Review of R&D results on sugar crystallization obtained at the University of Chemistry and Technology of Prague during last 25 years

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Abstract

This paper represents a summary of most important research activities in sucrose crystallization, in which the Department of Carbohydrates and Cereals, part of the University of Chemistry and Technology (UCT) Prague, have been focused over the last 25 years. A wide range of these projects has been carried out in cooperation with many research institutes, universities and industrial partners.
These activities can be divided into four main research areas that are interconnected and support each other.

1st area: Physical and chemical properties of sucrose and sugar solutions

The main condition for a successful control of the crystallization process is knowledge of physical properties of sucrose, other sugars and their impure solutions. At the beginning, it was necessary to obtain and verify these data experimentally. The most important properties to measure were: *(a)* density of sugar solutions (cooperation with Prof. Dandar, STU Bratislava); *(b)* solubility of sugars in technical sugar solutions (cooperation with Dr. Parkin, the British Sugar Research Centre in Norwich); *(c)* the effect of impurities on a shape of sugar crystals (cooperation with prof. Mantovani and Prof. Vaccari, University of Ferrara); and *(d)* the increase of boiling point of sugar solutions (Dr. Sarka, UCT Prague). This work involved a modification and/or design of new experimental devices. The most important data and results have been published in professional and scientific papers; included in the SUGAR TECHNOLOGY MANUAL (authors: Bubnik, Bruhns, Kadlec, Urban); and presented in congresses, such as CITS, ESST and AvH.

2nd area: The growth kinetics of sugar crystals in pure and impure sugar solutions

This area included work on gathering kinetic data that describe the growth of sugar crystals under conditions simulating the industrial environment. Equations describing the crystallization process have been suggested and verified using the data obtained from the 1st research area. Newly designed and built experimental equipment have been also used in laboratory and pilot plant trials.
Ultrasonic techniques for measurement of properties of sugar solutions and suspensions as well as US methods for determination of the metastable zone width have been developed and applied for sucrose crystallization control.
In cooperation with Prof. Mathlouthi from the Universite de Reims Champagne-Ardenne, a new image analysis method has been developed for control of the crystal formation and evaluation of crystal size distribution in crystallization processes.

3rd area: Simulation and mathematical modeling of new processes and technologies

Physical data about sugar solution properties and kinetic equations became an indispensable condition for further work on creation of new technological diagrams; simulation and modeling of processes; and not least, design of new manufacturing process diagrams for industrial partners. These activities were carried out under the European project Copernicus SUCLEAN that has been focused on raw juice crystallization and design and modeling of new sugar processing diagram. Partners in this project were: University of Ferrara, UMIST Manchester (Dr. Klemes), UCT Prague and Politechnika Warszawska Fillie Plock (Prof. Urbaniec). An essential part of the research was a study of application of membrane filtration (MF and NF) for purification of sugar solutions before crystallization carried out in cooperation with LSU Baton Rouge, USA.

4th area: Experimental work for industry and cooperation with industrial partners

The fourth part of our activities involves application of experimental data in measurement and modeling of processes in real sugar manufactures. Significant cooperating partners were VUC Prague (continuous crystallizer, Dr. Gebler), sugar factory TTD Dobrovice and other Czech sugar plants, ZVU Hradec Kralove, Czech Technical University Prague, and the Mikropur Company Hradec Kralove (Dr. Pridal).

Effect of supersaturation on the kinetics and thermodynamics of impurity transfer during sucrose crystallization

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The crystallization process is governed by interrelated thermodynamic and kinetic factors, which in turn affect the rate and extent of impurity transfer into crystals. The driving force for crystallization is supersaturation, which is defined as the difference between the chemical potential of the solute in the solution under the prevailing conditions, and that in the solution at equilibrium. Thermodynamics plays a key role in determining the driving force for the crystallization process but also determines the uptake of impurities under steady-state conditions. Therefore, the detrimental or beneficial effects of impurities/additives are hardly avoided once supersaturation, temperature, pH, and solution purity are established.

This work presents the rate of supersaturation variation as a variable that can be used to dramatically promote or inhibit crystal growth, relatively to steady-state conditions.

Constant supersaturation conditions are hardly verified in the practice of crystal growth. This is due to several different reasons that include solute depletion with time, solvent evaporation, or any other time course change of process variables such as temperature or impurity content. In a phenomenon called growth rate hysteresis, different crystal growth rates are observed in impure media as supersaturation is increasing or decreasing. This is the likely result of the competitive adsorption of impurities and solute on the crystal surface. In a first step, the effects of the impurity concentration on the crystal growth rate at constant supersaturation are quantitatively described. Growth rate curves obtained in pure and impure solutions are used to investigate the influence of supersaturation on the relative growth rates under equilibrium. The competitive adsorption model under unsteady state conditions (CAMUS) is then presented and validated against experimental results of crystal growth inhibition in the presence of impurities for changing supersaturation levels. Fast supersaturation changes with time lead to unsteady-state values of kink occupation by impurities, thereby contributing for the inhibition or promotion of crystal growth. Cases of non-conventional crystallization kinetics documented in literature are successfully explained through this model.

QUALITY OF CRYSTALS AND PRACTICAL ASPECTS OF SUGAR CRYSTALLIZATION

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Abstract

The quality of sugar crystals is defined commercially by the so-called European points based on the determination of aspect, colour 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 crystals might be acceptable according to specifications but it can evolve during storage due to instability of colour, size and moisture content and water activity which is at the origin of caking.

The major defects like impurity inclusions, habit modifications, the presence of twins, conglomerates, agglomerates and other defects like dusty or chalky sugar mostly originate from the composition of syrup, seeding, growth and brixing conditions, especially as regards the supersaturation (σ), temperature and pressure inside the vacuum pan.

Considering the importance of the first steps of production of sugar crystals, we intend to recall the practical aspects of crystallization, namely seeding and growth of crystals. The seeding of industrial pans remains a critical step which deserves optimization. The optimal quantity of seed crystals to use needs to be determined precisely, so that the correlation between the number and mass of crystals is known accurately. Supersaturation at seeding should remain in the metastable zone around $\sigma \leq 1.15 - 1.20$. During crystal growth, number of crystal defects may occur due to increased supersaturation or other boiling practices. At high supersaturation, above 1.3, sugar crystals conglomerates, twins and false grain may be formed. Brixing is generally regarded as a short period of evaporation to reach final Brix value before emptying the pan. In fact the Brixing requires a particular care and very often the addition of water, which helps controlling σ, avoiding false grain and gaining time.

Obtaining good quality sugar crystals and maintaining their quality and stability requires that some rules are adopted. All processing steps should be optimized in order to achieve the crystals quality target. Obtaining of high quality Sugar Crystals requires paying attention to each and every detail not only following crystal science principles (nucleation, growth …) but also rules of the thumb and instinct: *Crystallization is an art!*

Technical and economical comparison of the different crystallization schemes

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The actors of the sugar world must constantly face the economic risks which impact their management strategies in the more or less long term: evolution of the prices of ethanol, fossil energies, electricity, evolution of norms and economic policies (example the end of sugar quotas in Europe) and of course the evolution of sugar prices.

In the current context of the end of sugar quotas, French factories are asking themselves the question of optimizing their sugar production. This challenge requires an adaptation of the industrial tool and especially the crystallization workshop, at the heart of this challenge.

Historically, sugar crystallization worked in 3 strikes with refining; this scheme has subsequently evolved with the constraints of industrial sites and the production of fuel ethanol. A revision of the different schemes is now being considered in response to the end of the quotas. However, the techno-economic optimum is not always easy to determine.

BEMEIO software (Beet plant Model for Energy and Incomes Optimization) is a powerful modeling tool developed to optimize the operation and configuration of sugar complexes as a whole. Among other things, it makes it possible to model the crystallization scheme best suited to each plant in the current economic context.

For this presentation, based on a typical plant, several crystallization schemes were modeled with BEMEIO^{TM}. The impact on sugar production, energy consumption, changes in plant income and return on investment were then evaluated. The comparison of the various scenarios makes it possible to define the best development strategy for the plant.

Colorant inclusion into sugar crystals grown in blended beet and cane syrups

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With the decision of the EU market liberalization, the European sugar manufacturers are forced to optimize their process management and to increase factory utilization. The co-production of beet thick juice and raw cane sugar is a promising opportunity to increase the period of manufacturing in a beet sugar factory. Both raw materials comprise impurities (e.g. colorants) with different chemical and physical properties which influence final sugar quality in different manner and extent. Although the processing of mixed syrups is performed occasionally, practically no knowledge exists regarding the consequences on final sugar color. For this purpose, in the study presented crystallization experiments with mixed syrups were performed and the influence of raw material and process parameter on the final quality of sugar was investigated. Particular emphasis was given to the incorporation of colorants into the crystal.

The data collected indicate that the colorants from both sources mutually suppress their inclusion into the sucrose crystal. It is found that color transfer behaves exponentially as function of raw cane sugar level in the blend which was confirmed for different raw material qualities. On basis of the data, a model was defined to predict final sugar color value solely on the experimental color values of the single source syrups used. The generally acknowledged rule of thumb that a level of 20 g/100 g raw cane sugar does not lead to unpredictable issues during processing seems to be too limited. The data show that an addition of 40 g/100 g results in white sugar of highest quality with color values below 30 IU. However, high dextran levels in the raw materials promote color inclusion.

The results allow a differentiation between the contribution made by the three different mechanisms on final sugar color: Liquid inclusion, co-crystallization and adhesion. It was found that co-crystallization is the major inclusion mechanisms in mixed syrups. Furthermore, it was stated that color incorporation due to liquid inclusions and co-crystallization is strongly hampered if beet material is in the blend. This effect is more pronounced for liquid inclusions.

The work presented demonstrates the principles of color inclusion for sugars produced from blended syrups in detail and provides a comprehensive framework for manufacturers and researchers to produce sugars from mixed beet and cane syrups.

Effect of steam bubbling on crystal growth during the industrial crystallization of sugar: Investigations on vapor nucleation on the sucrose crystal surface

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The production and crystallization of sugar is a well-known process executed for many years. At first sight, this statement cannot be denied. Delving deeper into the matter, there are still unsolved questions and insufficiently understood (micro-) processes. Evaporation crystallization is a cornerstone regarding the conversion from dissolved sucrose in the thick juice to a high-grade crystalline product. Evaporation and crystallization are basic thermodynamic processes excessively studied. Explanations and models for numerous albeit simplified phenomena, are available.

Considering the complexity of sugar crystallization in terms of the amount and variation of process parameters, the applicability of the combination of simplified models is limited. The general development towards lower temperature differences between heating steam and massecuite poses a serious challenge to overcome, that requires in-depth knowledge of both crystallization and evaporation as well as their interactions. In common batch crystallization pans, the massecuite circulates in a vertical loop driven by density differences due to vapor formation and mechanical forces introduced by an impeller. The massecuite moves, supported by the impeller, downwards through the downcomer in the center of the pan. Within the tubes, heat is transferred to the massecuite supporting the density difference driven upwards stream. Above the heating chamber, the massecuite flows in radial direction into the downcomer completing the loop. Vapor formation is limited to superheated zones within the vacuum pan due to the necessity to overcome the contribution of the surface tension in nucleation. Saturation conditions of the massecuite depend on its composition (boiling point elevation) and the applied vacuum above the liquid surface coupled with the static pressure due to the massecuite level. Applying high temperature differences between heating steam and massecuite leads to saturated boiling within the heating tubes. The tubes provide overheated surfaces suited for heterogeneous vapor nucleation. Reaching a certain radius, the bubbles separate from the walls and keep growing through additional evaporation. This formation of vapor introduces strong buoyancy forces driving the massecuite flow. At lower temperature differences subcooled to no boiling within the tubes is observed. This effect is amplified towards the end of a strike by the increasing massecuite level and, hence, the increased static pressure. Possible vapor formation is displaced to zones above the heating tubes with reduced static pressures. As bubble formation at low to medium superheats is based on heterogeneous nucleation, possible sources of vapor nucleation have yet to be identified. Being the product of the process, sucrose crystals are dispersed within the whole massecuite and may represent suitable solid surfaces for vapor nucleation.

This study introduces a method to investigate bubble formation on sucrose crystal surfaces. A test droplet of sucrose suspension is heated within a liquid carrier above its saturation temperature. An energetical barrier inhibits vapor formation at the liquid-liquid phase boundary up to high superheats. Therefore, nucleation at the crystal surface is more likely to occur. The maximum achievable temperature with the given setup is measured at standard pressure. Additionally, the process is observed by a high-speed camera. Differently prepared sugar suspensions and sugar solutions of varying quality are investigated.

Optimal Plant-wide Control at the Interface of the Evaporation and Crystallization Stages of a Sugar Factory

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Abstract

The optimal plant-wide management of a process factory always poses significant challenges. In the case of food industries and, particularly, in the sugar case, the problem is aggravated by the difficulty of obtaining reliable models and the frequent lack of direct measurement of important quality related variables. In this contribution we put forward some ideas for approaching this task as applied to a case study that tries to capture some of the main trade-offs to be faced while coordinating, in an optimal manner, the workings of the evaporation section with the stage of semi-batch crystallizers.

In order to keep the size of the dynamic model and the resulting simulation time under check a scaled-down version of the flowsheet to the factory here taken as reference has been used. It represents the last three effects of a multiple effect feed-forward evaporation stage, which serves the resulting concentrated syrup and the reutilized heating steam from the III or IV effect to an array of three semi-batch evaporative crystallizers representing the first stage of the sugar house in charge of producing the commercial sugar grains. The dynamic simulation model also includes the series deployment of the level regulated melter, and of a standard liquor buffer tank connecting the output of evaporation station, providing the thick syrup, with the input of the crystallizers. At the output of the latter, the resulting massecuite is discharged into the strike receiver and from it, to the first stage centrifuges. The standard liquor used in the crystallizers is formed by adding to the thick syrup, the wash runoff syrup from the centrifuges and also, via dissolution, the sugar streams obtained from the second and third exhausting stages. The standard liquor buffer tank level moves freely, to fulfill its objective of accommodating the difference between the incoming, continuous flowrate from the melter with the intermittent feeding of the array of semi-batch crystallizers. The dynamical models used are simplified versions of those developed, using the object oriented physical model paradigm, for a previous training simulation application.

The problem here posed to be solved is basically related to the scheduling of the batches of three crystallizers, and, to a certain degree, to the pace of the workings of the same units, in order to keep up with the flowrate of thin juice at the entrance of the evaporator station, which along with its purity and concentration, are considered as disturbances. Other disturbances for the plant-wide problem are the flowrates of II and III sugar streams, since the corresponding stages are not modeled and, and also, the water into the centrifuges, and thus the purity, Brix and flowrate of the resulting wash runoff. The centrifuges water input is considered as given for the proposed exercise for the sake of simplicity, although it is acknowledged that, in real plant operation, it depends decisively on the quality of the size distribution of the crystals of the resulting massecuite. The task of being able to process all the incoming syrup, translates directly into keeping the level in the standard liquor buffer tank between safe values. The length of the cycle of each crystallizer can be impacted upon by manipulating the flowrate of the heating steam drawn from the evaporation station. Additionally, it is allowed to specify the setpoint of the concentration controller at the output of the evaporation station. The plant-wide management exercise proposed is interesting since it includes discrete and continuous degrees of freedom applied to a plant comprising units of a continuous and semi-batch character, which are closely integrated, interchanging mass and energy, in the presence of the uncertainties represented by the mentioned disturbances. The plant-wide problem is cast in a mathematical optimization setting.

Several strategies for facing the plant-wide optimal problem are discussed and simulation results are presented.

Keywords:
Sugar processing, Process control, plant wide control, batch crystallization, process system engineering, food processing

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Improved industrial crystallization by automation

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Compared with earlier times in beet sugar factories with manual or semi-manual operation, modern process automation is responsible for great improvements in sugar house processing. The practical experience gained in sugar factories shows the impact of automation e.g. on the improvement of crystal content and crystal quality as well as efficiency of the vacuum pans.

Generally, in industrial crystallization, the focus is on steadily improving the process control, with the aim to achieve additional yield increases. A new concept is presented, demonstrating how an improved process control can be implemented with the aid of supplementary sensors, while particularly observing the metastable limit.

Improved image analysis system for technical sugar crystal suspensions at Suiker Unie

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Abstract

Since 2003 Suiker Unie uses an off-line image analysis system to measure the size distribution of crystals in industrial massecuites. The practical range of the system was limited to suspensions with a mean particle size from 50 to 500 µm. Analyzing final A-product with a size of approximately 600 µm was not possible. This system was technically outdated and the opportunity was taken to extend the measuring range to include A product with an updated system. The original light-microscope and automated XY-stage have been extended with new components: XY-stage controller, high resolution camera and customized image analysis software. Combined hardware and software settings allow measurements in the crystal size range of 10 µm to 2000 µm. After image acquisition, the individual images are merged into a large mosaic image. The problem of edge-cut crystals is herewith avoided, providing a bigger size range and more accurate results with the same optical constellation. Detected crystals are particle sized and classified into four categories: fines, single crystals, and simple and complex conglomerates. Sample preparation procedure was modified to avoid false grain formation especially at suspensions of low purity. Taken samples of massecuite are directly fixated in a sucrose-fructose solution. The updated system and procedure show less variance in Mean Aperture (MA) and coefficient of variation (CV) compared to the formerly used. Both seed crystals and the final A-product can now be analyzed, thus covering the complete sugar crystallization process.

Optimization of massecuite production with a smart video pan microscope the Crystobserver

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Ensuring a factory can produce good massecuite quality is a key focus for any sugar factory operation. Managing the crystallization to produce homogeneous crystals while limiting the number of fines or the creation of false grains whoever the operator in charge is always challenging.

The paper describes the implementation of an ITECA high resolution camera on a batch pan. It shows how an accurate characterization of the pan operation helps establishing the best possible sequences to increase the overall pan floor extraction, whilst still guaranteeing the final massecuite quality remains stable. This is achieved by analyzing on-line the HD videos displaying crystal growth and by comparing different strikes between them at different stages of the process:

- Before seeding, the camera automatically detects any non conformity that may appear in the syrup , such as super coarse crystals, contaminants or air bubbles that will limit the production of high quality crystals
- At the seeding stage, the software counts and measures the crystals sizes from 4 µm, to make sure the good volume and crystal size have entered the pan as requested
- During the graining phase, the crystal growth is monitored in real-time and valuable statistical information are calculated (CV, MA, number of fines) to check normal crystal crop and trigger alarms on non conformity

The measurements made by the on-line camera are compared to the results obtained by a laboratory method in a German refinery, on crystals ranged from 50 µm to 700 µm. The various benefits brought by the camera are reported.

This new technology already marks a big step forward in improving the sugar pan yield. It lays the foundations for even more significant advances in the future when full automation will be achieved.