

## Comment on the Melting and Decomposition of Sugars

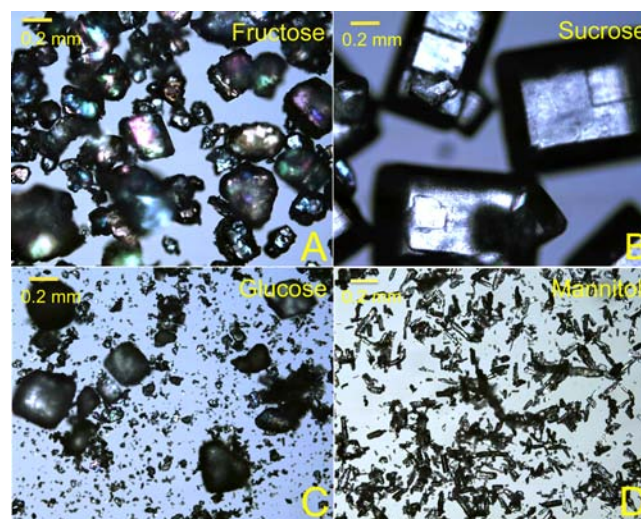
Melting of sugars has been studied by numerous authors, including Roos<sup>1</sup> and many others, as summarized in Lee et al.<sup>2</sup> Lee et al.<sup>2–5</sup> published a series of papers on melting of sugars, studied almost exclusively using variations of differential scanning calorimetry (DSC). These publications have opened up a serious discussion on the melting of sucrose and other sugars. A misinterpretation of the data published in the *Journal of Agricultural and Food Chemistry* was used in public media and the 2011 Annual Meeting of the Institute of Food Technologists and Food Technology magazine<sup>6</sup> to proclaim that “sugar does not melt, as previously believed, but rather decomposes”. We present here arguments that clearly refute the conclusions of Lee et al.<sup>2–5</sup> and express our concerns on published statements lacking scientific validation prone to devalue the food science discipline and mislead readers by fostering a misbelief that sugars do not melt.

Lee et al.<sup>2</sup> studied the heating rate dependency of melting of sugars. They hypothesized that “widely varying sugar melting parameters are not consistent with the definition of thermodynamic melting.” Such variation in melting temperatures of organic crystals is well-known and acceptable, because noncrystalline (amorphous) residues, large molecular sizes, highly variable crystal sizes, defects in crystal structures, impurities, superheating, isomerization and mutarotation, and, particularly, the presence of water (solvent) at normal atmospheric surroundings all contribute to variability in the melting behavior of organic crystals. The papers of Lee et al.<sup>2–5</sup> discuss these factors, but do not acknowledge that these important variables negate the main conclusion that “sugars do not melt”. Lee et al.<sup>2</sup> state the main, repeated conclusion of all four papers,<sup>2–5</sup> “We hypothesize that the kinetic process responsible for the “melting” of the sugars ... is thermal decomposition; thus, the heating rate dependency “melting” ... should be distinguished from thermodynamic melting. Herein, to prevent confusion, the term “loss of crystalline structure” will be used instead of melting.” This paper<sup>2</sup> concluded that “thermal decomposition was the kinetic process responsible for the loss of crystalline structure in the sugars ... and the term “apparent melting” was also introduced.” Lappalainen et al.<sup>7</sup> conducted a prior, careful study of the melting of xylose, using methodologies similar and complementary to those of Lee et al.<sup>2–5</sup> They concluded that, instead of thermodynamic melting, “anomalous melting” of xylose showed a change of conformation of molecules or decomposition during melting. Because of reactions (kinetic process) following but coinciding with ongoing melting of crystals, the temperature of melting was strongly dependent on the rate of heating.

Below, we will refute the conclusion of “loss of crystalline structure by decomposition” by pointing out some details of the experimental procedures utilized in the four studies of Lee et al.<sup>2–5</sup> and obvious pitfalls leading to this conclusion.

Lee et al.<sup>2</sup> reported that all of their sugars were supplied by Sigma-Aldrich Co., Inc., St. Louis, MO, USA, and were used without any purification. As shown here by microscopy (Olympus BX-51, Olympus, Inc., Japan, equipped with Linkam

LT350 cooling/heating stage, Pixelink PL-A662 camera, and Linksys32 version 1.6.2 software, Linkam Scientific Instruments, Waterfield, Tadford, Surrey, UK) in Figure 1, such



**Figure 1.** Crystals of fructose (A), sucrose (B), glucose (C), and mannitol (D) (10× magnification), showing highly varying crystal sizes and large differences across crystal sizes, individual crystal defects, and the “dust”-like noncrystalline, possibly milled particles in glucose as well as the small needle-like mannitol crystals.

sugars (corresponding products from Sigma-Aldrich) have very different crystal sizes. This leads to the conclusion that varying numbers of crystals of differing sizes were likely used by Lee et al.<sup>2</sup> in each analysis. “In each DSC pan, the study used 2.75 mg ... of each sugar.” An assumption of average crystal weight of 0.40 mg for sucrose, 0.04 mg for fructose, and 0.01 mg for glucose (based on weights of crystals shown in Figure 1) gives approximately 7 crystals for sucrose, 70 crystals for fructose, and 275 crystals for glucose (apparently, the glucose crystals had been milled). The samples also contained water, which may be mainly located in amorphous layers on crystal surfaces. The use of hermetic pans by Lee et al.<sup>2–5</sup> meant that practically no water was lost from samples at the lower experimental temperatures. Unfortunately, the weight of the samples after DSC experiments was not reported. Loss of sample mass would have indicated loss of water. Sample weighing after the experiment is considered a standard practice in this type of analyses. Furthermore, there is no reason to expect that any water or other impurities would have been homogeneously distributed; rather, water and impurities must have been present at significant concentrations within specific regions on the surfaces of individual crystals or entrapped in defects inside the crystals. Those authors also used mannitol (which is an isomer of glucitol/sorbitol, *not* the alcohol form of fructose, as

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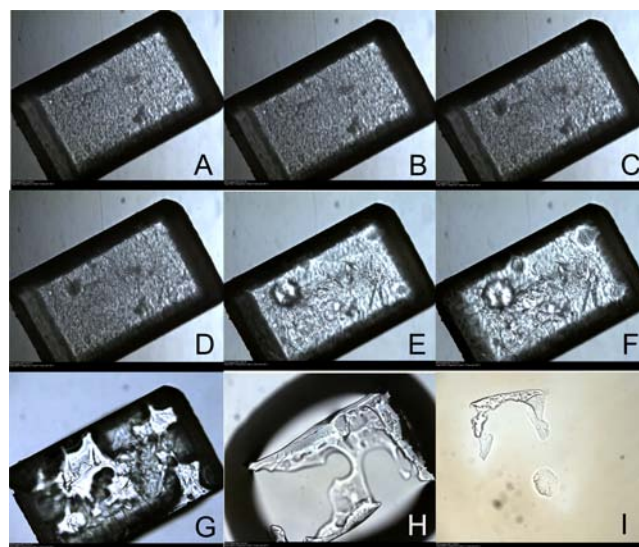
mistakenly stated<sup>2</sup>), as it was claimed to melt without “thermal decomposition”.

It appears that Lee et al.<sup>2–5</sup> did not take into account the presence of residual water, or water produced by decomposition of the sugars, in sample pans that were hermetically sealed. **Even traces of water and smaller sugars as impurities in sucrose can start a progressive melting/dissolution process, followed by partial decomposition of the sugar.** This is likely to initiate on crystal surfaces and becomes catalyzed by defects in the crystal structure. These decomposition reactions produce water that can cause an increase in the heat capacity reported in modulated DSC (MDSC) measurements. (The heat of evaporation of water is enormous, and even the loss of traces of water from sample pans produces a large endothermal shift in heat content.)

Lee et al.<sup>2</sup> based their conclusion of the loss of crystallinity by decomposition on the following statements: “... when the modulation temperature increases above the average temperature, some of the material melts, and when the modulation temperature drops below the average temperature, some of the material crystallizes ... the three sugars exhibited no collections of exothermic and endothermic peaks in the modulated heat flow ... supports that thermal decomposition is the kinetic process causing the loss of crystalline structure in the sugars.” We concur that the melting processes of indium and mannitol differ from those of fructose, glucose, and sucrose. We also agree that a part of these sugars can decompose during the measurements. However, such decomposition leads to liquid flow at crystal surfaces, which changes thermal conductivity and dissolution of molecules from the crystal. As this increases, there is increasing loss of water and enthalpy changes resulting from changes other than melting/recrystallization. Water was also retained as solvent. We can assume that these reactions at or near the crystal surfaces inhibit recrystallization. This results in a change in the amorphous content of the sugar, because of its melting and reduced recrystallization and because of decomposition and possible high viscosity of the surface liquid. Lee et al.<sup>2</sup> correctly discuss the effects of the decomposition products on recrystallization, possibly eliminating recrystallization. However, the authors seemingly ignored that the main component present after loss of the crystalline structure is the original sugar, which, by some process, must have transformed to a liquid, before recrystallization could possibly occur. Lee et al.<sup>2</sup> need to correct their conclusion to note that the crystals, instead of melting, dissolved time-dependently in an increasing quantity of decomposition products and water that formed as a result of the partial decomposition of the amorphous sucrose phase. This is very similar, conceptually, to the melting point depression of ice in frozen foods and can be related to the colligative properties and thermodynamics of solutions. Indeed, one of us has shown that sucrose dissolves, for example, in liquid sorbitol.<sup>8</sup>

Lee et al.<sup>3</sup> reported that “*These results prove not only that the loss of crystalline structure in sucrose is caused by thermal decomposition, but also that it is achieved via a time-temperature combination process.*” This statement, however, does not explain the fact that all sugars in the Lee et al.<sup>2</sup> study also exhibited a melting endotherm for the sugar. This must mean that the loss of crystalline structure did not occur by decomposition, but rather that there was melting/dissolution and associated decomposition. Such decomposition of liquid sugars is well-known and often referred to as caramelization.<sup>7</sup> In our own work, we do not see decomposition products (caramelization)

on crystal surfaces during heating, but we can see decomposition in the liquid phase of molecules released from the crystals (Figure 2). It should be noted that we confirmed



**Figure 2.** Images of a sucrose crystal at 20 $\times$  magnification, obtained using microscopy. The images were taken beginning at the start of heating at 80  $^{\circ}$ C (A). A heating ramp of 5  $^{\circ}$ C/min to 140  $^{\circ}$ C was applied, and an isothermal hold at 140  $^{\circ}$ C for 30 min followed (images at the beginning of the holding time, B, and at the end of holding, C, were taken). This isothermal holding showed some disintegration and cracking of the crystal at amorphous/defective regions, which continued during subsequent heating at 5  $^{\circ}$ C/min to 160  $^{\circ}$ C. An isothermal holding at 160  $^{\circ}$ C for 30 min increased the liquid phase of sucrose at the amorphous/defective regions (images at the beginning of the holding time, D, and at the end of holding, E, were taken). There was no observable discoloration of the crystal/liquid as heating was continued at 1  $^{\circ}$ C/min to 180  $^{\circ}$ C (image taken at 170  $^{\circ}$ C, F). Melting of the sucrose crystal, which started at the amorphous/defective regions, continued extensively during isothermal holding at 180  $^{\circ}$ C for 30 min (images at the beginning of the holding time, G, and at the end of holding, H, were taken). The liquid sucrose showed decomposition (discoloration) at the end of 180  $^{\circ}$ C isothermal holding, I, and melting of the remaining crystal was completed during final heating at 1  $^{\circ}$ C/min to 185  $^{\circ}$ C.

that the thermodynamic melting point (the temperature at which no crystalline material can exist) is about 185  $^{\circ}$ C for sucrose. If there is decomposition inside a crystal, the crystal must burst. We found some cracking at the crystal surface, in our microscopic observation of melting (Figure 2), but that occurred at defects or pre-existing cracks, after a liquid sucrose phase appeared, without decomposition of the sugar. Even heating of a mix of fructose and sucrose crystals showed melting of the crystals of both sugars prior to decomposition.

Lee et al.<sup>3</sup> made an interpretation that “*This heating rate dependency led to the hypothesis that a kinetic process was responsible for the loss of crystalline structure ... the most plausible kinetic process was thermal decomposition, not as an additional process accompanying thermodynamic melting, but as the kinetic process responsible for the loss of crystalline structure.*” This interpretation of the data raises serious concerns, because the loss of crystalline structure is reported, but no melting/dissolving of the crystals to liquid sugars is acknowledged. In fact, the materials, after complete loss of crystallinity, were primarily composed of the noncrystalline forms of the sugars,

and not of their decomposition products. This appearance of liquid sugar was acknowledged by Lappalainen et al.,<sup>7</sup> and we have confirmed this observation microscopically, as shown in Figure 2. The experimental evidence does not appear to support the conclusions made by Lee et al.;<sup>3</sup> rather, the evidence does suggest that the sugar molecules below their thermodynamic melting temperature gained mobility because of their dissolution/melting. There could be no chemical change of the sugar molecules before they were released from the crystal structure, as also shown by us in Figure 2. Lee et al.<sup>3</sup> proposed “*that thermal decomposition is the kinetic process responsible for the loss of crystalline structure ...; not that thermal decomposition occurs in addition to thermodynamic melting.*” But as noted earlier, the samples, according to the data presented by Lee et al.,<sup>2–5</sup> produced amorphous sugars with decomposition products, but not decomposition products with residues of the original crystals, which would have been the case if crystallinity were lost by decomposition.

Lee et al.<sup>3</sup> considered that a “*possible source of the H is surface water on the sucrose crystals.*” This hypothesis includes the presence of surface water, which means that there must have been dissolved sucrose, particularly at temperatures above 100 °C. In turn, this means that a portion of sucrose was mobile and available to initiate a progressive decomposition and increased dissolution/melting of sucrose with increasing temperature. This shows that sucrose was sucrose, as long as the molecules were accommodated in the crystals.

An interpretation of the melting endotherm for sucrose, obtained by standard DSC, “*indicates that thermal decomposition causes the loss of crystalline structure in sucrose, and the observed endothermic peaks measured by SDSC are due to the energy of amorphization ...*” However, the data reported<sup>3</sup> show an amorphous melt forming after heating to 192.7 °C, with complete loss of crystallinity, but very little degradation and discoloration. **The evidence for the loss of crystalline structure by decomposition is missing.** There are no results that could be used to prove that there was no melting/dissolution producing the endotherm. This endotherm has been shown by numerous authors in earlier studies,<sup>2,7</sup> and the melting can be proved by microscopy (Figure 2). Furthermore, the melting is proved by glass transition analysis and chemical techniques, which all show the presence of an amorphous sucrose melt.<sup>9</sup> Lee et al.<sup>3</sup> also provided some compositional data, which appear to prove that decomposition occurred after the melting of sucrose.

The loss of crystalline structure of sucrose was reported at various temperatures, but decomposition, after >50 h of holding at 120 °C in a sealed pan, is not surprising, as this condition is above the melting temperature of fructose (a possible first decomposition product), and there were water and impurities available to catalyze any decomposition reaction. Unfortunately, the acidity of the system is not known. It would also be imperative to report the loss of weight during such an extensive reaction period. The evidence, however, suggests that the loss of crystallinity must have occurred prior to any decomposition. The authors note correctly that “*the temperature at which sucrose decomposition begins may be related to the difference in the presence of trace amounts of water, salts, reducing sugars (i.e., glucose and fructose), and organic acids in the sucrose*”, but the same factors are likely causes of releasing and mobilizing sucrose molecules from the crystals, without prior or concurrent decomposition. Although mannitol was shown to decompose after 5555 min of heating at 159.9 °C, it was

concluded to show thermodynamic melting. We presume that some melting of mannitol could happen at the holding temperature in the vicinity of the melting temperature, being clearly the prerequisite of decomposition.

An HPLC study showed that “*upon complete loss of crystalline structure in the SDSC method (fast heating method) (sample temperature of 192.7 °C), the sucrose content decreased to 61.871% ... whereas, in the quasi-isothermal MDSC method (slow heating method) (120.0 °C for 3100 min), the sucrose content decreased to 24.043% ...*” These findings are completely contradictory to the conclusions made. The results show that sucrose, after loss of crystalline structure, was still sucrose. We cannot agree, because sucrose still exists after found completely losing crystalline structure by decomposition.

Lee et al.<sup>3</sup> concluded that “*caramelization of sucrose can simply be defined as browning of sucrose (or other apparent melting sugar) by applying heat for a length of time. In turn, the conversion of crystalline sucrose to amorphous sucrose by applying heat for a length of time (i.e., apparent melting) can be thought of as “controlled caramelization.”*” It seems that the authors, by this statement, conclude that sucrose was melted/dissolved; that is, melting/dissolution takes place to produce amorphous sucrose using heat, and that process can be used to control caramelization (decomposition of the amorphous sucrose). In our view, this has been known for centuries.

Additional data on the melting of sugars were produced by Lee et al.,<sup>4</sup> who reported results on applying various heating rates in DSC measurements. As shown here in Figure 1, the materials were very different in their crystal sizes, which is especially important to note in rapid-scanning DSC studies. That paper<sup>4</sup> reported that “*... the heating rate at which this thermodynamic melting temperature is achieved is most likely influenced by the type and amount of trace components (e.g., water and salts) ... In the case of sucrose and glucose, thermodynamic melting temperatures were not able to be obtained.*” Impurities affect the melting properties, and they must affect melting/dissolution. The explanation for the finding that glucose and sucrose did not show a temperature limit for heating rate dependence is obvious from our Figure 1. The heat transfer and diffusion of molecules from the large crystals cannot compete with the increase in external temperature. (Note that there are no details on how samples were prepared in Lee et al.<sup>4</sup> “*Because of the very small sample sizes used in the rapid-scanning DSC, these samples were prepared using a microscope.*”) Moreover, there were no data on the sample temperatures, and these data are perhaps impossible to obtain. We assume that the authors selected individual crystals of appropriate size: “*For sucrose and glucose (approximately 100 µg) samples, the rapid-scanning DSC measurements were performed in duplicate at heating rates of 250, 500, 1000, and 1500 °C/min.*” We note that the crystals selected were approximately 500 µm in size, which means that heat transfer could present a serious problem for such samples in rapid-scanning DSC. Also, the size of the sucrose molecule is double that of fructose and glucose, which is of great importance in crystallization/melting processes. Our experience supports and we recommend the use of different sample masses in all DSC studies, to separate sample size-independent instrumental artifacts.

Lee et al.<sup>4</sup> acknowledge that “*... trace components [e.g., water, salts, reducing sugars (i.e., glucose and fructose), and organic acids], which have been reported to accelerate sucrose decomposition, vary widely among different sucrose samples ... Therefore, the minimum heating rate required to reach the thermodynamic melting*

temperature, as well as the apparent melting temperature, could be different for every sugar sample studied." In other words, melting/dissolution of various crystals can happen differently and, also, in samples with multiple crystals (used for standard and modulated DSC), crystals can melt/dissolve at different temperatures and then accelerate other changes. Hence, "loss of crystalline structure by decomposition" may not be the right conclusion.

We finally comment on the findings of Lee et al.,<sup>5</sup> who "... investigates the effects of heating conditions used to produce amorphous sucrose on its glass transition ( $T_g$ ) parameters, because the loss of crystalline structure in sucrose is caused by the kinetic process of thermal decomposition ...." We find it contradictory that crystalline structure is found to be lost by decomposition, but, thereafter, the glass transition of amorphous sucrose in the same sample can be studied. We find that decomposing a glass-former means that the glass transition measured thereafter is not that of the original glass-former. Also, the decomposition that could cause the loss of crystalline structure cannot result in the formation of amorphous sucrose. **None of the data reported by Lee et al.<sup>2-5</sup> explain how decomposition can cause loss of crystalline structure of any sugar.** The findings of Lee et al.<sup>2-5</sup> are valid for melting sugars under different temperature conditions and for measurements of the properties of the melts with decomposition products formed subsequent to melting/dissolution. The only way that decomposition can be thought to cause loss of crystalline structure is if the presence of decomposition products accelerates the release of the sugar molecules from their crystals. This, however, requires a noncrystalline phase (molecules released from the crystals or pre-existing amorphous phase), before the decomposition reactions can start and produce decomposition products to further accelerate melting/dissolution.<sup>7</sup> This is proved by the images shown here in Figure 2.

Lee et al.<sup>5</sup> found that "a decrease in  $T_g$  values and an increase in  $\Delta C_p$  as heating rate decreases are accounted for by the plasticizing effect of the small molecular weight decomposition components." As a conclusion, this statement acknowledges that the decomposition products affect the melting/dissolution of the sugar crystals. This also means that sugars melt, and they melt differently in the presence of plasticizers, which can be their own decomposition products. We, however, cannot accept statements such as "sugars do not melt" or that sugars "lose (sic) crystalline structure by decomposition". These statements violate and argue against all the findings of Lee et al.,<sup>2-5</sup> as well as all the known thermodynamic consequences of impurities and solvents on melting/dissolution of crystals. The sugars are the same sugars released from their crystals, independent of the temperature at which the process takes place. This is what the authors also concluded in Lee et al.:<sup>5</sup> "The amorphous sample is not just amorphous sucrose, but rather amorphous sucrose plus the resultant decomposition components ... Because the kinetic process of thermal decomposition is responsible for the loss of crystalline structure in sucrose, the observed decrease in  $T_g$  values was ascribed to the plasticizing effect of small molecular weight decomposition components." The only problem is the lack of evidence for the "kinetic process of thermal decomposition" to be "responsible for the loss of crystalline structure". Lee et al.<sup>2-5</sup> have not explained or proved this hypothesis. The kinetics of decomposition may affect how fast melting/dissolution of sugars takes place, but the decomposition as such has nothing to do with the removal of molecules from the sugar crystals.

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### Notes

The authors declare no competing financial interest.

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