EFFECT OF MALTODEXTRIN ON THE FREEZING POINT AND THERMAL CONDUCTIVITY OF UVAIA PULP (*Eugenia piriformis* Cambess)

Efeito da maltodextrina no ponto de congelamento e condutividade térmica de polpa de uvaia (*Eugenia piriformis* Cambess)

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ABSTRACT

The freezing point depression (FPD) of uvaia pulp with and without additives - 10, 16, 22 and 28% of maltodextrin (MD), was measured using a simple apparatus consisting of two major sections: a freezing vessel and a data acquisition system. The thermal conductivity of the pulps was also investigated as a function of the frozen water fraction and temperature using a coaxial dual-cylinder apparatus. Above the initial freezing point, thermal conductivity fitted the polynomial equations well. Below the freezing point, thermal conductivity was strongly affected by both the frozen water fraction and the temperature. Simple equations in terms of the frozen water fraction and temperature could be fitted to the experimental data for freezing point depression and thermal conductivity.

Indexing terms: Freezing point depression, uvaia pulp, thermal conductivity.

RESUMO

O ponto de início de congelamento (FPD) da polpa de uvaia com e sem aditivos - 10, 16, 22 e 28% de maltodextrina (MD), foi medido por um aparelho simples, que consiste de duas seções principais: um vaso de congelamento e um sistema de aquisição de dados. A condutividade térmica foi calculada em função da fração de água congelada e da temperatura, usando um aparelho cilíndrico coaxial duplo. Foram empregadas equações polinomiais para descrever o comportamento do ponto inicial de congelamento e da condutividade térmica. Abaixo do ponto de congelamento, a condutividade térmica foi fortemente afetada pela fração de água congelada e pela temperatura. Equações simples em termos da fração de água congelada e da temperatura podem ser ajustadas aos dados experimentais no cálculo do início do ponto de congelamento e da condutividade térmica.

Termos para indexação: Ponto de início do congelamento, polpa de uvaia, condutividade térmica.

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INTRODUCTION

Brazil is the largest worldwide exporter of concentrated juices; principally of tropical and Amazonian fruits. Some tropical countries such as Thailand, India, the Philippines and China, have large crops grown for exportation (FAOSTAT, 2009) but part of the production does not meet minimal standards for exportation and is lost after harvesting. A similar case occurs with the Amazonian fruits, where production and industrial application are small (SCALON et al., 2004). The uvaia (*Eugenia pyriformis* Cambess) also known as uvalha, ubaia and avair-pear is a native of the Brazilian Atlantic forest. The fruit is a yellow, velvety, pyriform and edible berry chemically composed of 90.7% of water, 7.5% of soluble solids, with a total soluble solids (TSS)/total titratable acidity (TTA) ratio of 3.2, 33.0-39.5 mg $100g^{-1}$ of vitamin C and 1.5% of acidity (RUFINO et al., 2009; DONADIO, 1997). The fruits have a sweet, acidic mesocarp and are used to produce juice, vinegar, wine and liqueurs (GUEDES et al., 2009). Like most wild Brazilian fruit species, it is not marketed extensively, and basic information about its propagation, cultivation and industrialization is not available (CHOUDHARY; MEHTA, 2010).

Drying the fruit pulp converts it to a stable, easily-handled form that reconstitutes rapidly to a good quality product closely resembling the original. Dried pulp products are used mainly as convenience foods and have a long storage life at ordinary temperatures. Nevertheless, the drying of fruit pulps and other products with high sugar contents presents technical difficulties because of their hygroscopicity and thermoplasticity at high temperatures and humidities. The high hygroscopicity and thermoplastic nature of fruit juice powders give rise to problems such as: adhesion to the dryer walls; difficult handling; and caking (AHMED, 2011). Therefore, the use of additives such as maltodextrin and arabic gum (as well as other substances

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such as pectins, calcium silicate and carboxy-methyl cellulose) to facilitate drying and improve the transport and storage properties of the powder, is generally mandatory (ROUSTAPOUR et al., 2006; ADHIKARI et al., 2004).

Maltodextrins consist of β -D-glucose units linked mainly by glycosidic bonds (1 → 4) and are usually classified according to their dextrose equivalency (DE). The DE of a maltodextrin determines its reducing capacity and is inversely related to its average molecular weight (BEMILLER, 1996). This material is mainly used as an encapsulant of products that are difficult to dry – such as fruit juices, flavorings and sweeteners (REINECCIUS, 1991) - and to reduce stickiness and agglomeration problems during storage, thereby improving product stability (JAYA; DAS, 2004). In addition, they provide good retention of volatile substances and confer effective protection against oxidation (RIGHETTO; NETTO, 2005).

Knowledge of the thermal properties of frozen uvaia pulps is essential to calculate the temperature distribution during freezing and frozen storage, and to estimate the freezing time. Food engineers are interested in predicting freezing times in order to estimate the refrigeration requirements for freezing systems, and to design the necessary equipment for effective processing. Energy efficiency, reliability, safety, and quality of the final product must also be considered (DELGADO; SUN, 2001).

The freezing point temperature relative to 0ºC, also called the "freezing point depression" (FPD), which increases with increasing solute concentration, is an important thermophysical property in freezing processes. It is known that the freeze-drying process involves freezing of the fresh product, heating of the frozen foods at low temperature to induce sublimation, condensation of the water vapor and the consumption of mechanical energy to maintain the vacuum. The main disadvantage of this technique is the high capital and operating costs, limiting its use in the food industry and restricting freeze-drying to the dehydration of high-added value products such as instant coffee or baby foods. However, the freeze-drying of fruits and vegetables has recently been proposed for use as high quality ingredients in ready-to-prepare soups, snacks and delicacies (DI MATTEO et al., 2003). Considering this, knowledge of the thermophysical properties related to the freezing of fruit pulps is important in the wider context of freeze-drying research (CHEN et al., 1996; LERICI et al., 1983).

The aim of this work was to determine the freezing point depression and thermal conductivity of uvaia pulps with added maltodextrin, as affected by the frozen water fraction and temperatures from -25 to 75ºC.

MATERIAL AND METHODS

Raw materials: samples of uvaia (*Eugenia piriformis* Cambess) with soluble solid contents of 6.2 to 6.9 ºBrix; moisture contents of 87 to 89% (wet basis) and total sugars of 8.4g/100g, picked in the Ceara region, were obtained from a local market in São José do Rio Preto (SP, Brazil) and stored at 7ºC prior to use. A batch of uvaia pulp was prepared in a pilot plant finisher and sieved through a 1.6 mm-mesh.

Sample Preparation: an aqueous solution with 50% solids (mass basis) was prepared by dispersing the commercial maltodextrin MOR-REX® 1920 (Corn Products Brazil) in distilled water at 40ºC, using a mechanical stirrer. This solution was added to the uvaia pulp, and the mass ratio between the maltodextrin solution and pulp was calculated to provide 10, 16, 22 and 28% maltodextrin (MD) content on a dry weight basis (i.e. 10, 16, 22 and 28 g of maltodextrin/100 g total solids). According to the technical specifications provided by the manufacturer, maltodextrin MOR-REX® 1920 presents $17.0 \leq DE \geq 19.9$.

After processing, the pulps were quickly plate-frozen and stored at –20ºC until used in the experiment.

Determination of the freezing point depression: the FPD was calculated using equipment built on a laboratory scale, as described in Figure 1. The equipment consisted of an acrylic sample holder cylinder (inner diameter 2.7 cm, height 12.5 cm and a wall thickness of 1 mm), connected to a thermostatic cooling bath (Marconi, Brazil), using an ethylene glycol-water mixture (50:50) as the coolant, allowing it to reach cooling temperatures of -50 C. The temperature of the equipment was maintained at -30° C for all the experiments. For the experiments, each sample of uvaia pulp was placed inside the sample holder cylinder, which was cooled by the thermostatic bath. The

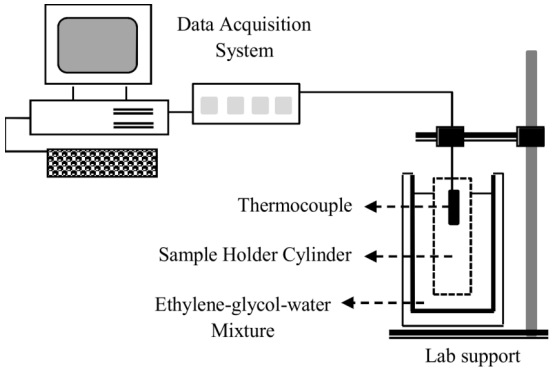

Figure 1 – Schematic diagram of the apparatus used to measure the freezing point depression.

temperature of the sample contained in the cylinder was measured using a thermocouple (calibrated with ethylene-glycol), fixed in a lab support. The thermocouple was placed at a distance of 9 cm inside the cylinder (from the surface to the base), and transmitted data at 1 min time intervals by means of a data acquisition system (Model NI 9213, National Instruments, USA) (TELIS et al., 2007; CHEN et al., 1996).

Before the experiment, the apparatus used to measure the freezing point depression was calibrated using ethylene glycol, which has a well-known FPD (TELIS-ROMERO et al., 1998). Eleven replicate experiments were carried out, obtaining a standard deviation of (SD = 0.737) and standard error of (SE = 0.145).

Determination of the thermal conductivity: the system used to measure thermal conductivity was a coaxial dual-cylinder apparatus, as per the schematic shown in Figure 2. This method was used by Telis-Romero et al. (1998, 2000) to measure the thermal conductivity of orange juice and coffee extract above the freezing point. The heat source was a uniformly distributed electric resistance heater inserted along the axis of the inner cylinder (1055 mm long and 127 mm in diameter) to provide a radial heat flux. The samples were loaded into the annular space between the inner and outer cylinders (inner diameter of 42 mm and length of 220 mm), with both ends fitted with nylon stoppers to prevent axial heat transfer. Before being loaded, the samples were degassed under vacuum for 20 min to remove air bubbles. Only 95% of the available volume was filled with sample in order to allow for expansion during freezing. The apparatus was then immersed in a thermostatic bath (model MA-184, Marconi, São Paulo, Brazil) containing ethyl alcohol. The

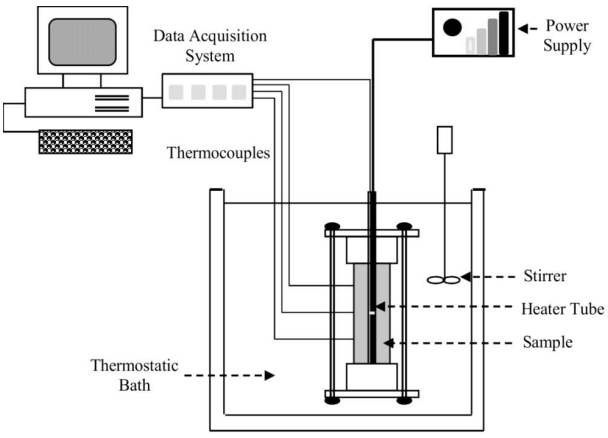

Figure 2 – Schematic diagram of the apparatus used to measure the effective thermal conductivity.

power input to the heater resistance was made by means of a laboratory DC power supply (model MPS-3006D, Minipa, São Paulo, Brazil), which allowed us to adjust the current, with a stability of 0.05%. The temperatures were monitored using a data logger (Model NI 9213, National Instruments, USA) and a LabVIEW data acquisition program written in C+. To measure the temperature, four copper-constantan thermocouples were fixed on the surfaces of the inner and outer cylinders, respectively. Steady state conduction inside the cell was described by the Fourier equation in cylindrical coordinates, with the boundary conditions corresponding to the heat transfer between the two concentric cylindrical surfaces kept at constant temperatures, as described by Gabas et al. (2005).

Equation (1), as described by Bellet et al. (1975), can be used to calculate the sample thermal conductivity, λ from the experimental measurements of T_1 and T_2 under steady state conditions.

$$\lambda = q \frac{\log\left(R_2 / R_1\right)}{2\pi l\left(T_1 - T_2\right)} \quad (1)$$

where q is the heat flux in the thermal resistance (W), r the radius (m), R_1 and R_2 respectively the external and internal radii of the cylinder (m), l = cell length (m), T the temperature (°C), T_1 the steady state temperature of the internal cylinder (°C), T_2 the steady state temperature of the thermostatic bath where the cell was immersed (°C), and λ the thermal conductivity of the sample at the average temperature $(T_1 + T_2)/2$ (W.m^{-1}.°C^{-1}).

The performance of the coaxial dual-cylinder apparatus was checked for accuracy according to the procedure indicated by Telis et al. (2007), using pure water containing 0.5% agar to prevent the effect of convection during the experiments, in the range from 0°C to –30°C.

RESULTS AND DISCUSSION

Freezing point depression: Figure 3 shows the experimental freezing curves for uvaia pulp in *natura* and with maltodextrin.

Figure 3 shows that the freezing point depression for uvaia pulp *in natura* and with maltodextrin has a significant difference for each treatment, which may be due to the high soluble solids content. Table 1 shows the results obtained for the initial freezing point (IFP) for uvaia pulp *in natura* and for that with maltodextrin, as calculated from the respective FPD curves.

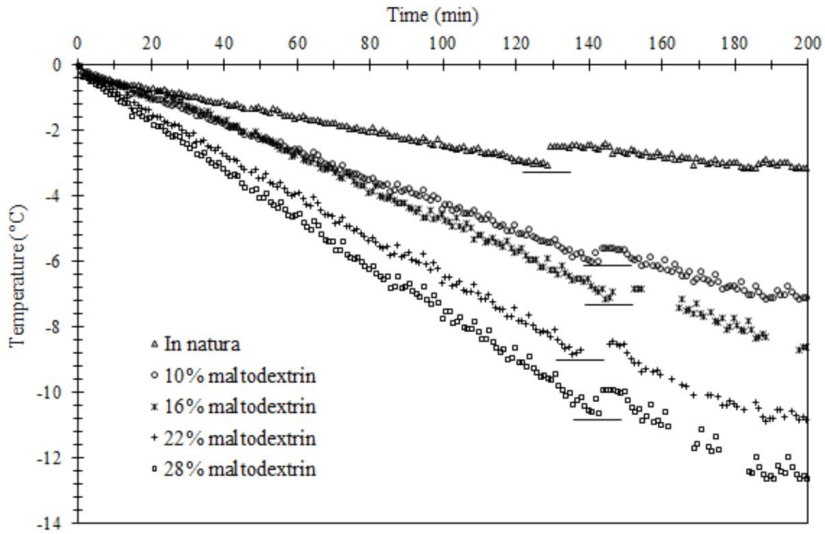

Figure 3 – Freezing point depression of uvaia pulp *in natura* and with 10, 16, 22, 28 % maltodextrin.

Table 1 – Values for IFP*.

Product	IFP (°C)
Uvaia pulp	-3.10 ± 0.02
Uvaia pulp with 10% maltodextrin	-6.00 ± 0.02
Uvaia pulp with 16% maltodextrin	-7.40 ± 0.02
Uvaia pulp with 22% maltodextrin	-9.10 ± 0.02
Uvaia pulp with 28% maltodextrin	-10.80 ± 0.02

*Mean and thermocouple sensibility range.

The results obtained above are similar to those found by Auleda et al. (2011) for fruits such as apple, pear and peach. Foods consist of solid and water fractions, and as sensible heat is removed, so the temperature of the mixture containing the solids and water decreases. Just below the initial freezing point, the water begins to convert into ice. As more heat is removed, more of the water converts into ice, and the remaining solution becomes more concentrated in terms of its solids content. Due to the higher solids concentration, the temperature at which freezing will occur is depressed (GEORG-WILHELM, 1999).

As shown in Table 1, the initial freezing point was reduced with the increasing percentage of maltodextrin in uvaia pulp. This can be explained by the nature of the maltodextrin, which, like any other starch derivative, has a remarkable ability to trap and bind water molecules by means of the hydroxyl group (LOPERA et al., 2009). This interaction of water with maltodextrin is extensive, because starch is highly hygroscopic ($17.0 \leq DE \geq 19.9$). At the cellular level, the heterogeneous maltodextrin coverage is fixed to the external structure of the material, facilitating the inclusion of water from the cells and osmotic mechanisms. The molecular force of hydration increases from the outer to the inner hydration layers, which is directly related to the decrease in initial freezing point (NESVADBA, 2008). To date only simple binary systems such as water–glucose have been investigated thoroughly enough. Authors such as Mackenzie et al., (1977) suggest that the addition of emulsifying agents may affect the equilibrium melting points, heterogeneous nucleation temperatures, homogeneous nucleation temperatures, glass transition and devitrification temperatures and re-crystallisation temperatures, as well as the frozen properties of the foods. Future research should focus on these properties to provide a better understanding of the influence of concentration by emulsifying agents on the initial freezing point.

Thermal conductivity: the results of the thermal conductivity experiment on uvaia juices with maltodextrin are presented in Table 2. Thermal conductivity was almost independent of temperature for all the juices above the freezing point. In the frozen state, however, the thermal conductivity was strongly affected by temperature, in such a way that it increased with decreasing temperature. This behavior was a consequence of the larger fraction of ice present in the samples, exposed to temperatures well below their initial freezing point. Schwartzberg (1981) presented a mathematical study of the food freezing process and reported that the thermal conductivity of ice is roughly 3.7 times larger than that of liquid water, which explains the marked increase in thermal conductivity of the foods during freezing.

Table 2 – Thermal conductivities of uvaia juice samples with different maltodextrin contents and temperatures above freezing point.

Temperature	-26	-24	-22	-20	-18	-16	-14	-10	-6	-2	0	10	20	30	40
% MD	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)														
0	1.409	1.396	1.380	1.383	1.383	1.353	1.315	1.193	0.909	0.485	0.486	0.492	0.499	0.507	0.515
10	1.177	1.154	1.126	1.093	1.098	1.045	0.992	0.771	0.701	0.444	0.450	0.456	0.461	0.468	0.475
16	1.014	0.994	0.979	0.957	0.911	0.852	0.777	0.538	0.425	0.427	0.428	0.439	0.444	0.450	0.456
22	0.892	0.873	0.838	0.795	0.743	0.700	0.636	0.551	0.416	0.418	0.419	0.426	0.433	0.438	0.444
28	0.780	0.808	0.767	0.717	0.656	0.581	0.526	0.389	0.391	0.394	0.395	0.401	0.408	0.414	0.421
%MD	Frozen water fraction*														
0	0.747	0.738	0.729	0.717	0.702	0.684	0.660	0.585	0.410	0	0	0	0	0	0
10	0.575	0.561	0.544	0.524	0.499	0.468	0.427	0.299	0	0	0	0	0	0	0
16	0.499	0.483	0.463	0.440	0.411	0.375	0.329	0.181	0	0	0	0	0	0	0
22	0.421	0.402	0.380	0.353	0.320	0.279	0.227	0.058	0	0	0	0	0	0	0
28	0.350	0.329	0.304	0.275	0.239	0.194	0.137	0	0	0	0	0	0	0	0

*Estimated using equation (2).

Table 2 shows that the thermal conductivities of uvaia pulp and of uvaia pulp with maltodextrin were not affected by a variation in temperature between 30 and 40 °C. This thermal property of food products is mainly a function of the water content and structure. The uvaia pulp presented a slightly higher thermal conductivity compared to fruits with similar moisture content, such as papaya and mango (TELIS et al., 2007). This behavior could be attributed to the higher water content of uvaia pulp (87 – 89 $kg \cdot kg^{-1}$, w.b) and its smaller soluble solids content, which lead to a greater frozen water fraction at any given temperature and a consequent increase in thermal conductivity (NESVADBA, 2008). It is well known from the literature that thermal conductivity decreases with increasing food concentration (DELGADO; SUN, 2001; CHEN et al., 1996). Some authors have reported that as the sugar content increases, so the quantity of free water in the material decreases, leading to a decrease in thermal conductivity (AULEDA et al., 2011). The values obtained for the frozen water fraction presented in Table 2 were calculated using Equation 2:

$$X_{ice} = X_w \left(1 - \frac{T_f}{T}\right) \quad (2)$$

where T and T_f are, respectively, the sample temperature and the initial freezing temperature (°C); and X_{ice} and X_w are the mass fractions of ice (wet basis, dimensionless) and of water (dimensionless), respectively.

According to Krokida et al. (2002) and Schwartzberg (1981), experimental results for the thermal conductivity of uvaia pulp with and without maltodextrin, above and below the initial freezing point, were represented by Equations (3) and (4), respectively.

$$\lambda = P_1 T^2 + P_2 T + P_3 \quad (3)$$

$$\lambda = P_1 \left(1 - \frac{P_f}{T}\right) + P_2 \quad (4)$$

where λ is the thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$) and T is the sample temperature (°C). The fitting procedure was carried out by linear regression, employing the tool solver from the excel workspace. This method involved minimization of the errors between the experimental and calculted data, by adjusting and identifying the parameters for each %MD. Tables 3 and 4 show the model parameters with their respective correlation coefficients (R^2) and standard errors (SE).

Figure 4 shows the agreement between the calculated and experimental data for the uvaia pulp with and without maltodextrin at different temperatures.

Results on the thermal conductivity and freezing point depression of uvaia pulp, are useful information to project industrial equipments and determine the molar mass of the aqueous solutions, respectively (KROKIDA et al., 2002).

Table 3 – Estimated equation (3) parameters and statistical results.

%MD	P_1	P_2	P_3	R^2	SE
0	4.64×10^{-6}	6.73×10^{-8}	0.099	0.998	5.81×10^{-4}
10	4.06×10^{-6}	6.73×10^{-8}	0.111	0.978	1.86×10^{-3}
16	3.98×10^{-6}	6.73×10^{-8}	0.101	0.978	1.75×10^{-3}
22	4.06×10^{-6}	6.73×10^{-8}	0.099	0.995	7.59×10^{-4}
28	3.64×10^{-6}	6.73×10^{-8}	0.099	0.998	2.72×10^{-4}

Table 4 – Estimated equation (4) parameters and statistical results.

%MD	P_1	P_2	R^2	SE
0	1.311	0.275	0.988	1.91×10^{-2}
10	0.584	0.700	0.898	5.80×10^{-2}
16	1.051	0.281	0.994	1.36×10^{-2}
22	0.848	0.339	0.939	3.16×10^{-2}
28	0.826	0.337	0.966	2.16×10^{-2}

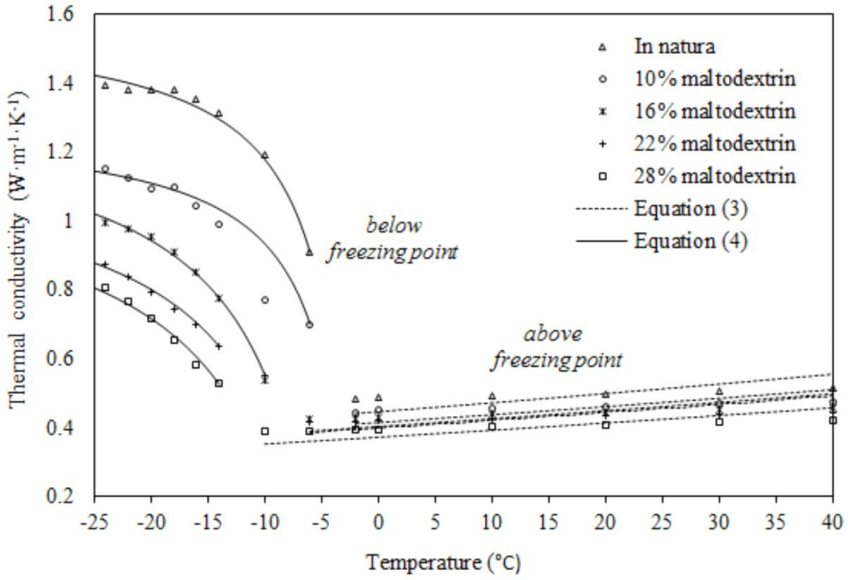

Figure 4 – Comparison between the calculated and experimental data for thermal conductivity of uvaia pulp with and without maltodextrin, at different temperatures.

CONCLUSION

The experimental values for the initial freezing point of uvaia pulp with and without maltodextrin were calculated. In the frozen state, it was observed that the thermal conductivity decreased with increasing temperature. Otherwise, the uvaia pulp alone presented a slightly higher thermal conductivity than the uvaia pulp with added maltodextrin, which could be attributed to differences in the total solids concentrations. The mass fraction of ice in both (with and without maltodextrin) pulps increased during freezing, causing an increase in thermal conductivity of the material due to the higher thermal conductivity of

ice as compared to that of liquid water. The thermal conductivities for uvaia pulp with and without maltodextrin, above and below the initial freezing point, were represented mathematically, obtaining good statistical results for each model used.

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