects the density. Because of increasing concentration, there is increased mass of starch granules. Increased temperatures also increase the thermal expansion of the solutions. Therefore, it is possible that a temperature of 50°C caused more volume expansion of CSS than lower temperatures of 30 and 40°C. Statistical analysis indicated that temperatures of 30, 40 and 50°C and concentrations of 20, 30, 40 and 50% w/w significantly affected the value of CSS \((p < 0.05)\). While the \( \rho \) of CSS was strongly affected by concentration, it was comparatively less affected by temperature.

### 3.4 Thermal diffusivity (\( \alpha \))

Table 4 shows \( \alpha \) values of CSS at various temperatures and concentrations. They were in the range of 0.770x10\(^{-7}\) - 0.831x10\(^{-7}\) m\(^2\)/s with standard deviations varying from 0.011x10\(^{-7}\) to 0.063x10\(^{-7}\) m\(^2\)/s. Statistical analysis indicated

<table>
<thead>
<tr>
<th>Concentration (%w/w)</th>
<th>Density*, ( \rho ) (kg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>20</td>
<td>1048.75±4.113a,A</td>
</tr>
<tr>
<td>30</td>
<td>1076.25±3.202a,B</td>
</tr>
<tr>
<td>40</td>
<td>1099.75±1.708a,C</td>
</tr>
<tr>
<td>50</td>
<td>1119.75±2.363a,D</td>
</tr>
</tbody>
</table>

*Means within a column (capital letter) or row (small letter) with different letters are significantly different \((p<0.05)\).

<table>
<thead>
<tr>
<th>Concentration (%w/w)</th>
<th>Thermal diffusivity*, ( \alpha ) (10(^{-7}) m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>20</td>
<td>0.799±0.047a,A</td>
</tr>
<tr>
<td>30</td>
<td>0.805±0.039a,A</td>
</tr>
<tr>
<td>40</td>
<td>0.827±0.015a,A</td>
</tr>
<tr>
<td>50</td>
<td>0.816±0.017a,A</td>
</tr>
</tbody>
</table>

*Means within a column (capital letter) or row (small letter) with different letters are significantly different \((p<0.05)\).
that neither concentration nor temperature significantly affected ($p>0.05$) the $\alpha$ of CSS.

Table 5 summarizes the relationships of thermal properties as functions of temperature and concentration using multiple linear regression equations. The $k$ of CSS was a weak function of concentration as indicated by the coefficient of temperature (-1.38$x_{10}^{-3}$) and concentration (-5.86$x_{10}^{-5}$). The error value of predicting an equation for experimental data was in the range of 0.12-4.94%. The $C_p$ of CSS showed negative influences of temperatures and concentrations with coefficients of -0.013 and -0.016 respectively. The error value of predicting an equation for experimental data was in the range of 0.02-1.84%. The $\rho$ of CSS decreased with increasing temperature with a coefficient of -0.462, but increased with increasing concentration with a coefficient of 2.116. The error value of predicting an equation for experimental data was in the range of 0.02-1.84%.

### 4. Conclusions

The thermal properties and $\rho$ of CSS were measured at temperatures 30, 40 and 50°C with varied concentrations of 20, 30, 40 and 50% w/w. Statistical analysis indicated that temperatures and concentrations significantly ($p<0.05$) affected $k$, $C_p$, and $\rho$ of CSS. The temperature had a more dominant influence on $k$ than did concentration, possibly due to the movement of molecules of CSS granules. The influence of temperature and concentration on the $C_p$ of CSS was similar to their influence on $k$. However, for $\rho$ temperature was less influential than concentration, because concentration had a positive effect on the mass of a cassava starch granule. The $k$ values were in the range of 0.307-0.333 W/m°C, with 8.50% change and decreased with increasing temperature and concentration. The $C_p$ values were in the range of 3.354-4.004 kJ/kg°C, with 19.58% change and decreased with increasing temperature and concentration. The $\rho$ values decreased with increasing temperature but increased with increasing concentration, and were in the range of 1044.0-1120.0 kg/m$^3$. The $\alpha$ was in the range of 0.770x$10^{-7}$ - 0.831x$10^{-4}$ m$^2$/s and increased with increasing concentration but was non-linearly related to temperature and concentration.

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### References


