QUALITY OF SUCROSE CRYSTALS AND STORAGE STABILITY OF WHITE SUGAR

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Introduction

The quality of sugar crystals is defined commercially by the so-called European points based on the determination of aspect, color in solution and ash. Other parameters are often listed among the specifications like moisture content and grain size distribution (M.A. and C.V.). All these quality parameters depend on the way crystallization was conducted, washing was made in the centrifugals as well as drying, cooling, handling and storage conditions.
The quality of white sugar might be acceptable according to specifications but it can evolve during storage to instability of color, size and sometimes caking. We have used water vapor sorption isotherms and image analysis of crystals to understand the origins of white sugar instability and especially to explain the conditions of breakage of sucrose crystals and dust formation.

1. Sucrose crystal defects

Defects of sugar crystals can be classified as internal and external defects. Among internal defects inclusions are the most important. External defects are those visually observed like twins, conglomerates, agglomerates and fragments of crystals obtained by the breakage of the most fragile needle-like single crystals.

1.1. Inclusions

The presence of impurities inside the crystal lattice has important effects on the sugar quality especially as concerns colour and ash content as well as the included fraction of moisture which may be released during storage and provokes in certain conditions the caking. The study of inclusions is well documented (Vaccari and Mantovani, 1995). The origin of

inclusions is mainly the capture of mother liquor droplets during fast growth of sugar crystals. In fact, the various faces of sucrose crystal have different rates of growth and the most rapid faces include mother liquor more rapidly than the others. It happens that inclusion is not visible in the crystal. In such case, heating at 105°C in the oven can reveal the colored drop included in the crystal lattice (Figure 1). The inclusion phenomenon can be limited by controlling the supersaturation of mother liquor to master growth kinetics.

1.2. External defects

The defects of crystals easily detected visually or under microscope are morphological. External habits of sugar crystallized under various conditions are described in Vavrinecz Atlas of sugar crystals (1965). Among the forms which are different from the simple 15 habits characterized by their Miller's indexes (Vavrinecz, 1965), there are different twins, conglomerates and elongated shapes.

1.2.1. Twins

In case of twins, 2 single crystals have a junction along a different plane depending on the type of twin (Vavrinecz, 1965)

(a) Type 1 twin crystals have their left poles turned towards each other while the right poles point outwards
(b) Type 2 twin crystals have their right poles grown together while the left poles are pointing outwards
(c) Types 3 twin crystals have both single crystals placed behind each other and are grown together along the a face (Figure 2).

The junction zone between the single crystals in a twin is, from the mechanical point of view, a weakness point where crystals can separate into fragments. Moreover, mother liquor retained between the crystals is not eliminated by washing in the centrifuge (Vaccari and Mantovani, 1995). Formation of twins depends on supersaturation, the higher the supersaturation, the most probable twin formation.

1.2.2. Conglomerates

In such assembling of crystals, the junctions are random. Many crystals attached to each other grow together. This phenomenon happens when very high supersaturation is obtained locally in boiling pans. The consequences of this defect are the increase of colour in solution and included moisture as well as friability (Figure 3).

1.2.3. Agglomerates

After drying of sugar crystals, it happens that an amorphous layer of dry sugar is formed at the surface above a thin film of saturated solution. This phenomenon together with the heterogeneity in moisture and the presence of fine particles lead to the agglomeration of two or more crystals. Here again the junction between particles includes moisture and can break during handling (Figure 4).

1.2.4. Other defects

Chalky white sugar crystals are observed when the amount of dust is high. This originates in case of abrasion by metal screens and scrolls or scratching in drum- dryers.
Irregular shapes especially needles are observed when sucrose is grown in presence of specific impurities (raffinose, dextran,…). A large C.V. of sugar crystals can have as its origin the use of seeds with large size distribution, spontaneous nucleation and rapid changes in vacuum or temperature during the boiling.

2. Consequences of crystals defects

The consequences of sugar crystal defects are numerous and economically detrimental. They may lead to the formation of fine particles by different breakage mechanisms (Verkoyen et al., 2002). Depending on the force applied and its direction (i.e; normal, tangential or any direction), the different breakage mechanisms observed are called attrition, abrasion, wear, fracture, fragmentation and chipping. Attrition (Figure 5a) and fragmentation (Figure 5b) are caused by normal forces, Abrasion (Figure 5c) and chipping (Figure 5d) by tangential ones and wear and fracture by forces of any direction. The size of particle after attrition, abrasion or wear remains almost the same and the shape becomes rounder. During chipping, small pieces of particles are broken and the particle becomes rougher. Fracture and fragmentation yield small fragments, this reducing the average size of particles.

The formation of fragments of particles and the change in size and shape of crystals makes sugar crystals more reactive towards water vapor. This is directly linked to the aptitude of white sugar to cake. The most detrimental factor on the flowability of sugar was found to be a high amount of fine particles (above 10 %) (Rogé and Mathlouthi, 2003)

On the other hand, sucrose crystals are sometimes defined as hard or soft depending on their friability. In fact hardness of sugar crystals is not well defined in the literature. A true hardness could be defined by objective test such as Brinnell index. Hardness according to Vickers for sucrose crystals is equal to 755 MPa (Bubnik et al., 1997). It seems that boiling at

low temperature yields soft crystals as compared to normal or high temperatures. Depending on the size of crystals, the large crystals appear to be hard and sharp and the small crystals feel to be soft by comparison.

All these defects end at an increased instability of bulk white sugar especially as water vapor pressure is increased.

3. Control of crystal defects and their consequences

3.1. Image analysis

Image analysis can be helpful and handy tool to determine and observe the breakage of sucrose crystals. Computer image analysis enables also evaluation of crystal size distribution and control of crystallization process in technical sugar solutions, which involves the evaluation of the produced crystals (Bubnik et al., 2001).

The Laboratory Universal Computer Image Analysis - LUCIA G system, which was applied in this work, is a product of the LABORATORY IMAGING Co., Prague, Czech Republic. LUCIA G is the true colour version and grabbing, processing and analysis of images are performed at RGB or HSI colour space. LUCIA includes a powerful, full-featured macro language and together with a rich image analysis library provides an excellent developer's environment for image analysis.

Three different kinds of images can be measured: colour, binary or so-called mask image. Colour image is used for intensity measurement or tone intensity determination. Binary image is useful for shape determination or size measurement (area, length, elongation). Mask image helps to reduce some area of measurement.

A wide spectrum of different objectives, microscopes, cameras and lighting systems enables the measurement of particles with different size range from several centimeters to microns. The program involves large amount of tools for adjustment and treating of the image to obtain the form suitable for optimal computer analysis.

Other components of the system used for image analysis were: digital camera JVC TK-C1380 with a resolution of 470,000 pixels, card Mu Tech 400 that is able to transfer the data from the camera to the computer, system of lenses Navitar, stand Kaiser and fiber optic lamp Hund Wetzlar. The Figure 6 shows the configuration of the system for image analysis.

3.1.1. Parameters for size distribution measurement

To determine the crystal size distribution different parameters were used:

- *Area (A)* is the main measured size parameter. It is expressed as a number of pixels (for uncalibrated measurements) and gives the true size of the object (if the calibration is made).
- *Maximum and minimum feret diameter (MaxFer) and (MinFer)* are measured as a length of an object projection under the angle 0 – 180 ° (measured by 10°).
- *Equivalent diameter (EqD)* is determined by the circle diameter, which would be of the same area as a measured object: $EqD = (4 A / \pi)^{1/2}$
- *Elongation (E)* is determined as a ratio of maximum to minimum Feret:

  $E = MaxFer / MinFer$

However, by the LUCIA system many other parameters can be evaluated, such as *perimeter* **(***Per)* of the measured object that is calculated from four different object projections under different angles (0, 45, 90 and 135 °), *length (L)*, which is calculated from perimeter value, *width (W)* is defined by the length *L* and area *A*, *mean chord (MCh)* is a mean value of secants of directions under angles of 0, 45, 90 and 135°, *cylindrical volume (VeqCy)* presents a volume of an equivalent cylinder, *spherical volume (Veq Sph)* is the volume of the ball of certain equivalent diameter, *circularity (Cir)* gives the degree how an object shape approximates the circle and is calculated from area and perimeter and its value for a circle is 1.

3.1.2. Object evaluation and separation

The ability to separate and differentiate scanned objects is a basic parameter for object measurement, which shows also a quality of used image system. Above all, four main functions *erosion, dilatation, open* and *close* can be used for this purpose. After using *erosion* (inner layer of object is subtracted) and *dilatation* (outer layer of the object is added) the object size is reduced (*erosion*) and or enlarged (*dilatation*) thus the results are affected. However using *open (erosion* followed by *dilatation)* and *close* (*dilatation* followed by *erosion*) the size of object is not affected. Other important functions are *CloseHole*, *SmoothBinary*, *CleanBinary*, *Contour* and others.

In many cases it is more useful to perform a manual separation of objects. The LUCIA system enables shift between an original (unmodified) image and modified image during manual processing. Manual separation allows excluding of irregular aggregates, which may be caused by imperfect sample preparation. In many difficult cases the operating personnel intervention is very meaningful and manual evaluation of the data depends strongly on experience and practice of the operating personnel.

3.1.3. Automatic measurement of scanned objects

The LUCIA system contains a program unit based on the programming language C++, which allows creating programs for evaluation and measurement of crystal size distribution and many others. All steps performed during picture evaluation are automatically saved in a subroutine and the whole process thus can be repeated if needed. Some steps can be changed or deleted. When the control of automatic evaluation is necessary, program can be stopped and then modified or confirmed.

The program has some additional functions like: addition of text labels for easier manipulation, limits and thresholds conditions (threshold setting, measurement of particles of a certain size, circularity utilization to exclude air bubbles, fibers from packages or admixtures), addition of different calculations for size, weight and area determination according to created relations, etc.

3.1.4. Result output

Output of results might be in a form of table, histogram, or it can be transferred into a spreadsheet for further processing. Program enables wide choice of evaluated parameters including statistical processing. All obtained images and tables can be saved and processed again. Additional scale, description, text label or legend can be added into images. An up-grade LUCIA version saves all original images and supplemental information in two levels so that measured image can be displayed in two versions, the original one and the modified one as well.

3.2. Study of the crystal breakage mechanism by image analysis

As already mentioned, the LUCIA system enables capture of colour pictures of different objects and can be used to observe and compare different breakage mechanisms. Figure7 show histograms (equivalent diameter distribution) of sucrose crystals before and after breakage treatment for sample with different mean apertures (in the range 100 - 1000

μm). It is clearly demonstrated that breakage yields a large C.V. and an increase in dust particles (< 150 μm). In addition, these results shows that the most friable crystals are those of 100-200 μm and those of 800 - 1000 μm. It is known that small crystals behave as soft as compared to standard sugar. The largest crystals are fragile due to the defects of inclusion and elongation.

3.3. Water location in the sugar crystal

Water content in sugar crystals was analyzed using an adapted method of Karl Fischer titration. Total water was obtained after complete dissolution of the sugar sample in methanol/ formamide mixture (2/3 - 1/3 (v/v)) at 50°C (Rogé and Mathlouthi, 2000). After analysis of total water, the solvent mixture is saturated with sugar. Addition of another sample of sugar and a very short agitation only allows release of surface water and its titration. This method permitted showing that about 80 % of moisture is located inside the crystal and only 20% at the surface. Moreover, water is not included in the crystal lattice as pure water but in mother liquor droplets observed by oven heating of crystals at 105°C (Figure 1). As already mentioned, included water increases the fragility of sugar crystals and yields fragments and dust.

3.4. Water vapor sorption of broken crystals

The drying and handling of sugar crystals with defects such as conglomerates, twins and inclusions increases the probability of dust formation. Likewise screening of crystals especially when it is repeated to obtain a certain grain size (M.A.) may be at the origin of the abrasion of large crystals and the sticking of fine particles at the surface of these crystals (Figure 8). Although commercial requirements of a certain mean aperture (M.A.) and size distribution (C.V.) are met, the sugar behaves as very hygroscopic and is subject to caking. The role of fine particles in caking phenomenon was already published (Rogé and Mathlouthi, 2003). We report here a series of water vapor sorption curves (Figure 9) showing the role of fine particles added to standard sugar. Moisture content increases at the surface of sugar crystals which are covered with fine particles. These particles rapidly dissolve and recrystallize releasing free water. A chain reaction of dissolution and recrystallization is initiated which ends with the lumping of the whole sample of sugar.

CONCLUSION

Image analysis of sugar crystals allows direct observation of the defects. It can help in determining the breakage mechanism by establishing crystal size distribution histograms.

Analysis of water content and water vapor adsorption isotherms informs on the quantity of water and its nature (surface or included water). The hygrosocpicity of sugar and its aptitude to break or to cake are directly linked to the quality of crystals. Such a quality is mainly obtained during crystallization in the boiler and also by controlling the steps of drying, handling and storage.

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