

THE EFFECTS OF MIXING SYRUPS FROM BEET AND CANE ORIGIN ON SUGAR QUALITY



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Dipl.-Ing.
Karl Schlumbach
geb. in Berlin

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Promotionsausschuss:

Vorsitzender: Prof. Dr. Stephan Drusch

Gutachterin: Prof. Dr.-Ing. habil. Cornelia Rauh

Gutachter: Prof. Dr.-Ing. Eckhard Flöter

Gutachter: Dr.-Ing. Arend Wittenberg

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ABSTRACT

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 operation in factory processing sugar beets. Both raw materials comprise impurities (e.g. colorants) with different physical and chemical properties which influence final sugar quality in differently. Although the processing of mixed syrups is already performed occasionally, practically no knowledge exists with respect to the consequences on final sugar color. For this purpose, crystallization experiments with mixed syrups were performed and the influence of raw materials and process parameters on the final quality of sugar was investigated. In particular, attention was paid to the incorporation of colorants into the crystal. Moreover, the influence of thermal stress on color formation in mixed syrups was investigated.

The results gathered indicate that the colorants from both sources mutually suppress their inclusion into the sucrose crystal. The initial finding that color transfer behaves exponentially as function of raw cane sugar level in a blend was confirmed to be of general validity with experimental data covering different raw cane sugar and beet syrup qualities. On basis of the data, a model was formulated to predict final sugar color values solely on experimental data (color values) of the constituting single source syrups. Based on the findings of this work the generally acknowledged rule of thumb that a level of 20 g/100 g raw cane sugar does not lead to unpredictable problems during processing of mixed syrups seems to be too restrictive. The data show that an addition of 40 g/100 g of a typical raw cane sugar results in white sugar of highest quality with color values below 30 IU (ICUMSA units). Considering also other impurities it was found that high dextran levels in the raw materials promote color inclusion.

Inclusion of colorants in sugar processing is related to three different processes, co-crystallization, liquid inclusion and adhesion. For the purpose of this study the contribution due to adhesion was mostly eliminated because affination, surface cleaning, was applied. It turned out that the major inclusion mechanisms in mixed syrups is co-crystallization. It was found that relative colorants' inclusion due to both liquid inclusions and co-crystallization are clearly reduced if beet material is present in the blend. In detail, it is observed that this effect is more pronounced for liquid inclusions.

Furthermore, the data from a detailed study on growth rate variation reveal that color incorporation increases linearly with growth rate. For liquid inclusions the effect of growth kinetics turned out to be hardly dependent when beet material is present (>33 g/100 g) in the blend. With increasing linear growth velocities, the model formulated significantly over-predicts the level of colorants' inclusion. This is due to the dramatically stronger effect of growth rate on the colorants' inclusion, for both mechanisms, in pure cane syrups.

Since colorants are also formed during the sugar production process a systematic study on the influence of thermal stress and the formation of colorants in mixed syrups was executed. The data gathered reveal that color values increase linearly with time and exponentially with temperature according to Arrhenius law. The hypothesis that the specific composition of the mixed syrups promotes excessive formation of colorants was not verified. Also for this process a framework was formulated that allows to predict the syrup color values dependent on the initial color values of the constituting raw materials, beet thick juice and raw cane sugar, temperature and treatment time.

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

ZUSAMMENFASSUNG

Mit dem Beschluss, den EU-Zuckermarkt zu liberalisieren, sind die Europäischen Zuckerproduzenten gezwungen, ihr Prozessmanagement zu optimieren und die Auslastung ihrer Fabriken zu erhöhen. Eine vielversprechende Idee den ca. 100-tägigen Kampagnenbetrieb in der Rübenzuckerverarbeitung zu verlängern, ist die Co-Produktion von Rübendicksaft und Rohrohrzucker. Beide Rohstoffe enthalten Unreinheiten wie z.B. Farbstoffe mit unterschiedlichen physikalischen und chemischen Eigenschaften, die sich auf unterschiedliche Weise auf die Zuckerqualität auswirken. Obwohl die Verarbeitung von gemischten Säften bereits seit Jahrzehnten vereinzelt durchgeführt wird, gibt es keinerlei Daten bezüglich der Konsequenzen dieses Produktionsansatzes auf die finale Zuckerqualität. Aus diesem Grund wurden in der vorliegenden Arbeit Kristallisationsversuche mit gemischten Säften durchgeführt und der Einfluss von Rohstoff- und Prozessparametern auf die Qualität des Zuckers untersucht. Im besonderen Fokus stand hierbei der Einbau von Farbstoffen in den Kristall. Darüber hinaus wurde der Einfluss von thermischem Stress auf die Farbbildung in gemischten Säften untersucht.

Die Betrachtung der Ergebnisse zeigt, dass sich die Farbstoffe der beiden Rohstoffe gegenseitig beim Einbau in den Kristall hemmen. Es wurde ein exponentieller Verlauf des Farbeinbaus als Funktion des Rohrohrzuckeranteils gefunden und für verschiedene Rohrohrzucker- und Rübendicksaftqualitäten bestätigt. Auf Basis der Daten wurde ein Modell entwickelt, das die finale Zuckerfarbe auf Grundlage der Sirup- und Zuckerfarben der vorliegenden Reinrohstoffe vorhersagt. Die Daten zeigen, dass die allgemein anerkannte Faustregel, 20 g/100 g Rohrohrzucker dem Rübendicksaft beigeben zu können, ohne dass unvorhergesehene Probleme bei der Kristallisation und Qualität auftreten, zu niedrig bemessen ist. Eine Zugabe von bis zu 40 g/100 g führt, nach der vorliegenden Arbeit bei typischen Rohstoffqualitäten, zu weißem Zucker höchster Qualität mit einer Farbe von maximal 30 IU (ICUMSA Einheiten). Allerdings wurde gezeigt, dass erhöhte Dextrangehalte im Rohmaterial den Farbeinbau fördern.

Farbstoffe können in Zuckerkristalle durch drei verschiedene Mechanismen eingebaut werden: Flüssigkeitseinschlüsse (Liquid inclusions), Co-Kristallisation und Adhäsion. In dieser Arbeit wurde der Beitrag der Adhäsionsfarbe durch einen Reinigungsprozess (Affination) weitestgehend eliminiert. Der Haupteinbaumechanismus für gemischte Säfte ist die Co-Kristallisation. Der Farbeinbau durch Co-Kristallisation und Flüssigkeitseinschlüsse wird in hohem Maße durch die Anwesenheit von Rübenmaterial unterdrückt, wobei dieser Effekt für Flüssigkeitseinschlüsse ausgeprägter ist.

Die gesammelten Daten zeigen weiterhin, dass der Farbeinbau mit der Wachstumsgeschwindigkeit linear steigt. Hierbei wurde beobachtet, dass der Einbau von Flüssigkeit (Liquid inclusions) nur minimal von der Wachstumsgeschwindigkeit beeinflusst wurde, wenn Rübenmaterial in der Mischung war (> 33 g/100 g). Aufgrund der Tatsache, dass der Einbau von Farbstoffen für reine Rohrsirupe deutlich stärker von der

Wachstumsgeschwindigkeit abhängt als für Sirupe, die Rübenmaterial enthalten, nimmt die Vorhersagequalität des Modells für Zuckerfarbe mit zunehmender Wachstumsgeschwindigkeit ab. Hierbei ist zu beachten, dass das Model konservativ ist, da es die Zuckerfarbe zunehmend als zu hoch vorhersagt.

Die Versuche zur Untersuchung des thermischen Einflusses auf gemischte Säfte haben gezeigt, dass die Farbbildung systematisch verläuft. Die Daten verdeutlichen, dass die Farbwerte als Funktion der Zeit linear steigen und die Farbbildungsrate in Abhängigkeit der Temperatur den Gesetzmäßigkeiten von Arrhenius folgt. Die Hypothese, dass es durch die Zusammensetzung der gemischten Sirupe zu einer exzessiven Farbbildung kommt, konnte nicht bestätigt werden. Des Weiteren wurde ein Model erstellt, welches die Farbe gemischter Säfte in Abhängigkeit der Anfangsfarbwerte der Rohmaterialien, Rübendicksaft und Rohrohrzucker, der Temperatur und der Behandlungszeit errechnet.

Die hier vorliegende Arbeit diskutiert erstmalig umfassend die Farbe von Zuckern, die aus Sirupen, die sowohl aus Rohr- und Rübenmaterial bestehen, kristallisiert wurden. Die gefundenen Zusammenhänge konnten in Modellen abgebildet werden, die es erlauben, aufgrund von Daten der Reinstoffe die gemischt werden, Vorhersagen zur Zuckerfarbqualität zu machen.

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LIST OF SYMBOLS, INDICES AND ABBREVIATIONS

Symbol	Description	Unit
A	Area	m ²
A _s	Absorption	-
b	Length of cuvette	cm
c	concentration	mol l ⁻¹ , kg m ⁻³
C	Conductivity	μS
C _{ash}	Ash content of affinated sugar	% (w/w)
C _{ash} [`]	Ash content of non-affinated sugar	% (w/w)
CV	Coefficient of variation	%
d	Diameter	mm
d ₅₀	Mean aperture	mm
D	Diffusion coefficient	m ² s ⁻¹
F ₄₂₀	Color value at 420nm	IU
G	Gibbs free Energy	kg m ² s ⁻²
G	Crystal mass growth rate	kg m ⁻² s ⁻¹
g	Gravitational acceleration	m s ⁻²
H	Enthalpy	kg m ² s ⁻²
h	Height	m
J	Relative crystal to solution velocity	m s ⁻¹
K	Constant	-
k	Transfer factor	%
k*	Transfer factor (* is related to corrected transfer factor)	%
k _D	Constant for diffusion reaction	m s ⁻¹
k _R	Coefficient for surface reaction	m s ⁻¹
L	Characteristic length	m
l	Length	m
m	Mass	kg
N	Number	-
n	Mole	mol
q	Purity	% (w/w)
S	Mass of sample (for ash content computation)	g
Sc	Schmidt number	-
Sh	Sherwood number	-
R	Gas constant	kg m ² s ⁻² mol ⁻¹ K ⁻¹

Symbol	Description	Unit
R_{ash}	Ash removal	%
R_{color}	Color removal	%
R^2	Correlation value	-
r	Radius	m
r_c	Critical radius	m
r_p	Radius where nuclei becomes a crystal	m
Re	Reynolds number	-
S	Supersaturation (ratio of concentrations c/c)	-
T	Temperature	K
V	Volume	m^3
v	Linear growth velocity	m s^{-1}
w	Mass content	$\text{g } 100 \text{ g}^{-1}$
x	Mass fraction of beet content	-
y_{sat}	Saturation coefficient (ratio of mass ratios w/w)	-
y_{ss}	Supersaturation	-
α	Volume shape factor	-
β	Surface shape factor	-
γ	Activity coefficient	-
δ	Boundary layer thickness	m
η	Viscosity	$\text{kg s}^{-1} \text{ m}^{-1}$
θ	Contact angle	°
λ	Rate constant for color transfer factor	-
μ	Chemical potential	J mol^{-1}
ρ	Density	kg m^{-3}
σ	Specific surface tension	kg s^{-2}
τ	Time	s
ϕ	Factor for free energy of heterogenous nucleation	-

Indices	Description
Ad	Adsorption
Air	Related to air
Ash	Related to ash
b	Bulk
c'	Crystalline deposit interface
Cr	Crystal
CC	Crystal content
Co	Co-crystallization
color	Related to color
CU	Control unit
DS	Dry substance
F	Color
i	Index
im	Impure, impurity
lab	Determined by laboratory analyses
LI	Liquid inclusion
l	Liquid phase
M	Molecular
MC	Massecuite
ML	Mother liquor
n	End point $\tau = n$
NS	Non-sugar or non-sucrose
p	Pure (q=100%)
S	Surface
s	Sugar
s'	non-affinated sugar
sat	Saturated state
seed	Related to seed crystal
sm	Small
sol	Solid phase
solution	Solution
sov	Solvent
TJ	Thick juice
V	Volume

Indices	Description
W	Water
x	Beet content in feed syrup
XL	Large
0	Point at $\tau = 0$, arbitrary reference

Abbreviation	Description
Aff.	Affination
ADH	Alkaline degradation products of hexoses
AP	After product
BCC	Beet crystal colorant
BCF	Burton-Cabrera-Frank
cm	Centimeter
Da	Dalton
DDS	De Danske Sukkerfabrikker
DOPA	Dihydroxyphenylalanine
g	Gram
h	Hour
ISP	Indigenous sugar cane polysaccharide
IU	ICUMSA units
K	Kelvin
KCl	Potassium chloride
l	Liter
m	Meter
min	Minute
mm	Millimeter
MV	Mean value
Nm	Newton meter
No.	Number
n/a	Not available
Repeat.	Repeatability
Reprod.	Reproducibility
RCF	Relative centrifugal force
rpm	Rounds per minute
RS	Raw sugar
s	Second
SD	Standard deviation
TU	Technische Universität
VHP	Very high polarity
vs	versus
WS	White sugar
μl	Microliter

Abbreviation	Description
μm	Micrometer

1 INTRODUCTION

Crystallization is one of the most effective methods in chemical, pharmaceutical, biochemical and food industry to separate a solute by phase transfer from the solvent and the impurities. In the sugar industry this is a crucial process step which influences final quality of the crystalline product. Although the image of sugar has changed negatively in our health-oriented society, its utilization in the food industry can hardly be replaced. Sucrose is a energy supplier, natural preservation agent, flavor carrier with a characteristic sweetness and gives volume and structure into the food product. However, the sugar price underwent fluctuations since years with a slight decrease in average (Figure 1-1). For sugar manufacturers in the EU, a new age started with the end of the Sugar Policy in 2017. With the elimination of the regulations, several Non-EU competitors might enter the European market on the one side, and EU sugar producers are able to export sugar worldwide. However, labor costs in the EU are higher compared to emerging countries which decreases the ability to compete. In Europe sugar is produced by beet sugar factories and raw cane sugar refineries. For EU manufacturers sugar refining is very cost intensive due to high fixed costs. Additionally, expenses for raw cane sugar transport are high due to the lack of availability in Europe. Furthermore, the price difference between raw cane sugar and white sugar is small (Figure 1-1). Thus, the operation is only worth if refineries run around the year. The beet sugar factories operate only some month per year due to the seasonal availability of sugar beets. Hence, for European sugar manufacturers, process innovations, the increase of capacities and flexibility regarding the sugar price will be crucial to ensure and strengthen their international competitiveness. The implementation of a thick juice inter-campaign can increase the operation time for some weeks. Nevertheless, alternative processes need to be implemented into the beet sugar factories, which solve the problem of seasonal raw material availability and increase operational flexibility and factory's utilization rate. A promising opportunity is the co-production of beet thick juice and raw cane sugar in an inter-campaign. Therefore, raw cane sugar is dissolved and blended with stored beet thick juice before the mixture is crystallized to sugar. This process is known since decades, but rarely performed due to the lack of knowledge and the protective, thus innovation inhibiting past EU quota system. Thus, co-production is in the focus of European, but also non-European manufacturers which have easy access to raw material from beet and cane origin (see Figure 1-2).

However, it is without saying that co-processed sugar has to meet quality standards such as purity, color value, ash content, particle size and distribution. Raw material quality and process parameters can influence these quality parameters. Particularly, the concentration and the physical and chemical properties of colorants and other non-sugars in the raw material have a major impact on final crystal quality. It is generally acknowledged that beet and cane plant provide different

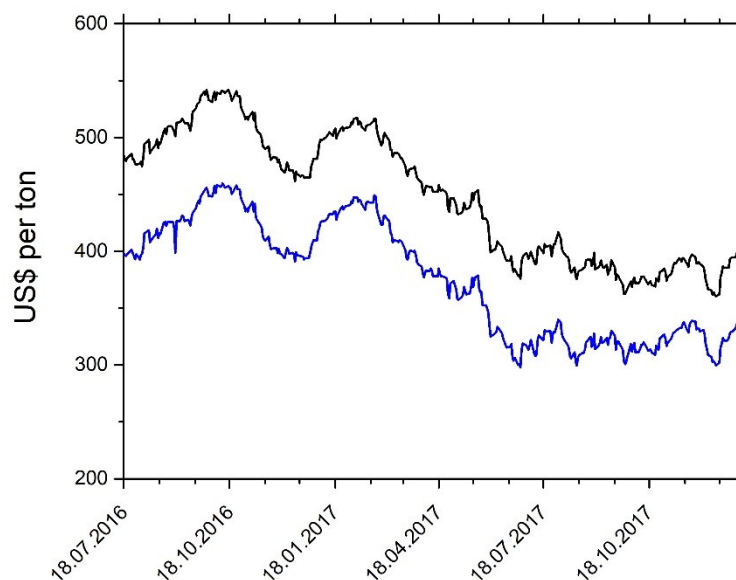


Figure 1-1: White sugar price (black line) and raw sugar price (blue line) according to White Sugar contract and the Sugar No. 11 contract, respectively. (Intercontinental Exchange Inc., 2018a, 2018b)

colored components into the process. Colorants present in cane sugar processing originate preliminary from the plant. These low colored substances, such as phenolics and indigenous sugar cane polysaccharides, react throughout the process into high molecular weight, dark colored compounds which have a high tendency for incorporation into the sucrose crystal (Tu et al., 1977; Godshall & Baunsgaard, 2000; Lindeman & O'Shea, 2001; Godshall et al., 2002). Additionally, raw cane sugar contains dextran, starch and glucose which influence final sugar quality, too. In contrast, prominent beet sugar colorants are formed during the process such as *Maillard* reaction products which are formed from reducing sugars and amino acids. Other colorants in beet sugar processing are melanins and alkaline degradation products of hexoses. However, beet colorants have a maximum molecular weight of 30 kDa (Godshall et al., 1991) and thus, only a slight tendency of incorporation into the sugar crystal is found (Godshall et al., 2002; Paton, 1992). When co-production is conducted, colorants and other non-sugars with different physical and chemical properties are mixed and thus unknown tendency for incorporation into the sugar crystal emerge. For this approach, the behavior and interactions of the colorants and other non-sugars throughout the process regarding the formation and inclusion of colorants are in essence unknown. In earlier work it was concluded that an addition of 20 g/100 g raw cane sugar into beet thick juice does not result in unpredictable issues during processing, which means that sugar quality standards are met (Kochergin et al., 2012).

Although co-production is conducted occasionally, the process is operated based on experience and hardly any experimental data are found in literature. The objective of the work presented here is to elucidate the behavior of mixed syrups during sugar crystallization with special focus on colorants' inclusion.

For this purpose, a laboratory crystallization process has been developed which produces sugar in an industrial relevant quality. The experiments were planned according to the most important quality and process parameters. Therefore, sucrose was crystallized from different blends of beet thick juice and dissolved raw cane sugar under controlled conditions to investigate the influence of different mixing ratios on colorant incorporation. In order to elucidate the influence of raw material quality on colorants' inclusion, experiments with various raw cane sugar qualities were conducted. The influence of crystal growth rate on sugar color inclusion was investigated by systematic crystallization experiments with varying temperature of the heating media. For the examination of color formation in mixed syrups, thermal treatment of various blends at different conditions was conducted.

Sugars and syrups were analyzed in detail to evaluate the contribution of syrup composition, raw material quality and crystal growth rate on final sugar color. With the data gathered a model to predict the final sugar color based solely on characteristic data of single source syrups was formulated, beet thick juice and dissolved raw cane sugar, respectively. Additionally, the results allow to differentiate between different inclusion mechanisms and their contribution on final sugar color. Based on the data from thermal treatment, a model to forecast color formation in mixed syrups dependent on temperature, time and initial color value of syrups solely from beet and cane origin was formulated.

The present study delivers a comprehensive framework for sugar manufacturers to apply co-production, because the principles of color inclusion in mixed syrups are outlined. These new insights allows the producers to quickly react on raw material or process variations and ensure that sugar quality standards are met.

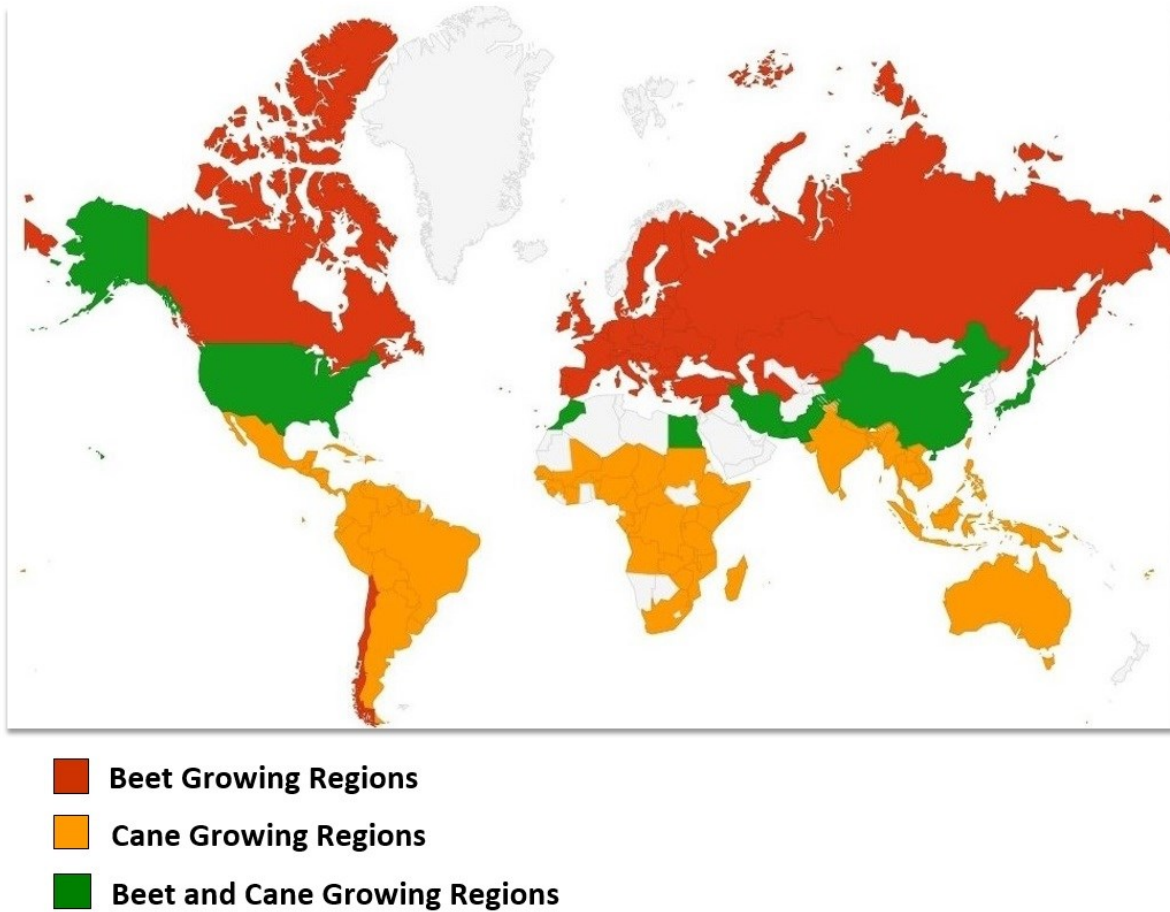


Figure 1-2: Beet and cane growing regions (reprinted with permission from International Sugar Organization (2017)).

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2 FUNDAMENTALS

2.1 Industrial sugar production

The most used important plants for industrial sugar production are sugar beet and sugar cane. In 2016/17, total world sugar production added up to 178 million tons. The ratio of beet sugar to cane sugar was approximately 22 to 78% (w/w). (Verein der Zuckerindustrie, 2017). Beet and cane plants contain nearly the same proportion of water (around 75% (w/w)), but show differences in solids' composition. Their composition of solids, as illustrated in Figure 2-1. The procedure of sugar production from both beet and cane is described in the following sections.

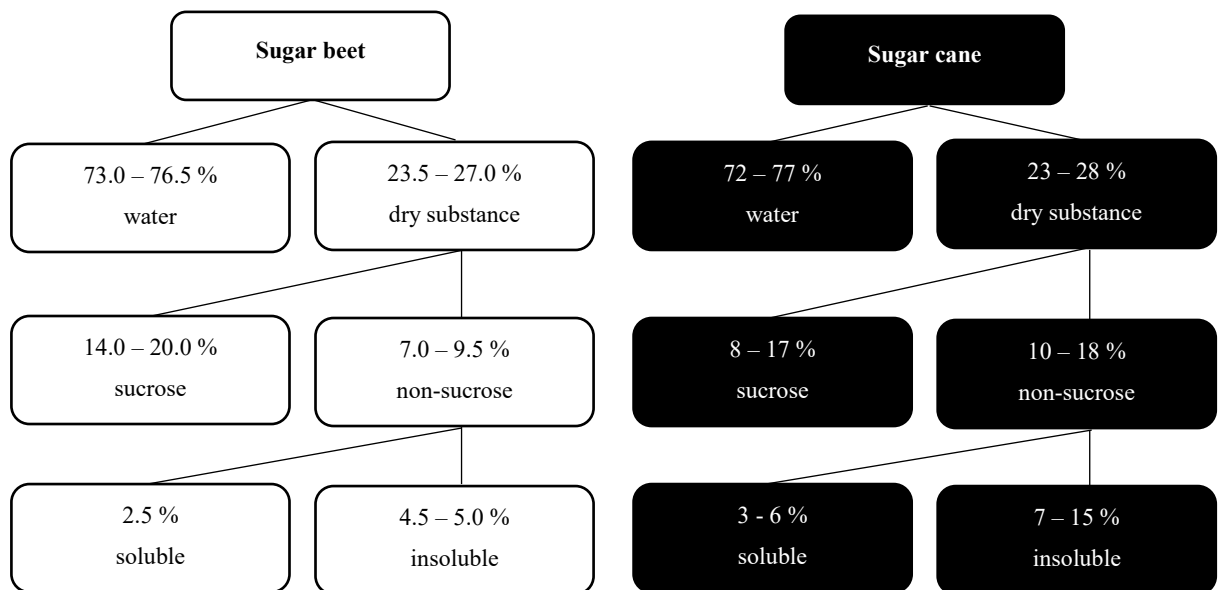


Figure 2-1: Comparison of sugar beet and sugar cane ingredients according to van der Poel, P.W. (2000).

2.1.1 Beet sugar production

Sugar beet (*Beta vulgaris*) is a plant which grows favourably in a temperate climate and contains 14 – 20 g/100 g of sucrose (van der Poel, P.W., 2000). In the European Union (EU), the plant is primarily used to produce white sugar. The EU is the world's major producer of beet sugar and achieved a production of 19.6 million tons in the campaign of 2014/15 (European Commission, 2017).

The seeds are planted in early spring and the roots are harvested between the end of September and mid-December. The beets of highest quality are rich in sugar and low in non-sugars. The

sugar and non-sugar composition is affected by the genetics of the variety, weather conditions, soil quality, diseases and fertilizing program (Asadi, 2007). The production campaign usually starts in October and lasts until mid-January. In 2015/16, the duration of the campaign ranged between 54 and 129 days in the EU countries (Bruhns, 2016). Additionally, some factories operate an inter-campaign in spring to crystallize sucrose from stored thick juice or syrups which are obtained by molasses desugarization.

2.1.1.1 Preparation

Before sugar beets enter the factory, the beets are defoliated, topped, uprooted and harvested by different machines. These process steps are already crucial for final sugar quality because improper procedure might lead to loss of sugar or introduction of undesired non-sugars into the factory.

Figure 2-2 illustrates the beet sugar production schematically. After unloading at the entrance of the sugar factory, a passage of wet transportation delivers the beets at the washing station. In several steps, soil, stones, sand, leaves and foreign matter such as metal are primarily removed. The mechanism is mechanical washing due to self-cleaning of the beets by friction while rolling in drum and paddle washers. Sugar loss, use of electrical energy and water demand should be minimized during the washing process. This is achieved by an optimum water-to-beet ratio, counter flow of washing water, smooth surfaces in the flume, short contact of beets with water, short transport distances and low falling heights. Soil stuck to beet nerve is removed by high pressure jet washing. Furthermore, rock and weed catchers withhold unwanted stones and leaves from the next process step: beet slicing. (Wittenberg, 2014)

2.1.1.2 Beet Slicing

The main purpose of beet slicing is to maximize the surface area of the material for the subsequent diffusion process. Material size and shape should be chosen in a way that ensures unhindered material transport in the extractor, efficient water permeation and minimized release of non-sugar compounds. This is achieved by the use of disc or drum slicing machines which cut the beets into V-shaped cosettes applying a certain slicing sequence of Königsfelder knives. The defined form and dimension of the cosettes provide a high surface-to-volume ratio for the extraction process (Bromm, 2014). The quality of the slicing process is expressed by two numbers: The Silin number is the total length of 100 g of cosettes, expressed in meters. High quality cosettes have a width of 3 – 6 mm and a length of 30 – 60 mm which corresponds to a Silin number of 10 to 18 m. The Swedish number expresses cosette permeability as the ratio of mass of cosettes longer than 50 mm to those shorter than 10 mm. A Swedish number higher than 10 is desirable (Asadi, 2007).

2.1.1.3 Extraction

In the sugar industry, the extraction process is strictly speaking rather a diffusion process than an extraction process, because the concentration balance is achieved by diffusion. The extraction process is conducted continuously. Its main scope is the production of a sucrose rich extract composed of the soluble constituents of the beet cells. The proportion of sucrose remaining in the cossettes should be as low as possible (w_s around 1 g/100 g in pressed pulp). Adequate process parameters are chosen to maximize sucrose yield and to minimize diffusion of non-sucrose compounds into the solution. In a countercurrent cossette mixer, cossettes are blended with hot raw juice (341 – 345 K) from the extraction tower. The increased temperature induces denaturation of the plant cells, the subsequent flow of water into the cells and the dissolution of cell constituents into the extract. The mass transfer is a result of diffusion and convection. Diffusion is described by the first law of Fick:

$$\frac{\Delta n}{\Delta \tau} = A \cdot D \cdot \frac{\Delta c}{\Delta l} \quad (2-1)$$

Where D is the diffusion coefficient and Δn is the amount of substance which passes the cross-section area A per time unit $\Delta \tau$ given that the concentration gradient is $\Delta c / \Delta l$. Hence, the process is influenced by temperature, cossette geometry and concentration gradient. A continuous concentration gradient is ensured by countercurrent principle: The cossettes are transported in the direction of the fresh water inlet by screw elements. Nowadays, most beet sugar factories have an extraction tower or a horizontal DDS (De Danske Sukkerfabrikker) extraction plant. The temperature of the extract is decreasing with increasing extraction of pulp (328 – 333 K). However, temperature is high enough to prevent microbiological activity. At the end of the process, the pulp (extracted cossettes) is pressed and the sucrose rich press-water is returned to the process. The pressed pulp is dried, enriched with molasses and pressed into pellets. The extract contains around 14 g sucrose/100 g and has a purity of around 90% before it is further processed in the juice purification station. (Schulze, 2014; Asadi, 2007)

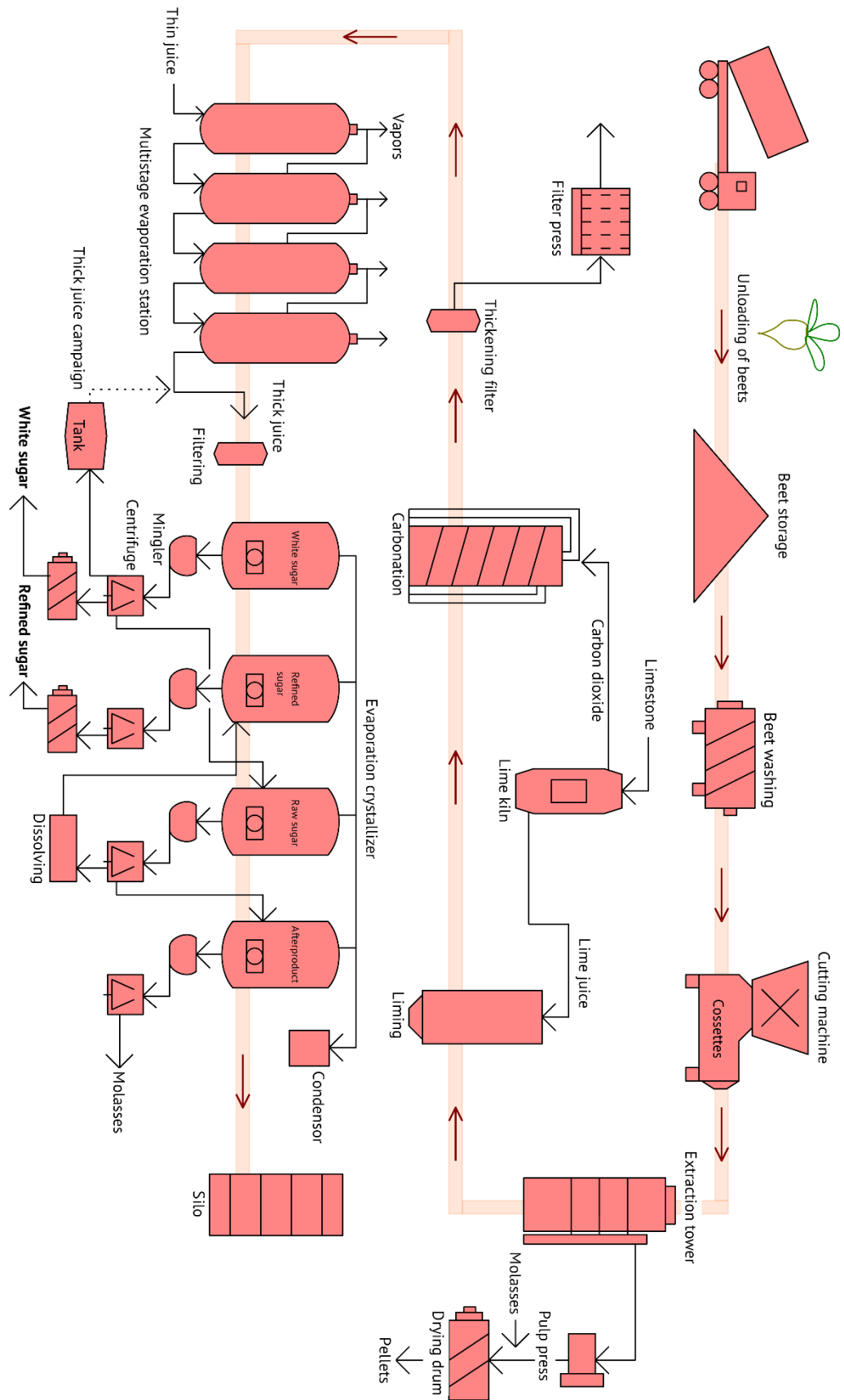
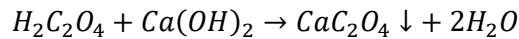


Figure 2-2: Schematic illustration of beet sugar process.

2.1.1.4 Purification

The objective of purification is the production of the thermostable juice by removal of possible non-sucrose contaminants which may have entered the process during extraction. The treatment thus enhances final sugar yield and crystal quality (purity, morphology). In addition to that, purification reduces crusting of the vessels. The whole purification process is divided into several parts: Preliming, main liming, 1st carbonation, 1st filtration, 2nd carbonation, 2nd filtration.

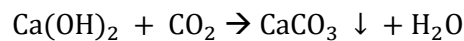
Preliming: The raw juice is limed stepwise with $\text{Ca}(\text{OH})_2$ to a pH-value of 11.2, whereas a constant temperature of 328 K is maintained. The increasing alkalinity results in neutralization reactions of inorganic or organic acids and calcium from the lime milk to form salts, e.g. oxalic acid and calcium hydroxide react to calcium oxalate, which has a low solubility, and water:



Additionally, colloidal non-sugars precipitate due to the alkaline conditions.

Main liming: During the subsequent main liming, temperature is increased to 353 K and pH-value is raised to 12.6 by continued addition of calcium hydroxide. These aggressive conditions result in saponification reactions and decomposition of reducing sugars (e.g. glucose, fructose) into lactic acid and other components. This reduces the occurrence of color generating reactions (e.g. *Maillard*-reaction, caramelization) throughout the process and leads to the formation of a thermostable juice.

1st Carbonation and filtration: During the next purification step, the excessive calcium hydroxide is removed by addition of carbon dioxide into the juice to initiate the formation of low soluble calcium carbonate. Precipitation of calcium carbonate is induced by raising the temperature to 363 K, because the solubility of calcium carbonate decreases with increasing temperature.



Consequently, the pH-value decreases to a value of 10.6 – 11.2. The calcium carbonate particles provide an adsorption surface for non-sugars. Additionally, these particles act as filter aid during the following filtration step which is conducted in candle and frame filters.

2nd carbonation and filtration: The second carbonation is performed to completely remove the lime salts and transfer the rest of calcium hydroxide into calcium carbonate. Therefore, the temperature is increased to 367 – 371 K and additional carbon dioxide is purged into the juice. When a pH-value of 9.2 is reached the juice is left unaltered for 10 min before filtration. This promotes formation and growth of calcium carbonate particles. The subsequently larger surface area is crucial for the adsorption of non-sugars. Furthermore, these larger particles are helpful during the filtration process. After filtration, a thermostable thin juice is obtained. It has a dry substance level of 15 g/100 g and a purity of more than 94%. (Asadi, 2007; van der Poel, P.W., 2000; Buczyś, 2014; Schlumbach & Abraham, 2016)

2.1.1.5 Evaporation

Evaporation of the purified thin juice is necessary to achieve supersaturation and, subsequently, crystallization. The liquid is evaporated under vacuum in multiple effect evaporators. Low pressure is applied to decrease the boiling point temperature and hence minimize color forming reactions which would occur at high temperatures. Nevertheless, the boiling point increases due to dry substance increase. This phenomenon is however counteracted by multiple effect evaporation which involves pressure decrease from effect to effect. Thin juice with a dry substance level of 15 g/100 g is heated to 363 K and enters the first evaporator. Under the given conditions, water is evaporating. It leaves the vessel as vapor which is directed to heat the second effect and is consequently condensing. The concentrated juice enters the next effect, and the process repeats. After the last effect the juice is concentrated to a dry substance level of 68 – 73 g/100 g and is prepared for crystallization. The multiple use of heat considerably reduces the energy consumption of a factory. Three to seven effects are used in beet sugar factories, but four to five are most common. In modern factories the formerly used Robert evaporators have been replaced by plate-heat exchangers or tube evaporators with rising or falling film. (Morgenroth, 2014; Asadi, 2007; van der Poel, P.W., 2000)

2.1.1.6 Crystallization

Crystallization is the most important process step in sugar production. Its purpose is the separation of solute from the solution by phase transfer from liquid to solid. A basic theoretical approach of crystallization is given in section 0. The main purpose of industrial sugar crystallization is the production of uniform crystals of highest quality and molasses of lowest purity with respect to highest space-time-yield. The driving force of the process is supersaturation which can be achieved by evaporation or cooling. When a certain level of supersaturation is attained, seed crystals are added into the supersaturated mother liquor which consists of solvent, solute and dissolved impurities. The scope of this procedure is that no other but the added seed crystals grow during crystallization strikes and ensure a narrow particle size distribution at the end. There are two different seeding materials: Slurry and footing massecuite. In modern beet sugar factories, two step footing massecuite is produced according to the Braunschweig procedure. The first step is the preparation of footing one by controlled cooling crystallization of slurry particles of 10 μm . Within four hours, the process temperature is decreased from 333 K to 298 K. In the end, crystals have grown to a size of 100 μm and account for 20% of the total massecuite mass. The second step is the continued growth of these crystals in a process of evaporation crystallization. The resulting massecuite contains 45% of crystals (w/w) which have grown to a size of 300 – 350 μm . These crystals are used as seeding material for the actual production crystallization strike.

There are two different ways of crystallization: batch and continuous. Batch crystallization starts with feeding the pan. Usually, this is followed by a thickening phase to obtain a certain level of supersaturation before adding the seed crystals. It is also common practice, however, to add the

footing to the undersaturated liquid so that fine crystals dissolve resulting in narrow particle distribution. After seeding, the crystals grow and the pan is continuously filled with feed syrup while evaporation ensures supersaturation. When the massecuite level reaches a defined maximum, the filling process is stopped and the tightening phase is initiated. Evaporation is continued until the crystal content is around 50 –55% (w/w). For continuous crystallization, a horizontal or vertical multichamber crystallization vessel with typically four chambers is used. Compared to batch crystallization, space-time-yield is increased, but particle size distribution is broadened due to a broader residence time distribution in the chambers.

Figure 2-3 illustrates a four-product crystallization scheme with footing massecuite production. Thick juice is used to produce white sugar “two” or “B” – a sugar with a sucrose content above 99.5 g/100 g and color values below 150 IU. For seeding, footing massecuite is used. At the end of each batch, massecuite is collected in a mixer which distributes the suspension to numerous centrifuges. In the centrifuge, the sugar is separated from the mother liquor. Afterwards, the sugar is dried, sieved and packed. The mother liquor is used as feed syrup for raw sugar production. It still consists of around 70 g/100 g dissolved sucrose. The raw sugar crystallization process is conducted in the same ways as described above, but centrifugation is continuous and performed twice. After the first centrifugal step mother liquor is separated and used as feed syrup for after product crystallization. The sugar crystals are affinated in a second centrifugal step which means for the here described case that they are washed with thick juice or raw sugar feed syrup to remove the more impure residue film from their surface. The affination run-off syrup is again recycled as after product feed. The centrifuged raw sugar is melted (dissolved) and used as feed syrup for crystallization of white sugar “one” or “A”– sugar of highest quality ($w_s > 99.7$ g/100g, color below 60 IU). The after-product process starts with evaporation crystallization which is followed by cooling crystallization to exhaust the molasses. The molasses is separated within the first centrifugation step of continuous centrifugation. The sugar is affinated in a second step, melted afterwards and used as white sugar feed just as the raw sugar before. The white sugar “one” production is well controlled and matches white sugar “two” crystallization. This production scheme ensures the production of high quality white sugar, less sugar loss and a high space-time-yield. (Asadi, 2007; Michelberger, 2014; van der Poel, P.W., 2000)

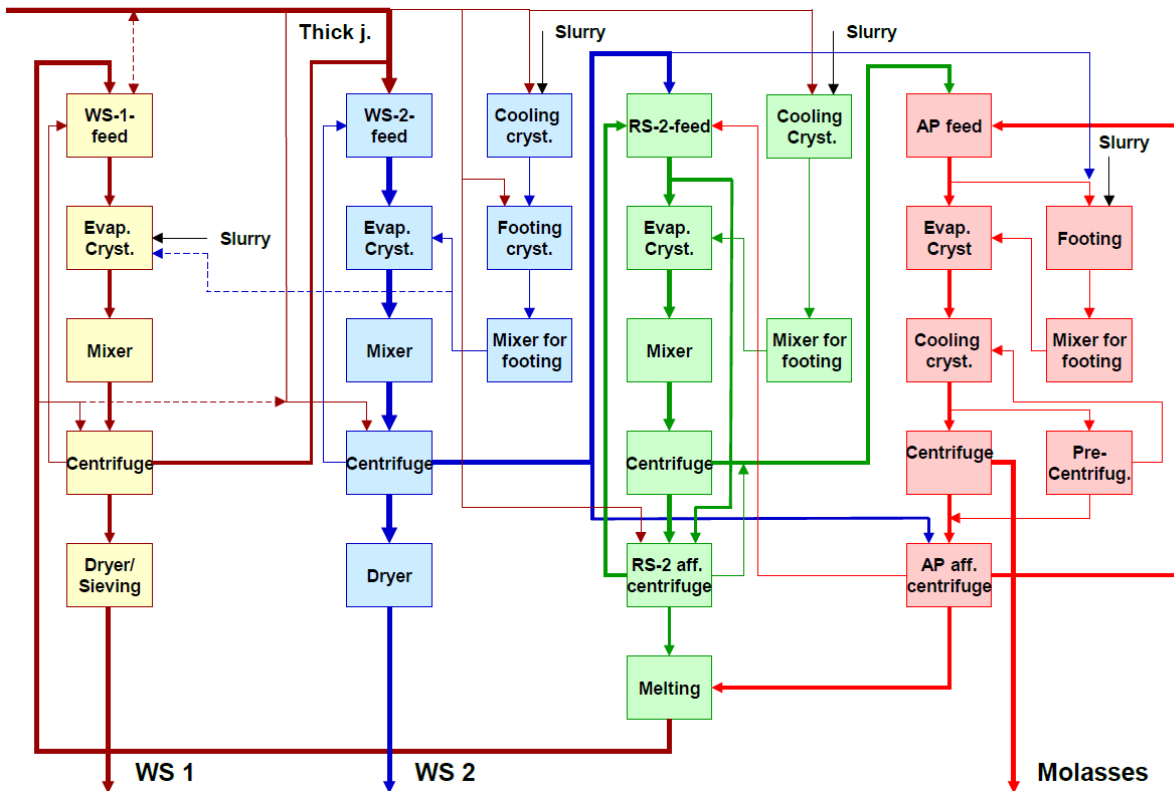


Figure 2-3: Four product scheme with affination of raw and after product sugar. Aff. – affination, AP – after-product. RS – raw sugar, WS – white sugar. Reprinted with permission from Michelberger (2/26/2014).

2.1.1.7 Separation and drying

In order to separate the sucrose crystals from the surrounding mother liquor centrifugal forces are used. Therefore, the massecuite is separated in either batch or continuous centrifuges depending on the quality of the sugar. Continuous centrifuges are applied for low quality sugar such as raw or after product sugar and run with constant revolution. Due to constant rotation and feeding the suspension is distributed evenly at an equal G-force. While mother liquor runs through the basket, sugar is moving upwards to the edge of the basket and is washed with water. At the edge of the basket the crystals are collected in a chute. However, usually continuous double centrifuges are used to enhance separation efficiency. Then, sugar is centrifuged again and washed with liquid. Afterwards the sugar is dissolved in a melter in condensate and used as feed syrup for white sugar crystallization (see Figure 2-3). (Asadi, 2007; Rénevier, 2014; van der Poel, P.W., 2000)

For production of saleable white sugar batch centrifuges are used and the residual mother liquor on crystal surfaces is removed by washing water. First the rotating basket of the centrifuge is filled with massecuite. The rotation speed increases to increase G-forces and yields improved separation efficiencies. Mother liquor passes through the basket screen and sugar crystals are hold back. For washing the crystals water is sprayed evenly on the sugar surface while the basket is

still rotating. Rotation is continued until the moisture of sugar is around 0.3% (w/w). Afterwards mechanical brakes slow down rotation. Then the centrifuge is discharged and sugar is transported to the drying station. (Asadi, 2007; Rénevier, 2014; van der Poel, P.W., 2000)

Sugar is dried to reduce moisture to a minimum which prevents microbiological activity and color reactions. Different dryers are used in the sugar industry which mainly differ in the way the wet sugar and the conditioned air are introduced into the process. The air flow is either co-current, counter current or cross-current. Independently from drying equipment and flow scheme hot, filtrated air evaporates adhesive water by flowing through thin sugar layers. Then sugar is cooled down to a suitable storage temperature (below 303 K). In the end the sugar is stored in silos.

2.1.2 Raw cane sugar production

Sugar cane (*Saccharum officinarum*) is a perennial crop which grows in tropical and subtropical regions. The largest industries are, however, located in subtropical regions, more precisely between 15° and 30° latitude. The highly versatile grass plant can be grown under a broad range of weather and soil conditions making it a popular and comparatively more flexible resource for sugar production. The optimal growth of the sugar cane crop requires a warm climate with an average daytime temperature of about 303 K. An adequate moisture and high solar radiation are additionally necessary for proper sugar cane growth. The ripening (storage of sucrose in stems) and harvesting of sugar cane should preferably take place in a cool and dry season (mean temperatures between 283 K – 293 K) using controlled irrigation.

Since sugar cane is globally the dominant raw material for sugar cane manufacture, the following sections are intended to also describe the process steps from harvesting to crystalline sugar in cane sugar factories. (Blackburn, 1984; Hugot, 1972)

2.1.2.1 Harvesting

The target of cane harvesting is to supply high quality sugar cane stalks to the mill which means high sucrose and low trash content. Therefore, tops and leaves need to be removed, because they are high in reducing sugars, colorants and starch which lowers the sugar yield in the evaporation and crystallization station.

There are generally two main procedures for sugar cane harvesting, namely hand cutting and mechanical harvesting, while both procedures comprise several technical variants. During the time of slavery, field work was cheap and hand cutting was therefore the preferential harvesting method. Hand cutting is characterized by less cane damage which prevents sugar loss due to microbial activity. It is hence generally known that hand cutting results in higher sugar yields. With the abolition of slavery pre-harvest burning (intended to remove leaves and trash) started to increase the output of cutters. This method spread during the years of war when man power was rare and is now standard in many countries. Burning of cane has, however, the disadvantage of increased cane surface damage promoting microbial activity. The associated sucrose hydrolysis

and also the production of unwanted metabolic products results in a higher sugar loss and also in an increased amount of molasses. Therefore, burnt cane must be processed within 24 h.

Cutting by hand is nowadays replaced by machines in modern countries. Mechanical harvesting requires an adequate field preparation. A large, stone-free and even field area with a row length of 200 – 400 m is in particular essential for efficient mechanical harvesting. Whole-stick and chopper harvesting systems are used and adapted for certain harvesting conditions. Whole-stick harvesters are suitable for straight and upright grown, pre-burnt cane. Cane burning is hence also for mechanical harvesting a widely-used auxiliary method, which, again, requires a short subsequent storage time. In case of heavy, recumbent or green (not burnt) crops, choppers are the better suited choice. In addition to considering field conditions for choosing an appropriate harvesting method, the existing extraction system needs to also meet the requirements for either chopped or whole sugar cane. Either way the following transport to the factory should be carried out in a continuous and uniform way in order to avoid any changes due to microbial activity. (Hugot, 1972; Chen & Chou, 1993; van der Poel, P.W., 2000)

2.1.2.2 Extraction in cane mills

Extraction of sucrose from cane plant can be carried out using either a mill or a diffuser system. This first section is related to the mill station and the following is concerned with diffuser extraction.

In order to obtain raw juice from sugar cells, cane stalks need to firstly be crushed into a fibrous mass. Therefore, swing hammer shredders are used to divide the stalk into particles of 100 mm length and below 2 mm width to facilitate diffusion (1 in Figure 2-4). If whole stalk cane is delivered, sticks are cut by one or two knives into smaller pieces prior to shredding. Afterwards

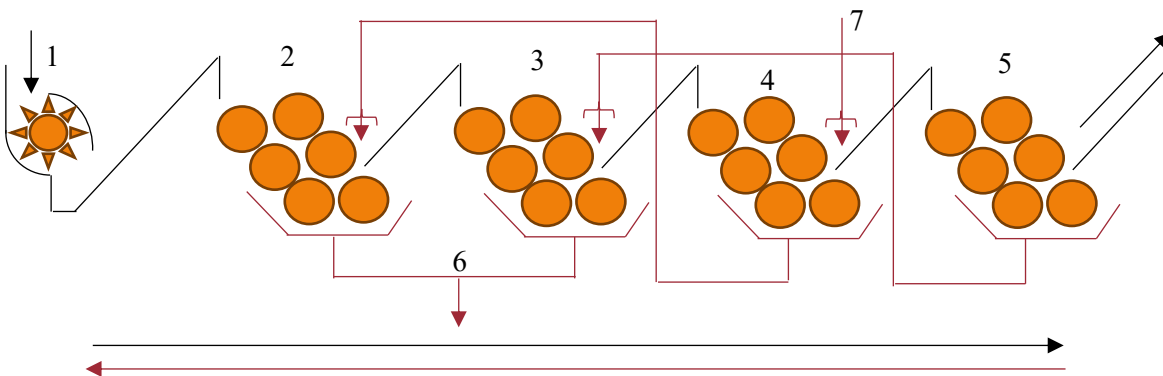


Figure 2-4: Schematic illustration of cane mill with shredder (1), six-roll mills (2-5), mixed juice (6), fresh water supply (7), flow of cane (black arrows) and flow of liquid (red arrows).

the fibrous mass is transported to the mill station where extraction of sugar from cane takes place. To do so, extraction units composed of four six-roller mills are used (2 – 5 in Figure 2-4). It should be noted that various mill compositions such as three-roller mills are found in the sugar cane processing industry. The process outlined here is representative for modern factories.

Similar to beet cossette extraction, sucrose containing water is directed in counter-current flow to bagasse transport. Juice from first and second mills are collected and transported as 'mixed juice' to the purification station. It should be noted that the term 'mixed juice' is not to be confused with 'mixed syrup' which means the blend of beet thick juice and dissolved raw cane sugar in this work. The resulting juice has a dry substance level of approximately 17 g/100 g. At the third mill (4) water (condensate) (7) with a temperature of about 358 K is sprayed on the bagasse. In theory, the bagasse absorbs the liquid like a sponge and releases sucrose containing juice from cane cells when squeezing it between the rolls. Juices from third and fourth mill are used in the first and second mill, respectively, for counter current extraction. After the last mill bagasse is exhausted to 95% of its initial sucrose content and subsequently used as fuel for boilers. The extraction process is finished after approximately 20 minutes.

As already mentioned, cane burning is a well-known method to improve processability and final product quality despite the aforementioned increased need of short storage times. This becomes especially evident during extraction whereat burnt cane shows clearly advantages over green cane: 20 – 30% less suspended solids, lower consumption of power, increased extraction yield and higher milling capacity can be achieved by cane burning. The result of mill extraction is called mixed juice which then needs to be clarified in the following process step of juice purification. (van der Poel, P.W., 2000; Chen & Chou, 1993)

2.1.2.3 Extraction in diffusers

The principle of cane diffusers is similar to extraction in the beet sugar factory. Thereby, the raw material is sliced into pieces to obtain an adequate ratio of surface and volume. In a counter current flow, the liquid and raw material are transported to ensure a uniform concentration gradient. Cane diffuser have similarities with beet diffusers and run for over 50 years in Egypt. Since the 1970th about 90% of cane is processed in diffusers.

Figure 2-5 illustrates a schematic diagram of a cane diffuser with a length of 50 – 60 m. Before cane enters the diffuser, raw material has to be prepared to achieve high extraction yields. Therefore, cane stalk is shredded into long fibers which provide a stable and open bed for continuous flow. Furthermore, cane cells are ruptured which facilitates diffusion. The prepared cane then enters the diffuser and is transported on a screen through 12 stage trays (length of approximately 4 m) counter current to liquid flow. According to that, juice from one tray is sprayed on cane material of the previous tray. After passing the last tray, bagasse leaves the diffuser and is dewatered in a mill. Conventional cane mills are, however, in this case not suited. A grooved top squeezing roll and a perforated bottom drum roll are used instead to achieve satisfactory moisture of bagasse. (Rein, 2007)

The extraction yield can be affected by several parameters such as temperature, imbibition rate, resistance time or raw material preparation. First of all, an adequate temperature control is essential to achieve high extraction yields and also to reduce enzymatic and microbial activity.

The temperature is therefore preferentially maintained between 348 – 358 K. Although higher temperature increases the extraction rate due to a higher diffusivity, the effect of cane preparation and flow rate is much more important. It is intuitively that the higher the imbibition rate, the higher the final yield of extraction. However, conversely higher imbibition rates result in a necessary increase of evaporation capacity increasing production costs. Thus, this process design is based on a compromise taking both factors into account. The residence time of cane material in diffusers is generally between 54 – 90 minutes. Within that window 96 – 98% of the initial sucrose content can be extracted from the raw material.

Extraction by diffusers achieves higher yields of sugar compared to mill stations. Further advantages of diffusers are lower capital, maintenance and operational costs. Additionally, the starch content of juices from diffusers is much lower than from a sugar mill tandem. Disadvantages are increased concentrations of sand and higher color values. However, it should be noted that the color value is also affected by other parameters such as cane variety, quality due to storage between harvest and mill, time-of-season, and temperature.

Unlike to juice obtained from mills, the resulting juice from diffusers is called draft juice. In order to simplify the ongoing phrasing, the term “raw juice” is generally used for both, the beet and the cane extraction product.

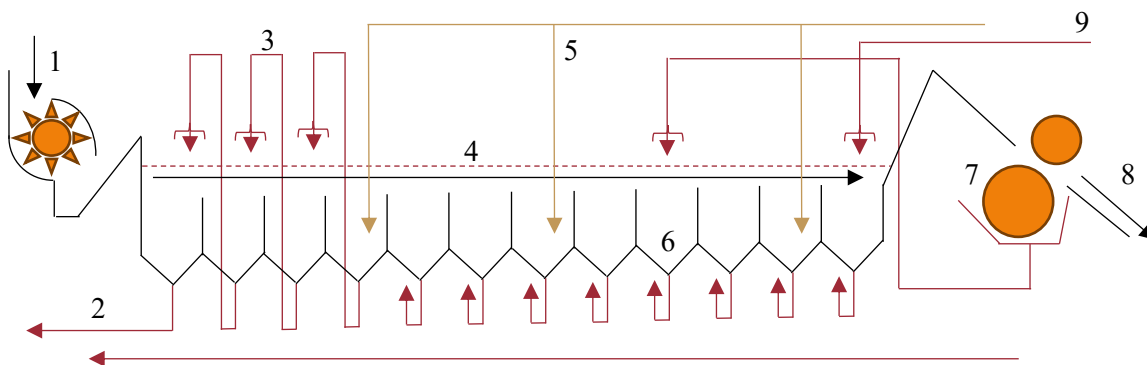


Figure 2-5: Schematic illustration of cane diffuser with shredder (1), draft juice (2), imbibition juice (3), diffuser with screen (4), direct injection vapor (5), 12 stage trays (6), dewatering mills (7), final bagasse (8), fresh water supply (9), flow of cane (black arrows) and flow of liquid (red arrows).

2.1.2.4 Purification

The syrup resulting from cane extraction is turbid, high in color and contains several soluble and insoluble non-sugars. The intention of juice purification is to remove such non-sugars as far as possible. The purification of raw cane juice is quite different to the procedure used in beet processing.

In order to prevent problems of subsequent process steps (blockages of heaters), raw juice is firstly screened to remove suspended solids such as small pieces of bagasse, sand and soil. Colorants and turbidities are then removed by a defecation clarification process with multiple options such as cold liming, warm liming, intermediate liming or hot liming. Although liming is practiced

throughout the sugar cane industry, the knowledge about the chemical and physical reactions is limited. Thus, is the detailed design of suitable liming processes rather a result of historical experiences than a priori knowledge. To exemplify, intermediate liming which is widely used in Australia is described here: Subsequently to screening, the raw juice is heated in tube or plate heat exchangers to approximately 349 K. Then lime is added in an amount such that the pH-value increases to 7.8. Ca^{2+} -ions react with dissolved phosphate to insoluble tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Other inorganic acids such as PO_4^{3-} or SO_4^{2-} precipitate, too, due to the presence of Ca^{2+} ions. The heat provokes denaturation of proteins, waxes, and gums. These conditions favor the formation of colorants, such as melanoidins due to the reaction of amino acids with reducing sugars. In contrast to liming of beet raw juice, the pH-value is kept intentionally low (7.8) to avoid decomposition of reducing sugars. Since the concentration of reducing sugars is much higher in cane raw juice, the resulting amounts of decomposition products would not be remediable during juice purification. Detrimental effects on later sucrose crystallization would be the consequence. After a holding period of 10 – 15 min, in which previously outlined physical and chemical reactions occur, limed juice is heated above the boiling point of 376 K. Subsequently, the overheated juice is delivered to flash tanks to enable the release of dissolved air. Afterwards juice needs to settle in order to remove precipitated salts, proteins and other flocculants. Therefore, continuous clarifiers separate clarified sucrose containing liquid from mud. However, the mud still contains relatively high amounts of juice. In order to separate the juice from the solids, mud is mixed with bagacillo, fine bagasse particles, which act as filter aid in the following separation process. The mixed mud is then clarified in rotary drum vacuum filters and collected before it enters the evaporation station.

The cane raw juice purification process does not result in a thermostable thin juice which is conversely found in beet sugar production. Thus, high temperatures in subsequent process steps such as evaporation and crystallization, promote the formation of colorants and acids. (Rein, 2007; Chen & Chou, 1993)

2.1.2.5 Evaporation

Due to the similarity of sugar beet and cane sugar evaporation procedure, detailed description of this process step can be found in section 2.1.1. As mentioned in the previous section, cane thin juice is much more thermolabile than beet thin juice. It hence still contains considerable amounts of invert sugar. Therefore, high temperatures should be avoided and a homogeneous mixing should be applied in order to minimize color forming reactions. (Rein, 2007)

2.1.2.6 Syrup clarification

In order to increase quality of syrup prior to crystallization process, fine suspended solids which are formed during evaporation, are removed by flotation clarification. Therefore, small air bubbles, flocculants and chemicals (e.g. phosphate) are introduced into the syrup. Hence, fine

suspended matter agglomerates and floats onto the syrup surface due to their surface properties, size and relative density. (Rein, 2007)

2.1.2.7 Crystallization, separation and drying

Crystallization is also the most important purification step in raw cane sugar production. Just as in beet sugar production, different crystallization schemes are possible to achieve high quality raw cane sugar and low molasses purity. The crystallization step is generally quite similar for beet and cane processing. Crystallization parameters such as pressure, temperature and final crystal content are practically the same. Even the designs of the boiling pans and centrifuges for batch and continuous processing as well as the drying drums do not differ much. Again, details on this process step are described in the previous sections 2.1.1 on beet production.

It is nevertheless worth to mention that the boiling scheme can be different between beet and raw cane sugar production. Figure 2-6 shows the conventional three step boiling scheme with A, B and C crystallization redesigned according to Rein (2007). The clarified syrup from the previous process step feeds pan A and B. For both pans, a massecuite containing pan C sugar (purity of 85%) and water is used as footing massecuite. The crystallized sugar from pan A (purity of 89 – 99%) and B (purity of 97 – 98%) are both of saleable quality. The run-off syrup from A product (purity 60 – 70%) feeds pan B and C. Pan C is also fed by the run-off syrup of pan B. To achieve sugar of high polarity, the purity of pan B has to be kept between 70 – 75%. Therefore, clarified syrup is added into the pan. Batch centrifuges are used for the production of raw sugar of saleable quality. The separation of C sugar from C molasses is conversely performed by continuous centrifuges.

Anyway, other modified process schemes are found in raw cane sugar factories: For the purpose of the crystallization of VHP-sugar (very high polarity: 99.3 – 99.5%), B and C sugar are remelted and used as feed for pan A.

In the end, it should be mentioned, that especially raw cane sugar factories are designed to meet the quality criteria of customers' demands. In general, the production of high quality raw sugar is aimed for. However, in emerging or third world countries the purity and quality of sugar might be less relevant than just covering volume demand.

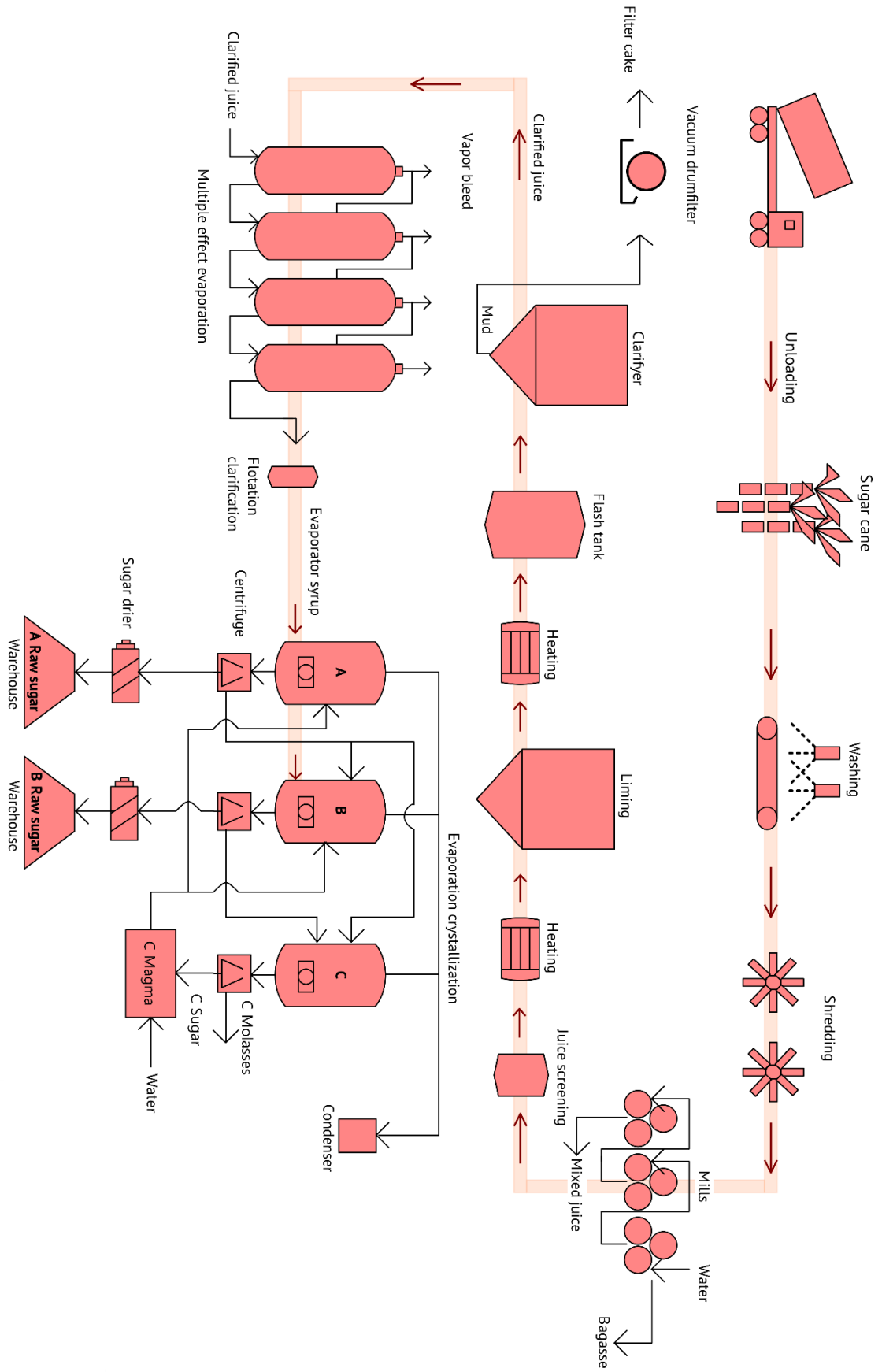


Figure 2-6: Process scheme of raw cane sugar factories.

2.1.3 Co-production in beet sugar factories

Co-production in beet sugar factories refers to processing of raw cane sugar during the regular sugar beet campaign or during thick juice campaign. The additional implementation of this divergent process is intended to increase utilization of the factories which, apart from that, stand still most time of the year due to seasonal availability of sugar beet. This is especially relevant for beet sugar manufacturers where raw cane sugar is easily accessible such as North America, Iran or Egypt. In past (e.g. in GDR) and present, co-production is an occasionally used procedure. Since the decision of the 2017 EU market liberalization this process gained more attention. Nevertheless, information about this modified process is rare and experiences are not shared. This section should give a brief overview about application opportunities for co-processing.

Figure 2-7 shows process schemes for co-production during regular beet and thick juice campaign. The schemes shown represent only a small selection of a wide variety of potential procedures. However, the actual factory design as well as thick juice and raw cane sugar quality have to be taken into account when implementing co-processing. Due to the fact that raw cane sugar contains undesired colorants which are preferentially incorporated into the sugar crystals (see section 1.1), purification steps are usually applied before the sugar is introduced into the process. If co-production is conducted during the regular sugar beet campaign, raw cane sugar is hence usually subjected to an affination step, in which adhering dark colored molasses films on crystal surfaces are removed as far as possible. Therefore, a saturated sugar solution is mingled with the raw sugar under controlled conditions. Using this procedure, the color value of raw cane sugar can be reduced by 50 – 70% (Rein, 2007). The affinated sugar is then separated by the means of centrifugation. The affination syrup is added to beet raw juice. The resulting blended juice is then purified using common beet juice purification conditions (2.1.1). The affinated sugar is dissolved in thin juice before the solution is subjected to evaporation and crystallization.

The thick juice campaign is another suitable period of time for co-production of raw cane sugar resulting in an improved factory utilization. Two different options for that are shown in Figure 2-7. Option A is designed for raw sugar of very high polarity (VHP), which has a sugar content of at least 99.3% (w/w) and a color between 1100 – 2000 IU. In a first step the sugar is affinated as explained above. The affination syrup needs further to be decolorized. Therefore, liming and carbonation followed by filtration are adequate process steps. Ultrafiltration and ion exchange systems are optionally used for decolorization of the affination liquor. The affinated sugar is melted and blended with decolorized affination syrup and stored thick juice. If raw cane sugar quality is very high, it is possible to omit the affination as well as the decolorization step. In this case raw sugar is completely dissolved and the resulting liquor is filtered to remove fine dispersed particles. Afterwards it is blended with thick juice and subsequently crystallized. This scheme would decrease production costs due to the absence of juice decolorization. However, the filtration system has to be maintained continuously to ensure high flow rates.

A processing option for raw cane sugar of lower quality is illustrated as Option B in Figure 2-7. For this purpose, raw cane sugar liquor is made from crystals and decolorized in previous outlined process steps such as liming, carbonation, filtration, ultrafiltration and ion exchange. A comparison of different decolorization systems and schemes is presented by Rein (2007). The purified liquor is mixed with thick juice prior to crystallization.

It is generally acknowledged that an addition of 20 g/100 g raw cane sugar does not result in unpredictable issues during co-processing. Furthermore, at this concentration color values below 30 IU can be achieved (Kochergin et al., 2012). For Eastern European Factories an addition of even 70 g/100 g raw cane sugar has been reported. The crystallization of sugar in general is not supposed to be critical when co-production is applied. However, both sources supply colorants with different physical and chemical properties into the process which results in a yet unknown transfer of colorants. The incorporation of colorants is affected moreover by the quality of beet and cane material. Additionally, other factors such as growth rate affect the quality of sugar crystals, in particular particle size, size distribution, color and ash inclusion. In conclusion, the quality of sugars produced from co-processing of beet and cane material cannot be understood and controlled based on the knowledge of either pure beet or cane processing due to the unknown interactions of minor components. Thus, a systematic study is necessary to understand the mechanisms of color inclusion into sugar crystallized from mixed syrups. In particular the effects of co-processing on particle size and distribution of sugar crystals are of interest.

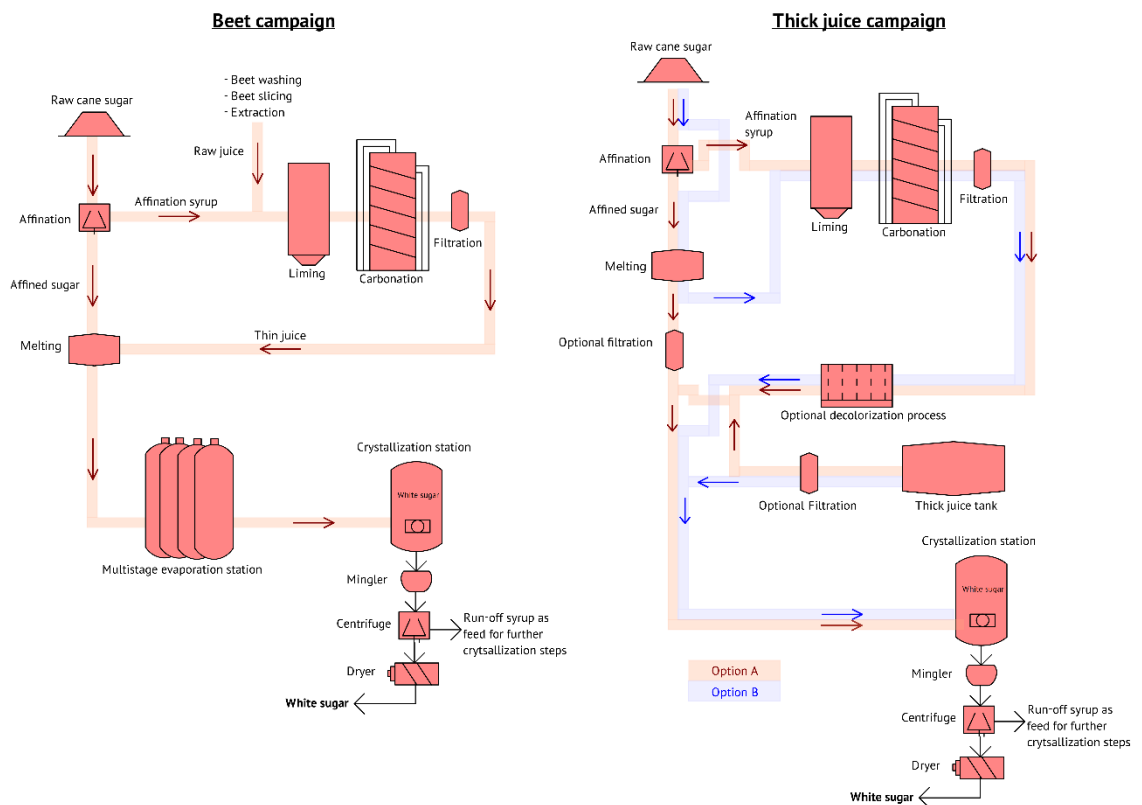


Figure 2-7: Process schemes for co-produced white sugar in beet and thick juice campaign.

2.2 Colorants in sugar production

Color is the perception of visible light (wavelength between 390 – 700 nm) which is reflected by an object or fluid. In the food industry, it is a key quality parameter which describes the characteristic of a product. Sucrose crystals contain minute concentrations of impurities which are bound to the crystal due to adsorption and inclusion. These impurities are often colored and might dye solutions or products made from sugar. The colored constituents are not easy to identify and quantify, because their actual chemical structure is unknown. Additionally, technical sucrose solutions contain mixtures of various colorants which have different absorption properties. Hence, the total effect of colorants is determined and compared by light absorbance at one wavelength (Rein, 2007). For sugar, worldwide quality standards are set by ICUMSA, but also by customers such as Coca-Cola Company, to ensure uniform quality of the final product regarding color, taste, turbidity and shelf life. For example color of white sugar A and B has to be below 60 and 150 IU, respectively (van der Poel, P.W., 2000). These standards are independent from sugar source. Typical non-sugars in sucrose crystals are colored light brown to dark brown and even black. It is generally acknowledged that the coloring matter in beet and cane sugar differ regarding their physical and chemical properties such as molecular weight, electrical charge and pH-sensitivity. Thus, it is not surprising that the colorants behave differently with respect to adsorption onto and inclusion into the sucrose crystal. The following sections give a brief overview about the colorants in beet and cane sugar production.

Colorants in beet sugar production are preliminary formed during the process due to sugar degradation reactions. Reducing sugars, such as glucose and fructose as products of sucrose hydrolysis, form highly reactive intermediates under acidic or basic conditions. Hence these can react to colored compounds in condensation and polymerization reactions (Coca, 2004). However, other substances are responsible for color reactions during beet sugar processing as well. Precursors, colorless or slightly colored constituents from beet plant like amino acids, nitrogenous and phenolic compounds enter the process and act as reaction partners in color forming enzymatic and non-enzymatic reactions.

Colorants in cane sugar production originate mainly from the plant and undergo polymerization reactions during the process. They are responsible for two third of raw cane sugar color. Thus, it is of greatest interest to remove color-containing parts of the plant, such as leaves, before the cane enters the extraction unit (e.g. by pre-harvest burning). The color in cane varies by its growing condition, time of season and cane variety. Due to process conditions, most colorants in cane sugar manufacturing remain soluble throughout the process. Thus, if no decolorization such as ion exchange system, activated carbon system or membrane filtration is applied, these compounds are incorporated into the sucrose crystal. (Rein, 2007)

2.2.1 Phenols and flavonoids

Phenols and flavonoids, also known as light yellow plant pigments, are found in green plants and enter the process during sugar extraction from raw material. Phenols consist of an aromatic hydrocarbon group with a hydroxyl group attached. Caffeic acid, Ferulic acid and chlorogenic acid are phenolic acids found in cane juices. Flavonoids consist of a heterocyclic ring and two phenyl rings. Both, phenols and flavonoids, are highly soluble at increased temperatures and mild pH-conditions (4.5 – 7.5) which are found in cane processing. In addition, these compounds are precursors for further color reactions. They take part in oxidation as well as enzymatic catalyzed reactions and form melanins of very high molecular weight ($> 250,000$ Da). The reaction products, known as melanins, are the major contributors for raw cane sugar color (see 2.2.2). Moreover, the color forming reactions of the aromatic compounds are promoted by iron which is often found in cane juices due to iron-containing plant equipment. Beet and cane plants contain high amounts of phenolics. However, beet phenolics contain nitrogen and cane phenolics do not. Hence, beet phenolics are reactants in *Maillard*-reactions. (van der Poel, P.W., 2000; Godshall & Baunsgaard, 2000; Rein, 2007; Chen & Chou, 1993)

2.2.2 Melanins

Melanins are dark brown to black enzyme-catalyzed oxidation products of phenolics (see section 2.2.1). The most common enzymatic browning reaction in beet sugar processing starts immediately after cutting beets into cosettes: Tyrosine is catalyzed by a polyphenol oxidase (tyrosinase) to DOPA which is formed in further steps to dopachinone, dopachrome and dark colored melanin. The enzymatic reaction occurs even at high temperatures (343 K) and under middle acidic conditions (reaction optimum at pH- value of 5.5 – 6.5) during extraction (pH-value 5.0 – 6.6). The reaction stops during liming where high pH-values result in low solubility. Hence, they are separated during purification step and rarely found in sucrose crystals from beet. However, if melanins pass the purification station they are preferentially included into the sucrose crystal. (van der Poel, P.W., 2000; Godshall & Baunsgaard, 2000; Shore et al., 1984; Bourzutschky, 2005)

In cane sugar processing melanins are formed throughout extraction, too. However, the enzymatic reactions are more promoted during milling (up to 333 K) than in cane diffusers (363 K) due to lower temperatures. Enzymes in cane sugar processing have their optimum at a pH-value between 4.5 – 7.5. Throughout the whole cane sugar process this optimum is nearly always found. In contrast to beet sugar production, melanins remain dissolved after the purification station due to milder pH conditions (max. 7.8). Thus, melanins with a molecular weight above 250,000 Da are common colorants in sugar from sugar cane origin. (Bourzutschky, 2005; Rein, 2007)

2.2.3 Melanoidins

Melanoidins are dark-brown to black, polymeric, non-enzymatic reaction products from reducing sugars and compounds containing amino groups. The formation of melanoidins, generated by *Maillard* reactions, is important for the entire food industry. While this color forming reaction is intended for most products it is undesired in sugar processing.

The *Maillard* reaction follows a typical Arrhenius temperature dependency and hence increases in its rate significantly in the temperature range of 293 – 373 K. At low dissolved dry substance level and neutral or slightly acidic conditions (e.g. extraction) *Maillard* reaction can actually be neglected (van der Poel, P.W., 2000). However, although in cane extraction the amount of N-containing compounds is low and conditions are slight acidic conditions (pH 5 – 6), melanoidin formation is observed in cane diffusers due to high temperatures (363 K) (Bourzutschky, 2005). The reaction has its optimum between a pH-value of 9 – 10 (van der Poel, P.W., 2000) and a dry substance level of 80 – 90 g/100 g (Heitz, 1995). The polymerization degree increases with increasing temperature and extended reaction time. In addition color, thus the optical effect, is intensified at higher degrees of polymerization (above 10,000 Da) (Coca, 2004; Bourzutschky, 2005). Hence, color formation due to *Maillard* reactions is of major importance during evaporation and crystallization steps due to increasing dry substance levels, high temperatures and the duration of high temperature exposure.

According to Coca (2004) *Maillard* reactions can be divided into three stages:

1. The *Maillard* reaction starts with a condensation reaction between a compound containing a free amino group and the α -hydroxyl carbonyl group of a reducing sugar. The condensation product releases water and converts into a Schiff base. Further steps including the *Amadori*-rearrangement result in the formation of *Amadori* compounds which are not colored.
2. The *Amadori* compounds are degraded in enolization and condensation reactions to fission products. Subsequently Strecker degradation forms aldehydes and α -aminoketones from dicarbonyl compounds and amino acids.
3. The highly reactive intermediate compounds of the last stages are polymerized in further reactions such as dehydration, cyclisation, isomerization, rearrangement, retroaldolisation and condensation. Thus, brown to black colored, nitrogen-containing polymers are formed, which are known as melanoidins. It is without saying that with increasing polymerization molecular weight increases, too.

2.2.4 Alkaline degradation products of hexoses (ADH)

As their name suggests ADHs are formed under alkaline conditions. Their exact reaction pathways are not known. First sucrose is inverted into glucose and fructose. Afterwards mainly the latter is involved in further decomposition steps. The reaction forms colorless carboxylic acid constituents with less than six carbon molecules such as lactic, acetic or oxalic acid. These compounds can participate in polymerization reactions and form colored compounds. In addition, considerable amounts of brown colored products with more than six carbons are formed which are polymerized to compounds with molecular weights up to 10,000 Da. The formation of ADH starts at ambient temperature but is accelerated with increasing temperature. The optimum pH-value is 11. Thus, their formation is more pronounced in beet sugar production due to alkaline conditions in the purification station. It is mentioned that ADHs are responsible for 80% of ICUMSA color value in beet sugar processing. (Rein, 2007; Bourzutschky, 2005; Davis, 2001)

2.2.5 Caramels

Caramels are yellow to brown compounds with a characteristic taste and flavor. These compounds are formed via decomposition of sucrose to fructose and glucose at very high temperatures (> 393 K). The monosaccharides are rearranged and α -dicarbonyl compounds such as 3-deoxyhexosulose are formed. Further condensation, isomerization and dehydration reactions occur and form different colloidal compounds. Color formation is promoted by increasing pH-values and temperatures. In the evaporation and crystallization station caramelization is induced due to elevated temperatures, long heating times, recirculation of syrup and overheating caused by inadequate circulation. Another source of caramel formation is the built up of sucrose based incrustations on heat transfer surfaces in evaporators where colorants can easily form due to very high temperatures and long heat exposure. The reaction products have a molecular weight of 500 – 1,000 Da which is increasing above 10,000 Da with time and elevated temperatures due to polymerization. Caramels are preferentially found on the surface of the sucrose crystal. In general, caramelization plays a minor role in beet processing, because the presence of amino acids favors *Maillard* reaction instead. (Bourzutschky, 2005; Coca, 2004; Godshall & Baunsgaard, 2000; Rein, 2007)

2.2.6 Indigenous sugar cane polysaccharides

Indigenous sugar cane polysaccharides have their origin in the cane plant. The molecules are soluble in water and have a concentration of 200 – 1000 mg/kg dry substance in fresh cane juice. The chemical structure consists of an arabinogalactan backbone with glucuronic acids, esterified phenolic groups and dicarboxylic functionalized lipids attaches. It is reported that this large molecule can form complexes with other colorants. The resulting complex is of very high

molecular weight and surprisingly included into sucrose crystals. (van der Poel, P.W., 2000; Godshall & Baunsgaard, 2000; Bourzutschky, 2005)

2.3 Theoretical approach of sucrose crystallization

Industrial crystallization processes are used as a separation and purification technique to form solid crystals from a solution or melt. A solution is a homogeneous single phase which consists of a blend of two or more components - the solvent and the solutes. In case of the industrial sugar production, the solvent is water and the solutes are both sucrose and non-sucrose compounds. The solubility of the sucrose is affected by different parameters e.g. temperature, pressure, concentration of sucrose and non-sucrose components, which influence the crystallization process, respectively. The goal of every crystallization process is a high yield and purity of the valuable material, in this case sugar crystals. The following sections give a brief overview about the basics of solubility, nucleation and crystal growth in the sugar production.

2.3.1 Solubility

An industrial sucrose solution is obtained by the extraction of sucrose from sugar beets or cane. The sucrose molecules diffuse from the plant cells into the solvent (water). Besides sucrose also impurities such as peptides and minerals are extracted. The impure solution, called raw juice, is purified to increase the purity of the sucrose solution. In a next step the solution is evaporated to achieve a supersaturated state. The solubility in pure sucrose solutions is expressed as a relation of the sugar to water content at a given temperature as illustrated in Figure 2-8.

The solubility of a substance is driven by its molecular structure and its conformation in solution. The sucrose molecule comprises eight hydroxyl groups. Intermolecular hydrogen bonds can be formed by five of eight hydroxyl groups, which are involved during crystallization and dissolution. The other three can form intramolecular bonds. A complete hydration of the solvate-able hydroxyl groups is present in aqueous solutions with a low sucrose content. The free hydroxyl groups form hydrogen bonds and a hydrate structure, respectively, which explains the high solubility of sucrose in water. Hence, primarily the collisions of sucrose molecules have an effect on the physical properties of

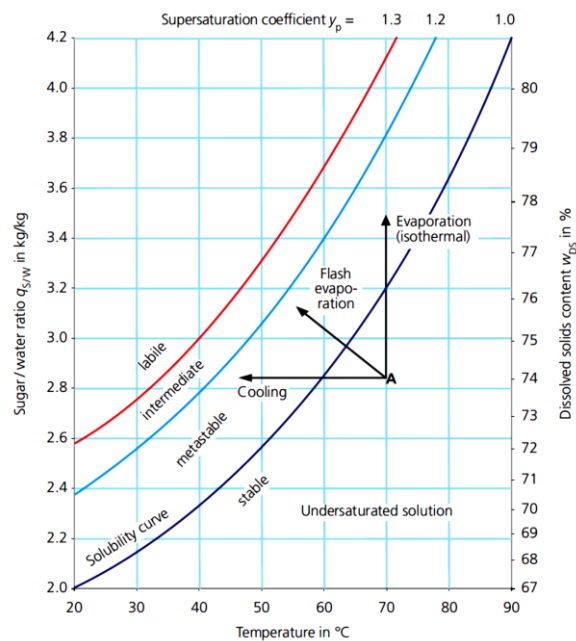


Figure 2-8: Solubility of pure sucrose solution as a function of temperature. Permission from Rein (2007).

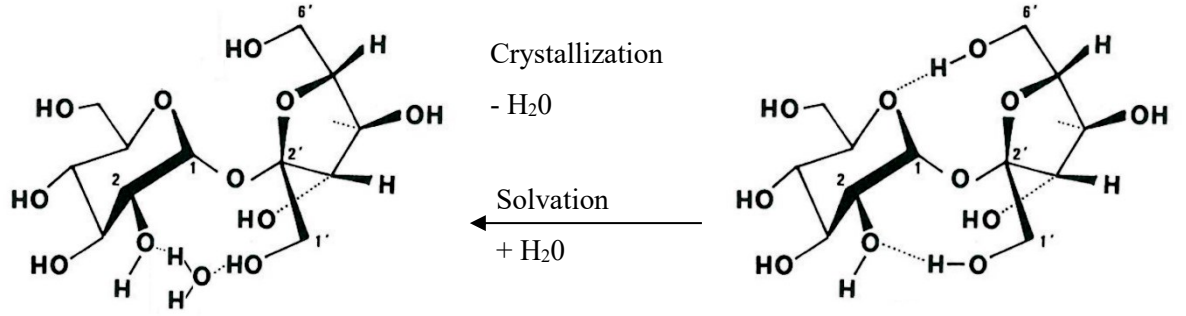


Figure 2-9: Conformation of sucrose molecule in dissolved and crystalline state (reprinted from Wittenberg (2001)).

the solution (van der Poel, P.W., 2000). In highly diluted aqueous solutions ($< 40 \text{ g/100 g}$) this behavior follows in general ideal solution behavior (Schliephake, 1963). Lichtenthaler et al. (1996) found that sucrose possesses a preferred conformation: a hydrogen bond persists between the Glucose 2^g-O and the Fructose 1^f-OH groups. This conformation limits the flexibility of both rings to each other and is similar to that in the crystalline state (Figure 2-9) (van der Poel, P.W., 2000). When the sucrose concentration in the solution is higher, the distance between the sucrose molecules is decreasing and not all hydroxyl groups form bonds with water. Thus, interactions between the sucrose molecules occur and leads possibly to aggregation or an so-called ‘associated structure’, respectively. If the size of the resulting cluster (Figure 2-10) exceeds the critical radius a three-dimensional nuclei is formed (see 2.3.2) (van der Poel, P.W., 2000).

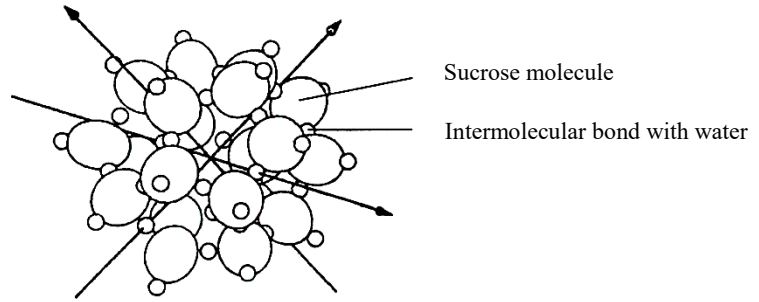


Figure 2-10: Cluster of sucrose molecules (reprinted from Schliephake (1963)).

A solution is saturated with the solute i if the chemical potential of the species in the solid phase (sol) is equal to the one in the solution (l):

$$\mu_i^{sol} = \mu_i^l \quad (2-2)$$

The chemical potential μ_i is defined as:

$$\mu_i = \mu_i^0(T) + RT \ln(\gamma_i c_i) \quad (2-3)$$

with the chemical potential of an arbitrary reference state μ_i^0 , the gas constant R , the temperature T , the activity coefficient of the species γ_i and the molar concentration c_i (Myerson, 2001).

The usual unit to describe the solubility of a solute (sucrose) in a solvent (water) is the ratio of their masses. In sugar industry the solubility coefficient $q_{sat,p}$ is defined as:

$$q_{sat,p} = \left(\frac{w_s}{w_w} \right)_{sat,p} \quad (2-4)$$

But technical solutions in the sugar factories contain impurities which affect the solubility in dependence of their amount and type. Therefore, the term $q_{sat,im}$ is used for the solubility coefficient of technical sucrose solutions. It is calculated analogous to equation (2-4). The quotient of the solubility coefficient of the technical to the pure sucrose solution is defined as the *saturation coefficient* (van der Poel, P.W., 2000):

$$y_{sat} = \frac{(w_s/w_w)_{sat,im}}{(w_s/w_w)_{sat,p}} = \frac{q_{sat,im}}{q_{sat,p}} \quad (2-5)$$

The knowledge of the solubility of a solute in a liquid is necessary for calculation of the driving forces of the crystallization processes. Nevertheless, it provides neither information about the formation of crystals nor growth rates. The driving force for these processes is the difference between the chemical potential of the current and the saturated state (see equation (2-3)):

$$\frac{\mu - \mu_{sat}}{RT} = \ln \left(\frac{\gamma \cdot c}{\gamma_{sat} \cdot c_{sat}} \right) \quad (2-6)$$

where μ is the chemical potential, γ is the activity coefficient and c is the molar concentration. The index *sat* indicates the saturated state. Usually the driving force is expressed as supersaturation S , which can be described by:

$$S = \exp \left(\frac{\mu - \mu_{sat}}{RT} \right) = \frac{\gamma \cdot c}{\gamma_{sat} \cdot c_{sat}} \quad (2-7)$$

Due to the fact that thermodynamic data are regularly unavailable, ideality is assumed ($\gamma = \gamma_{sat}$) and hence the supersaturation S is often constituted by the ratio of the concentrations (Myerson, 2001; Mullin, 2001):

$$S = \frac{c}{c_{sat}} \quad (2-8)$$

For practical reasons, in the sugar industry the *supersaturation coefficient* y is defined as the quotient of the ratio of the mass fractions of sucrose to water in the actual solution and the ratio of the mass fractions of sucrose to water in a saturated solution at a given temperature. In impure solutions the denominator is the product of the saturation coefficient (equation (2-5)) and the solubility coefficient of a pure sucrose solution at given temperature:

$$y = \frac{(w_s/w_w)}{(w_s/w_w)_{sat}} = \frac{(w_s/w_w)}{y_{sat} \cdot (w_s/w_w)_{sat,p}} \quad (2-9)$$

The solubility curve of a pure sucrose solution as a function of the temperature is illustrated in Figure 2-8. The solution is in a stable state if the sucrose to water ratio at a given temperature is below the solubility curve (undersaturated $y < 1$). Above the solubility curve, the solution is supersaturated ($y > 1$) with different merging zones. The metastable stable zone is the most interesting in the industrial sugar crystallization to obtain a pure product with a narrow particle

distribution and less false grain. If the supersaturation increases nucleation might occur spontaneously at a certain limit which is called the metastable limit also, known as the spinodal curve, respectively. It is the boundary between the metastable zone and the unstable region (Myerson, 2001). In the intermediate zone, the crystallization process is less controllable due to an accelerated crystal growth and nucleation. The rate of spontaneous nucleation increases in the labile zone. A supersaturated solution can be achieved from an undersaturated stable solution by cooling, isothermal evaporation or flash evaporation (van der Poel, P.W., 2000).

2.3.2 Nucleation

The crystallization can be divided into two steps: nucleation and crystal growth. The nucleation can be further subdivided into primary and secondary nucleation (Figure

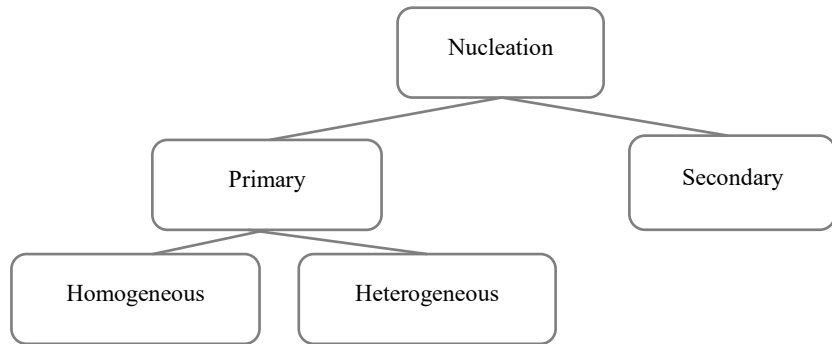


Figure 2-11: Mechanisms of nucleation.

2-11). Primary nucleation proceeds without existing crystal surfaces. It can be divided into homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs solely by the participation of solute molecules. Although, it occurs rarely in practice as individual phenomenon, it is the basis of various nucleation theories. Heterogeneous nucleation is provoked by the presence of dissolved impurities or surfaces. Differences in surface tension form the basis for heterogenous nucleation. Secondary nucleation occurs due to the presence of crystals. (Myerson, 2001)

2.3.2.1 Homogeneous nucleation

The thermodynamic considerations for crystal nuclei from solutions are analogous to the condensation of vapor from a liquid. The phase transition occurs by a change in the Gibbs free energy ΔG . It is the sum of change of the surface free energy ΔG_S and of the volume free energy ΔG_V :

$$\Delta G = \Delta G_S + \Delta G_V \quad (2-10)$$

The crystallization is an exothermal process where $\Delta G_S > 0$ and $\Delta G_V < 0$. Thus, ΔG_S is the work required for the formation of a particle–solution interface. Assuming that the sucrose nucleus is a spherical particle with radius r and the specific surface tension σ the surface free energy is expresses as:

$$\Delta G_S = 4\pi \cdot r^2 \cdot \sigma \quad (2-11)$$

The volume free energy ΔG_V can be considered as the released energy by transferring the particle constituting solute molecules for the bulk solution into the crystalline state:

$$\Delta G_V = -\frac{4}{3V_M}\pi \cdot r^3 \cdot \Delta\mu \quad (2-12)$$

with ρ_{cr} as the density of the crystal, V_M the molecular volume and $\Delta\mu$ the difference of the chemical potential of a molecule which transforms from solution into the crystalline state.

Figure 2-12 illustrates the trend of ΔG , ΔG_S and ΔG_V as a function of the cluster size. The Gibbs free energy change of a solid particle is decreasing for nuclei greater than the critical radius r_c .

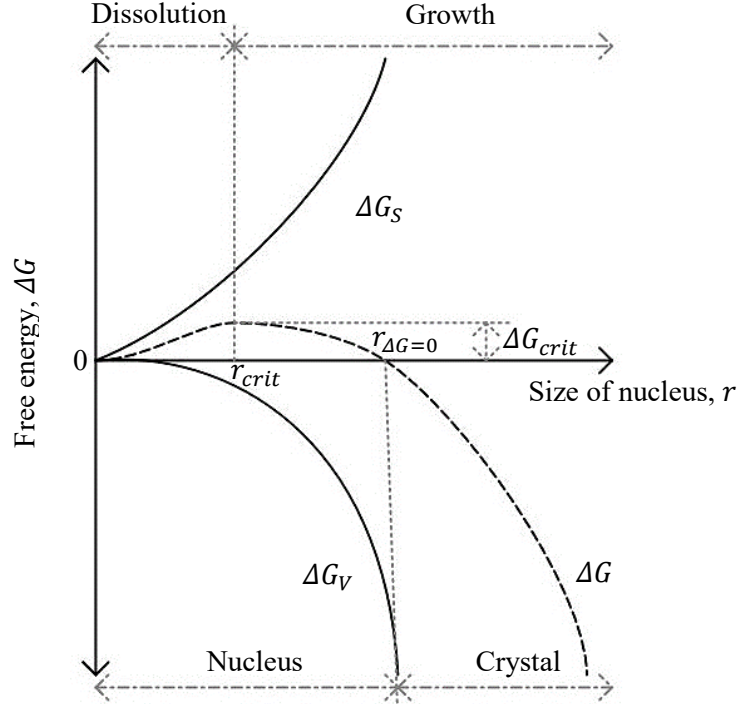


Figure 2-12: Free energy diagram for nucleation explaining the existence of a 'critical nucleus' according to Mullin (2001) and modified.

Therefore, molecular aggregates with $r < r_c$ are unstable and dissolve easily because further growth would increase the driving force for dissolution. For agglomerates with a radius r_{crit} the driving force for dissolution ΔG_{crit} is actually maximal. For particles with $r > r_{crit}$ the gradient of the change of the free volume energy exceeds the one of the surface free energy. Hence is further growth improving the energetical state of a particles in this size range. However, a stable crystalline state of the particles is only achieved once r exceeds the size $r_{\Delta G=0}$ so that $\Delta G < 0$. From this point ($r_{\Delta G=0}$) on the particles are actually not nuclei but stable crystals. The critical size of the nucleus is computed by the minimum of the gradient of the free energy with respect to the radius (Myerson, 2001; van der Poel, P.W., 2000):

$$\frac{d(\Delta G)}{dr} = 8\pi \cdot r \cdot \sigma - \frac{4\pi}{V_M} \cdot r^2 \cdot \Delta\mu = 0 \quad (2-13)$$

$$r_{crit} = \frac{2\sigma \cdot V_M}{\Delta\mu} \quad (2-14)$$

If ideality is assumed and equation (2-6) and (2-7) are regarded, it is clear that the size r_{crit} is decreasing with increasing supersaturation and decreasing temperature:

$$r_{crit} = \frac{2\sigma \cdot V_M}{\Delta\mu} = \frac{2\sigma \cdot V_M}{RT \ln S} \quad (2-15)$$

The required activation energy ΔG_{crit} to form a stable particle can be computed by combining equations (2-10) to (2-12) and (2-15) (Myerson, 2001; van der Poel, P.W., 2000):

$$\Delta G_{crit} = \frac{16\pi \cdot \sigma^3 \cdot V_M^2}{3(RT \cdot \ln S)^2} \quad (2-16)$$

The number of stable nuclei formed per unit time and unit volume is expressed as the rate of nucleation. It is given in the form of the Arrhenius reaction velocity equation and can be combined with equation (2-16):

$$\frac{dN}{dt} = A \cdot \exp\left(-\frac{\Delta G_{crit}}{RT}\right) = A \cdot \exp\left(-\frac{16\pi \cdot \sigma^3 \cdot V_M^2}{3T^3 R^3 (\ln S)^2}\right) \quad (2-17)$$

It is evident that the nucleation rate increases with increasing supersaturation. Under the condition that supersaturation is constant nucleation rate is increasing with increasing temperature. Additionally, nucleation rate also increases with reduced interfacial tension. The nucleation rate follows an exponential trend once the critical supersaturation is reached. In practice, the viscosity of the solution increases with decreasing temperature which slows down the motion of the molecules and reduces nucleation rate (Myerson, 2001).

2.3.2.2 Heterogeneous nucleation

Heterogeneous nucleation occurs in the presence of foreign particles which decreases the surface tension work required to generate the new surface. This is a function of the surface tension σ , between the crystal and the other liquor and the crystal and the foreign surface. Heterogeneous nucleation occurs if the adsorption of the crystal to the foreign surface is beneficial in this respect. Hence, regarding equation (2-15) and (2-16) both the critical radius and the required activation energy to form a stable nucleus are decreasing. This means that the maximum of the critical free energy is lower during the heterogeneous $\Delta G'_c$ compared to the homogeneous ΔG_{crit} nucleation (Mullin, 2001):

$$\Delta G_{crit} = \phi \Delta G'_c \quad (2-18)$$

With ϕ as a factor which is < 1 . The forces of the interfacial tensions between the solid crystalline phase (c), the liquid (l) and the foreign solid phase (im, sol) can be expressed by the following equation:

$$\sigma_{sol,l} = \sigma_{c';im,sol} + \sigma_{c';l} \cos \theta \quad (2-19)$$

or

$$\cos \theta = \frac{\sigma_{im,sol;l} - \sigma_{c';im,sol}}{\sigma_{c';l}} \quad (2-20)$$

with the contact angle of the solid phase θ .

The decrease of the activation energy ΔG_c due to foreign particles depends θ . Therefore, the factor ϕ can be described by:

$$\phi = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (2-21)$$

Considering the affinity between the crystalline matter and the foreign particle, $0^\circ < \theta < 180^\circ$, the factor $\phi < 1$ indicates that heterogeneous nucleation is favorable over homogeneous nucleation. Meaning that taken the appropriate foreign material heterogeneous nucleation occurs at lower supersaturation than homogeneous nucleation.

2.3.2.3 Secondary nucleation

Secondary nucleation proceeds at much lower supersaturation in the presence of crystals of the solute. The process can occur due to different mechanisms such as initial breeding, needle breeding or collision breeding. According to each of these processes one can query if it is nucleation or just the reproduction of crystals. However, this question is not discussed because it is not within the scope of this work.

The first one takes place on the surface of seed crystals during growth. On the surface an organized structure of solute molecules is present until shear forces remove the cluster from the surface which subsequently forms a nucleus (Wittenberg, 2001). Needle breeding takes place when parts of dendritic crystals are detached and operate as new nucleation or growth sites. Collision breeding is induced mechanically. Either the crystals collide with each other or with a part of the vessel such as the stirrer or the wall. This leads to micro abrasions or the dislocation of clusters from the crystal surface (Myerson, 2001; Mullin, 2001). Secondary nucleation can be induced in the sugar industry by adding just a small amount of powdered sugar into a batch. The amount is actually too low to allow to control the crystallization. However, the microcrystals provoke the formation of nuclei. The application of this procedure results in a very broad particle size distribution, which is not recommended. The application of this procedure is also described as seeding (van der Poel, P.W., 2000). In this case it is hard to distinguish between seeding and nucleation. However, the abovementioned procedure is contrary to the actual objective of seeding: the control of the end crystal size by introducing seed crystals of defined size and distribution into the process. In sugar industry seeding is usually performed in combination with cooling crystallization. This is used for a controlled footing massecuite procedure as described in 2.1.1.

2.3.3 Crystal growth

Crystal growth is the second phase of the crystallization. After the formation of nuclei, or presence of possible growth sites, the particle size increases by the inclusion of solute molecules into the crystal lattice. The understanding of crystal growth is besides nucleation management crucial to control the final size and distribution of the particles. Furthermore, the crystal growth rate and the system conditions can take influence on the crystal habit and impurity inclusions. In the following

two different mechanisms involved in crystal growth are presented, the *Adsorption Layer Theory* and the *Diffusion Layer Model*. In addition, two different approaches for the computation of crystal growth rates are outlined.

2.3.3.1 Adsorption layer theory

The general theory of crystal growth ergo the incorporation of a solute molecule into the lattice starts with its adsorption onto the crystal surface which is illustrated in Figure 2-13. The molecule is deposited on the crystal surface. Subsequent it diffuses along the surface (1) until it is attached to a step or a kink (2). From a thermodynamic point of view the probability of incorporation is more

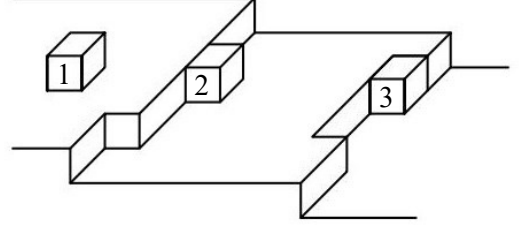


Figure 2-13: Surface structure of a growing crystal according to Myerson (2002).

likely with a higher number of closest bonding sites (3). If the molecule is not incorporated, it will desorb back into the solution phase. Thus, crystals grow layer by layer because it is more difficult to form a new layer than both spreading across and binding into an existing network. But under ideal conditions the growth continues until the face is plane. Hence arises the question how a new step is formed. The Two-Dimensional Growth Theories and Burton-Cabrera-Frank (BCF) Surface Diffusion Model try to explain the origin of a new step. The first one describes the formation of a new stable nucleus on the crystal surface by reaching the critical radius analogous to the previous explained nucleation of three-dimensional cluster formation. Thus, molecules will absorb onto the crystal surface and collide with each other which results in the formation of a two-dimensional aggregate, e.g. a nucleation of a new layer on the surface, taken the critical free energy is exceeded. For two-dimensional nuclei follow from equation (2-10) the Gibbs free energy ΔG , the critical radius r_c and the height h :

$$\Delta G = 2\pi \cdot r \cdot h \cdot \sigma - \frac{\pi \cdot r^2 \cdot h}{V_M} \cdot RT \cdot \ln S \quad (2-22)$$

$$r_{crit} = \frac{\sigma \cdot V_M}{\Delta\mu} = \frac{\sigma \cdot V_M}{RT \ln S} \quad (2-23)$$

From equation (2-22) and (2-23) the critical Gibbs free energy to form stable two-dimensional nuclei on the crystal surface is derived:

$$\Delta G_{crit} = \frac{\pi \cdot h \cdot \sigma^2 \cdot V_M}{RT \cdot \ln S} \quad (2-24)$$

Although the critical Gibbs free energy is lower for two- than for three-dimensional nuclei (compare equation (2-16) and (2-24)), the nucleation rate is about zero for low supersaturation. Furthermore, this growth principle is not continuous and the nucleation of two-dimensional nuclei

on the crystal surface is the rate-controlling step. (Myerson, 2001; Mullin, 2001; van der Poel, P.W., 2000)

The BCF Model assumes that surface nucleation is not necessary for crystal growth. New steps are formed by a spiral growth starting from existing steps or defects as illustrated in Figure 2-14. Therefore, if a surface is completely overgrown with a layer of molecules the step is still existing just one layer higher. In this case diffusion of solute molecules to the crystal surface is the rate-limiting step.

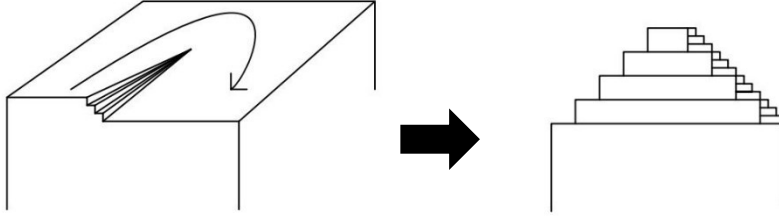


Figure 2-14: Development of a growth spiral starting from a screw dislocation according to Mullin (2001).

2.3.3.2 Diffusion layer model

The previously explained *Two-Dimensional Growth* and *BCF Model* regard the general idea of crystal growth. However, both models neglect concentration differences as the driving force for crystal growth. Furthermore, the diffusion of the solute in the boundary layer and the thickness of the latter are influencing the crystal growth rate. Therefore, the *Diffusion Layer Model* simply describes this relation: Before a solute molecule is built into the crystal lattice and the crystal grows, the solute must diffuse from the supersaturated bulk solution to the crystal surface. Hence, the concentration of solute molecules in the interfacial region is decreasing with crystal growth to allow for adequate mass transfer. Thus, a concentration gradient develops and solute molecules diffuse towards the surface of the crystal. The region of this gradient is called concentration boundary layer and has a thickness of δ (Figure 2-15A). A simple mathematical approach of crystal growth ($dm/d\tau$) by the *Diffusion Layer Model* is given in the following equation (Myerson, 2001):

$$\frac{dm}{d\tau} = D \cdot A \cdot \frac{\Delta c}{\Delta l} \quad (2-25)$$

where Δc is the concentration difference, Δl is the position difference in the boundary layer, A is the surface area and D the diffusion coefficient. The relation between concentration differences and their positions in the boundary layer can be described by:

$$\frac{\Delta c}{\Delta l} = \frac{c_b - c_i}{\delta} \quad (2-26)$$

with δ as the boundary layer thickness, and c_b and c_i as the concentrations of solute in the bulk and at the interfacial region, respectively. Thus equation (2-25) and (2-26) can be summed up to:

$$\frac{dm}{d\tau} = D \cdot A \cdot \frac{c_b - c_i}{\delta} = k_D \cdot A \cdot (c - c_i) \quad (2-27)$$

with k_D , the constant for diffusion reaction. Nevertheless, this equation disregards that the solute molecules are involved in further steps until they are included into the crystal lattice. The different steps were outlined among others by Ekelhof (1996):

1. Diffusion of the solute molecules through the boundary layer
2. Partly dehydration of the molecules
3. Adsorption onto the crystal surface
4. Diffusion along the crystal surface
5. Inclusion on the most energetic favorable site

A mathematical description of each single step is quite complex. It is rather recommended to focus on the meaningful steps 1, 4 and 5 (Ekelhof, 1996). Additionally, the process of crystal growth is on the one hand a diffusional process, forced by the concentration difference between the bulk and the solid surface. On the other hand the incorporation of the solute molecules into the crystal lattice can be regarded as a first-order “reaction”. The kinetics of any crystal growth depends on the respective rate-limiting step. For sucrose, the diffusion along the surface (4.) proceeds very quick compared to the diffusion through the boundary layer and the inclusion reaction (Ekelhof, 1996). The integration of the solute can hence be described in simplified manner with the following equation:

$$\frac{dm}{dt} = k_R \cdot A \cdot (c_i - c^*) \quad (2-28)$$

where k_R is the coefficient for the surface reaction and c^* is the concentration of the solute at the equilibrium on the crystal surface (Ekelhof, 1996; Mullin, 2001; van der Poel, P.W., 2000). The connection of equation (2-27) and (2-28) leads to a general crystal mass growth rate:

$$\frac{dm}{dt} = k_G \cdot A \cdot (c_b - c^*) \quad (2-29)$$

with k_G the overall growth constant:

$$k_G = \frac{(k_D \cdot k_R)}{(k_D + k_R)} \quad (2-30)$$

The coefficients for diffusion and surface reactions are dependent upon the crystallization conditions such as stirring, non-sucrose components, or temperature. It is generally acknowledged that the crystallization process of sucrose is limited by the surface reaction at temperatures below 313 K and depending on the diffusion at temperatures above 323 K (van der Poel, P.W., 2000). The thickness of the interfacial region δ can be described by the relation between the Reynolds (Re), Schmidt (Sc) and Sherwood number (Sh):

$$Sh = \frac{l}{\delta} = \frac{2}{3} \cdot Re^{1/2} \cdot Sc^{1/3} \quad (2-31)$$

which results in the following equation after converting:

$$\delta = \frac{3}{2} \cdot L \cdot \left(\frac{J \cdot L \cdot \rho}{\eta} \right)^{-1/2} \cdot \left(\frac{\eta}{\rho \cdot D} \right)^{-1/3} = \frac{3}{2} \cdot L^{1/2} \cdot \left(\frac{\eta}{\rho} \right)^{1/6} \cdot \frac{D^{1/3}}{J^{1/2}} \quad (2-32)$$

l is the linear dimension of the crystal, J is the relative crystal to solution velocity, D is the diffusion coefficient and ρ and η are the density and the dynamic viscosity of the solution, respectively (van der Poel, P.W., 2000).

The *Diffusion Layer Model* (Figure 2-15A) assumes that the concentration of the solute is decreasing from bulk to crystal surface. Thus, it describes the flow of solute molecules from the bulk of solution through the stagnant layer to the boundary of the crystal lattice. However, it is

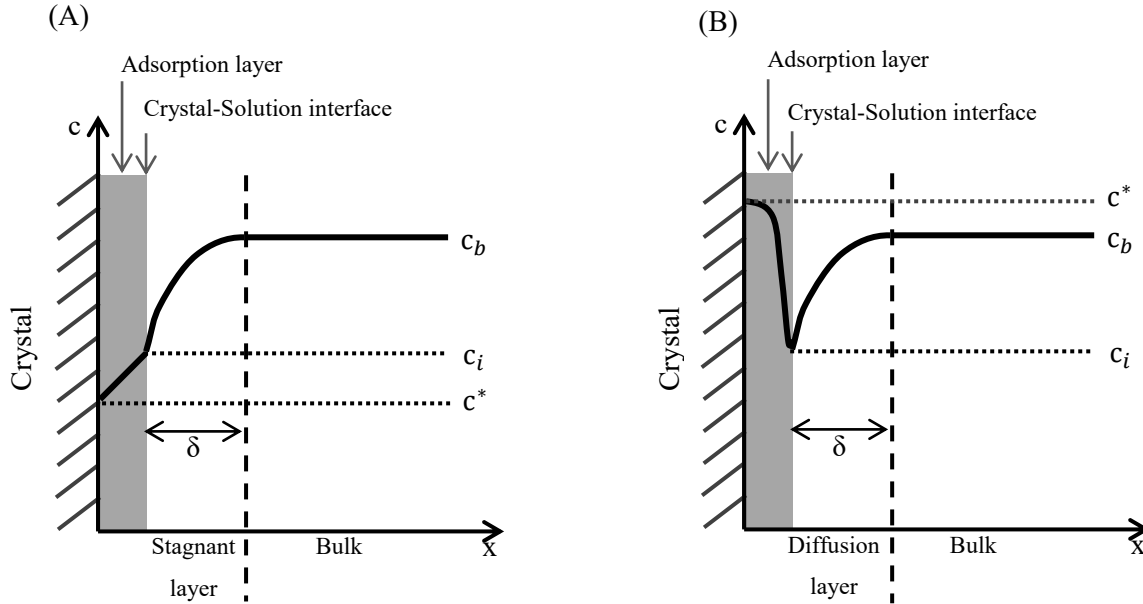


Figure 2-15: Concentration profile near the crystal surface according to Myerson (2002) (A) and an alternative approach (B).

hard to imagine that the concentration at the surface of the crystal and consequently in the adsorption layer is decreasing below the concentration of the solute in the bulk and at the crystal-solution interface. Actually, the solute concentration is the highest on the crystal surface and its direct surrounding as outlined in Figure 2-15B. Thus, the concentration is increasing from the crystal-solution interface to the crystal surface, ergo throughout the adsorption layer. In this layer the orientation and configuration of the molecules occur, and the solute molecules diffuse along the crystal surface until a favorable binding site is found. However, compared to the *Diffusion Layer model* this idea of crystal growth cannot be explained by diffusion through concentration differences. Nevertheless, this apparent contradiction can be overcome by a more appropriate approach for the diffusion in the explanation by existing gradients in the chemical potential (Bird et al., 2007).

2.3.3.3 Crystal growth rate

Multiple options exist to compute the crystal growth rate due to the dependency on temperature, particle size, supersaturation, and others. In this work, two different approaches based on mass deposition, crystal growth rate G , and linear growth velocity v are used and compared to each other.

The first approach, the crystal growth rate G , is computed by the change of the crystal mass m with time τ and per surface A . Therefore, the linear growth rate and shape factors are used for the computation (Mullin, 2001):

$$G = \frac{1}{A} \cdot \frac{dm}{d\tau} = \frac{3\rho \cdot \alpha}{\beta} \cdot \frac{dL}{d\tau} \quad (2-33)$$

with L as the characteristic dimension, ρ the crystal density, and the volume and area shape factors are α and β , respectively. It is obvious that a crystal has various faces which can have different growth rates. However, the linear growth rate alone considers only one characteristic dimension. Thus, it describes a mean crystal growth rate of different faces in dependence of the chosen characteristic dimension. The combination of the linear growth rate and the shape factors makes it possible to conclude easily from linear to mass growth rate. Furthermore, the shape factors allow calculating the growth rate of the crystals from an equivalent spherical particle although crystals have usually not a simple spherical shape. In this work, the characteristic dimension is related to the mean aperture d_{50} of the sucrose crystals which are obtained by sieve analysis. The shape factors are set to $\alpha = 0.75$ and $\beta = 5.02$ according to Bubnik & Kadlec (1992).

The second approach, considering the linear growth velocity v , is directly related to crystal masses. It is useful in agitated vessels and if the amount of seed crystals is known (Mullin, 2001).

$$v = \frac{\sqrt[3]{m_{Cr,n}} - \sqrt[3]{m_{Cr,0}}}{\sqrt[3]{\alpha \cdot \rho \cdot N \cdot \Delta\tau}} \quad (2-34)$$

with m_{Cr} the mass of crystals at the end (n) and the begin of crystallization (0) strike and the number of crystals (N).

2.4 Inclusion of impurities

Crystallization is a separation method with a high segregation level. In industrial applications, process parameters are chosen such that a product of high quality is achieved in consideration of an economic space-time yield. Thereby, quality loss due to impurity incorporations is practically unavoidable. The final crystal product contains minor quantities of colorants, ash material and other organic substances. To determine and compare impurity inclusion the transfer factor can be used (2.4.1). In order to achieve high quality products with a minimum of incorporated impurities, it is mandatory to understand the underlying incorporation mechanisms. Impurities are usually found randomly distributed inside the crystal but possibly also on the surface due to the incomplete separation from the mother liquor (e.g. centrifugation). Thus, one should distinguish between adsorption and inclusion of impurities (2.4.2). Some factors, which affect impurity inclusions are the unpredictable natural variability of the raw material and minor changes in process conditions. The latter will be discussed below (2.4.3).

2.4.1 Transfer factor

In a general thermodynamic approach, a partition coefficient K can be calculated to estimate the separation of impurities between the two phases. It is the ratio of the concentrations of impurities in the solid phase ($x_{im,sol}$) and in the liquid phase ($x_{im,l}$). Analogous to the calculation of ideal solubility it can, presuming that both phases are ideal and at equilibrium, at a given temperature (Myerson, 2001) be calculated:

$$K = \frac{x_{im,sol}}{x_{im,l}} = \exp\left(\frac{\Delta H_{im}^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{im}}\right)\right) \quad (2-35)$$

with the heat energy of fusion of the impurity ΔH_{im}^{fus} ; the universal gas constant R and the crystallization temperature of the pure impurity T_{im} .

Building on to equation (2-35) the sugar industry established the color transfer factor k_{color} to estimate the final sugar color $F_{420,s}$ (determined at a wavelength of 420 nm) as a function of the color value of the feed syrup $F_{420,ML,0}$ (Lionnet & Moodley, 1995):

$$k_{color} = \frac{F_{420,s}}{F_{420,ML,0}} \cdot 100\% \quad (2-36)$$

The transfer factor k_{color} is very useful but neglects the actual concentration of colorants in the mother liquor due to the ongoing crystallization. This approach can only be valid under two assumptions: a) no additional colorants are generated during the crystallization process, source term = 0; and b) all crystallizations considered yield the same crystal content and hence concentration factor. To improve on this, a corrected color transfer factor (k_{color}^*) considering the color value of the mother liquor also at the end of the crystallization strike ($F_{420,ML,n}$) is introduced:

$$k_{color}^* = \frac{F_{420,s}}{(F_{420,ML,0} + F_{420,ML,n}) \cdot \frac{1}{2}} \cdot 100\% \quad (2-37)$$

In addition to colorants, ash material is incorporated into the sucrose crystal. The transfer factor for ash is computed accordingly with equation (2-37):

$$k_{ash}^* = \frac{C_{Ash,s}}{(C_{ash,ML,0} + C_{ash,ML,n}) \cdot \frac{1}{2}} \cdot 100\% \quad (2-38)$$

Furthermore, in industrial crystallization impurity inclusion is related to non-equilibrium growth processes such as defect formation resulting from local conditions. Hence, the transfer factors integrate the contribution of different inclusion mechanisms such as adsorption, liquid inclusions and co-crystallization.

Since the interactions of numerous factors are responsible for impurity incorporation, it is useful to consider the processing factors affecting the final sugar color (section 2.4.3) and to examine the different inclusion mechanisms (section 2.4.2).

2.4.2 Inclusion mechanisms

The characteristic of inclusion is primarily intended by the strength of intermolecular bonds between solvent, crystal surface and impurities during crystal growth (Myerson, 2001). As illustrated in Figure 2-16 impurities can be:

- adhesion on the crystal surface
- entrapped into liquid inclusions
- co-crystallized into the crystal lattice.

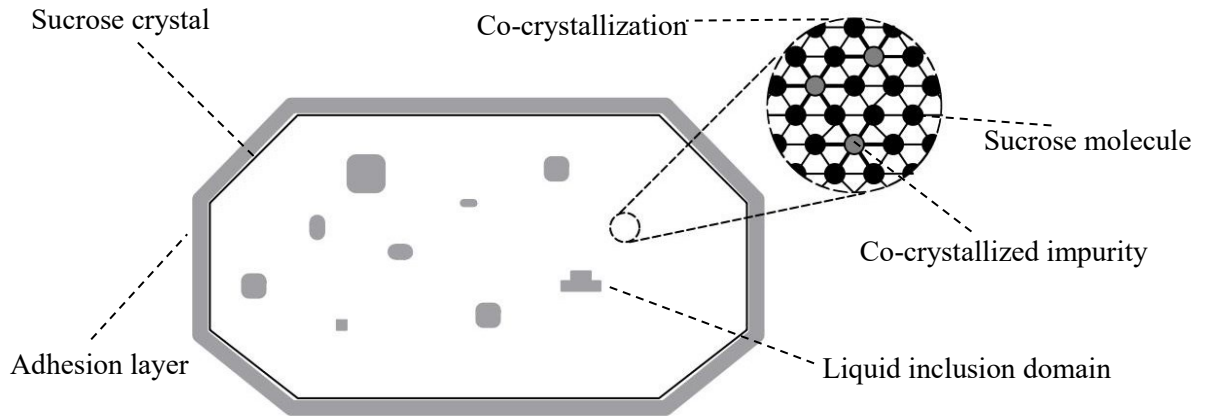


Figure 2-16: Inclusion mechanisms for sucrose crystals.

According to the inclusion mechanism, impurities need to undergo the following steps analogous to solute molecules during crystal growth before they are attached onto or included into the crystal: volume diffusion, surface transport and inclusion. There are mobile and immobile impurities which show different behavior on the crystal surface ergo inclusion properties: Mobile impurities form weak bonds on the crystal surface and have a smaller effect on growth velocity,

because they are “swept” away during growth. In contrast, immobile impurities are forming strong bonds with solute molecules on the crystal surface and thus effectively disrupt crystal growth (Myerson, 2001). Hence, these immobile impurities are preferentially found on or inside the crystal. This is in line with the general knowledge that high molecular weight colorants are preferentially included into the sucrose crystal (Godshall et al., 1987; Shore et al., 1984; Godshall et al., 1991; Godshall et al., 2005), because such substances have a low diffusion coefficient ergo these molecules are less agile due to their molecular mass (Edward, 1970).

2.4.2.1 Adsorption/Adhesion

Adsorbed or rather adhered impurities are bound to the crystal surface by van der Waals forces, hydrogen and ionic bonds. In sugar manufacturing, this describes in general mother liquor remaining on the crystal surface after the centrifugation process. The so-called outer or surface color can be removed by the affination procedure. If the surface color is not removed satisfactorily an increase in sugar color value will occur during storage (Godshall et al., 2005) due to oxidative processes. Grimsey and Herrington (1996) found that caramels have a higher tendency for surface adsorption than glycosylglycine melanoidin. Both have approximately the same molecular weight. For beet sugars low molecular weight colorants are rather found on the crystal surface whereas colored high molecular weight compounds are included into the crystal (Shore et al., 1984). Eggleston et al. (2012) described the adsorption mechanisms rather as adsorption-occlusion which is the first step of inclusion into the crystal. It means that impurities are included inside the crystal when they occupy suitable adsorption sites on the crystal surface and are overgrown. For the purpose of this study the mechanisms outlined by Eggleston et al. (2012) is categorized as co-crystallization. In this work, adsorbed or adhered colorants relate to substances on the crystal surface after centrifugation procedure, thus the outer color.

2.4.2.2 Liquid inclusions

Different approaches of liquid inclusions exist but all combine the fact that it is a result of surface defects during crystal growth. Most likely these defects are a result of repeated dissolution and regrowth of the sucrose crystal (Mullin, 2001). This dissolution of the crystal surface occurs due to inhomogeneities in the vessel which results in different undersaturated regions. The dissolution leads to pits on the crystal surface. As soon as the interfacial region is again in contact with

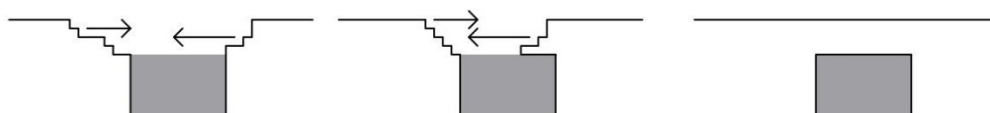


Figure 2-17: Development of a mother liquor inclusion by the interaction of growth layers of different height and velocity according to Mullin (2001).

supersaturated mother liquor, rapid crystal growth occurs as a result of repair phenomena (Mullin, 2001). It is mentioned as well that the size of the pits increases to grooves since the crystal

continues to grow (van der Poel, P.W., 2000). If the mother liquor is adhered in such a pit or groove, the liquid will be entrapped (Figure 2-17) (Vaccari et al., 1990b; Saska, 1988; Grimsey & Herrington, 1994).

The mechanism of liquid inclusions is prominent for seed crystals due to their rough surfaces possibly resulting from grinding or milling. Vaccari et al. (1990b) pointed out two ways of color incorporation during the transformation from seeds to crystals. For the same growth conditions, the growth rate of a rough surface is higher than that of a flat one which supports color inclusion. In addition, growth instabilities such as the formation and disappearance of uncommon faces promote syrup inclusions due to dendritic growth. The authors detected no color inclusion of spontaneously nucleated crystals compared to seed crystals obtained by milling under the same growth conditions.

Further reasons for surface defects are local differences in supersaturation on the crystal surface or local adhesions of impurities on the crystal which hinder growth in a particular direction (Mackintosh & White, 1968).

Although other authors outline that liquid inclusions can have higher concentration of impurities than the mother liquor (Myerson, 2001), for this work, it is however assumed that the inclusion at the moment of inclusion is representative of the respective mother liquor. Building on this, impurity concentrations according to this mechanism are proportional to the impurity concentration in the mother liquor and considering ash insert proportional to the level of ash inclusion. Once mother liquor is included the concentration within this inclusion might change, because solute molecules in entrapped mother liquor crystallize after the crystallization strike is finished due to cooling crystallization. Consequently, the concentration of non-crystallizing impurities in liquid inclusions is increasing.

2.4.2.3 Co-crystallization

Co-crystallization describes the homogeneous incorporation of impurities into the crystal matrix: This happens after initial adsorption onto the growth site at the crystal surface and the impurity becomes part of the crystal lattice on further crystal growth (Singh & Delavier H.J., 1974; Promraksa et al., 2009; Zhou et al., 2016). It should be noted that in sugar industry this process is sometimes also referred to adsorption-occlusion (Promraksa et al., 2009). If an impurity is included into a crystal lattice, similar growth properties as the solute molecules are required. Additionally, the guest molecule has to interact with the crystal surface and needs to fit into the kink site ergo the crystal matrix (Zhou et al., 2016). Since it is difficult to evaluate if these conditions are strictly fulfilled or also kinetic effects that support the formation of an imperfect crystal play a role, it is difficult to distinguish between kinetic colorants occlusion and co-crystallization as equilibrium state. However, for the purpose of the present thesis and the sake of clarity this type of inclusion irrespective of the detailed mechanism is considered co-crystallization. It was found that substances with carbohydrate (sucrose-like) structure are despite

of their high molecular mass are preferentially included into the sucrose crystal lattice. For beet sugar these colored substances are called BCC (beet crystal colorant), which are a complexes of polysaccharide, calcium and colorants (Godshall et al., 2005). In cane sugar, indigenous sugar cane polysaccharides (ISP) are found to be the primary reason for high color transfer factors found (Godshall & Baunsgaard, 2000; Godshall et al., 2002; Bourzutschky, 2005). These substances consist of an arabinogalactan backbone with glucuronic acids and a colorant. It is assumed that these colorants (BCC and ISP) form clusters with sucrose (Grimsey I.M. & Herrington, 1996). In other words, the sucrose molecules appear to functionalize the surface of the polysaccharide so that these colored compounds are incorporated more easily. Here the impurity can be seen analogous to a Trojan Horse.

2.4.3 Factors affecting impurity inclusion

In industrial crystallization, process parameters are chosen to achieve high-quality end products and simultaneously maximize the space-time yield. However, process parameters affect the final sugar quality. Thus, it is crucial to know the influence of certain process parameter on impurity inclusion. Therefore, three important parameters are reviewed in detail in the following sections: crystal growth rate, relative velocity between crystals and mother liquor and crystal size.

2.4.3.1 Crystal growth rate

It is generally acknowledged that rapid crystal growth increases the rate of impurity inclusions in the crystal. In this context van der Poel, P.W. (2000) stated that high crystal growth rates mechanically entrap mother liquor or suspended solids into the crystal. Furthermore Singh & Delavier H.J. (1974) outlined that the concentration of salts (ash) in sugar crystals increases with increasing growth rate. Lionnet (1988) revealed a color transfer increase of 13% as a result of a crystallization rate increase of about 45%. In addition Mackintosh & White (1968) and Guo (1984) showed that the level of impurities included inside the crystals is higher with higher growth rates. Vaccari et al. (1990a) observed inhomogeneous inclusions of colorants into the crystal. Crystal surfaces with higher growth rates appear to incorporate more impurities. Other authors also confirmed that high crystallization rates increase the transfer of color into the sucrose crystal (Mantovani et al., 1986b; Donovan & Williams J.C., 1992; Guo, 1984; Saska, 1988).

The reason for higher inclusion levels with increased growth kinetics is outlined by Myerson (2001) and illustrated in Figure 2-18: Due to growth of the crystal and a mass flow to the growing surface impurity molecules accumulate in the diffusion layer above the crystal-solution interface. The resulting concentration gradients are such that impurities are diffusing back into the bulk solution. At higher growth rates the gradients in impurity concentration have to be steeper to maintain this balance. Hence, the impurity concentration in the interfacial region is higher with higher growth rates to establish a sufficiently higher impurity concentration than in the bulk

solution. As a result, the impurity molecules accumulate in the boundary layer which consequently leads to an increased transfer rate. (Myerson, 2001)

Furthermore, high growth rates favor that solute molecules are build into the crystal lattice without assuming the appropriate configuration. Thereby more defects evolve on the crystal surface and the likelihood of impurity capture increases even more (Myerson, 2001).

Considering this phenomenon of increased concentrations of impurities close to the crystal surface due to high growth rates an assumption previously made has to be reconsidered. In section 2.4.2 it is postulated that the concentration of impurities in included mother liquor is equal to their concentration in the bulk at the specific moment of inclusion. However, due to increased growth rates impurities are concentrating in the diffusion and possibly also adsorption layer (Figure 2-18). As a result liquid inclusions might have higher concentration of impurities than the surrounding mother liquor (Mullin, 2001). However, this concentration effect is essentially valid for all impurities and hence is the postulated proportionality of ash inclusion and color contribution due to liquid inclusion still valid.

2.4.3.2 Relative velocity between crystals and solution

The relative velocity between crystals and solution is in first place caused by ascending steam bubbles. However, the resulting relative motion of the particles and the fluid is not sufficient to avoid inhomogeneities in the pan. Stirring maintains and improves the circulation and homogeneous distribution of the suspension in the vessel. It increases the heat transfer coefficient of evaporative crystallizers and reduces concentration differences. Thus, mechanical stirrers

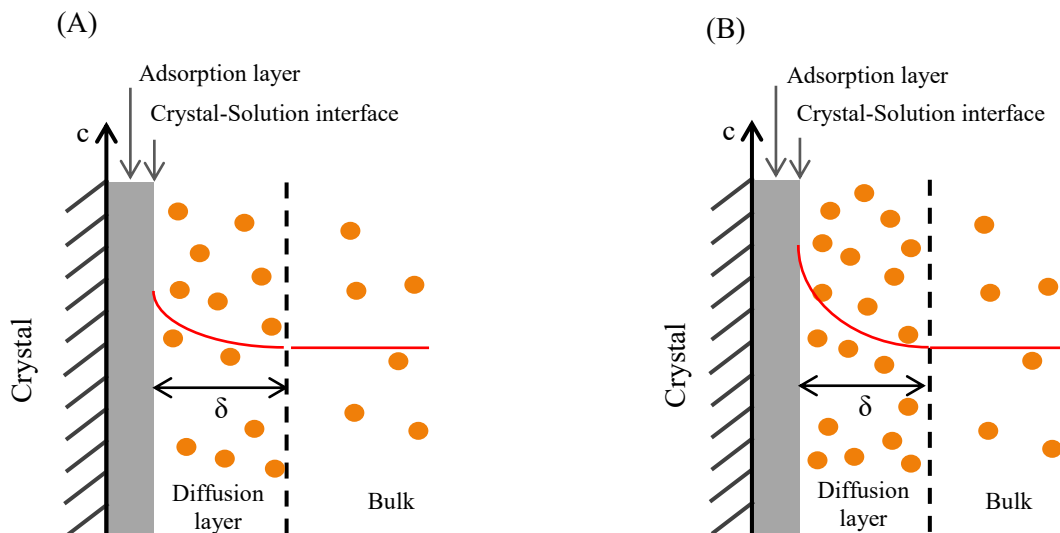


Figure 2-18: Concentration profile of impurities in bulk and diffusion layer (A) and concentration of impurities in diffusion layer due to increased growth rates (B) according to Myerson (2002) (modified).

improve the quality of the sugar crystals by reducing mother liquor inclusions and leading to a more even particle size distribution (van der Poel, P.W., 2000). This phenomenon of reduced color transfer due to increased relative velocity (e.g. by stirring) between crystals and mother

liquor is observed by other authors, too (Donovan & Williams J.C., 1992; Saska, 1988; Guo, 1984; Lionnet, 1988). Saska (1988) reasoned that the diffusion layer thickness is decreasing with increasing crystal fluid velocity. As a consequence, the concentration gradient necessary to establish mass transfer balances at a specific growth rates can be established with less increased impurity concentrations in the diffusion layer close to the crystal surface (see Figure 2-19). Following the reasoning above this consequently yields less impurity incorporation.

2.4.3.3 Crystal size

The optimization parameters for industrial sugar processing are in the end determined by the needs of the customers. According to van der Poel, P.W. (2000) sugar can be categorized in different grades (90% (m/m of sugar)): powder (< 0.1 mm), fine 3 (0.1 – 0.35 mm), fine 2 (0.2 – 0.5 mm), fine 1 (0.2 – 0.75 mm), medium (0.5 – 1.25 mm), coarse (1.0 – 2.20 mm). In North America fine sugar (< 0.400 mm) is preferentially used in the households, Europeans like fine to medium sugars (0.300 – 0.800 mm) and in Africa and the Arab countries coarse sugar is favored. In general, a narrow particle size distribution is pursued to achieve a high separation efficiency of molasses and crystals in the centrifuge. Furthermore, an increased proportion of very fine sugar crystals can lead to processing difficulties causing interruptions on the centrifugation process due to blocking or high amounts of dust. If very fine sugars are desired, these are concentrated by sieving or generated by milling. In the following the influence of crystal size on the sugar color value is discussed.

It is without saying that smaller crystals provide relative to mass a higher surface area than larger crystals. Thus, a higher amount of colorants carrying mother liquor can adhere to smaller crystals and negatively affect the sugar quality. If a given amount of monodisperse crystals are compared to another batch of crystals of half the size, the total surface area is 8-fold higher for the latter one. Hence, the 8-fold amount of mother liquor is attached to the surface of the sugar causing increases in the color and ash values of the final product. It was shown that between 25 and 50% of the sugar color value is found on the crystal surface (Shore et al., 1984; Godshall et al., 1991). The higher surface area furthermore influences the rate of color increase over time when sugar is stored for longer periods because this process relates to exposed surface. However, it should be noted, that the contribution of colorants in the adhered mother liquor to sugar color values depends on the efficiency of the centrifugation and washing process as well as the color value of the mother liquor at the end of the crystallization process.

As outlined above another significant part of the sugar color value is due to material distributed inside the sugar crystal. These colorants are not removable without dissolving the sucrose crystal. It was found in earlier studies that larger crystals have a higher ash and color level than smaller ones (Singh & Delavier H.J., 1974; Delavier H.J. & Hirschmüller H., 1968; Vaccari et al., 1990b; Mantovani et al., 1986a, 1986b). Initially, this seems to be contradictory to the statement made

previously. Therefore, the factors influencing the color value of a sugar crystal due to colorants inside the crystal are discussed here:

- Concentration of impurities during the process
- Increased growth rate
- Increased surface roughness
- Nucleated versus seeded crystals

First, it goes without saying that with crystal growth and increasing process time, concentration of impurities in the mother liquor is increasing. Thus, crystals grow in an environment with increasing degree of pollution. This suggests that larger crystals contain more impurities. This is strictly valid in comparing crystals grown for different time scales in the same process.

Furthermore, increasing crystal size moreover leads to an increased growth rate, which itself is responsible for higher inclusion rates: taking into account that small and large crystals grow from a solution of same conditions, it is obvious that viscosity η , density ρ and diffusion coefficient D (equation (2-32)) are equal for both approaches. However, the linear dimension of the crystal L and the relative crystal to solution velocity J are different. The Stokes equation can be used to describe the relative motion between crystal and solution:

$$J = \frac{2 \cdot r^2 \cdot g \cdot (\rho_c - \rho_{ML})}{9 \cdot \eta} \quad (2-39)$$

with the radius of the particle r , the gravitational acceleration g and the density of the crystal ρ_{cr} and solution ρ_{ML} . The parameters of equation (2-39) are equal for small and big crystals except the particle size. Thus, the parameter can be summed to a constant K and the radius, r , can be approximated with the half of the characteristic dimension L of the crystal:

$$J = K \cdot \frac{L^2}{4} \quad (2-40)$$

If one combines equation (2-32) and (2-40) for small and large crystals, with subscript sm and XL respectively, the relation of the thickness of the interfacial regions δ is expressed as:

$$\frac{\delta_{XL}}{\delta_{sm}} = \left(\frac{L_{XL}}{L_{sm}} \right)^{1/2} \cdot \left(\frac{J_{sm}}{J_{XL}} \right)^{1/2} = \left(\frac{L_{sm}}{L_{XL}} \right)^{1/2} \quad (2-41)$$

It is obvious that δ_{XL} is smaller than δ_{sm} since L_{sm} is smaller than L_{XL} . According to this, two different approaches are considered which result in contradictory effects. First, if it is assumed that crystal mass growth rate is equal for small and large crystals, the concentration of impurities at the adsorption layer is lower for large crystals (see Figure 2-19). This would result in decreased impurity inclusion. On the other side, if the size of the interfacial region is decreased for large crystals, the growth rate is increasing (equation (2-27)) (Mantovani et al., 1986b). And it is generally acknowledged that higher growth rates increase impurity inclusion (see 2.4.3.1).

Additionally, with increasing process time the crystal surface roughness increases significantly as a result of faulty integration of growth clusters (Ferreira et al., 2008). This means that the number of persistent growth promoting imperfections such as dislocations increases since their generation per time is assumed to be constant. Consequently, higher impurity transfer rates emerge because growth rate increases and the increased number of imperfections itself promotes impurities transfer as well.

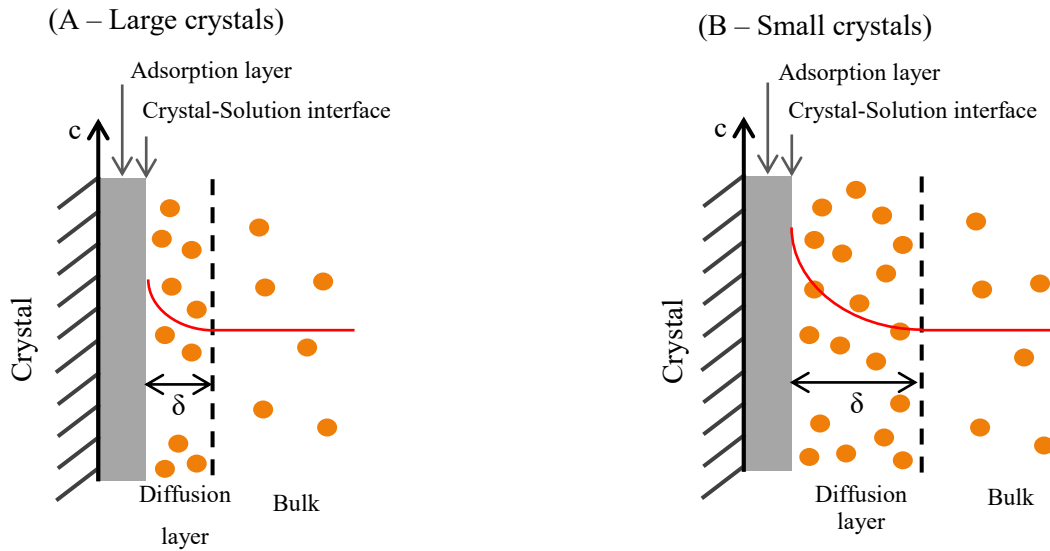


Figure 2-19: Concentration profile of impurities in bulk and diffusion layer for crystals with small (A) and large (B) interfacial region.

It was found that crystals spontaneously nucleated throughout the crystallization strike contain less impurities than crystals originating from seeds obtained by a milling process (Vaccari et al., 1990b). Considering the fact that impurity concentration is increasing with increasing process time, these observations seem to be counterintuitive. However, it is assumed that the surface of nucleated crystals is nearly perfect and hence, the amount of surface defects is low. In contrast, the surface of large crystals possibly carries the accumulated defects generated throughout the crystallization process. The resulting difference in “surface density of defects” between small and large crystals has consequently an effect on growth rate and impurity inclusion.

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3 CONTROLLED SUCROSE CRYSTALLIZATION AT PILOT- PLANT SCALE

*Schlumbach, Karl^a; Pautov, Alexander^a; Göckeritz, Lukas^a; Bagherzadeh, Arash^b; Flöter,
Eckhard^a*

^a TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

^b EnProCo Berlin GmbH, Volmerstr. 7A, 12489 Berlin, Germany

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Abstract

The industrial production of sugar is structured such that the development of process innovations is difficult. The evaluation of ideas directly at full scale is risky and costly. Testing basic feasibility at small scale is hence desirable. To this end a pilot scale crystallizer and adequate processing developed is described here. The evaluation covers next to basic quality parameters also the comparison of computed online data with laboratory analysis on samples drawn. The designed evaporating crystallization appeared to be well controlled. At constant supersaturation approximately 50 g/ 100 g of crystals were produced reliably. It turned out that next to the actual well controlled crystallization process the separation and drying processes are very important to produce relevant data. Centrifugation at high relative centrifugal forces (1,450 RCF) for 120 s with dosage of plain water (2.5 g/100 g massecuite) as washing fluid yielded best results. Drying in a fluidized bed at temperatures of 343 K for 10 min was superior to drying at open air or in climate cabinets, this with respect to formation both of agglomerates and fine crystals. It is shown that the designed process allows to crystallize sucrose in small scale with industrially relevant characteristics of process and product.

3.1 Introduction

The industrial sugar production process is highly optimized due to the fact that its basic unit operations have not been subject to radical changes lately. However, scientists and engineers are continuously searching innovations and further optimization. Key areas of improvement are energy consumption, effluent, and yield practically relating to all steps of the chain from field to sugar storage. Technical progress in sugar production is hampered by the nature of the sugar factories. At first, production of sugar from sugar beet is in fact a seasonal business so that during the harvesting season high utilization of equipment is paramount. During the campaign it is difficult to accommodate any experimental process variations. This problem of limited opportunity for experimentation is even further condensed due to the fact that factories typically operate a single production line with incoming beet volumes clearly in excess of 10,000 tons per day. This configuration results in prohibitive costs for factory trials that put a charge of material at risk. Furthermore, factories have limited experimental possibilities beyond daily routine analysis. Consequently, relevant pilot plant facilities and respective personal are rare. As a result, potential improvements and possible innovation ideas remain not evaluated and unrealized. In order to improve on this situation a small scale evaporating crystallization pilot plant was installed at the Technical University Berlin (TUB), Germany. In this work the crystallization pilot plant and peripheral processing units are described. The different processing steps are discussed and compared to industrial reference data. Data computed based on process control readings are validated against laboratory analysis of samples drawn. Overall a validated versatile design that allows performing relevant experiments at small scale is presented.

3.2 Material and methods

3.2.1 Material

3.2.1.1 Pilot plant set up

In order to establish a downscaled pilot plant operation for sucrose crystallization from thin juice the following unit operations are necessary. To start the process from clarified thin juice an evaporation unit is necessary to generate thick juice. Even though this is installed currently in TUB's laboratory the evaporation unit will not be discussed in detail here. To crystallize sucrose from thick juice or other syrups a 0.005 m³ volume evaporating crystallizer was installed. Further processing of the massecuite necessitates the separation of the crystals from the mother liquor. The combination and adequate execution of the separation and the subsequent drying step are of

utmost importance for the production of industrially relevant sugar qualities at small scale.

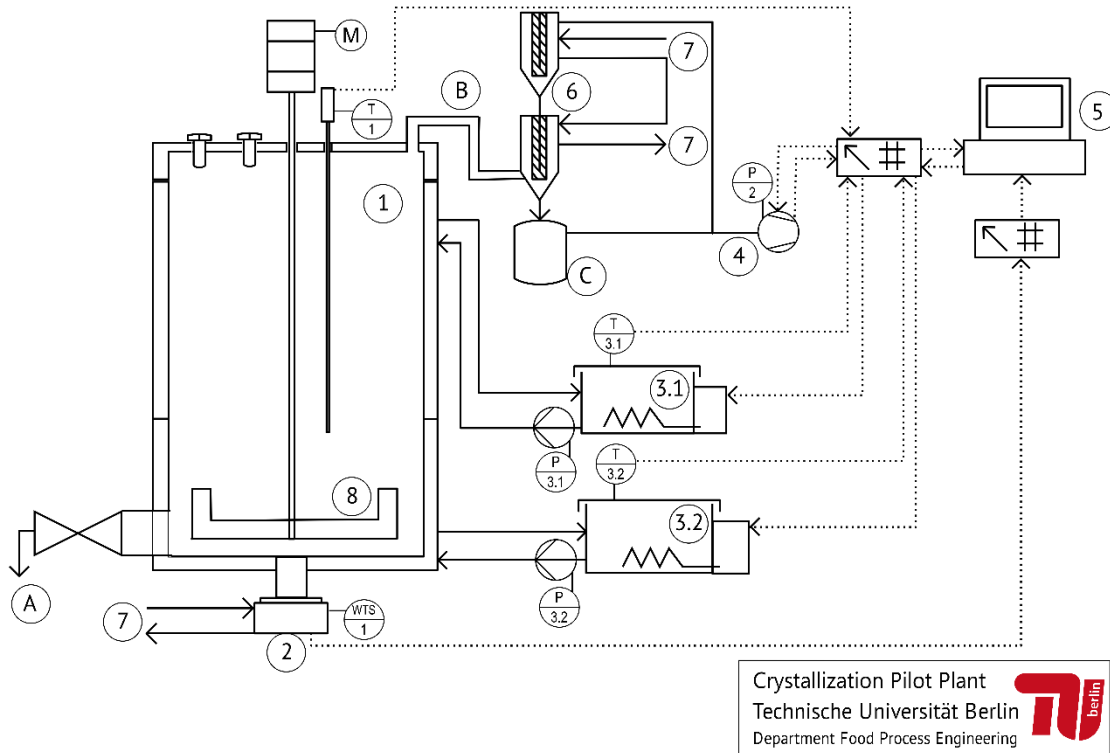


Figure 3-1: Crystallization pilot plant and ancillary equipment. 1 Vessel; 2 Refractometer; 3.1 Thermostat; 3.2 Thermostat; 4 Low pressure pump; 5 Data processing unit; 6 Cooler; 7 Cooling water; 8 Stirrer; A In-/outlet valve for feed and massecuite; B Vapor outlet; C Condensate outlet.

3.2.1.1.1 Crystallizer

Figure 3-1 illustrates the scheme of the crystallization unit. The evaporating crystallizer consists of a stainless-steel vessel with a glass jacketed cylindrical vessel mounted on top. The total juice capacity is 0.005 m³. The vessel is temperature controlled by independent hot water flows through the double walled stainless-steel and glass jacket. The water is in both cases brought to desired temperatures by thermostats (F32-HD and F12-MC, both Julabo Seelbach, Germany). A Pt 100 thermo element is immersed into the fluid inside the crystallizer monitoring the actual temperature of the sample. An agitator (RZR 2102 control, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany) is connected to a gastight permanent magnetic coupling on top of the vessel. The agitator moves a stirrer inside the vessel and measures the increasing torque during the crystallization. The torque is used as indication for the end of the crystallization strike. A process refractometer (iPR 2-3, Schmidt & Haensch GmbH & Co., Berlin, Germany) (index 2 in Figure 3-1) is mounted to the bottom of the vessel to determine the dry substance content of the mother liquor.

Flow rates in and out of the systems are monitored in order to allow mass balances. A positing system at the bottom of the crystallizer makes sampling possible. The mass of the feed syrup and of the samples are determined with the help of a scale (LC6200 (± 0.01 g), Sartorius AG, Göttingen, Germany). The steam leaves the crystallizer at the top into a vent condenser where it is condensed. The condenser feeds an Anschuetz-Thiele-receiver to determine the condensate formation. The pressure is established using a low pressure pump (PC 3001, Vacuubrand GmbH & Co KG, Wertheim, Germany).

3.2.1.1.2 Process control

The process control of the crystallization unit is programmed in LabVIEW (National Instruments Corporation, Munich, Germany). It allows to control the different active units and to record processing parameters (Figure 3-2). The thermostats and low pressure pump are actively controlled. Data recorded cover temperature, pressure, and signals of the process refractometer.

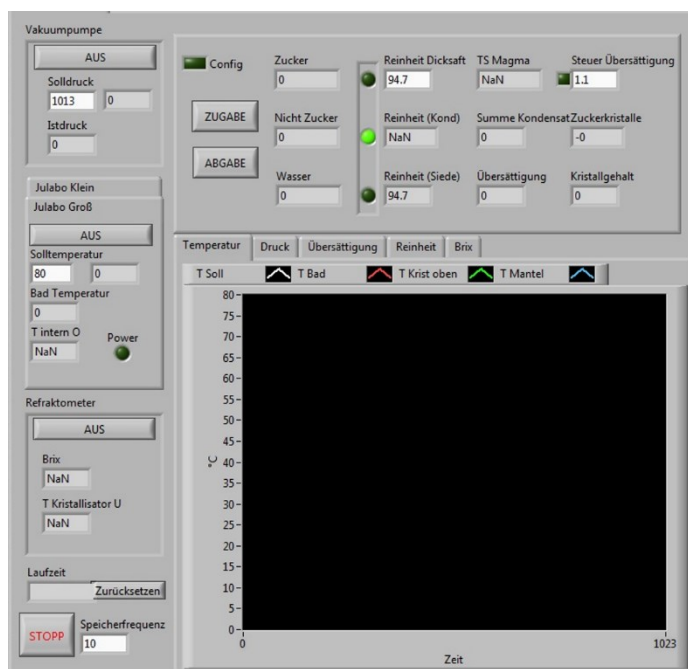


Figure 3-2: Process control panel recording unit. Control of the vacuum pump, two thermostats and the refractometer. Display of current temperatures (inside vessel and from thermostats) and dry substances. Values of total content of dry substance, actual purity, crystal content, and supersaturation are calculated.

Additional data are fed manually into the system. These are on one hand the flow rates of feed and condensate. On the other hand, analytical data of samples drawn are fed into the system. Based on repeated linear regression of three consecutive condensate readings the supersaturation and purity are determined during the crystallization. This approach allows the computation of the crystal content, the mass of sucrose crystals, the dry substance level and amount of water present. The data recording rate is typically set to once per 20 s.

3.2.1.2 Separation

After crystallization the separation of the sucrose crystals and mother liquor is achieved by centrifugation (Centrifuge DM 2250, Gebr. Heine, Viersen, Germany). This centrifuge is temperature controlled by pumping hot water through its double jacket. This way the massecuite is practically not cooling down after crystallization and experimental errors due to post crystallization are minimized. Additionally, the high temperatures maintained ensure good separation because the viscosity of the mother liquor is not further increased. The maximum

filling volume of the centrifuge is 0.003 m³. The separation process is assisted by addition of washing fluid during the centrifugation. The self-constructed washing unit in essence distributes the washing fluid, after dispersion with 2.5 bar pressure through a flat jet nozzle, evenly on the massecuite surface. This way the remaining mother liquor on the sugar crystals is in part replaced and diluted with the washing fluid.

3.2.1.3 Fluidized-bed drying

The wet sugar obtained after centrifugation still has a water content of 0.12 g/100 g. To make sure that no agglomeration occurs, the crystals need to be dried additionally without continuous mutual contact. This is secured by sugar drying in a self-constructed fluidized-bed dryer. Dry ambient and unconditioned air is sucked into the system and heated by an electric heating unit. The volume flow is controlled by a frequency converter (Micromaster 420, Siemens, Berlin, Germany). The flow rate is measured and displayed by Ursaflux W4 (Junkalor, Dessau-Roßlau, Germany). The temperature of the air flow prior to entry into the fluidized bed is measured by a Pt 100 and the power of the electric heater is adjusted accordingly. Optionally also the incoming air flow, humidity and temperature of the exhaust air can be determined. The wet sugar is placed on a 0.063 mm mesh size sieve. The fluidized bed is confined by a conical polymethyl methacrylate pipe of 0.5 m height. The sugar is easily fluidized by the hot air flow.

3.2.2 Methods

3.2.2.1 Batch crystallization process

The crystallization vessel is filled with 5,000 g of feed juice with dry substance content of 66 – 67 g/100 g and purities varying 95 – 99%. During subsequent processing no additional feed juice is supplied into the vessel. The crystallization is carried out at a pressure of 270 mbar (± 1 mbar) and at a stirrer rate of 60 rpm. As described the vessel is heated by two independent thermostats. For evaporation of the mother liquor one thermostat (3.2 in Figure 3-1) heats the stainless-steel vessel. The temperature of the heating fluid (water) is kept at 361 K (± 0.01 K). The other thermostat (3.1 in Figure 3-1) feeds the glass jacketed body of the crystallizer. The heating water was kept at a temperature of 343 K (± 0.01 K) to prevent nucleation and crystallization on the side walls. To suppress foam formation during the process 100 μ l of Struktol SB 2433 (Schill + Seilacher "*Struktol*" GmbH, Hamburg, Germany) is added to the system at the beginning of the strike.

Two syrup samples were taken prior to the actual seeding. At first the starting juice is characterized once a homogeneous sample occurs. A second sample was taken before the supersaturated ($v_{ss} = 1.10$) solution is seeded. The data reported in this manuscript refer to crystallization processes seeded at a supersaturation of 1.10. The supersaturation during the process was determined using the data from the process refractometer, temperature, and purity of

the solution. The seed crystals added had an average size of $d_{50,0} = 0.28$ mm and a color value of 35 IU. This fraction was obtained by sieving industrial sugar. The desired final crystal size ($d_{50,n}$) was 0.80 mm aiming at a low coefficient of variation (CV). The mass of seed crystals $m_{Cr,0}$ is calculated by d^3 -Rule (Witte, 1987):

$$m_{Cr,0} = m_{Cr,n} \cdot \left(\frac{d_{50,0}}{d_{50,n}} \right)^3 \cdot \frac{N_{Cr,0}}{N_{Cr,n}} \quad (3-1)$$

with $m_{Cr,n}$ as the mass of crystallized sucrose. The number of crystals in seed and product are indicated by $N_{Cr,0}$ and $N_{Cr,n}$, respectively.

During the strike a supersaturation of 1.07 (± 0.01) was maintained by control of pressure and external heat supply.

Different from standard operation samples were taken regularly during the strike to validate process readings and computed data. Sampling was done via the valve at the bottom of the vessel after homogeneity of the massecuite was achieved through temporarily increased stirrer rates of 200 rpm. Mother liquor for additional analysis was produced from the sampled massecuite through straight application of a strainer.

The crystallization was stopped once the torque of the agitator increased by a value of 0.06 Nm from the starting value. This torque increase as a function of the viscosity of the massecuite relates for commonly used juices to a crystal content of 45 – 50 g/100 g. While the massecuite is drained from the crystallizer samples of massecuite and mother liquor were taken for detailed analysis.

3.2.2.2 Separation

After crystallization the sucrose crystals and mother liquor are separated by centrifugation. To optimize the separation process an experimental program considering the type of washing fluid, the amount of washing fluid, and the moment of washing was executed. Conflicting performance indicators for the separation process are the reduction of the color contribution due to adhesion of mother liquor to the crystals and minimization of the loss of crystals due to dissolution of crystalline material in the washing fluid.

The optimization of the separation process was for reasons of simplicity performed with a synthetic massecuite. This suspension with a crystal content of 50 g/100 g was prepared by mixing industrial white sugar with saturated thick juice. In detail a solution of 1,200 g saturated thick juice (color value, $F_{420} = 1,938$ IU) was mixed with 1,200 g industrial white sugar with an initial color value of 21 IU and an initial mean aperture of 0.534 mm. Prior to filling the synthetic massecuite into the centrifuge it is homogenized at room temperature by agitation with a stirrer (20 min, 100 rpm). Throughout the different washing experiments the centrifuge was running at 3,000 rpm which translates to a separation factor of 1,450 RCF.

Since the synthetic massecuite is in equilibrium at 293 K also the separation process is performed at this temperature. Either demineralized water or dissolved sugar syrup (each at 293 K) were tested as washing fluids. The amounts of washing fluid administered were 0, 20, 30, 40, 60, 80

and 100 ml. These doses related to 0, 0.83, 1.25, 1.67, 2.5, 3.33, 4.17 g of washing fluid per 100 g of massecuite.

To study in how far the effectivity of the washing step depends on other factors than the type and amount of washing fluid, two different washing cycles were compared. Unavoidably all centrifugation processes begin with a 25 s acceleration period. In cycle 1, the washing fluid was sprayed on the centrifuged massecuite surface after 60 s at maximum velocity (3,000 rpm, 1,450 RCF). In this case the process is stopped after 120 s. Also in cycle 2 the centrifuge operates initially at a speed of 3,000 rpm. After 45 s the angular velocity is reduced to 1,500 rpm which translates to a separation factor of 360 RCF. Adjustment of speed takes about 10 s. After further 15 s at the reduced angular velocity the respective washing fluid is added. The reduced angular velocity was maintained for another 30 s to possibly cause a slower passage of the washing fluid through the cake resulting in a better purification as discussed elsewhere (van der Poel, P.W., 2000). Subsequently, final centrifugation is performed for 30 s at again 3,000 rpm to achieve best separation results. Hence, both cycles have an effective cycle time of 120 s with cycle2 extended by 2 times 10 s adjustment time.

3.2.2.3 Drying

Three different drying methods were compared in this study: Fluidized bed drying (10 min at 343 K), open air drying (30 min at 293 K) and drying in a heating cabinet (20 min, 343 K). The methods were compared with respect to the resulting variations of the average particle size, the coefficient of variation, and the content of agglomerates and fine crystals. Additionally, color formation during drying is monitored without any indication for any color formation.

3.2.2.4 Lab analysis

Lab analyses were performed to verify the data directly monitored or computed from process monitoring data. Analysis were executed according to ICUMSA (ICUMSA, 2011) standardized methods. Samples studied were feed juices, process samples and the end products (massecuite, run-off syrup and sucrose) of the crystallization, separation and drying process. Table 3-1 and Table 3-2 list the materials, chemicals and devices used for the analysis. An automatic dilution and dosing system (DDS, Anton Paar, Graz, Austria) was used to dilute the massecuite and (run-off) syrup samples 1:1 (mass/mass) with demineralized water prior to analysis. The dry substance content w_{DS} was determined by refractometer. The sucrose content w_S was analyzed by polarimetry after clarification with *Carrez* in agreement with ICUMSA Method GS8-2 (ICUMSA, 2011). These data allow computation of the purity q in % according to equation (3-2):

$$q = \frac{w_S}{w_{DS}} \cdot 100 \quad (3-2)$$

The crystal content w_{CC} (in g/ 100 g) was computed based on the respective sugar content w_s of the massecuite (MC) and mother liquor (ML):

$$w_{CC} = \frac{w_{s,MC} - w_{s,ML}}{100 - w_{s,ML}} \cdot 100 \quad (3-3)$$

The color of the feed juice, massecuite, run-off syrup and sugars was determined based on absorbance of light at a wavelength of 420 nm (A_s) according to the analytical methods GS1/3-7 and GS2/3-10 (ICUMSA, 2011). The pH-value was adjusted with hydrochloric acid or sodium hydroxide solutions. The color value in IU in solution can be calculated by:

$$F_{420} = \frac{10^8 \cdot A_s}{b \cdot w_{DS} \cdot \rho} \quad (3-4)$$

with b the length of the cuvette (1 cm for syrup, 5 cm for sugar), w_{DS} the dry substance content and ρ (kg m⁻³) the density of the solution.

The particle size determination was conducted according to ICUMSA Method GS2/9-37 (2007) (ICUMSA, 2011). Each sample of the final dried sugar was categorized by means of sieve analysis with the following classes of sieves: 0.315 mm, 0.400 mm, 0.500 mm, 0.630 mm, 0.800 mm, 1.00 mm and 1.25 mm. The mechanical shaker (AS 200 Control, Retsch Technology GmbH, Haan, Germany) separated the sucrose crystals for 10 min and the mass fractions were weighted subsequently. The mean aperture (d_{50}) is calculated according to *Powers Method* (van der Poel, P.W., 2000).

Table 3-1: Material and chemicals used for laboratory analysis.

Chemicals & Materials	Distributor
Carrez I solution (21.9 g of zinc acetate dihydrate and 3 g of glacial acetic on 100 ml water)	Bernd Kraft, Duisburg, Germany
Carrez II solution (10.6 g of Potassium hexacyano ferrate(II) trihydrate on 100 ml water)	Bernd Kraft, Duisburg, Germany
Celite Hyflo Super Cel®	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
CHROMAFIL® membrane filters GF/PET 0.45 µm	Machery-Nagel GmbH & Co. KG, Düren, Germany
Filter paper MN 631	Machery-Nagel GmbH & Co. KG, Düren, Germany
Hydrochloric acid solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
Sodium hydroxide solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
10 mm UV-cuvette (612-5685)	VWR International, Darmstadt, Germany
50 mm glass cuvette 100-OS (634-9017)	VWR International, Darmstadt, Germany

Table 3-2: Devices used for laboratory analysis.

Device	Labelling	Manufacturer
Centrifuge (laboratory)	Sieva-2	Hermle Labortechnik GmbH, Wehingen, Germany
DDS	Automatic dilution and dosage system	Anton Paar, Graz, Germany
pH-meter	Seven Excellence	Mettler Toledo, Gießen, Germany
pH-electrode	Inlab Routine Pro	Mettler Toledo, Gießen, Germany
Polarimeter	Saccharomat NIR W2	Schmidt & Haensch, Berlin, Germany
Refractometer (laboratory)	ATR W2 plus & ATR	Schmidt & Haensch, Berlin, Germany
Sieve shaker	AS 200 Control	Retsch Technology GmbH, Haan, Germany
Spectrophotometer	SPEKOL 1300	Analytic Jena, Jena, Germany

3.3 Results and discussion

3.3.1 Crystallization

3.3.1.1 Observation of process

The process parameters such as temperature, dry substance, and supersaturation are recorded or computed during the process by the process control unit (see 3.2.1.1.2). Figure 3-3 shows the development of these parameters for a representative experimental run. The data points in Figure 3-3 are smoothed to remove background noise by an adjacent-average method. The moving averaging interval used is 15 points.

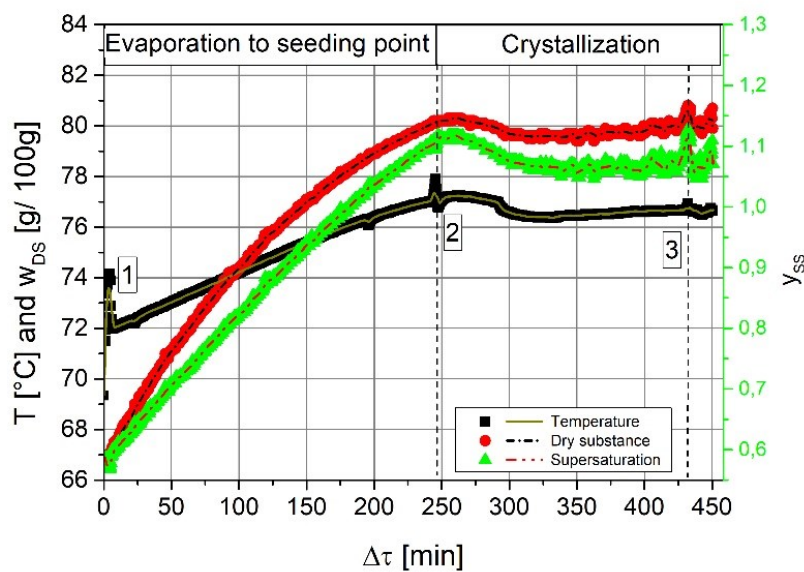


Figure 3-3: The graph illustrates the development of the temperature (black line), dry substance (red, dashed-dotted line) and supersaturation (green, dashed-double-dotted line) in the mother liquor during one experiment. First the mother liquor starts to boil (1). When a supersaturation of 1.10 is achieved, seed crystals are added to the solution (2). Further equilibrium of crystal growth and evaporation develops. The process is finished at point (3) where the torque of the agitator indicated a crystal content of approximately 50 g/100 g.

Zero time actually marks the start of solution boiling. In line with expectations the solution was initially overheated and the temperature decreased sharply after boiling set in (see point 1 in Figure 3-3). The dry substance in the mother liquor increased smoothly due to the evaporation of water. This increase in dissolved matter was nicely accompanied by a boiling point elevation, hence increase in temperature. The increase of dissolved dry substance in the mother liquor was obviously related to an increased supersaturation. Once a supersaturation of 1.10 was achieved (point 2 in Figure 3-3) seed crystals are administered to the system. To do so the pressure needed to be changed temporarily, because the system has no pressure lock allowing isobar seed dosing. This process takes approximately 1.5 minutes and lead to temporarily increased system temperatures. Once the low pressure is applied again temperature dropped to the boiling point at process pressure. After seeding crystal growth occurs and the content of dissolved solids and

hence supersaturation, too, are decreasing until a balance between evaporation rate and development of crystals is achieved. If the balance is achieved the dry substance content in solution remains nearly constant. At constant driving force the evaporation rate and crystal growth appeared to be in good balance. The encountered small fluctuation of the dry substance value of the mother liquor during further processing is most likely due to inhomogeneities in the vessel. This became more apparent with increasing levels of dispersed solids in the crystallizer, see point 3 Figure 3-3. This interpretation is supported by the fact that temporarily increases of the stirring rate yielded the expected reduction of the dry substance content reading accompanied by an increased temperature reading. However, reduction of the stirring rate to the original values causes the increased indication of dry substance again. This observation indicates to the authors' interpretation that the temperature in bottom part of the crystallizer is higher than at the position of the temperature probe. This locally higher temperature yielded a locally higher solubility which could be eliminated once stirring rate was increased. At industrial crystallizers effects from hydrostatic pressure have to be considered. With liquid heights of 20 cm this is however considered insignificant here. Looking at Figure 3-3 it is not surprising that the supersaturation computed based on the dry substance level determined for the mother liquor is following the fluctuations of the lead signal.

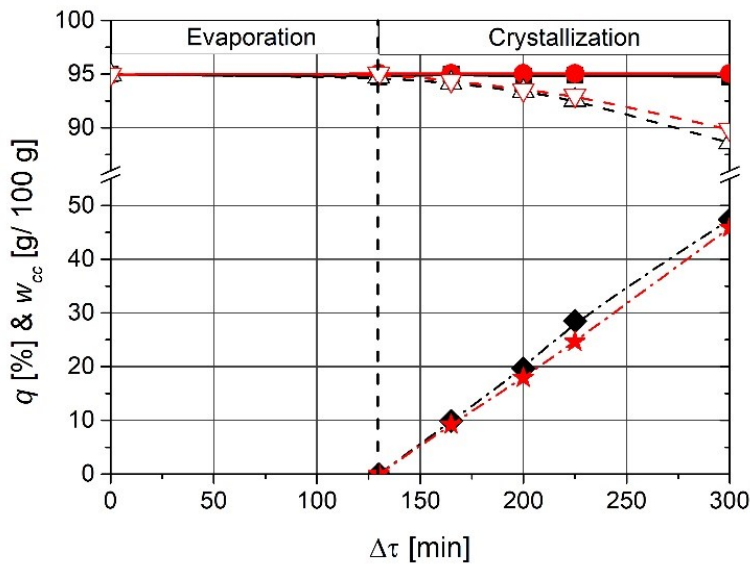


Figure 3-4: Comparison of online and offline data during the crystallization process: Purity q determined by experimental analysis: masseccuite (\blacksquare , straight) and mother liquor (Δ , dashed); Purity q calculated by mass balance: masseccuite (\bullet , straight); mother liquor (∇ , dashed); Crystal content w_{cc} determined by laboratory analysis (\blacklozenge , dashed-dotted) and calculated by mass balance (\star , dashed-dotted).

3.3.1.2 Comparison online data with laboratory experiments: Crystal content and purity

The process control unit calculates the current crystal content and purity during the process based on mass balances. To evaluate the quality of these calculated properties computed from process data they were compared with analytical data on samples taken during the process. This comparison is illustrated in Figure 3-4 to Figure 3-6. Figure 3-4 illustrates the trend of the parameters during the evaporation and crystallization. As expected the purity of the massecuite is not changing during the process. Overall the data computed based on process control data and data generated offline are in very good agreement. This holds on one hand for the continuously decreasing purity of the mother liquor due to the increase of non-sugar content in the solution. Secondly also the values describing the increase of the crystal content of the massecuite with process time were in good agreement for online and offline determinations. To further illustrate this good agreement Figure 3-5 and Figure 3-6 show a parity plot of either the purity of the mother liquor and crystal content of the massecuite for various experimental runs. In both graphs data gathered by online and offline methods for different feedstocks are compared. The good agreement of the purity values is illustrated by the high correlation value, $R^2 = 0.973$. It has however to be acknowledged that the data suggest that with decreasing purity the agreement of methods becomes less good. To further substantiate this finding, additional experiments with less pure feed juices will need to be performed. Figure 3-6 illustrates the good agreement between the values obtained by both methods for the crystal content, $R^2 = 0.952$. The data however suggest that there is systematic difference with data from offline measurements indicating higher crystal contents in the massecuite. Possible causes for this deviation are the inhomogeneity during sampling from the bottom part of the crystallizer and/or the incomplete accounting of condensed

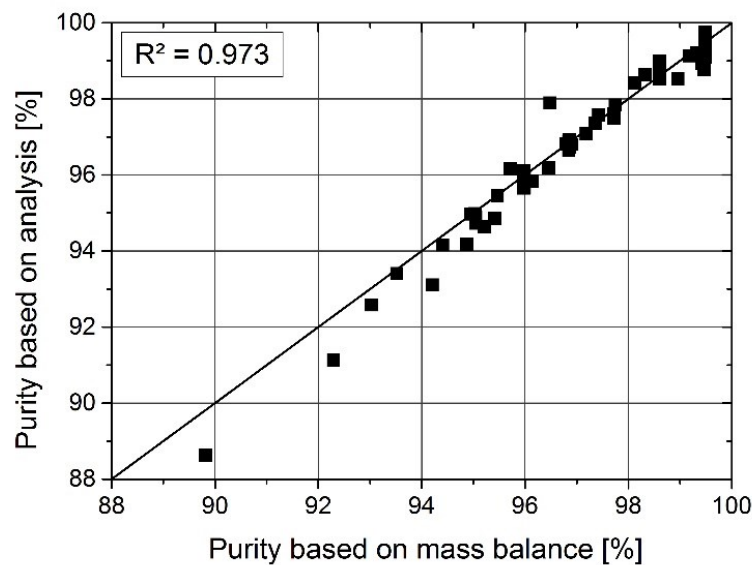


Figure 3-5: Parity plot of the purity data. Laboratory analytical data on samples vs calculated data based on mass balance and process monitoring data.

steam. The later could be caused by either incomplete condensation in the condenser or condensation at other cold spots different from the condenser.

In general, it is fair to conclude that the purity and crystal content were accurately determined based on online measurements and mass balances. This allows in particular better determination of the right moment to end the process aiming for specific crystal contents.

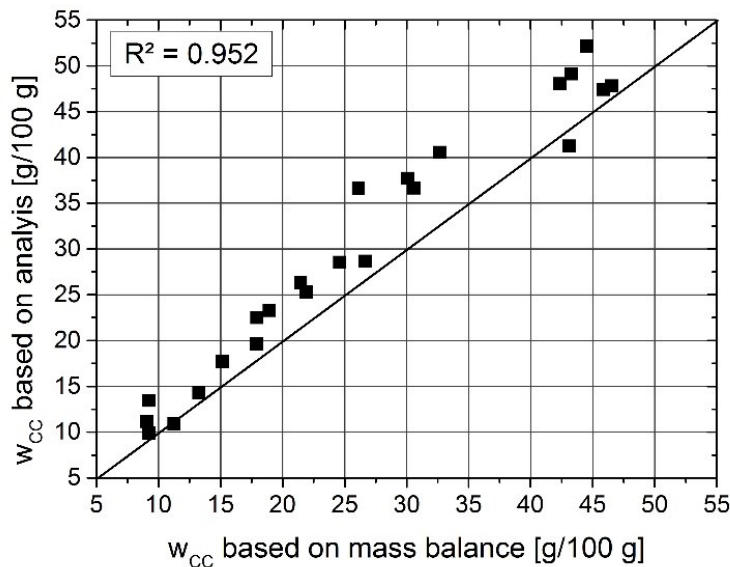


Figure 3-6: Parity plot of the crystal content w_{cc} . Laboratory analytical data on samples vs calculated data based on mass balances and process monitoring data.

3.3.2 Separation

The separation process was optimized by investigating the influence of the washing fluid, the amount, and process of dosing.

Figure 3-7 shows the color values in IU obtained for the different separation treatments. The color value of the sucrose crystals after separation in the centrifuge without any washing was irrespective of application of cycle 1 or 2 33.7 IU. This shows that the basic separation potential of both cycles is comparable. In general, it was observed that the resulting sugar color value decreased linearly with amount of washing fluid up to a level of approximately 2.0 g washing fluid per 100 g of massecuite. In this linear region actually three treatments practically yielded identical results. The cycle 1 with continuously high rotational velocity is for both washing fluids, water or saturated sucrose syrup, as effective as cycle 2 with water as washing fluid. Cycle 2 in combination with syrup as washing fluid results in only a third of the reduction of the color value compared to the other treatments. For this treatment additional washing fluid up to 4 g/100 g results in further improved color values. For the other treatments it appears that further dosing of washing fluids does not result in significant improvements. This is easily understood because the color values achieved with 2.5 g/100 g washing fluid are close to the color value of the sugar

crystals themselves, 21 IU. Most consistent low values, between 21 and 23 IU, were achieved with treatment cycle 1 utilizing water as washing fluid.

One can conclude that the treatments to remove syrup from the crystals' surface performed better when water instead of saturated sugar syrup is used. Secondly, it appeared that cycle 1 with continuously high angular velocity is more effective than cycle 2 which is designed for longer contact times. Consequently, washing with 2.5 g/100g of water on mass of massecuite by applying cycle 1 is the best candidate to be chosen as standard operation if crystal sizes are not changed too much by this treatment.

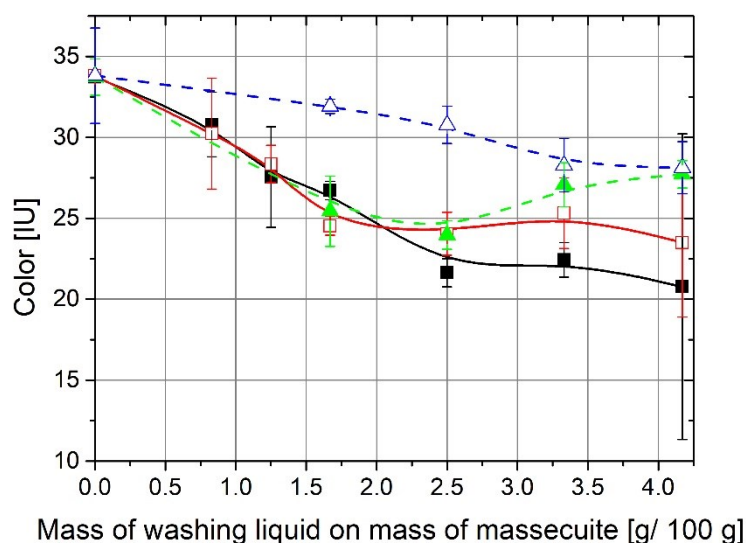


Figure 3-7: Color value of sugars as function of different centrifugation treatments including washing fluids: (■) water, cycle 1; (□) water, cycle 2; (▲) syrup, cycle 1; (Δ) syrup, cycle 2. Lines drawn to guide the eye.

3.3.3 Drying

Three different drying methods were considered for the treatment of the different wet centrifuged crystal masses. Since agglomerates and fine crystals are considered most disturbing fractions of the standard sucrose crystals their amounts were considered key quality markers for the drying process. In detail the mean aperture and the mass fractions of the upper sieve ($d > 1.00$ mm) concerning agglomerates and the collecting pan ($d < 0.315$ mm) concerning fine crystals were determined to evaluate the drying methods.

The illustration of the sugar qualities resulting from the different drying treatments will be limited to samples resulting from the separation process according to cycle 1 with utilization of water as washing fluid. The different separation treatments appear only to have an insignificant effect on the result of the drying processes. Hence, only one out of four data sets is shown to illustrate the effect of amount of washing water and drying process. The results of the mean aperture of the dried sugars are illustrated in Figure 3-8A. For the three different drying methods, air, climate cabinet, and fluidized bed the mean aperture as function of amount of washing fluid is given. In

contrast to the two other drying methods the fluidized bed drying results consistently in low mean apertures that were practically independent of the dosing of the washing fluid. Also for the two other methods the mean aperture appears to be independent of the dosing of the washing fluid. However, with these processes the mean aperture is clearly larger and data are more fluctuating irregularly. The superiority of the fluidized bed drying is further illustrated by the fact that mean aperture of the dried sugar ($0.54 \text{ mm} \pm 0.02 \text{ mm}$) is practically coinciding with the mean aperture of the sugar that has been used to manufacture the synthetic massecuite prior to the centrifugation (0.534 mm).

Figure 3-8B shows the corresponding mass fraction of the agglomerates ($d > 1.00 \text{ mm}$) per process and setting. The data clearly illustrate that for both the air drying and the drying in climate cabinets a significant amount of agglomerates appears. The reason for this formation of agglomerates is the lack of movement and proximity of the sugar crystals during the drying processes. The wet sugar crystals stuck together when dried at open air or in climate cabinets. In this case the sugar was agitated gently by hand after drying to basically make sieving possible. But the formation of agglomerates was practical irreversible. In line with the data on the aperture the fluidized bed dried sugar contained in essence no agglomerates ($< 0.5 \text{ g/100 g}$) and resembled the initial industrial sugar used for the synthetic massecuite. These results were confirmed by the data on dried sugar separated differently as described above. This illustrates that meaningful study on the crystallization of sucrose which entangles analyses on dry sugar particle sizes can only be realized if adequate drying processes are ensured. Drying at open air or in heating cabinets intrinsically has the risk to falsify results on particle sizes making them irrelevant. In contrast the fluidized-bed drying suppresses the formation of agglomerates by constant movement of the wet sugar. To verify that the drying process does not generate excessive amounts of fine crystals, the fraction of particles with diameters of less than 0.315 mm was determined. Figure 3-9 depicts the relation of the amount of smallest particles determined by sieve analysis ($d < 0.315 \text{ mm}$) and the dose of washing fluid. The samples shown are all fluidized-bed dried and concern the application of different washing fluids, water or saturated syrup. For water washed samples, the fine crystals level varied between 5 and 7 g/100 g without showing any clear relation to the dosage of the washing water. These values are lower than for original value of the industrial sugar. This apparent reduction is probably caused by dissolution of the small crystals during the preparation of the synthetic massecuite and possibly also the centrifugation. Furthermore, it is found that the content of fine crystals increased almost linearly with the dosage of saturated syrup as washing fluid. This indicates that sucrose containing fluid adhering to the crystal surface corresponds to fine crystals formation during the fluidized bed drying in line with earlier observations. It is however well acknowledged that fine crystals or dust formation is primarily caused by crystal collisions promoting abrasion. This effect is most likely the cause for the minimum level of 5 g/100 g fine crystals found in all samples independent of the washing treatment.

In summary best results were obtained when massecuite separation is performed with the centrifuge operating continuously at high angular velocity, when the separation is supported by washing with 2.5 g plain water per 100 g massecuite and when subsequent drying is performed in a fluidized bed. Operating in this way produced crystalline sucrose without excessive production of either agglomerates or fine crystals.

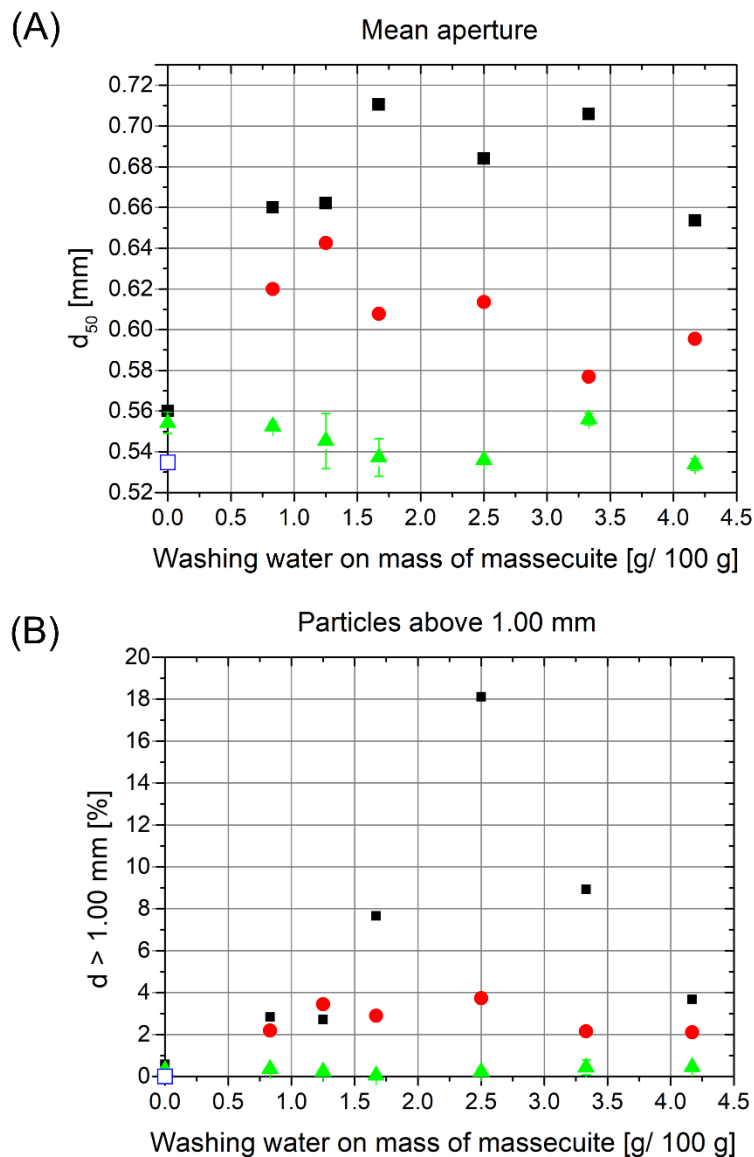


Figure 3-8: Mean aperture (A) and content of particles above 1.00 mm (B) from sieve analysis of dried sugar which was previously washed by different amounts of washing water in the centrifuge. All samples treated according to Cycle1. Drying methods: (■) air, (●) heating cabinet and (▲) fluidized-bed. For reference initial industrial sugar (□).

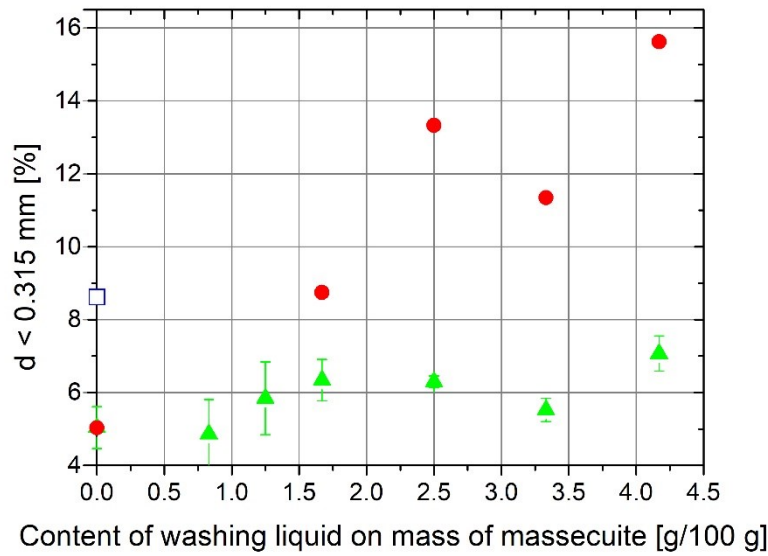


Figure 3-9: Content of fine crystals (particles $d < 0.315$ mm) for fluidized-bed dried samples. Washing media: water (▲); saturated sugar syrup (●); initial industrial sugar (□).

3.4 Conclusion

In this manuscript the setup of a pilot plant scale crystallization unit including separation and drying processes is described. This entangles also the general software used for online process control and monitoring of the crystallization process. Aim of the design is to produce at small scale sugar that in its characteristics and dependency of the characteristics on process parameters resembles industrial sugar. To this end supersaturation, purity and crystal content were computed based on process control and monitoring data in combination with mass balances. Comparison of these data with offline standard laboratory analyses showed a high level of agreement. The separation process using a centrifuge was optimized with respect to two conflicting parameters. These were low sugar color increased due to mother liquor adhesion and minimal crystal dissolution in the washing liquid. Best washing was achieved with 2.5 g of plain water per 100 g of massecuite. From the three different drying methods evaluated, open air, climate cabinet, and fluidized bed the later proved clearly superior.

Applying fluidized-bed drying for 10 min at 343 K lead to minimal formation of agglomerates yet not generating excessive amounts of small particles (< 0.315 mm). The two other drying methods proved to be only of limited value for reliable evaluation of the crystallization.

One can conclude that the work presented here demonstrates that if the suggested procedures are executed diligently the pilot plant crystallization design described is capable to produce sugar at industrially relevant quality. The described capability to perform relevant sucrose crystallization at small scale should benefit the evaluation of innovation and process optimization ideas.

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4 COLOR TRANSFER INTO SUCROSE CRYSTALLIZED FROM BLENDED BEET AND CANE SYRUPS

Schlumbach, Karl; Scharfe, Maria; Flöter, Eckhard

TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

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Abstract

Following the changes in legislation the situation for sugar production in Europe is going to change in the near future. Due to market liberalization the option to co-process raw materials from beet and cane origin becomes more attractive. To this end the crystallization of sugar from blended syrups was studied with particular emphasis on the color inclusion. Evaporation crystallization was performed for various blended syrups and the feed syrups and resulting sugar were characterized in detail. The crystallization is performed at practically constant supersaturation followed by centrifugation and drying. It is found that the colorants from the different origin mutually suppress their inclusion or adhesion. For the industrial raw materials based system it is indicated that color values of less than 30 IU can be achieved with levels of up to 40% of cane material. Based on the experimental finding a simple relation to predict the color of sugars crystallized from blended syrups is formulated. The input data to the model are the color values of both the two pure feed syrups mixed and their respective sugars.

4.1 Introduction

Due to the raw material availability sugar production in Europe is seasonal. With the combination of two production periods based on either fresh-beet-based or stored thick juice with sufficient storage capacity the annual demand is met. This approach has obvious economical drawbacks. With the EU sugar quota regime ending in 2017 liberalization of the European sugar market allows import and export of raw materials and finished sugar into and out of the EU. One possible reaction to this development is the increased use of imported cane or semi-finished cane sugar products (raw cane sugar) as source of sugar produced in European sugar factories. One could

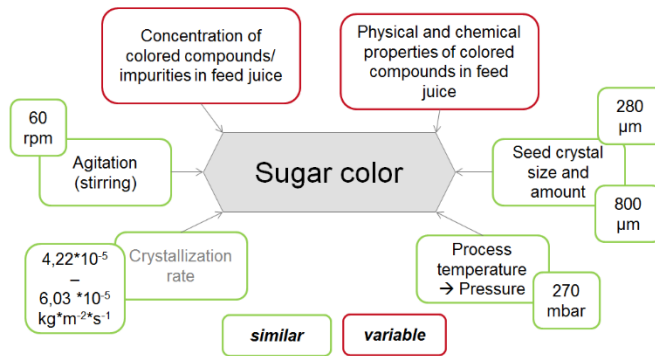


Figure 4-1: Factors affecting sugar color.

image to either seize this opportunity by sequential utilization of different raw materials or by co-production of beet thick juice and raw cane sugar to extend the inter-campaign and to increase the sugar production. Since several years the co-production process is already applied by different sugar

companies. Obviously, the sugars produced from mixed raw materials have to meet quality standards such as color and ash levels. The processing parameters temperature and agitation intensity as well as desired end crystal size influence these quality parameters. In particular the properties and concentration of colorants and other non-sugars present in the feedstock have a profound effect on the final sugar quality. The different factors influencing sugar color levels in sugar are listed in Figure 4-1. Their settings and variation within the work reported are given as well. For practical reasons the so-called color transfer factor (k_{color}) has been introduced. It allows to estimate the final sugar color $F_{420,s}$ (determined at a wavelength of 420 nm) as a function of the color value $F_{420,ML,0}$ of the feed syrup (Lionnet & Moodley, 1995):

$$k_{color} = \frac{F_{420,s}}{F_{420,ML,0}} \cdot 100\% \quad (4-1)$$

This transfer factor should not be mixed up with partitioning coefficients which relate the distribution of a species between two coexisting phases. The transfer factor k_{color} is highly practical but completely ignores the process of concentration of colorants in the mother liquor due to the ongoing crystallization. Since sucrose solutions from beet and cane are introducing different non-sucrose components the respective color incorporation appears to be quite different which is found back in the significantly different transfer factors of 6% and 1% for cane and beet, respectively. The colorants originating from the sugar beet and the production process contain a high proportion of melanoidins and have a maximum molecular mass of 30 kDa (Godshall et al., 1991). These

colorants only have a limited tendency to be incorporated into the sucrose crystal (Paton, 1992), the average transfer factor in beet sugar production is 1% (Godshall et al., 2002).

In contrast, the colorants and their precursors present in cane sugar production predominantly originate from the cane plant material. Plant pigments such as phenolics are precursors of high molecular mass colorants found downstream in the process (Lindeman & O'Shea, 2001). During milling and extraction colorants and polysaccharides (e.g. indigenous sugar cane polysaccharides) are forming complexes of higher mass which due to their saccharide nature incorporate more easily into the sucrose crystal (Godshall et al., 2002; Godshall et al., 1987; Tu et al., 1977; Godshall & Baunsgaard, 2000). Furthermore, melanins are formed by enzymatic catalysis immediately after shredding and cutting of cane until the enzymes are deactivated by heat (Bucheli & Robinson, 1994). These melanins cannot be separated during juice purification because the high invert sugar content of the juices dictates milder processing conditions such that the melanins remain soluble (van der Poel, P.W., 2000; Rein, 2007). The resulting enzymatic browning products give color to the final sucrose crystal as they are incorporated during the crystallization strike (Paton, 1992). Additionally, color generating reactions such as *Maillard* reactions, alkaline degradation and caramelization lead to additional colorants with high molecular mass (Rein, 2007). The molecular mass of the colorants occurring in cane sugar production is up to 1,000 kDa (Godshall et al., 1987) and the average color transfer factor ranges from 6 to 10% (Godshall et al., 2002; Godshall & Baunsgaard, 2000).

Currently, it is generally acknowledged based on practical experience that an addition of 10 to 20 g/100 g raw cane sugar to beet thick juice results in acceptable high quality white sugar with a color value of less than 30 IU (Kochergin et al., 2012). However, this evidence based value is in conflict with basic engineering considerations taking the differences in transfer factors of beet and cane sugar production into account.

Two simple approaches to predict the color values for sugars produced from blended syrups can be formulated by assuming either independent inclusion processes for colorants from different origins or a linear conversion of the color transfer factors applicable to the color of the blended syrups. In detail, one could assume that the transfer factor for cane based colorants solely applies to the cane based colorants present in the blended syrup. Simultaneously, the transfer factor for the beet based colorants allows assessment of the color contribution to the final sugar color resulting from the beet colorants. Consequently, this independent contribution of the sugar color values of the two original syrups mixed are simply combined linearly to derive the color value for sugars crystallized from the blended syrups. Applying this approach to the material used throughout this work the calculation is based on a beet thick juice color value of approximately 2,000 IU and a raw cane sugar color value of 1,600 IU. Color transfer factor k_{color} is as mentioned above 1% for beet and 6% for cane (Godshall et al., 2002; Godshall & Baunsgaard, 2000). For an 80 to 20 mix of the beet thick juice and raw cane sugar, color values of the syrup of 1,600 IU and 320 IU result from beet and cane respectively. Multiplied with the respective transfer factors these

translate to a predicted sugar color value of 35.2 IU, of which 16 IU are beet contributed and 19.2 IU from cane origin.

Alternatively, an approach to predict the sugar color from the blended syrups could be based on the color value of the actual syrup and a linearly mixed color transfer factor. Applying this approach, the color transfer factor of an 80:20 beet to cane blend is predicted to be 2%. Combining this transfer factor with the color value of the mixed syrup (1,920 IU) the predicted resulting sugar color value is 38.4 IU. Both approaches hence predict that the quality criteria of sugar color values of less than 30 IU cannot be met with 20 g/100 g incorporation of raw cane sugar in mixed thick juices considering the material characteristics present in this work.

Publications on the topic of co-production of beet and cane material are rare. With the change of the market situation the work presented here aims to elucidate the relation of the sugar quality produced from blended syrups with the properties of the raw materials and the mixing ratio. To this end, different blends of beet thick juice and dissolved raw cane sugar were processed under controlled conditions. Both blended syrups and resulting sugars were characterized in detail. Based on the experimental information gathered a framework to predict the color value of sugars produced from blended syrups is formulated. This prediction is based on the properties of the blended syrup constituting single source syrups and the respective sugars produced out of them.

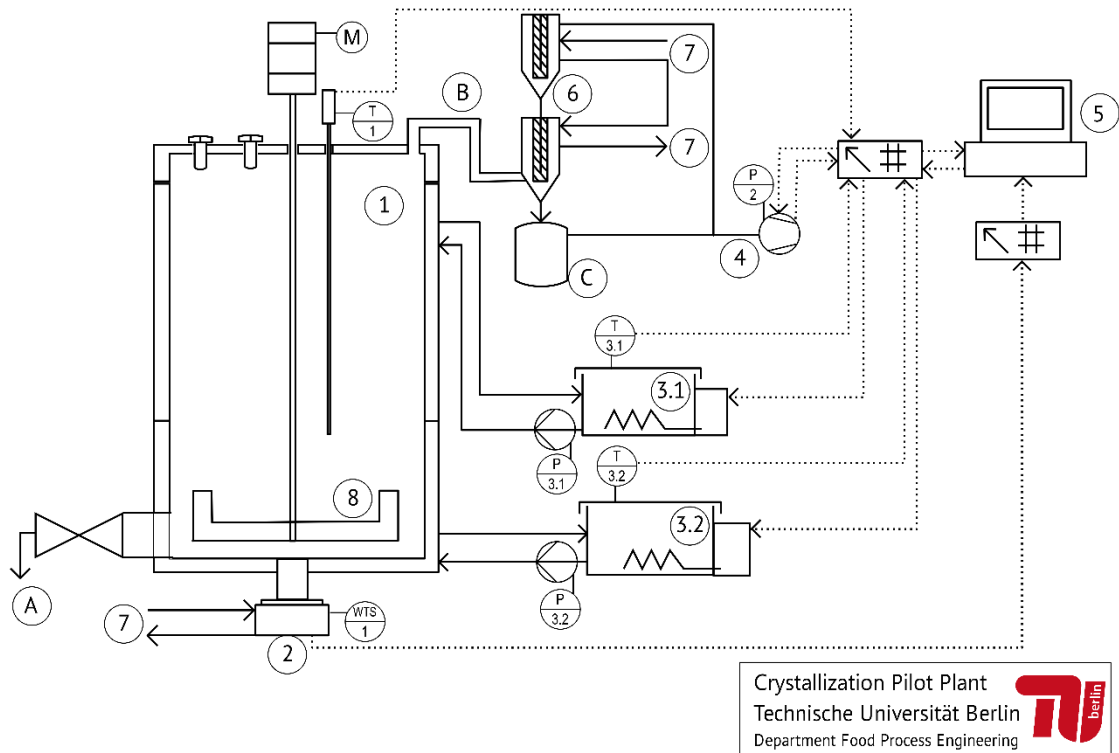


Figure 4-2: Crystallization pilot plant and ancillary equipment.

1 Vessel; 2 Refractometer; 3.1 Thermostat; 3.2 Thermostat; 4 Low pressure pump; 5 Data processing unit; 6 Cooler; 7 Cooling water; 8 Stirrer; A In-/outlet valve for feed and massecuite; B Vapor outlet; C Condensate outlet.

4.2 Material and methods

4.2.1 Crystallization plant, separation and drying

All crystallization experiments are executed in a 0.005 m³ evaporating crystallizer, which is described in detail elsewhere. It was shown before that the crystallization and supporting other unit operations allow production of sugar of industrially relevant quality (Schlumbach et al., 2015).

The temperature of the fluid in the vessel is controlled using two independent thermostats. One thermostat (F32-HD, Julabo, Seelbach, Germany) (3.2 in Figure 4-2) feeds the main heating surface, the double-walled stainless-steel bottom part of the vessel. The water temperature was kept at 366 K (± 0.01 K). The other thermostat (F12-MC, Julabo, Seelbach, Germany) (3.1 in Figure 4-2) feeds the glass jacketed body of the crystallizer. It was kept at a lower temperature (343 ± 0.01 K) in order to keep a homogeneous temperature distribution and to avoid nucleation on the wall. The temperature is monitored via a Pt 100 placed inside the crystallization vessel. A process refractometer (iPR 2-3, Schmidt & Haensch GmbH & Co., Berlin, Germany) (2 in Figure 4-2) is mounted to the bottom of the vessel to determine the dry substance content within the mother liquor. The pressure is controlled by a vacuum pump (PC 3001, Vacuubrand GmbH & Co KG, Wertheim, Germany).

The experimental set-up is controlled, and data are recorded on-line with the help of a PC. Control and monitoring routines are realized in a LabVIEW (National Instruments Corporation, Munich, Germany) environment.

Subsequent to the crystallization the sugar is separated from the mother liquor using a temperature controlled basket centrifuge (Centrifuge DM 2250, Gebr. Heine, Viersen, Germany). The speed of 3,000 rpm is equivalent to a G-force of 1,450. A self-constructed washing unit is installed to wash the residue syrup from the surface of the crystals. The amount of water which was used to displace the residual syrup film of the sugar surface was 2.5 g/100g of the mass of the massecuite. Finally, the wet sugar is dried in a fluidized-bed dryer, designed by TU Berlin. The sugar was dried for 10 minutes with conditioned air at a temperature of 343 K to yield a residual humidity of $0.04 (\pm 0.01)$ g/100 g.

4.2.2 Raw materials

To ensure that the work is industrially relevant the beet thick juice was sourced directly from a German sugar factory. The raw cane sugar originating from Brazil was also supplied by a sugar factory. The raw cane sugar solution was prepared using two parts of mass of raw sugar and one part demineralized water ($< 2 \mu\text{S/cm}$). Prior to blending the syrups each syrup was filtered using a stainless-steel mesh (nominal 5 μm , absolute 8 μm ; TEDRA Dahmen GmbH & Co. KG, Wassenberg, Germany). The same batches of beet thick juice and raw cane sugar were used

throughout the experiments. The mixed feed syrups for the different crystallization experiments were blends with the following mass ratios: 100:0, 80:20, 60:40, 40:60, 20:80, 0:100. Here, the first number expresses the beet and the second the cane content in g/100g. Furthermore, 100 µl of Struktol SB 2433 (Schill + Seilacher "Struktol" GmbH, Hamburg, Germany) were added to inhibit foam forming during evaporation and crystallization.

4.2.3 Batch crystallization process

All crystallization processes started with the vessel filled with 5,000 g of the respective syrup. Throughout the crystallization no further feed was supplied to the vessel. The system pressure is maintained at 270 mbar ($< \pm 1$ mbar) throughout the process. Homogeneity of the sample is achieved through agitation with a U-shaped stirrer at 60 rpm (see Figure 4-2).

Samples were taken prior to cooking when a homogeneous blend was achieved. Seeding was conducted at a supersaturation coefficient of 1.05 (± 0.01). Seed crystals had an average particle size of 0.283 mm and color value of 30 IU. The desired end crystals size was 0.800 mm. The supersaturation level during crystallization was found to be 1.10 (± 0.01).

The crystallization strike was finished once the torque of the agitator increased by a value of 0.06 Nm from the starting value. This torque increase as a function of massecuite viscosity relates to a crystal content of 45 to 50 g/100g. At this incident samples of the massecuite and the mother liquor were taken. Subsequently, the sucrose crystals were separated from the mother liquor by centrifugation as described above.

4.2.4 Analytical methods

The equipment, materials and chemicals used for the analytical procedures are listed in Table 4-1 and Table 4-2. The dry substance content (w_{DS}) of the feed syrup, the massecuite and run-off syrup is determined by refractometry. The sucrose content (w_S) was analyzed by polarization after clarification with *Carrez* reagent following the ICUMSA Method GS8-2 (ICUMSA, 2011). According to this method the purity q in % of the samples or sugar is calculated:

$$q = \frac{w_S}{w_{DS}} \cdot 100 \quad (4-2)$$

Simple mass balances allow determination of the crystal content w_{CC} (in g/100 g) from the sugar content w_S of the massecuite (MC) and mother liquor (ML):

$$w_{CC} = \frac{w_{S,MC} - w_{S,ML}}{100 - w_{S,ML}} \cdot 100 \quad (4-3)$$

The color of the feed syrup, massecuite, and run-off syrup and sugar is determined using modified versions of the analytical methods GS1/3-7 and GS2/3-10 (ICUMSA, 2011). The pH-value was adjusted with hydrochloric acid and/or sodium hydroxide solutions. In the modified method applied, the color determination is not only performed at pH 7 but also at the pH-values of 4 and

9 (Smith & Gregory, 1971). The color value (in IU) in solution can be calculated from the spectrophotometrically determined absorption (A_s) at 420 nm as follows:

$$F_{420,pH} = \frac{10^8 \cdot A_s}{b \cdot w_{DS} \cdot \rho} \quad (4-4)$$

with b the length of the cuvette (1 cm for syrup, 5 cm for sugar), w_{DS} the dry substance content and ρ (kg m^{-3}) the density of the solution. Furthermore, the color value of affinated sugar crystals was determined. To this end, sugar was mixed with a saturated sugar solution of refined sugar with a color value of less than 15 IU for 15 min. Once the surface color is released into the solution the suspension was centrifuged as described above. This process was repeated with an additional mixing time of 5 min. Prior to the determination of the sugar color, the sugar was dried in an exsiccator.

The size of the sugar crystals resulting from different blended syrups was determined according to ICUMSA Method GS2/9-3 (ICUMSA, 2011). Samples of the dried sugars were categorized according to the classes of sieves: 0.180 mm, 0.250 mm, 0.400 mm, 0.630 mm, 0.710 mm, 0.800 mm, 0.900 mm, and 1.00 mm. A mechanical shaker (AS 200 Control, Retsch Technology GmbH, Haan, Germany) classified the sugar crystals for 10 min. The mean aperture (d_{50}) and coefficient of variation (CV) were calculated according to Powers Method (van der Poel, P.W., 2000). From the crystal sizes and the duration of the crystallization strike ($\Delta\tau$) the average crystal mass growth rate G ($\text{kg m}^{-2} \text{s}^{-1}$) was derived (Bubnik & Kadlec, 1992):

$$G = \frac{3\rho \cdot \alpha}{\beta} \cdot \frac{\Delta d_{50}}{\Delta\tau} \quad (4-5)$$

The constants $\alpha = 0.75$ (crystal shape factor) and $\beta = 5.02$ are set according to Bubnik & Kadlec (1992). The density ρ of sucrose crystals is $1,587 \text{ kg m}^{-3}$ and Δd_{50} is the difference between the average size of the crystals from seeding and at the end of the process.

Table 4-1: Material and chemicals used for laboratory analysis.

Chemicals & Materials	Distributor
Carrez I solution (21.9 g of zinc acetate dihydrate and 3 g of glacial acetic on 100 ml water)	Bernd Kraft, Duisburg, Germany
Carrez II solution (10.6 g of Potassium hexacyano ferrate(II) trihydrate on 100 ml water)	Bernd Kraft, Duisburg, Germany
Celite Hyflo Super Cel®	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
CHROMAFIL® membrane filters GF/PET 0.45 µm	Machery-Nagel GmbH & Co. KG, Düren, Germany
Filter paper MN 631	Machery-Nagel GmbH & Co. KG, Düren, Germany
Hydrochloric acid solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
Sodium hydroxide solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
10 mm UV-cuvette (612-5685)	VWR International, Darmstadt, Germany
50 mm glass cuvette 100-OS (634-9017)	VWR International, Darmstadt, Germany

Table 4-2: Devices used for laboratory analysis.

Device	Labelling	Manufacturer
Centrifuge (laboratory)	Sieva-2	Hermle Labortechnik GmbH, Wehingen, Germany
Conductometer	Seven Easy	Mettler Toledo, Gießen, Germany
Conductometer electrode	InLab 730	Mettler Toledo, Gießen, Germany
DDS	Automatic Dilution and Dosage System	Anton Paar, Graz, Germany
pH meter	Seven Excellence	Mettler Toledo, Gießen, Germany
pH electrode	Inlab Routine Pro	Mettler Toledo, Gießen, Germany
Polarimeter	Saccharomat NIR W2	Schmidt & Haensch, Berlin, Germany
Refractometer (laboratory)	ATR W2 plus & ATR	Schmidt & Haensch, Berlin, Germany
Sieve shaker	AS 200 Control	Retsch Technology GmbH, Haan, Germany
Spectrophotometer	NANOCOLOR UV/VIS	Machery-Nagel GmbH & Co. KG, Düren, Germany

4.3 Results and discussion

4.3.1 Batch crystallization process

In order to verify that the crystallization of the different blended syrups was performed in a consistent manner characteristic data of the different crystallization runs were gathered and compiled in Figure 4-3. Most consistent processing is desired in order to relate occurring differences in color values primarily to the compositional variation of the blended syrups because crystal size and particle distribution are influencing the color transfer as well. Not surprisingly, the data on the purity of the feed syrup and the respective massecuite (Figure 4-3A) show a linear dependence on the beet syrup content. The data on the purity of the run-off syrup evolve proportionally to the purity data of the feed syrup. This is perfectly in line with mass balances according to the experimental design aiming at a constant final crystal content of 50 g/100g. Figure 4-3B illustrates that the process monitoring via the torque of the agitator ensured that this is widely achieved with final crystal contents varying between 48.2 and 49.7 g/100 g.

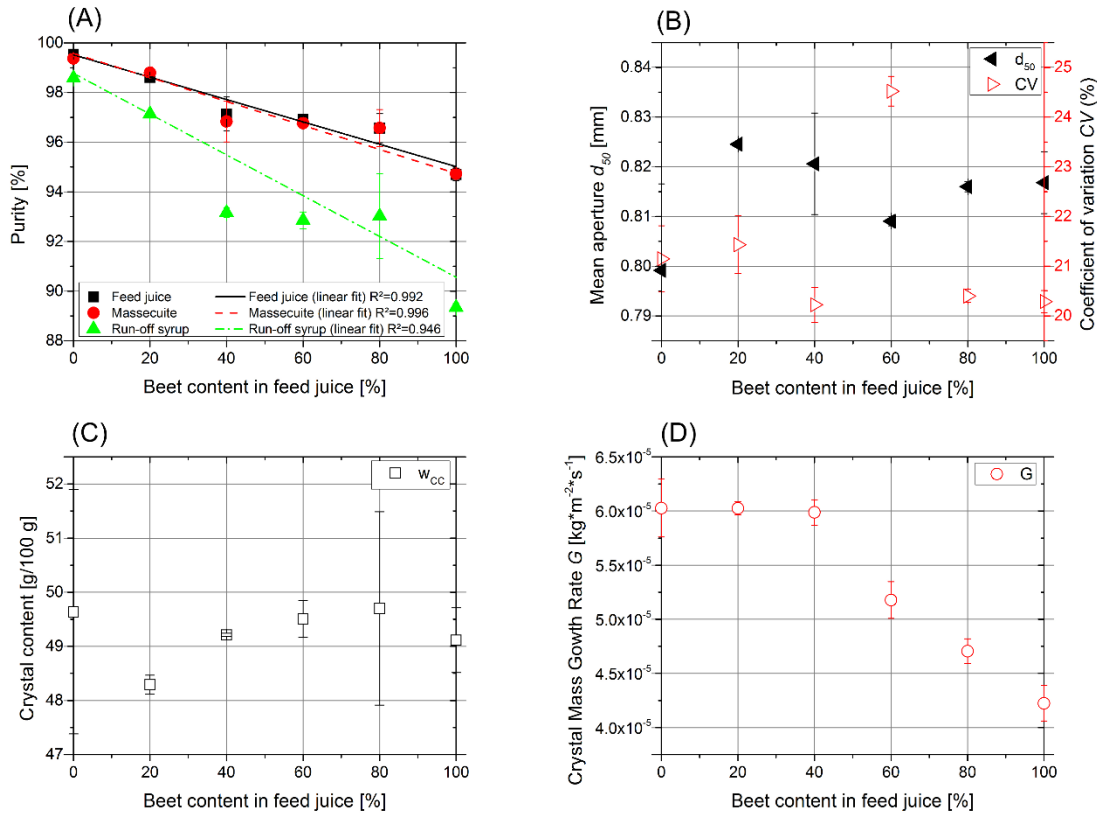


Figure 4-3: Data of general analyses from the crystallization experiment: (A) Purity of the feed syrup (■, solid line), massecuite (●, dashed line) and run-off syrup (▲, dash-dotted line). (B) Mean aperture (◄) and coefficient of variation (►) determined by sieve analysis. (C) Crystal content (□) at the end of crystallization strike and (D) crystal mass growth rate (○).

The desired mean aperture was 0.800 mm. The experimental data illustrated in Figure 4-3C show that values between 0.799 and 0.825 mm were achieved. Furthermore, the coefficient of variation

is between 20.22 and 24.52% indicating a good and narrow particle size distribution (van der Poel, P.W., 2000).

Crystallization rates determined according to equation (4-5) are depicted in Figure 4-3D. With increasing inclusion levels of beet syrup the crystallization rates remained practically constant up to levels of 40 g/100 g of beet syrup. At higher inclusion levels of beet syrup the data suggest that the growth rates decrease linearly from $5.99 \cdot 10^{-5}$ to $4.22 \cdot 10^{-5} \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. This trend corresponds fairly well with purity data of the respective mixed feed syrups. This variation in the crystal growth rates has to be taken into account during interpretation of color values because higher growth rates are considered to result in increased color values (Lionnet, 1998a; Grimsey & Herrington, 1994). However, the effects of crystal growth rates on color values of crystalline sugar most likely vary depending on the type of colorant and the respective inclusion or adhesion process (Godshall et al., 2002; Lindeman & O'Shea, 2001; Godshall & Baunsgaard, 2000; Shore et al., 1984).

Overall, the data in Figure 4-3 show that crystallization strikes were performed according to experimental design very consistently to eliminate strong influences of process variations on the color transfer/inclusion processes.

4.3.2 Color transfer

The results on the color transfer observed for the different mixed syrups are shown in Figure 4-4. The color values of the feed syrups and affinated sugars shown are determined at pH 7 and relate to the main y-axis which is broken between 100 and 1,500 IU. Color transfer factors were calculated according to its definition and are shown against the secondary y-axis. Not surprisingly, the color value of the feed syrups increased linearly with increasing beet syrup content. As the data illustrate the color value of the sugars is increasing exponentially with increasing cane content. For obvious reasons the color transfer factor consequently also shows an exponential dependence on the composition of the mixed syrups. The transfer factors determined for both unmixed beet syrup and unmixed cane syrup are in good agreement with literature (Godshall et al., 2002; Godshall & Baunsgaard, 2000). The exponential relation found indicates that the colorants from different origins have a significant interaction with each other. It seems hence that even though the color inclusion mechanism is generally acknowledged to be quite different for colorants originating from either beet or cane (Paton, 1992; Godshall et al., 2002; Godshall & Baunsgaard, 2000; Grimsey & Herrington, 1994; Grimsey I.M. & Herrington, 1996) that color inclusion is mutually suppressed. A possible explanation is based on the inclusion mechanism, transfer factors, and diffusivities of the beet and cane colorants. It is generally acknowledged that colorants from cane have higher molecular masses, lower diffusion coefficients (according to *Stokes-Einstein* equation (Edward, 1970)), and are due to their complexion built into the crystal lattice. This is reflected in the high transfer factor of 6%. Responsible for this behavior are

probably colorants which are attached to polysaccharides forming colored high mass compounds. These polysaccharides act as color inclusion carriers due to their sucrose affinity. These

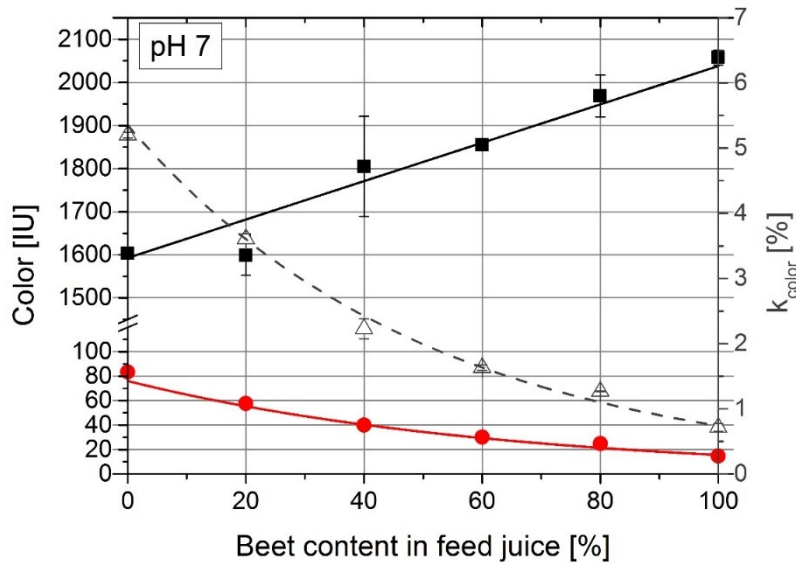


Figure 4-4: Color determined at pH 7 from feed syrup (■, solid line) and affinated sugar (●, solid line), and the resulting color transfer factor (△, dashed line).

compounds are hard to remove during sugar cane refining (Godshall et al., 1987). In contrast, the colorants originating from beet syrups have smaller molecular masses, a high diffusion coefficient, and are most likely included as liquid inclusion or via surface adhesion (Paton, 1992; Shore et al., 1984; Grimsey I.M. & Herrington, 1996). Combining these attributes, it appears likely that the colorants originating from beet temporarily adsorb to the crystal surface and hence block the surface for the adhesion and subsequent incorporation of the colorants originating from cane. Additionally, the different colorants most likely reduce mutually the mass transport to the crystal surface by means of a pseudo polarization due to the accumulation of non-integrated colorants.

The color analyses were also performed at different pH-values to get more detailed information about the incorporation processes and adhesion effects of the different colorants. In Figure 4-5 the coloring of the sugars crystallized from different mixes measured at pH-values of 4, 7, and 9 are expressed as color transfer factors. For mixed syrups rich in beet syrup practically no differences were observed. With increasing level of cane syrup in the blended syrups higher transfer factors are found. However, under acidic conditions (pH 4) the values are increased by approximately 25% compared to the measurements at pH-values of 7 and 9. This behavior is in line with the statement that color measurements at pH 4 are more sensitive to colorants with high molecular mass. These typically originate from cane syrup and tend to be incorporated more easily into the sucrose crystal (Paton, 1992; Godshall et al., 1987; Wright, 2002). Between the measurements at pH 7 and 9 no significant difference was observed. Determinations at pH 9 are

said to be particularly sensitive to ionized colorants predominantly found in cane syrups (Wright, 2002). As Figure 4-5 illustrates also the measurements at the different pH-values suggest that the evolution of the color transfer factor behaves exponentially with the mixing for the syrups. Furthermore, the reduction of the color value by affination was investigated. Affination processes should be more effective in reducing sugar color values for colorants that are adhering to the

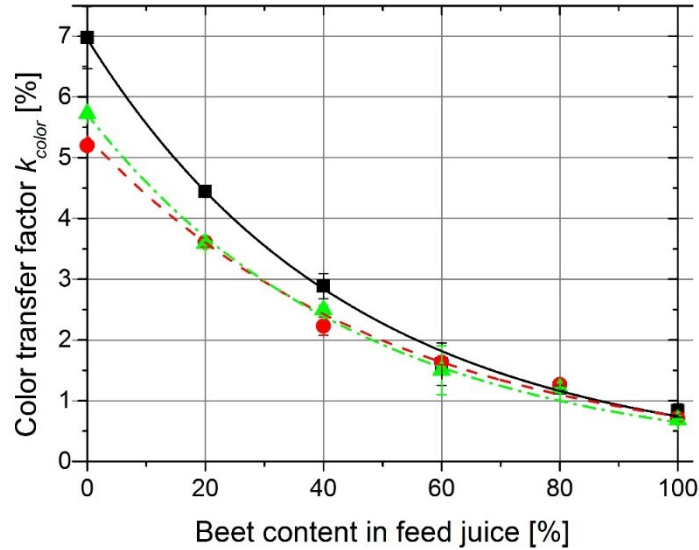


Figure 4-5: Color transfer factors determined at pH 4 (■, solid line), pH 7 (●, dashed line) and pH 9 (▲, dash-dotted line).

crystal surface than for those which are built into the crystal structure. The relative reduction of the color value of sugars crystallized from mixed syrups is depicted in Figure 4-6. With increasing beet content of the mixed syrup affination has a greater effect on the sugar quality. For syrups with high incorporation levels of cane it is found that the reduction of the color value based on measurements at pH 4 is as small as 15%. This confirms that the colorants originating from cane syrup are significantly more difficult to remove than those from beet syrups because they are believed to be incorporated into the crystal matrix (Paton, 1992; Godshall et al., 2002; Godshall, 1997).

Building on the experimental data shown in Figure 4-5 a model to calculate the color transfer factors for mixed syrups $k_{color,x}$ from the color transfer factors constituting of the pure beet syrup $k_{color,x=1}$ and the pure cane syrup $k_{color,x=0}$ is formulated. Equation (4-6) expresses that the color transfer factor for any mixture can be calculated by a simple exponential function.

$$k_{color,x} = k_{color,x=0} \cdot \exp(-\lambda x) \quad (4-6)$$

x is the beet content in the blended syrup and λ the system specific ‘rate constant’. The specificity to a certain system is obtained by simply fitting the ‘rate constant’ λ such that the function connects the color transfer factors of the two pure syrups. Hence, no data on mixed syrups are necessary to define equation (4-6).

Figure 4-7 shows the experimental values of sugar colors (pH 7) for the syrups used throughout this work as a function of the beet content of the mixed syrups. Different from the general rule of thumb that only up to one fifth of cane material can be co-processed with beet thick juice it was found that for the industrial material studied here double the amount of cane material appears to be tolerable. The lines drawn in Figure 4-7 represent the three different approaches to predict the color value of sugars crystallized from mixed beet and cane syrups. Only input to all predictions

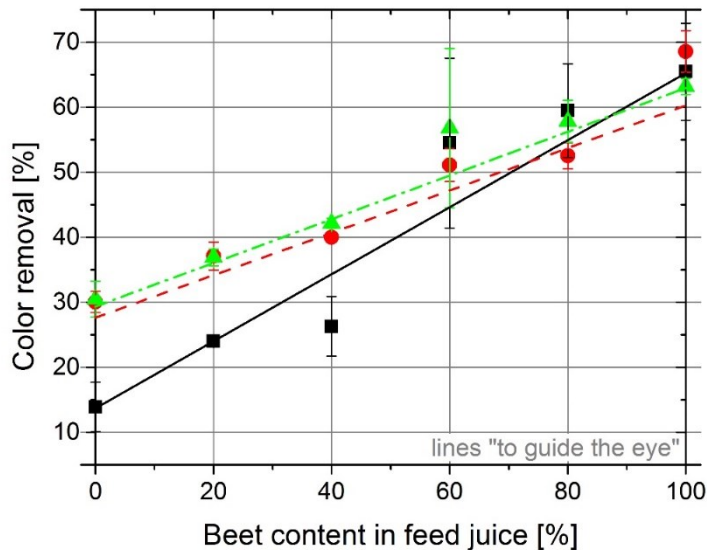


Figure 4-6: Color removal by affination determined at pH 4 ■ (solid line), pH 7 ● (dashed line) and pH 9 ▲ (dash-dotted line) of crystallized sucrose from blends of beet thick juice and dissolved raw cane sugar.

are the color values of the feed thick juices and crystallized sugars for the two pure syrups, 100% beet and 100% cane, which constitute the mixed system. The models for the colorants inclusion as formulated above are described shortly:

- Independent: Interpolation of sugar color values based on independent inclusion per origin.
- Linear: Total color value of the blended syrup with a linearly interpolated color transfer factor.
- Exponential: Total color value of the blended syrup with an exponentially interpolated color transfer factor.

As Figure 4-7 reveals the experimental data for color values of sugars crystallized from blended syrups shows a systematic pattern. The linear model significantly overestimates the sugar color. A significantly better result is obtained for the independent model which still overpredicts the sugar color by up to 30%. Utilizing the exponential model to derive color transfer factors for the blended syrups a very good match of the experimental data is achieved. It has to be emphasized here that the predictions of the three modelling approaches are based on the experimental data of the pure syrups, 100% beet and 100% cane, only. The findings of this work give hence hope to

predict the color of sugars crystallized from blended syrups on basis of the experimental values solely on the pure syrups constituting the mixtures.

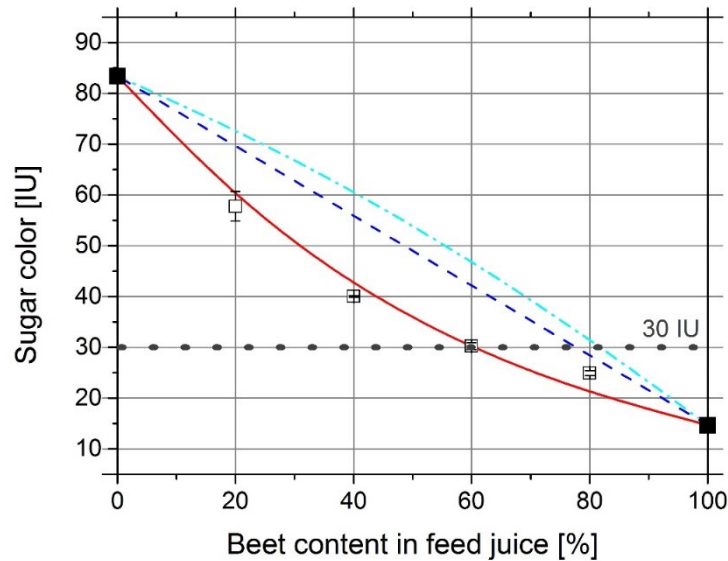


Figure 4-7: Calculated trend of the sugar color by the independent (dashed line), linear (dash-dotted line) and exponential (solid line) model with the knowledge of the color transfer factors and feed juice colors of the single source syrups. The experimental sugar colors from the single source syrups (■) and blends (□) are compared with the models.

4.4 Conclusion

The work reported here is concerned with the quality of sugar crystallized from blended syrups originating from both beet and cane. Especially, the question how the colorants from the different origins influence the resulting sugar color is of key interest. A general rule of thumb states that inclusion levels of up to 20 g/100 g raw cane are not problematic. Since the colorants originating from the two sources are quite different in their nature it appears fair to assume that their respective color inclusion processes progress independently. This suggests that the color of sugars from blended syrups is a simple linear interpolation between the color values obtained for the constituting pure syrups, 100% beet and 100% cane. Since the color values for sugars are predicted by simply combining a color transfer factor with the color value of the feed thick juice another technical approach is formulated by averaging the color transfer factors k_{color} of the two pure syrups. This average transfer factor is then applied to actual color values of the mixed feed thick juice. This approach predicts color values in excess of the linear interpolation described above.

The evaporating crystallization was executed in such a way that practically constant supersaturation was maintained. The detailed execution of the process is described elsewhere (Schlumbach et al., 2015) but it should be mentioned here that all processing steps, crystallization, centrifugation, and drying are performed such that the resulting sugar is comparable to industrial

Conclusion

quality. For the study of the color values of sugars crystallized from blended syrups it appeared that neither of the two models formulated a priori, either independent color contribution or linearly mixed transfer factors, describe the experimental results properly. Intermediate mixes result in sugar color values lower than a simple linear interpolation suggests. A simple exponential function, equation 6, was adjusted by fitting parameter λ such that it connects the transfer factors of the two pure syrup transfer factors. Transfer factors for the blended syrups were hence calculated without any data on blended syrups. Combination of the resulting transfer factors with the linear interpolated color values of the thick feed juice result in a very good match of predicted and experimental color values for sugar crystallized from blended syrups.

For the system studied here the experimental data indicate that the rule of thumb dictating a maximum of one out of five inclusion of cane material appears to be too restrictive since a level of two out of five resulted in a sugar color value of 30 IU.

Furthermore, the experimental data obtained at different pH-values confirmed the difference of the colorants from different origin indicating that the colorants dominating the absorption at pH 4 originating from cane are more difficult to wash off by affination than other colorants.

To formulate an explanation for the mutual suppression of color inclusion for the colorants from the two different sources appears easy at first sight. The colorants originating from beet are significantly smaller than the complexes resulting from cane material. With the respective diffusivities, high for beet colorants, and preference to be built into the crystal lattice, high for cane colorants, a surface poisoning by the beet colorants, analogue to polarization in membrane processes, is likely. However, no framework is formulated yet to explain the identified evolution of the experimental data.

Consequently, future work will focus on a mechanistic explanation of the relationship found. None the less the evidence to support the exponential relationship formulated here needs to be substantiated by additional experiments with different raw materials and process parameters.

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5 CRYSTALLIZATION AND ANALYSIS OF BEET AND CANE SUGAR BLENDS

Schlumbach, Karl; Pautov, Alexander; Flöter, Eckhard

TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

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Abstract

The work presented here is concerned with the production of sugar from mixed syrups that origin from both cane and beet. This is of interest because with the end of the regulation of the European sugar market in 2017 producers aim for higher utilization of their production sites. This can for example be achieved by co-processing of raw cane sugar and beet juice. Despite the abundant body of work concerning the colorants inclusion in either beet or cane sugar manufacturing practically no detailed information on this important parameter is available for mixed syrups. The systematic study reported here reveals that colorants from different origin show a mutual suppression of their incorporation into the crystal. This is particularly surprising because these colorants are reported to follow specific incorporation mechanisms on different faces of the growing crystal. Further analysis reveals that the color contribution due to liquid inclusions, hence crystal imperfections, starts to increase only at high cane inclusion levels (80%), while the color effects of co-crystallization dominate and increase systematically with cane levels. Finally, a model to forecast the color values of sugars crystallized from mixed syrups is formulated.

5.1 Introduction

With the end of the EU Sugar Policy in 2017 the European sugar factories are forced to enhance their capacity by optimizing their processes and thereby improving their efficiency. One approach is co-processing beet thick juice and raw cane sugar, a process already applied for years by sugar companies. In doing so quality standards such as the color which is the most important quality parameter in sugar production have to be met. It is generally acknowledged that an addition of 10 - 20 g/100 g raw cane sugar does not lead to unpredictable difficulties in the production of high quality white sugar (color value of less than 30 IU) (Kochergin et al., 2012). It is expected that a variation in the raw cane sugar quality leads to processing and quality issues during co-processing. As a result, the white sugar color value would increase. This problem becomes even more apparent with the desire to use larger fractions of raw cane sugar. A better knowledge of the chemical and physical properties of the compounds causing a shift in the color of the resulting sugar is required. In particular as in beet and cane sugar production different colorants with different chemical and physical properties like molecular mass, pH-sensitivity and electrical charge are responsible for the resulting sugar color. Only an increased understanding of color formation and transfer during co-processing allows producers to quickly react on quality variations of the raw materials while maintaining highest quality standards of the end product. The prediction or even description of the sugar color after co-processing has practically not been studied yet. The lack of any reliable experimental data does certainly not allow to formulate a hypothesis on the interaction of colorants originating from different sources.

Figure 5-1 illustrates simplified the operational steps in a typical beet and cane sugar factory. It disregards the emerging by-products and used processing aids. The main purpose of sugar production is the separation of sucrose from non-sucrose components followed by the crystallization obtaining sugar crystals of desired quality, e.g. purity, size distribution and color. Without going into any detail it should be mentioned here that the cane sugar production process typically ends with raw sugar while beet sugar processing directly delivers white sugar. The quality standards are monitored using the standardized methods as published by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA, 2011).

One important quality parameter is the color, a result of a variety of brownish to yellowish components in the raw sugar juices. However, color cannot be quantified as such. Hence, a

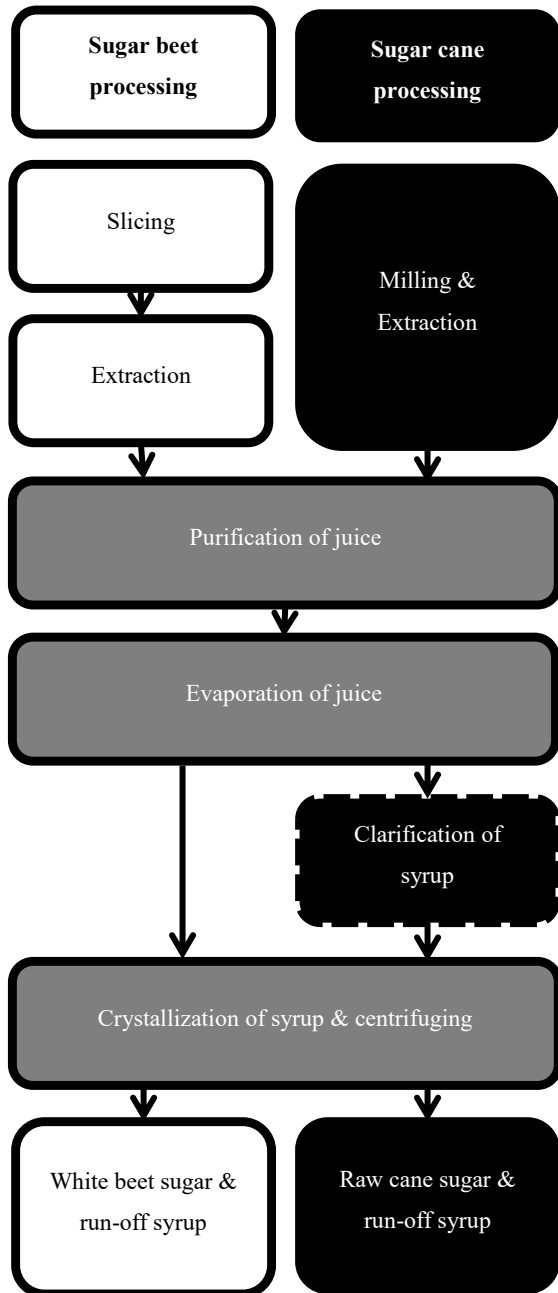


Figure 5-1: Simplified schematic flow diagram of general sugar production in sugar beet and sugar cane industry.

practical quantification is usually performed based on the total effect of all coloring components on light absorbance (Rein, 2007).

The precursors and colorants originate either directly from the plant or are formed by degradation reactions during processing. Colorants which are formed during the process are divided into enzymatic colorants such as melanins and non-enzymatic colorants such as melanoidins, caramels and alkaline degradation products of hexoses (ADHs).

Melanins are oxidation products of phenolics (e.g. tyrosine) and also products of phenol-amine reactions. Phenolics are nearly colorless precursors present in the beet and cane plant with the difference that phenolics in beet contain higher concentrations of nitrogen than in cane. They oxidize preferably in presence of enzymes (e.g. polyphenoloxylase) resulting in dark, yellow to brown colored pigments (Godshall et al., 1991; Davis, 2001; Godshall & Baunsgaard, 2000).

Melanoidins are dark-brown to black reaction products of reducing sugars and compounds containing amino groups. The *Maillard* type reaction is obviously promoted at high temperatures (> 363 K) and pH-values > 7 (Martins et al., 2000). For sugar syrups

originating from beet dry substance levels (w_{DS}) from 80 to 90 g/100 g syrup are reported to be most reactive (Heitz, 1995). Furthermore, color intensification occurs due to increased polymerization on extended exposure to elevated temperatures (Coca, 2004). The molecular mass of the coloring components depends on the degree of polymerization and is commonly larger than 2,500 Da (Davis, 2001).

Alkaline degradation products of hexoses (ADH) represent another class of colorants. Before alkaline degradation products can form, sucrose needs to be inverted in a lye catalyzed reaction. In further steps glucose and fructose are decomposed at elevated temperatures under alkaline

conditions. The reaction results in carboxylic acids with less than six carbon atoms, e.g. lactic, acetic and oxalic acid. In addition, considerable amounts of brown-colored hydrocarbons with more than six carbon atoms and color darker than caramels are formed. However, the exact suite of reactions relating to color formation is currently not fully understood (Shore et al., 1984; Godshall et al., 1991; Davis, 2001; Coca, 2004; Bourzutschky, 2005).

Caramel compounds are by-products of the decomposition of sucrose to fructose and glucose at very high temperatures (>433 K). Other by-products are a variety of colloidal polymeric components occurring due to condensation, isomerization, and dehydration reactions. Again molecular masses in excess of 2,500 Da are found (Godshall & Baunsgaard, 2000; Davis, 2001; Coca, 2004; McKee et al., 2011).

The indigenous sugar cane polysaccharides, a type of arabinogalactan, end up in the sugar or molasses stream as they are not affected by the process. They are highly soluble, contain glucuronic acid units and have molecular masses up to 300,000 Da (Clarke et al., 1986). Furthermore, polyphenolic acids and functional dicarboxylic groups are attached. Literature suggests that these components form dark-colored structures with high molecular mass. These components are preferentially incorporated into the sucrose crystal matrix (Godshall & Baunsgaard, 2000; Godshall et al., 2002).

In the beet sugar production melanins are formed due to the oxidation of cell substances (e.g. tyrosine) primarily introduced due to beet slicing and the extraction step. These melanins are insoluble in aqueous solutions. They precipitate and are hence predominantly separated from the juice during the various purification steps due to precipitation (van der Poel, P.W., 2000). If the melanins however pass carbonation, darkening of the produced sugars can occur (Shore et al., 1984). The nitrogen content in the beet sugar production is usually higher than in the cane sugar production. This high nitrogen content induces melanoidin formation due to *Maillard* reaction even at the low process temperatures (ambient temperature). At higher temperature and alkaline conditions ($\text{pH} > 11$ and $T = 358$ K) in the subsequent process steps, such as extraction and juice purification, the *Maillard* reactions are further enhanced. During the liming and carbonation steps process conditions are such that amides are saponified (approx. 70%) and most of invert sugars, polysaccharides (e.g. pectins), organic acids, and polyphenols are decomposed or removed from the juice (van der Poel, P.W., 2000). Even though this reduces the relevant concentrations the *Maillard* reactions still proceed due to the high temperatures (up to 393 K) and long downstream retention times (Coca, 2004). As pointed out by Asadi (2007) caramelization as color generating process is not relevant here since temperatures remain below 433 K. Next to the *Maillard* reactions, alkaline degradation of invert sugars during carbonation generates additional coloring compounds with higher molecular mass (Godshall et al., 2005; McKee et al., 2011).

In summary the colorants in beet syrups contain a high proportion of melanoidins with relative low affinity to incorporation into the sucrose crystal structure (Paton, 1992). In contrast most of the precursors and colorants found in cane sugar production originate from the plant. These plant

pigments are low molecular mass compounds such as phenolics and flavonoids and serve as precursors for the high molecular mass colorants present downstream (Lindeman & O'Shea, 2001). After the milling and extraction processes cane juices contain a range of colorants composed of e.g. pigments and polysaccharides of high molecular mass (e.g. indigenous sugar cane polysaccharide, starch and arabinogalactan) which tend to form complexes. These coloring complexes are preferentially incorporated into the sucrose crystals (Godshall et al., 2002; Godshall et al., 1987; Tu et al., 1977; Godshall & Baunsgaard, 2000).

Another source of colorants is enzymatic browning (melanin formation) immediately after cutting and shredding the sugar cane. As Bucheli & Robinson (1994) point out this process stops due to thermal deactivation of the enzyme or substrate depletion. The solubility of melanin pigments is sensitive to pH making them practically insoluble at higher pH-values. Because of the elevated concentration of invert sugar in the juices milder conditions are applied during the purification of cane juices. The harsh conditions of the beet sugar purification process favor the degradation of invert sugars. Applying these conditions during cane processing is consequently not recommended because the resulting degradation products would be detrimental for the crystallization process. The consequently applied lower pH-value in cane processing favors that melanins remain dissolved (Rein, 2007; van der Poel, P.W., 2000) and are subsequently incorporated into the sucrose crystal (Paton, 1992). Additionally, *Maillard* reactions and alkaline degradation occur leading to darker color values and colorants of higher molecular mass (Rein, 2007).

In general, incorporation is affected by the crystal growth rate, nature and concentration of the impurities (Ferreira et al., 2009; Lionnet, 1998a; Godshall et al., 2002; Mantovani et al., 1986b, 1986a; Rein, 2007). In depth knowledge on the incorporation mechanism of colored compounds and other impurities such as ash is necessary in order to improve the final white sugar quality and to optimize process conditions accordingly. Three different color incorporation mechanisms are considered. These are namely adsorption onto the crystal surface, liquid inclusion and co-crystallization.

At first adsorption is nothing else than binding of coloring molecules onto the crystal surface. Obviously, this relates to the so-called surface color. The color effect due to adsorption is however reduced during the centrifugal washing step (Grimsey I.M. & Herrington, 1996; van der Poel, P.W., 2000).

The liquid inclusion mechanism relates to the inclusion of the mother liquor into crystal voids. This happens when liquid is adhered in a defect of the crystal surface like a groove. On further crystal growth this liquid is overgrown and hence entrapped within a void of the crystal matrix (Grimsey & Herrington, 1994; Mackintosh & White, 1968; Saska, 1988; Vaccari et al., 1990b). It goes without saying that high growth rates support this color inclusion mechanism. The so-called phenomenon of inner color is commonly explained by liquid inclusions (Singh & Delavie H.J., 1974). Furthermore it is generally acknowledged that ash inclusion is also related to this

mechanism (Grimsey I.M. & Herrington, 1996). The contribution to color values according to this mechanism is hence proportional to both the colorants concentration in the mother liquor and the level of liquid inclusion.

In the co-crystallization process it is assumed that co-crystallizing impurities have similar crystal growth properties and lattice parameters as sucrose (Singh & Delavie H.J., 1974). Grimsey I.M. & Herrington (1996) stated that some colorants depending on their molecular structure tend to form clusters with sucrose in the mother liquor due to their physical and chemical properties being similar to sucrose. These clusters of high molecular mass appear to have a high affinity with the sucrose crystal matrix and consequently co-crystallize despite the size differences (Grimsey I.M. & Herrington, 1996).

One can distinguish between liquid inclusion and co-crystallization by considering the concentrations of impurities and colorants in the mother liquor and the sugar crystal. Simple mass balances reveal that liquid inclusion can only lead to sugar color values dramatically lower than the color value of the mother liquor.

In sugar industry the so-called color transfer factor k_{color} (Chiu & Sloane G.E., 1980) has been introduced to pragmatically estimate the final sugar color. The color transfer factor is expressed as the ratio of affinated sugar color value $F_{420,s}$ to the feed syrup color value $F_{420,ML,0}$ (Lionnet & Moodley, 1995):

$$k_{color} = \frac{F_{420,s}}{F_{420,ML,0}} \cdot 100\% \quad (5-1)$$

Usually the color transfer factor in beet is lower than in cane sugar manufacturing. Typical values for sugars produced from beet are around 1% while for cane sugar production values from 6 to 10% are reported (Godshall et al., 2002; Godshall & Baunsgaard, 2000). Beet sugar with acceptable color values of 20 to 30 IU (ICUMSA units) is usually crystallized from thick juices with color values between 2,000 and 3,000 IU. Raw cane sugar of high quality has a color value of 1,000 to 2,000 IU and is crystallized from thick juices with color values between 10,000 and 18,000 IU.

The differences in the behavior of the colorants in beet and cane sugar production are also manifested in the process steps yielding the final white sugar. While in beet sugar production the white sugar can be produced in one crystallization step, white cane sugar production is only possible after re-dissolution of the brownish raw cane sugar. Prior to the final crystallization of white cane sugar the resulting syrup needs to be purified. A detailed description of the beet and cane sugar processing can be found elsewhere (Asadi, 2007; Rein, 2007; van der Poel, P.W., 2000). It is known that the final color of the end product of cane and beet sugar production relates to the physiology of the plant. The components responsible for the colorants have different physical and chemical properties. Consequently, the colorants' incorporation mechanisms are different.

From the excessive body of work covering the color in sugar crystallization the work reported by Kochergin et al. (2012) is the only one concerning sucrose crystallization from blended beet and cane syrups. The results reported suggest that in mixed syrups the colorants originating from cane have a stronger relative contribution to the resulting sugar color value than colorants of beet origin. However, the reported data do not allow to draw firm conclusions on the interactions of the colorants from different origin because of insufficient control of the crystallization process. The focus of the work reported here is the identification of the effect of colorants from either beet or cane origin on the color value of sugars produced from mixed syrups. To this end sucrose has been crystallized from various mixed syrups composed of beet thick juice and dissolved raw cane sugar. The colorants and ash incorporation for resulting sugars were analyzed. Additionally, to the evaluation of the contribution of the different color incorporation mechanisms an attempt is made to formulate a framework describing the systematic evolution of sugar color during co-processing. Without being bound by any experimental data one could formulate two simple mixing models. On one hand one could assume that colorants from beet and cane origin behave completely independently from each other. This implies that the color transfer factors per origin are applied exclusively to respective color contribution (colorants) in the mixed feed syrup. Simple summation of both contributions yields a forecasted final sugar color value. For example the final sugar color value for the currently acknowledged cane inclusion level (80% beet syrup and 20% cane syrup) is:

$$F_{420,s,x=0.8} = \frac{k_{color,x=1}}{100\%} \cdot F_{420,ML,0,x=1} \cdot 0.8 + \frac{k_{color,x=0}}{100\%} \cdot F_{420,ML,0,x=0} \cdot 0.2 \quad (5-2)$$

Another practical approach, technically less sound though, assumes a linear combination of the color transfer factors applied to the color value of the complete mixed feed syrup, which is obviously a linear combination of value of the two original syrups:

$$F_{420,s,x=0.8} = \left(\frac{k_{color,x=1}}{100\%} \cdot 0.8 + \frac{k_{color,x=0}}{100\%} \cdot 0.2 \right) \cdot (F_{420,ML,0,x=1} \cdot 0.8 + F_{420,ML,0,x=0} \cdot 0.2) \quad (5-3)$$

Applying these models to forecast sugar color values based on the feed syrups used in this work - color values of 2000 IU for beet syrup and 1200 IU for cane syrup - and the typical color transfer factors in the beet and cane sugar industry, 1% and 6% respectively (Godshall & Baunsgaard, 2000; Godshall et al., 2002), the color value for sugars crystallized from blended syrups can be computed. For an 80:20 beet to cane mixture the forecasted sugar color value is 30.4 IU for an independent inclusion process and 36.2 IU for a linear dependence of the color transfer factors. These values are close to the above-mentioned quality threshold of 30 IU and hence correspond to the acknowledged safe inclusion level of 20% raw cane sugar. Based on the data gathered these models are evaluated and a new correlation for the prediction of color values of sugars produced from mixed beet and cane syrups is suggested.

5.1 Material and methods

5.1.1 Experimental set-up

The crystallization experiments are performed in an evaporation pilot-plant (volume 0.005 m³). The schematic set-up is given in Figure 5-2. After the crystallization, the crystals are separated from the mother liquor (impure sugar solution) using a centrifuge (DM 2250, Gebr. Heine,

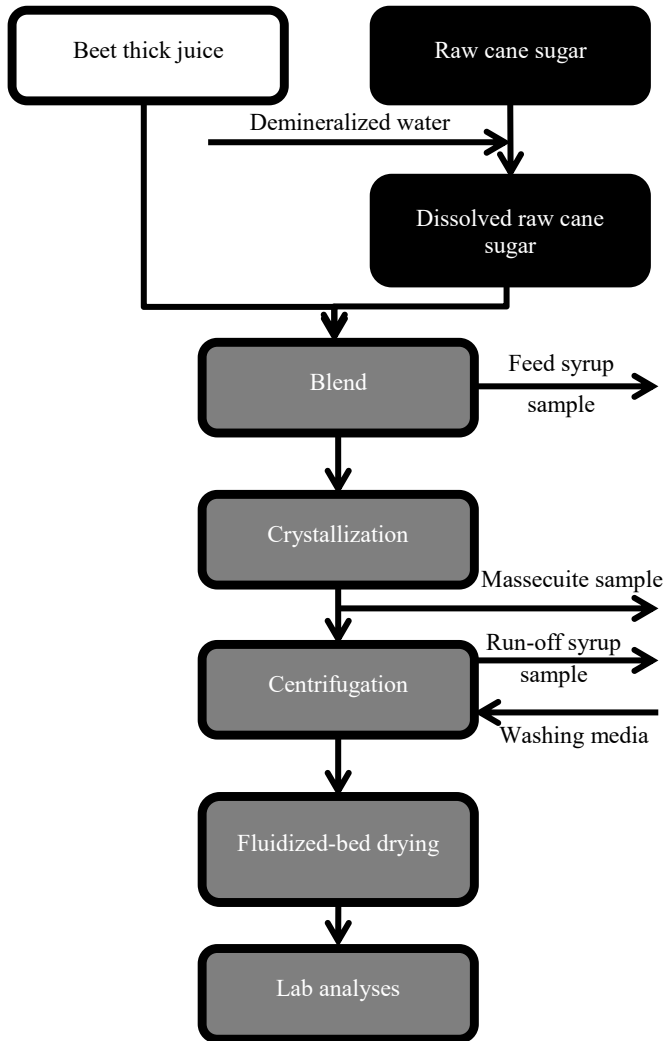


Figure 5-2: Procedure of the executed experiments.

A process refractometer (iPR 2-3, Schmidt & Haensch GmbH & Co., Berlin, Germany) (2 in Figure 5-3) is mounted to the bottom of the vessel to determine the dry substance content of the mother liquor. The pressure is established using a low pressure pump (PC 3001, Vacuubrand GmbH & Co KG, Wertheim, Germany).

With the help of a PC the experimental set-up is controlled and experimental data are recorded on-line. Software based on LabVIEW (National Instruments Corporation, Munich, Germany) was developed for this purpose.

Viersen, Germany) and dried in a fluidized-bed. The complete design of the pilot-plant and supporting units are described in detail elsewhere (Schlumbach et al., 2015)(Figure 5-3). It was shown earlier that the crystallization and subsequent process steps, such as separation and drying, allow the production of sugar of industrial relevant quality (Schlumbach et al., 2015).

The vessel is kept at a constant high temperature by two independent hot water flows through the upper and lower jackets. The temperature of the heating water is controlled by thermostats (F32-HD and F12-MC, both Julabo, Seelbach, Germany). A Pt-100 thermo element is submerged into the mother liquor to monitor the temperature during the experiment.

Subsequent to the crystallization strike the sugar is separated from the mother liquor in a temperature controlled basket centrifuge. In analogy to the industrial practices a self-constructed washing unit with a flat-jet nozzle is installed to wash the residue syrup from the surface of the crystals during the centrifugation process. The experiment is completed by drying the sugar in a TU Berlin designed fluidized-bed dryer.

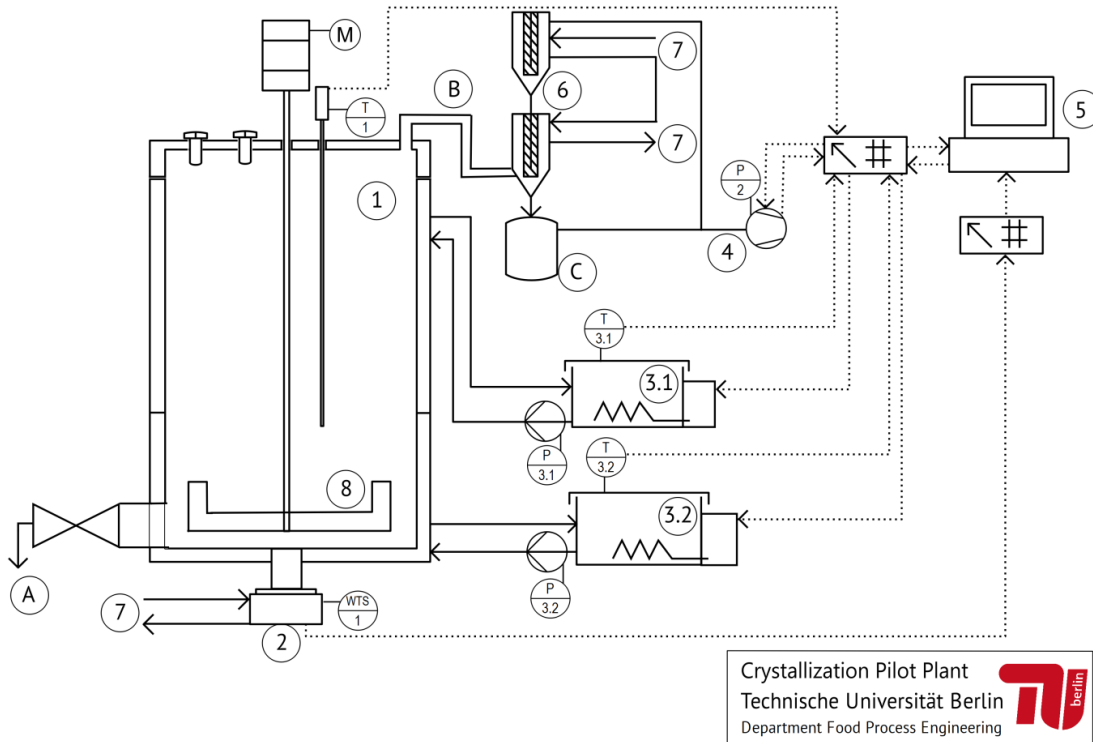


Figure 5-3: Crystallization pilot plant and ancillary equipment. 1 Vessel; 2 Refractometer; 3.1 Thermostat; 3.2 Thermostat; 4 Vacuum pump; 5 Data processing unit; 6 Cooler; 7 Cooling water; 8 Stirrer; A Massecuite outlet; B Vapor; C Condensate

5.1.2 Experimental procedure

In Figure 5-2 the experimental procedure is described schematically. The feedstock for crystallization runs are blends of beet thick juice from a German sugar factory and a solution of dissolved raw cane sugar (Brazil) with different mixing ratios (Table 5-1). Prior to each experimental run the solution of dissolved raw cane sugar was prepared using demineralized water ($< 2 \mu\text{S/cm}$). For all experiments two parts of mass of raw cane sugar and one part of water were mixed at ambient temperature.

For the crystallization 5000 g of blend are sucked into the vessel (Figure 5-3), after the vessel was evacuated (270 mbar (± 1 mbar)) by means of the low pressure pump. During the experiment no further feed syrup was added. After the crystallizer was filled the blend was stirred and kept homogeneous by means of an agitator (60 rpm) (RZR 2102 control, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany). The vessel was heated via the jackets. One thermostat (3.2 in

Figure 5-3) was kept at a high temperature of 361 K (± 0.01 K) to heat the stainless-steel vessel to drive water evaporation from the mother liquor. The other (3.1 in Figure 5-3) was kept at a lower temperature of 343 K (± 0.01 K) acting as an active insulator of the vessel to avoid nucleation and sucrose deposition on the wall.

Table 5-1: Quality parameters of the blended feed syrups according to refractometric dry substance, purity, color value measured at pH 7 and ash content.

Beet content	Cane content	Dry substance	Purity	Color at pH 7	Ash content
%	%	g/100 g	%	IU	%
100	0	67.22	94.91	2021	1.19
80	20	67.11	95.99	1733	0.97
60	40	66.97	96.76	1681	0.86
40	60	66.71	97.57	1459	0.57
20	80	66.59	98.53	1362	0.33
0	100	65.89	99.16	1221	0.10

Table 5-2: Material and chemicals used for laboratory analysis.

Chemicals & Materials	Distributor
Carrez I solution (21.9 g of zinc acetate dihydrate and 3 g of glacial acetic on 100 ml water)	Bernd Kraft, Duisburg, Germany
Carrez II solution (10.6 g of Potassium hexacyano ferrate(II) trihydrate on 100 ml water)	Bernd Kraft, Duisburg, Germany
Celite Hyflo Super Cel®	Carl Roth GmbH & Co. KG, Karlsruhe, Germany
CHROMAFIL® membrane filters GF/PET 0.45 µm	Machery-Nagel GmbH & Co. KG, Düren, Germany
Filter paper MN 631	Machery-Nagel GmbH & Co. KG, Düren, Germany
Hydrochloric acid solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
Sodium hydroxide solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
10 mm UV-cuvette (612-5685)	VWR International, Darmstadt, Germany
50 mm glass cuvette 100-OS (634-9017)	VWR International, Darmstadt, Germany

After sufficient stirring time a sample was taken from the homogeneous sample and analyzed. These data define a reference state. The actual crystallization was started once a supersaturation of 1.10, determined using the data of the process refractometer, temperature and purity of the solution, was achieved. At that point seed crystals of a size of $d_{Cr,0} = 282.5 \mu\text{m}$ and a color value of 35 IU obtained by sieving industrial sugar were added. The amount of seed crystals $m_{Cr,0}$ was calculated by the d^3 -Rule (Witte, 1987):

$$m_{Cr,0} = m_{Cr,1} \cdot \left(\frac{d_{Cr,0}}{d_{Cr,n}} \right)^3 \cdot \frac{N_{Cr,0}}{N_{Cr,n}} \quad (5-4)$$

with $N_{Cr,i}$ the number and $m_{Cr,i}$ the mass of crystals. The index '0' indicates the state at the beginning of the crystallization, the index 'n' the end of the crystallization, and thus the end of the experiment. For the calculation the desired crystal size $d_{Cr,n} = 800 \mu m$ and the number of crystals $N_{Cr,n} = N_{Cr,0}$ was used.

Due to the constant pressure and heat supply the supersaturation was kept constant at a value of $1.07 (\pm 0.01)$ throughout the crystallization process. The end of the crystallization strike is indicated once the torque of the agitator increased by a value of 0.06 Nm compared to the starting value. This increase relates to a crystal content of approximately 50 g/100 g . A sample of the massecuite was taken. After crystallization the sucrose crystals were separated from the mother liquor using a centrifuge. The G-force was $1,450$ which is close to typical industrial values (van der Poel, P.W., 2000; Schlumbach et al., 2015). Also a sample of the run-off syrup was taken. A self-constructed washing unit washed the residual syrup film from the crystal surface to ensure low sugar color and to inhibit subsequent agglomerate formation. The optimum amount of water (343 K) for the washing was determined in earlier experiments, 2.5 g/100 g of the mass of the massecuite (Schlumbach et al., 2015). After separation the sugar was dried in a fluidized-bed for 10 minutes with conditioned air at a temperature of 343 K to a residual water content of $0.04 (\pm 0.01) \text{ g/100 g}$.

Table 5-3: Devices used for experiments and lab analysis.

Device	Labelling	Manufacturer
Agitator	RZR 2102 control,	Heidolph Instruments GmbH & Co.KG
Centrifuge (process)	DM 2250	Gebr. Heine, Viersen, Germany
Centrifuge (laboratory)	Sieva-2	Hermle Labortechnik GmbH, Wehingen, Germany
Conductometer	SevenEasy	Mettler Toledo, Gießen, Germany
Conductometer electrode	Inlab 730	Mettler Toledo, Gießen, Germany
pH-meter	Seven Excellence	Mettler Toledo, Gießen, Germany
pH-electrode	Inlab Routine Pro	Mettler Toledo, Gießen, Germany
Polarimeter	Saccharomat NIR W2	Schmidt & Haensch, Berlin, Germany
Refractometer (laboratory)	ATR W2 plus & ATR	Schmidt & Haensch, Berlin, Germany
Refractometer (process)	iPR 2-3	Schmidt & Haensch, Berlin, Germany
Sieve shaker	AS 200 Control	Retsch Technology GmbH, Haan, Germany
Spectrophotometer	SPEKOL 1300	Analytic Jena, Jena, Germany
Thermostats	F32-HD F12-MC	Julabo, Seelbach, Germany
Ultrasonic bath	Sonorex RK 100H	BANDELIN electronic GmbH & Co. KG, Berlin, Germany
Vacuum pump	PC 3001	Vacuubrand GmbH & Co KG, Wertheim, Germany

5.1.3 Analysis and data processing

The analysis is conducted according to the analytical methods used in the sugar industry given in detail elsewhere (ICUMSA, 2011). In Table 5-2 to Table 5-4 the materials, chemicals, and devices used for the analyses are listed.

All analytical methods are applied to solutions. Prior to analysis the massecuite and the (run-off) syrup samples needed to be diluted 1:1 (w/w) with demineralized water. The dry substance content (w_{DS}) of the feed syrup, massecuite and run-off syrup were determined by refractometer; the sucrose content (w_S) by polarization after clarification with *Carrez* following the ICUMSA Method GS8-2. With these data the purity q (in %) of a solution or sugar sample can be calculated:

$$q = \frac{w_S}{w_{DS}} \cdot 100 \quad (5-5)$$

The ash content is determined using ICUMSA Methods GS1/3/4/7/8-13 and GS2/3/9-17 (ICUMSA, 2011) which are based on conductivity. The ash content C_{Ash} (in % (w/w)) is calculated using the conductivity of water, C_w , and of the sample at 293 K, C_I :

$$C_{Ash,s} = 6 \cdot 10^{-4} \cdot (C_I - 0.35 C_w) \quad (5-6)$$

The ash content of the syrup $C_{Ash,s}$ (in % (w/w)) is calculated by:

$$C_{Ash,ML} = (16.2 + 0.36 \cdot \frac{w_{DS}}{100}) \cdot 10^{-4} \cdot (C_I - C_w) \cdot \frac{5}{S} \quad (5-7)$$

with w_{DS} the dry substance and S the mass of the sample in 100 ml. The ash transfer factor is calculated by:

$$k_{Ash} = \frac{C_{Ash,s}}{C_{Ash,ML,0}} \cdot 100\% \quad (5-8)$$

The color of the feed syrup, massecuite, run-off syrup, sugar and affinated sugar is determined using the modified analytical methods GS1/3-7 and GS2/3-10 based on absorbance at a wavelength of 420 nm (ICUMSA, 2011). In this modified method the pH-value was adjusted with hydrochloric acid or sodium hydroxide solutions to values of 4, 7, and 9 (Smith & Gregory, 1971). The color value (IU) of the solution is given in ICUMSA units according to:

$$F_{420} = \frac{10^8 \cdot A_s}{b \cdot w_{DS} \cdot \rho} \quad (5-9)$$

with b the length of the cuvette (1 cm for syrup, 5 cm for dissolved sugar), w_{DS} the dry substance and ρ (kg m⁻³) the density.

To quantify the colorants and ash removal from the crystals these were subjected to affination. This means that the sugar crystals subsequent to centrifugation and washing were exposed to a saturated sugar solution with a color value of less than 15 IU under stirring for 15 min and 5 min. In the following the affinated – surface cleaned – sucrose crystals were separated from the solution by means of a lab centrifuge (3,600 rpm). This procedure was repeated twice. After the affination the sugar crystals were dried in a desiccator before analyzing.

The color removal R_{color} after affination was computed by:

$$R_{color} = 100 - \frac{F_{420,s}}{F_{420,s'}} \cdot 100\% \quad (5-10)$$

where $F_{420,s}$ and $F_{420,s'}$ are the color values of affinated and non-affinated sugar. The ash removal R_{ash} is calculated analogous to equation (5-10).

The particle size determination according to ICUMSA Method GS2/9-37 (2007) (van der Poel, P.W., 2000) gives the mean aperture (d_{50}) and the coefficient of variation (CV). Based on these data the crystal growth rate G ($\text{kg m}^{-2}\text{s}^{-1}$) can be calculated according to Bubnik & Kadlec (1992):

$$G = \frac{3\rho \cdot \alpha}{\beta} \cdot \frac{\Delta d_{50}}{\Delta \tau} \quad (5-11)$$

wherein the crystal shape factor α is set equal to 0.75 for sucrose crystals and Δd_{50} is the difference between the mean aperture size of the end and seed crystals. Furthermore, the surface area shape factor β is set to 5.02. The density of sucrose crystals ρ is $1,587 \text{ kg m}^{-3}$. The duration of the crystallization process is expressed by τ and is the period between seeding and end of the crystallization.

Table 5-4: Analytical methods for determination of quality parameters.

Parameter	Method	Analytical device
Dry substance	Refractometric	ATR & ATR W2, Schmidt & Haensch
Polarisation of sugar syrups	Polarimetric (GS8-2)	Saccharomat NIR W2, Schmidt & Haensch
Ash content	Conductometric (GS1/3/4/7/8-13 (1994), GS2/3/9-17 (2011))	SevenEasy, Mettler Toledo, Inlab 730
Color	Spectrophotometric (GS1/3-7 (2011), GS2/3-10 (2005))	Spekol 1300, Analytik Jena
Particle size distribution	Sieving (GS2/9-37)	AS 200 Control, Retsch
pH-value	Electrometric	SevenExcellence, Mettler Toledo InLab® Routine Pro, Mettler Toledo

Table 5-5: Mean values and standard deviation of mean aperture d_{50} and coefficient of variation CV from sieve analyses and crystal mass growth rates G of duplicated crystallization experiments.

Beet to cane content	d_{50}	\pm	CV	\pm	G	\pm
%	mm	mm	%	%	kg m ⁻² s ⁻¹	kg m ⁻² s ⁻¹
100:0	0.736	0.008	27.12	0.47	$2.88 \cdot 10^{-5}$	$2.18 \cdot 10^{-6}$
80:20	0.751	0.012	18.75	0.16	$3.03 \cdot 10^{-5}$	$4.91 \cdot 10^{-6}$
60:40	0.797	0.029	20.06	0.93	$3.63 \cdot 10^{-5}$	$9.72 \cdot 10^{-6}$
40:60	0.799	0.003	19.93	0.14	$3.52 \cdot 10^{-5}$	$8.36 \cdot 10^{-6}$
20:80	0.759	0.004	18.87	0.03	$3.91 \cdot 10^{-5}$	$6.22 \cdot 10^{-6}$
0:100	0.797	0.034	18.79	0.26	$4.66 \cdot 10^{-5}$	$2.26 \cdot 10^{-6}$

5.2 Results and discussion

5.2.1 Crystallization process

All crystallization runs were performed in duplicate. The processing was conducted in a most consistent manner to avoid that variations of the color transfer are a result of varying process conditions. This because particle size distribution and crystal growth conditions might affect the color inclusion (Singh & Delavie H.J., 1974; Lionnet, 1998a, 1998b). Characteristic data illustrating the consistency of experimentation are shown in Figure 5-4 and Table 5-5. The purity data of the feed syrup and the massecuite (Figure 5-4A) are in good agreement and show the expected linear decrease with increasing beet content. The decrease in purity of the run-off syrups corresponds very well with the data of the feed syrup and the final crystal content (50 g/100 g). Figure 5-4B depicts the values on the final mean aperture. The desired mean aperture of 0.800 mm is not reached perfectly in all experiments. However, an average value of 0.77 with a SD of 0.03 supports that only minimal process variations were encountered (Delavie H.J. & Hirschmüller H., 1968; Lionnet, 1998a, 1998b). The coefficients of variation (Figure 5-4C) between 18.7% and 20.0% indicate a narrow particle size distribution. For the pure beet syrup a *CV* of 27.1% is found which is still considered an adequate grain size distribution (van der Poel, P.W., 2000).

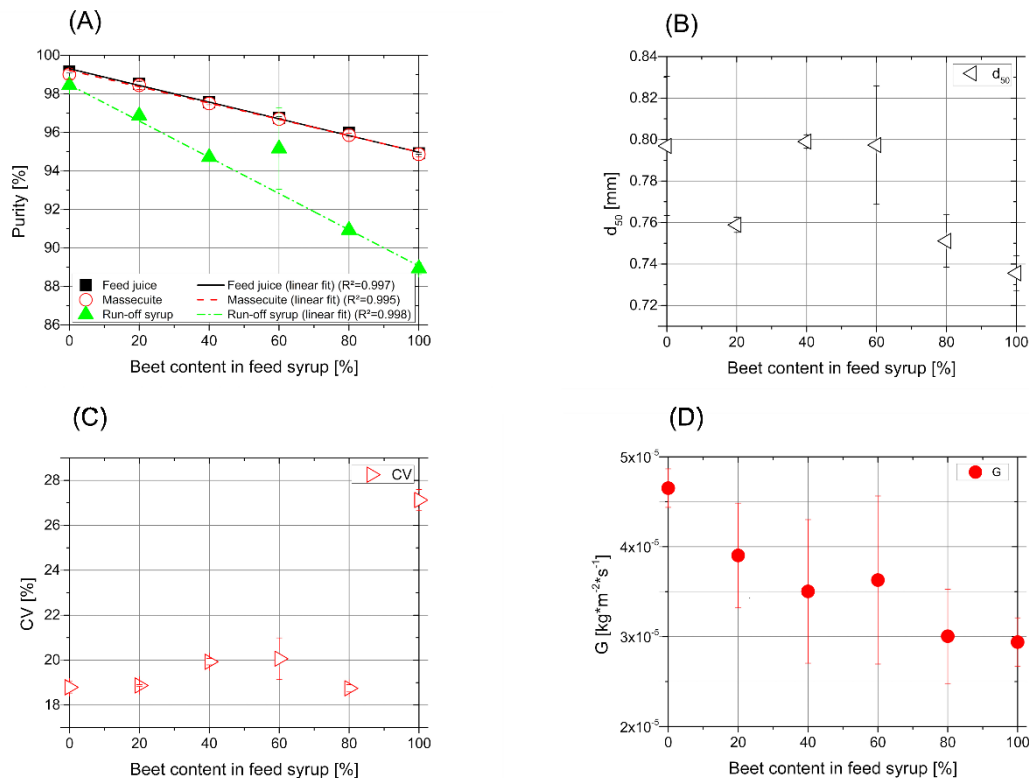


Figure 5-4: Data of general analyses from the crystallization experiment: (A) Purity of the feed syrup (■, solid line), massecuite (○, dashed line) and run-off syrup (▲, dash-dotted line). (B) Mean aperture (◁) and (C) coefficient of variation (▷) determined by sieve analysis. (D) crystal mass growth rate (●).

The crystallization rates according to Bubnik & Kadlec (1992) are displayed in Figure 5-4D. They are decreasing with increased beet content in the mixture from $4.65 \cdot 10^{-5}$ to $2.93 \cdot 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$.

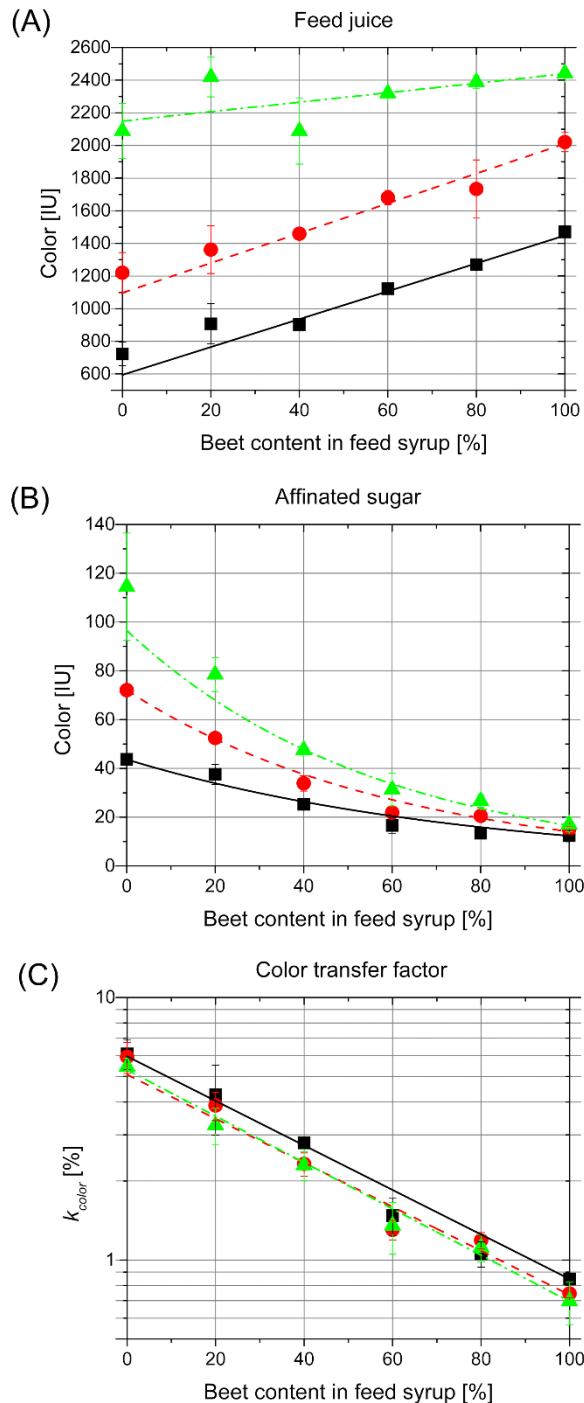


Figure 5-5: Color of feed syrup (A) and affinated sugar (B) determined at different pH-values and the resulting color transfer factor (C): pH 4 ■ (straight line), pH 7 • (dashed line), pH 9 ▲ (dash-dotted line). The lines from (A) are linear fitted and the curves in the graphs (B) and (C) are exponential fitted.

This behavior is probably due to increasing purity of syrups richer in cane syrup accelerating crystal growth (van der Poel, P.W., 2000). Also this trend has to be taken into account when discussing color and ash inclusion levels because higher crystal growth rates are known to lead to increased transfer rates (Lionnet, 1998b; Singh & Delavier H.J., 1974; Saska, 1988; Guo, 1984).

5.2.2 Color transfer

The color values of the feed syrups and affinated sugars and the resulting color transfer factors are shown in Figure 5-5. The analyses are performed at different pH-values to obtain more detailed information on the transfer mechanism of the different colorants.

Regarding the color values for the series of syrups from pure beet thick juice to raw cane sugar solution it is not surprising that a linear relation is found for each pH-value (Figure 5-5A). At higher pH-values higher color values are found. As reported earlier phenolic colorants originating from the cane plant cause higher color values at higher pH (Lindeman & O'Shea, 2001; Godshall, 1997; Davis, 2001). This

correlates well with the increased relative contribution of the cane colorants to the mixture

properties resulting in the change of the slope of the color values found for the absorption measurements at pH 9 in Figure 5-5.

The color data of the affinated sugars produced from the syrups characterized in Figure 5-5A are illustrated in Figure 5-5B indicating an exponential increase with increasing cane levels at pH-values of 4 and 7. At pH 9 the values at high cane content appear elevated beyond this relation which is due to their prominent pH sensitivity as shown already in Figure 5-5A. The color value of the pure beet syrup based sugar is around 20 IU at all pH-values. The color values for pure cane sugar are 43 IU, 72 IU, and 115 IU for pH-values of 4, 7, and 9 respectively. The different sensitivity of the color value determination of the pure syrups is perfectly in line with expectations (Lindeman & O'Shea, 2001; Godshall, 1997; Davis, 2001). The color values of sugars crystallized from mixed syrups show a systematic behavior increasing with increasing cane content.

The color transfer factors derived from the primary data according to equation (5-1) are depicted in Figure 5-5C. It is obvious from the results in Figure 5-5A and B that the color transfer factors determined at pH-values of 4, 7 and 9 are increasing exponentially with the composition. For pH 7 the data for pure syrups are in good agreement with literature (Godshall & Baunsgaard, 2000; Godshall et al., 2002). Beyond the clear systematic found in the semi-logarithmic graph it is remarkable that the transfer factors appear to be the highest when derived from the absorption measurements at pH 4. This result is in agreement with the literature suggesting that coloring matter particularly active at pH 4 is preferentially incorporated into the sucrose crystal. The relating non-phenolic high molecular weight colorants originate from the cane plant (Paton, 1992; Godshall et al., 1987; Wright, 2002).

The systematic study reported here confirms our initial results indicating that the colorants from different origin, beet or cane, suppress the mutual incorporation into the sugar crystal (Schlumbach et al., 2016).

The data displayed in Figure 5-5C allow to formulate another approach to forecast the color value of sugar produced from mixed syrups. Based on an exponential evolution of the transfer factors $k_{color,x}$ with composition equation (5-12) is derived.

$$F_{420,s,x} = \frac{k_{color,x=0}}{100\%} \cdot \exp(\ln(k_{color,x=1}/k_{color,x=0}) \cdot x) \cdot (F_{420,ML,0,x=1} \cdot x + F_{420,ML,0,x=0} \cdot (1 - x)) \quad (5-12)$$

In Figure 5-6 the three different approaches (equations (5-2), (5-3) and (5-12)) to forecast the color value of sugar crystallized from mixed syrups are compared. In detail these are:

- Linear: Linearly interpolated color transfer factor applied to color values of the mixed feed syrup.
- Independent: Summation of the contribution from colorants per origin determined independently from each other.

- Exponential: Exponentially interpolated color transfer factor applied to color values of the mixed feed syrup.

Since the color values and transfer factors for the pure beet and cane syrups are input data to all calculations it is inherent that the deviations between experimental and forecasted data displayed are zero for syrups from a single origin. In this light it is not surprising that the relative deviations found for all pH-values are most prominent in the intermediate composition range. It is remarkable that all forecasting methods overestimate the color values found. This is valid for all pH-values studied. Both the Linear and Independent model indicate color values with continuously positive deviations in excess of 50%. In contrast the Exponential model formulated in this work describes the data quite consistently. Since the deviations found are much less systematic than for the other models these could be due to the experimental accuracy as indicated by the error bars given. The data clearly indicate that the colorants originating from different sources appear to suppress mutually their inclusion into the crystalline sugar. Colorants originating from cane have high molecular masses and hence low diffusion coefficients (Edward, 1970). These compounds consist of colorants and polysaccharides giving them a sucrose-like outer structure supporting incorporation into the crystal lattice (Tu et al., 1977; Godshall & Baunsgaard, 2000; Godshall et al., 1987; Godshall et al., 2002). This process is generally recognized to be the reason for high color transfer factors (5 to 6%) in cane sugar processing. In contrast the smaller and thus more diffusive colorants occurring in beet sugar production have a high affinity to adsorb onto the crystal surface or to be subject to liquid inclusions (Grimsey

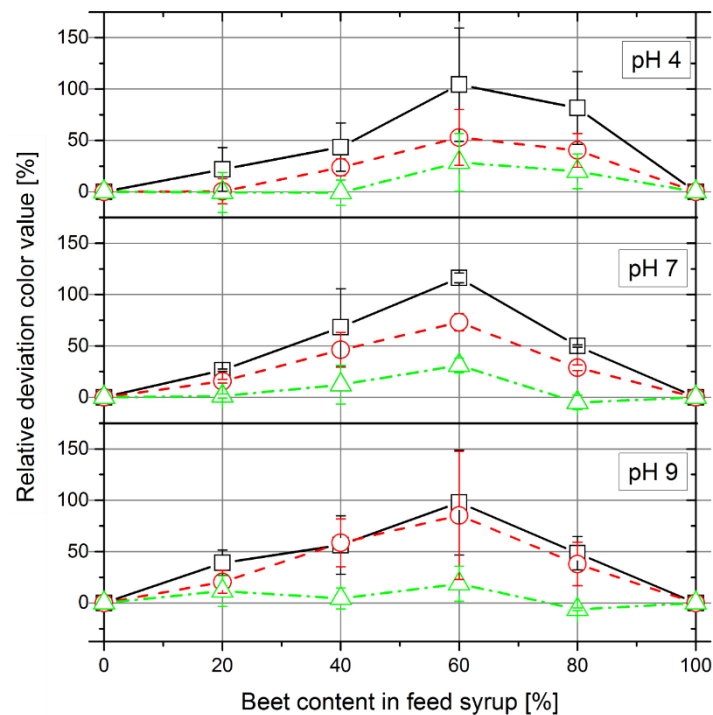


Figure 5-6: Relative deviation of experimental to modelled sugar color values computed by linear (□, straight line), independent (○, dashed line) and exponential (△, dash-dotted line) model.

I.M. & Herrington, 1996; Shore et al., 1984). This results in color transfer factors of less than 1%. Combination of these two mechanistic views suggests the mechanistic hypothesis that compounds originating from beet juice temporarily or permanently adsorb onto the crystal surface and consequently prevent incorporation of the colorants originating from cane. The more mobile beet colorants prevent or at least disturb the development of an adsorption layer based on cane colorants which can be regarded a prerequisite for the inclusion.

5.2.3 Ash transfer

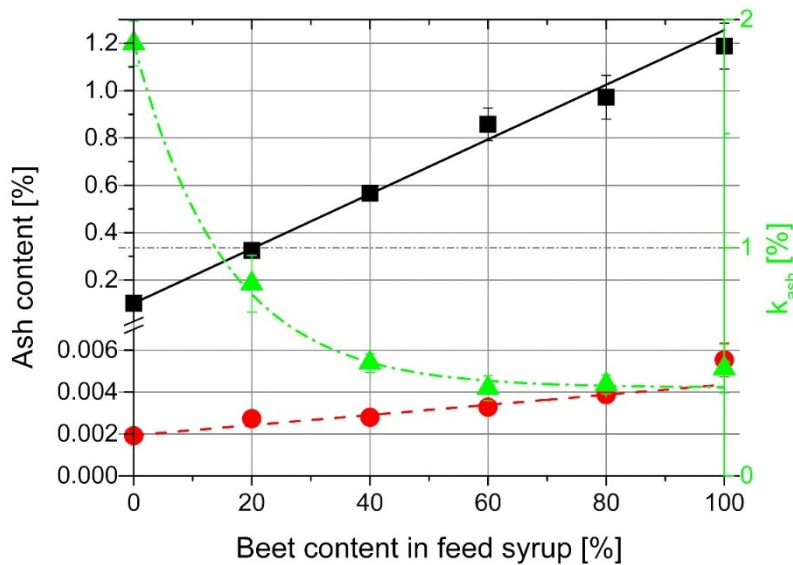


Figure 5-7: Ash content of feed syrup (■, straight line), affinated sugar (●, dashed line) and the resulting ash transfer factor (▲, dash-dotted line) which is related to the secondary y-axis.

Ash from the mother liquor is found in the crystal due to liquid inclusion. The simultaneous study of the ash inclusion allows drawing conclusions on the coloring of sucrose crystals based on liquid inclusion. The data on ash levels of the feed syrups, affinated sugars and resulting ash transfer factors according to equation (5-8) are displayed in Figure 5-7. The values of the feed syrups and affinated sugars refer to the primary y-axis which is broken between 0.006 and 0.2%. The computed ash transfer factors are plotted against the secondary y-axis. The values found for both the syrups and the affinated sugars increase linearly with increasing beet content in the syrup. For the ash content of affinated sugars the composition dependency is hence inverted compared to the one found for color values. This indicates that the results found for the color transfer in the mixed syrups is not based exclusively on liquid inclusion. The significantly higher ash transfer factors found for mixed syrups rich in cane material is most likely due to the presences of non-sucrose components which interact with the sucrose surface. For instance polysaccharides such as dextrans and starches can change the crystal habit by inhibiting the growth of a face (van der Poel, P.W., 2000; Mathlouthi & Reiser, 1994).

5.2.4 Color and ash removal by affination

The effect of the affination process on color values and ash content is documented in Figure 5-8. The affination process is designed to primarily remove material, colorants and ash, adhering to the crystal surface. This concerns material actually adsorbed onto the crystal surface but also mother liquor remaining attached to the crystal surface after centrifugation. The fact that ash

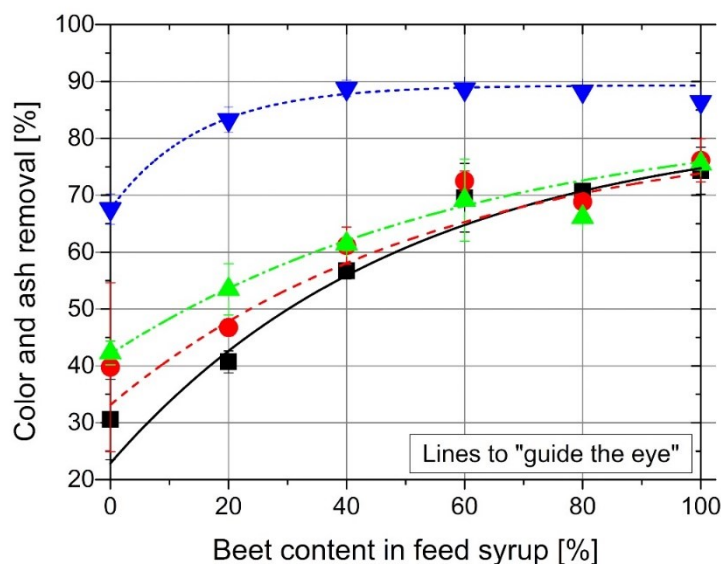


Figure 5-8: Color removal, determined at pH 4 ■ (solid line), pH 7 ● (dashed line), pH 9 ▲ (dash-dotted line), and ash removal ▼ (short dashed line) by affination of crystallized sucrose from blends of beet thick juice and dissolved raw cane sugar.

removal appears to be more effective than color removal is counter intuitive because ash levels in sugars are said to be predominantly due to liquid inclusions. However, for the non-affinated sugars the attached liquid had a significant contribution to both color and ash values. It turns out that the concentration differences of ash and color between the attached mother liquor and actual sugar crystal concentration – affinated sugar – are almost one order of magnitude larger for ash levels than for color levels. This explains the higher relative removal effect of affination on ash levels compared to color levels. The lower relative ash removal found for increasing levels of cane in the mixed syrup indicates that the level of liquid inclusions is increased with increasing cane levels. This is either due to the possible presence of dextran driving crystal imperfections or could be a side effect of the incorporation of the color-polysaccharide-complexes. This reasoning on liquid inclusion of ash holds simultaneously for the color inclusion. However, the increased level of cane in the mixed syrups causes an even more pronounced reduction of the color removal efficiency of the affination process. This is most likely due to the fact that the effect of color co-crystallization becomes more prominent on this composition change. The observation that the color values determined at pH-value 4, strongly related to colorants originating from cane, shows this effect most prominently further supporting this interpretation. This is in line with earlier work stating that colored components with high molecular mass in cane sugar are preferentially

included into the crystal lattice and hence difficult to remove during refining (Godshall, 1997; Paton, 1992; Godshall et al., 2002).

5.2.5 Mechanistic interpretation

The data presented in the previous section are used to derive a hypothesis on the contribution of the different inclusion mechanisms. The relative contribution according to the adsorption, liquid inclusion, and co-crystallization mechanism is expressed via the respective color transfer factors shown in Figure 5-9.

The color transfer according to liquid inclusion is assumed to occur simultaneously with the ash inclusion. This because for affinated sugar ash is assumed to be exclusively included due to liquid inclusions (Grimsey I.M. & Herrington, 1996; Singh & Delavier H.J., 1974). This way the color contribution due to inclusion of mother liquor is calculated. Since either liquid inclusion or co-crystallization contributes to the inner color the remaining proportion of the inner color value is due to co-crystallizing colorants.

The implication of these assumptions yields the picture shown in Figure 5-9. The color transfer factor for adhesion is calculated in line with equation (5-1) based on the difference of the color value for affinated and non-affinated sugar as input. It increases linearly from 2.5 to 5.0% on changing the composition from pure beet to pure cane syrup. It should be noted here that this specific color contribution is not part of Figure 5 which relates to affinated sugar. In contrast the transfer factor for color due to liquid inclusion, correlating to ash inclusion (see above) remains practically constant at 0.5% for inclusion levels up to 60% of cane syrup. At higher cane inclusion levels it increases to a maximum of 2.0% for pure cane syrup. The most dramatic change is found for the color transfer factor accounting for effects of co-crystallization. It increases exponentially

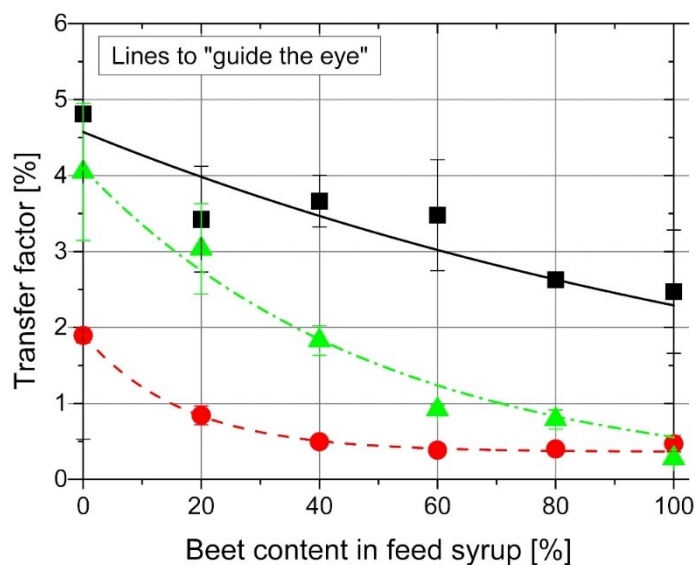


Figure 5-9: Mechanism specific color transfer factors determined at pH 7: Adsorption (■, solid line), liquid inclusion (●, dashed line) and co-crystallization (▲, dash-dotted line).

from 0.3% to approximately 4.0% on cane level increase. As this analysis illustrates the different mechanisms show a specific dependency on the composition of the mixed syrups. However, it has to be noted that the conclusion drawn here certainly needs further validation based on additional experimental results.

5.3 Conclusion

Sugar crystallization from sucrose solutions made up from mixtures of syrups originating from both cane and beet origin was studied systematically. The primary focus was the elucidation of the mutual effect of the coloring components from different origin on each other. Therefore, all process parameters were carefully controlled. In contrast to the abundant literature on the color incorporation in sugar crystallization from juices of a single origin, practically no data exist on the crystallization from mixed syrups. It is found that the different types of colorants have a profound effect on the overall color incorporation. The color values found are significantly lower than predictions based on either treating all colorants as one species ignoring their differences or the assumption that each type of colorants is incorporated independently. This mutual suppression of incorporation is particularly surprising because the earlier works on single origin syrups indicate that the colorants originating from cane or beet are incorporated via different crystal faces of the sucrose crystal (Mantovani et al., 1986a; van der Poel, P.W., 2000). The findings reported here further indicate that the current recommendation not to include more than 20% (w/w) of cane material into mixed syrups in order to meet quality standards (Kochergin et al., 2012) - color values of less than 30 IU - is way too conservative. Further analysis of the data allowed evaluation of the relative contribution of the different color incorporation processes considered in sugar processing. The contribution of adsorption was derived from differences between affinated and non-affinated sugar crystals. Evaluating the inclusion of mother liquor in the crystal via ash analysis allowed to disentangle both contributions to the so-called inner color, namely inclusions of the mother liquor and co-crystallization. Expressing these contributions in transfer factors, a kind of cumulative partitioning coefficient, shows a linear development of this factor for adsorption and an exponential evolution for the color incorporation due to co-crystallization as a function of cane syrup levels. The color transfer based on liquid inclusion remains nearly constant up to high levels of cane syrup (80%). This possibly indicates that at these high inclusion levels the bulky co-crystallizing molecules originating from cane start to cause additional crystal imperfections. The data further allow the formulation of a model to forecast the sugar color values resulting from mixed syrups crystallization based on the analysis of the respective pure cane and beet syrups. Since the work reported here is the first of its kind dealing with mixed syrups additional work is needed to solidify the conclusions drawn. It remains anyhow remarkable that different solutes that are known to interact with different faces of the growing crystal have such a profound effect on their mutual rate of inclusion. Consequently, additional specific experiments are needed to elucidate the underlying mechanisms of the observations made.

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6 EFFECT OF QUALITY AND ORIGIN OF TECHNICAL SUCROSE SOLUTIONS ON THE INCLUSION OF COLORANTS INTO THE SUGAR CRYSTAL MATRIX

Schlumbach, Karl; Scharfe, Maria; Flöter, Eckhard

TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

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Abstract

BACKGROUND: Due to the liberalization of the European sugar market the pressure to improve factory utilization is growing. Currently, beet and cane as sucrose sources are produced in isolation, according to geography. Co-production of sugar from beet and cane origin in one stream is a promising option. However, the knowledge base for production sugar is practically non-existing. This paper is part of our contribution to this field and specifically addresses effects of raw material quality.

RESULTS: This framework formulated for the coloring of sugars crystallized from mixed syrups is also valid for different raw material qualities: raw cane sugars: color values 1221 to 2505 IU, dextran levels 50 to 1200 mg kg⁻¹; beet syrups: 1509 to 2058 IU. Co-crystallization is the main color incorporation mechanism. Color due to liquid inclusion increases strongly at cane inclusion levels in excess of 60%. The prediction of final sugar color based on characteristics of pure mixture constituents is verified and indicates significant differences to current recommendations.

CONCLUSION: A first comprehensive description of the color values in sugars produced from mixed cane and beet syrups is presented. Prediction of color values from data on sugar color of single sources marks a major contribution to future applications of co-production.

6.1 Introduction

Due to the availability of sugar beets sugar production in Europe is limited to two periods, either the fresh-beet or the thick juice campaign. This seasonal production meets the annual demand, but production capacities do not remain fully utilized. With the end of the EU Sugar Market Policy in 2017, and hence market liberalization, growing competition for market shares will start. The possibility of increased imports, but also the freedom to export, combined with prices according to world market, generate new opportunities and pose a threat. Therefore, European sugar producers need to enhance their capacities and improve their efficiency. One route to achieve this is the use of raw cane sugar either by just refining it as such or in co-production with beet syrup. Different manufacturers have already apply the latter for several years to extend the inter-campaign and thus utilization. It is understood that products from co-processing have to meet the same specifications as single source products in order to meet customers' demands. Considering the production of sugar from mixed syrups it was demonstrated earlier that high-quality white sugar (color of less than 30 IU (ICUMSA Units)) can be produced only with limited addition of raw cane sugar. Admixing levels of 10 to 20% (w/w) raw cane sugar into the beet thick juice were tolerable applying conventional beet juice processing (Kochergin et al., 2012). In a previous contribution it was shown that actually higher raw cane sugar levels of up to 40 g/100 g in the blends still result in white sugars of highest quality with color values < 30 IU (Schlumbach et al., 2016). It is assumed that this is due to the interaction of the colorants from different origin mutually suppressing incorporation into the sugar crystal. In this context also the relative contribution of the different color incorporation mechanisms on final sugar color values was discussed (Schlumbach et al., 2017). However, it is fair to assume that the colorants' transfer into the sucrose crystal strongly depends on the quality and quantity of the colorants in the mixed feed syrups. The colorants originating from the different sources differ in their physical and chemical properties but are usually not distinguished in the assessment of the final sugar color value. These colorants are typically sub-divided into two classes, original biotic and process-induced (Figure 6-1). Although the exact chemical structures of these compounds is irrespective of origin, are not fully understood, the types of colorants and their formation mechanisms are generally known and described elsewhere (Bourzutschky, 2005; Davis, 2001; Godshall & Baunsgaard, 2000; Godshall et al., 2002; Coca, 2004; Martins et al., 2000; Shore et al., 1984; Schlumbach et al., 2017). In contrast to the colorants in beet juices being primarily process induced, the colored components in cane sugar juice originate directly from the plant material. The concentrations and detailed characteristics of these colored impurities and their precursors depend on many factors, e.g. age of stalk, growth and weather conditions, crop damage due to insects, diseases, occurring frosts, soil type, fertilizers, harvesting method, and microbiological activity (Clarke & Godshall, 1988; Chen & Chou, 1993). It is of primary interest for manufactures considering co-processing to

develop a better understanding of the coloring components and their behavior in order to design blends and processes such that the desired quality of sugars can be produced reliably.

To achieve this goal, it is necessary to consider the different color incorporation mechanisms. In general, three different mechanisms (adhesion, liquid inclusion, and co-crystallization) for the incorporation of colorants are considered (Delavier H.J. & Hirschmüller H., 1968). Because there is no commonly acknowledged terminology the terms used throughout this work are defined as follows:

- **Adhesion:** This process causes the outer color of the sugar crystal. It refers to mother liquor still adhering to the crystal surface after centrifugation. It subsequently solidifies on drying. The amount of mother liquor remaining on the surface depends on factors such as the viscosity of the mother liquor and the centrifugation process. The respective color value due to adhesion is additionally influenced by the concentration of colorants in the mother liquor, type of colorants, and their tendency to temporarily adhere. Some studies suggest that for normal operations adhesion accounts for 20 - 50% of the total color value of the sugar crystal (Shore et al., 1984; Godshall et al., 1991). Since the process described above and by Delavier and Hirschmüller (Delavier H.J. & Hirschmüller H., 1968) does not involve the selective concentration of molecules at an interface, but the inability to remove a liquid film, adhesion appears to be the appropriate name. Adsorption, on the contrary, is an essential step in crystallization and co-crystallization.
- **Liquid inclusion:** A prerequisite for this phenomenon is the presence of imperfections in the crystal lattice. Defects such as grooves, or generally rough surface growth can cause voids in the crystal structure once roughness is overgrown. If these voids are filled with mother liquor they contain colored mother liquor. Colorants and other non-sugar material in the mother liquor incorporated this way can consequently not be removed by washing processes (e.g. during centrifugation, affination). They are only accessible by dissolving the crystal (Mackintosh & White, 1968; Shore et al., 1984). The quantity of liquid inclusions is stated to be proportional to the amount of surface defects which itself is influenced by the crystal growth kinetics (Grimsey & Herrington, 1994; Singh & Delavier H.J., 1974). Observations of fast growing crystal faces promoting the inclusion of colorants (Mackintosh & White, 1968; Vaccari et al., 1990a; Vaccari et al., 1990b) support this view. It is generally accepted that liquid inclusions are exclusively responsible for incorporation of ash components, such as KCl, into sugar crystals. The concentrations in the originally entrapped liquid hence equal those of the mother liquor at the moment of inclusion (Grimsey & Herrington, 1994; Grimsey I.M. & Herrington, 1996). It is thus fair to assume that the concentration of other non-sugar components (e.g. colorants) present in liquid inclusions corresponds to the ash concentration. However, the absolute concentrations of all non-sugar substances in the entrapped liquid change due to

partial sucrose crystallization from the entrapped mother liquor induced by temperature reduction (Guo, 1984).

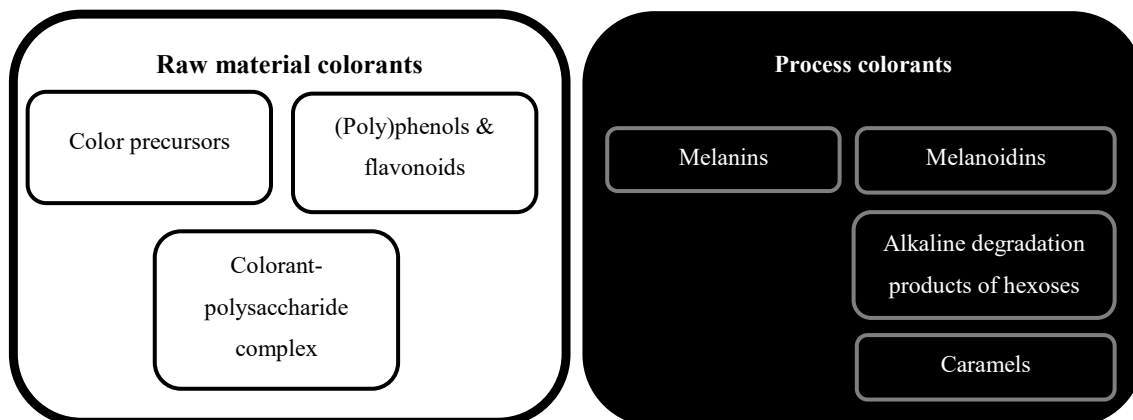


Figure 6-1: Raw material and process colorants which are influencing final sugar color.

- Co-Crystallization:** In sugar research this process is sometimes also referred to as adsorption-occlusion (Promraksa et al., 2009). A key feature that distinguishes this mechanism from those previously described is the possibly homogeneous distribution of guest molecules throughout the crystal structure. Guest molecules, for the purpose of the manuscript colorants, adsorb to the growth site and become on further growth part of the crystal matrix (Promraksa et al., 2009; Zhou et al., 2016). A prerequisite for this process is hence a sufficient level of interaction with the kink site and a reasonable geometrical fit with the hosting crystal matrix (Zhou et al., 2016). Fulfilment of the above conditions is difficult to judge. Consequently, the distinction between adsorbed and occluded molecules and adsorbed and crystallized molecules is far from trivial. However, for the purpose of this manuscript the incorporation of molecules into the crystal lattice is considered co-crystallization irrespective of complete or limited miscibility in the solid phase or incorporation due to kinetic effects. Colorants with a sucrose-like structure and high molecular mass are incorporated predominantly into the sucrose crystal lattice. Due to their low diffusion coefficients a concentration increase close to the crystal surface emerges on crystallization, polarization, so that the driving force for co-crystallization is increased (Schlumbach et al., 2017). A variation in the interpretation of this process is based on the assumption that, actually, sucrose-colorant complexes are present in the mother liquor which are more easily built into the lattice (van der Poel, P.W., 2000; Singh & Delavie H.J., 1974; Grimsey I.M. & Herrington, 1996).

It is common practice to express the color value of sugar crystals as percentage of the color value of the feed material. The ratio of these values is referred to as the transfer factor. Typical values for color transfer factors are 1% in beet sugar processing and 6 – 10% in cane sugar processing, respectively (Godshall et al., 2002; Godshall & Baunsgaard, 2000). This concept finds application for both beet and raw cane sugar manufacturing and allows the estimation of allowable color

values for starting materials. To produce sugar with color values of 20 – 30 IU from beet syrups these should have color values not exceeding 2000 – 3000 IU. Since raw cane sugar has color value targets in the range of 2000 to 3000 IU cane syrup with color values in between 10,000 and 18,000 IU can be processed. It is obvious that this practical concept of constant transfer factors is valid within tight boundaries. For example, Lionnet et. al. state that the color transfer factor in cane syrups increases with decreasing syrup color (Lionnet & Moodley, 1995).

Crystallization experiments with blends from beet thick juice and dissolved raw cane sugar were performed earlier (Kochergin et al., 2012). It was reported that cane-related colorants were preferentially adsorbed onto the crystal surface and are more easily incorporated into the sucrose crystal making them difficult to remove. This was basically reconfirmed by additional studies (Schlumbach et al., 2016). The results gathered allowed the derivation of a correlation showing that the color transfer factor in mixed syrups develops exponentially with increasing cane levels in the mixed syrup. The data hence suggested that there is mutual suppression of incorporation for colorants of different origin. Additional work revealed that with increasing levels of cane material in the blend, co-crystallization, in particular, is promoted (Schlumbach et al., 2017).

However, the previous studies were conducted with a limited set of raw materials. Raw material quality (e.g. raw cane sugar) varies greatly due to origin, plant quality, processing and storage conditions. To verify the general applicability of the findings described above it is necessary to study raw materials of different quality. To this end the work reported here addresses the influences of different raw material qualities on the color values of sugars produced. Building on earlier results the relative contributions of the different color incorporation mechanisms was studied as well.

6.2 Material and methods

6.2.1 Experimental set-up

The crystallization experiments were carried out in a 0.005 m³ evaporation crystallizer (Figure 5-3). After crystallization the slurry was centrifuged (DM 2250, Gebr. Heine, Viersen, Germany) to separate the mother liquor (impure sugar solution) from the crystals. A subsequent drying takes place in a fluidized-bed dryer (TU Berlin-design). A detailed description of the crystallization equipment and supporting units is given elsewhere (Schlumbach et al., 2015). The sequence of processing steps was designed such that sugars produced are of industrial relevance.

In short, the crystallization vessel was heated and temperature-controlled by two separate hot water flushed jackets. Two thermostats controlled the temperature of the respective heating water (F32-HD and F12-MC, both Julabo, Seelbach, Germany). The temperature of the mother liquor was monitored throughout the crystallization run by a thermo element (Pt100) submerged into the mother liquor. To determine the dry substance content of the mother liquor continuously a process refractometer (iPR 2-3, Schmidt & Haensch GmbH & Co., Berlin, Germany) (2 in Figure 5-3)

was utilized. The LabVIEW (National Instruments Corporation, Munich, Germany) environment was used to control the process equipment and record on-line data.

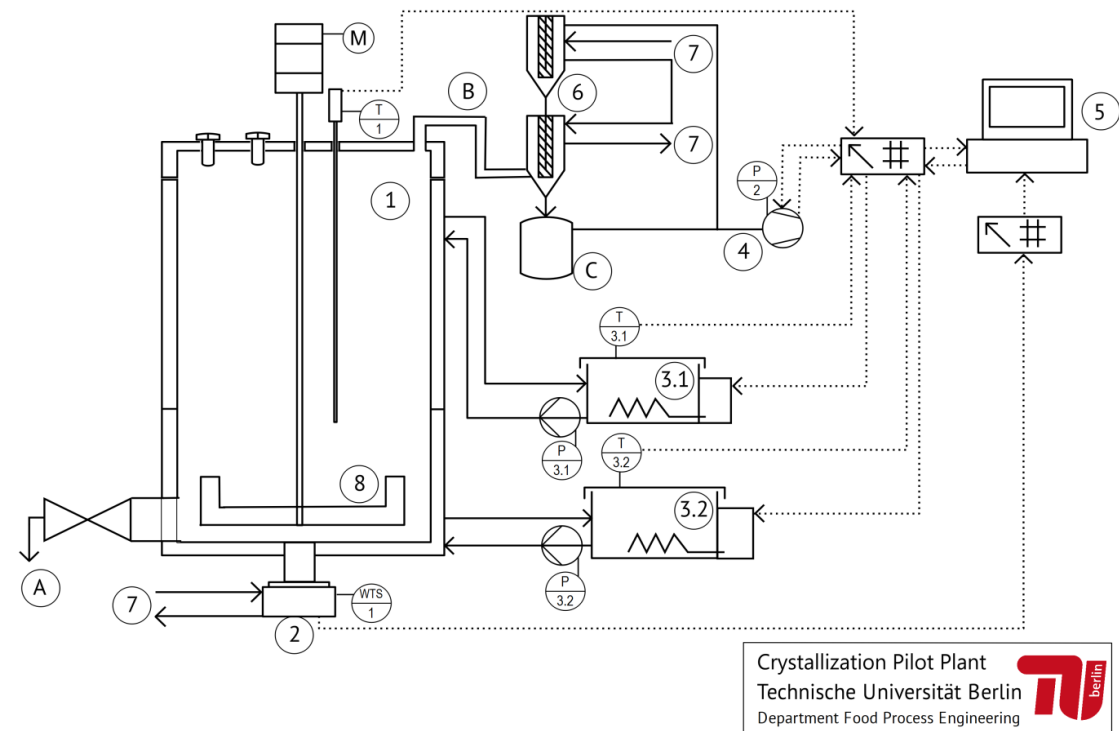


Figure 6-2: Crystallization pilot plant and ancillary equipment. 1 Vessel; 2 Refractometer; 3.1 Thermostat; 3.2 Thermostat; 4 Low pressure pump; 5 Data processing unit; 6 Cooler; 7 Cooling water; 8 Stirrer; A Masecuite outlet; B Vapor; C Condensate.

6.2.2 Raw materials

In the present study beet feedstocks were kindly provided directly from German sugar factories. White and raw cane sugars were sourced from sugar factories in Brazil and Cuba. The characteristic properties of the raw materials are given in Table 6-1. Prior to each experiment the white and raw sugars were dissolved using demineralized water ($< 2 \mu\text{S cm}^{-1}$). All syrups, including beet thick juices, were centrifuged through a stainless-steel mesh (nominal $5 \mu\text{m}$, absolute $8 \mu\text{m}$; TEDRA Dahmen GmbH & Co. KG, Wassenberg, Germany) prior to crystallization. One hundred microlitres of Struktol SB 2433 (Schill + Seilacher 'Struktol' GmbH, Hamburg, Germany) was added to the feed syrups to inhibit the formation of foam.

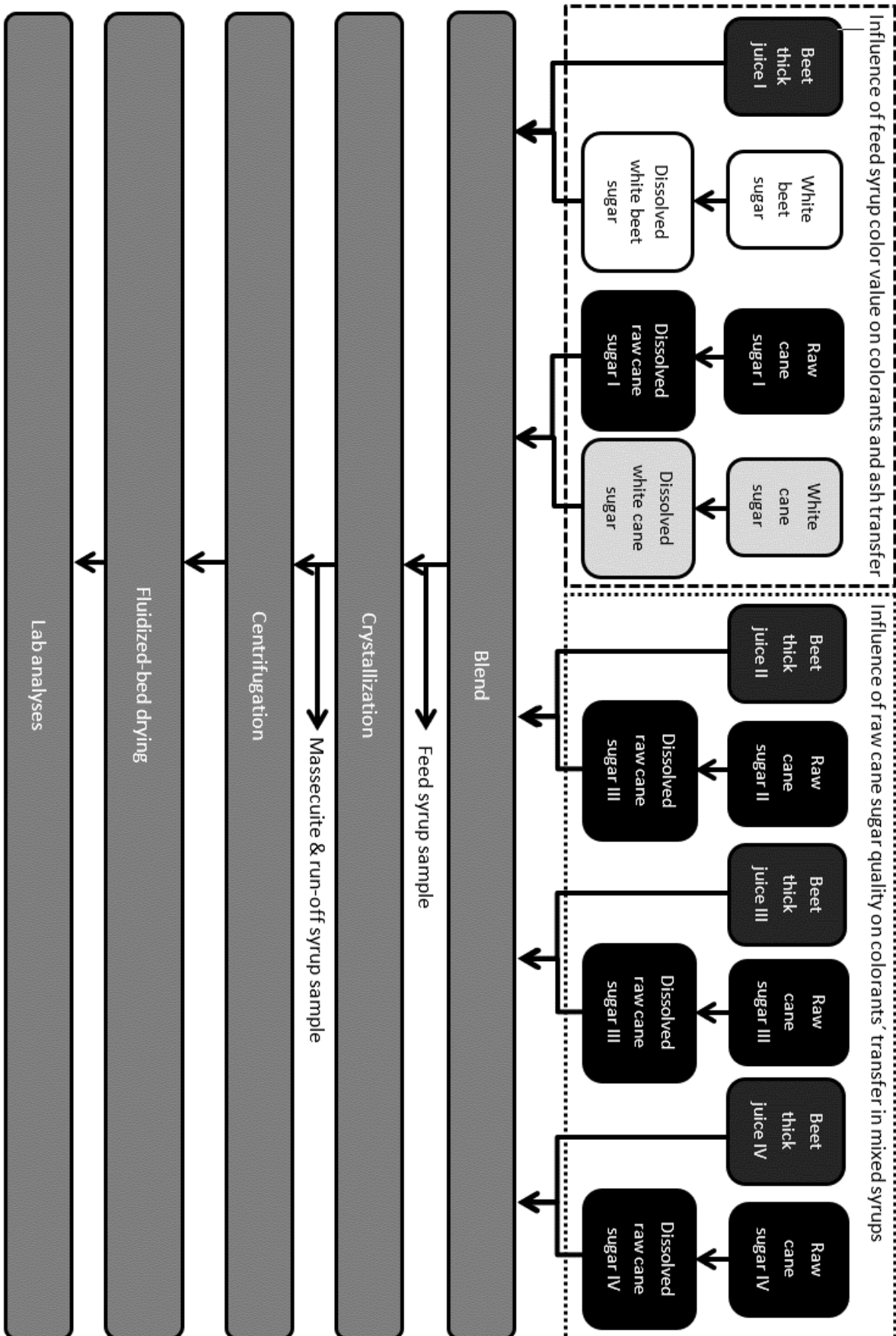


Figure 6-3: Procedure for the crystallization experiments.

6.2.3 Experimental procedure

Various blends based on different combinations of raw materials were studied. Figure 6-3 illustrates the experimental design schematically. Each crystallization run started with 5,000 g of the respective feed syrup in the crystallizer. The homogeneity of the syrup was maintained by continuous stirring (60 rpm) (RZR 2102 control, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany). The system pressure was set to 270 mbar (± 1 mbar) and kept at this value throughout the crystallization run (low pressure pump, PC 3001, Vacuubrand GmbH & Co KG, Wertheim, Germany). The temperature of the heating water in the lower jacket, the heating jacket of the crystallizer, was adjusted for different syrups to ensure smooth operation. In general, the temperature of the heating fluid was 361 K (± 0.01 K). For crystallization runs involving raw cane sugars III or IV this set point was increased to 366 K (± 0.01 K). The upper jacket was temperature-controlled mainly to avoid crystal nucleation on the wall. The heating fluid in this jacket had a temperature of 343 K (± 0.01 K) throughout the experimental campaign.

Table 6-1: Quality parameters of the raw materials.

Raw material	Origin	Dry substance g/100 g	Purity %	F ₄₂₀ IU	Ash % (w/w)	Dextran mg kg ⁻¹
Beet thick juice I	Germany	67.84	95.11	1915	1.134	-
White beet sugar	Germany	-	99.97	21	0.005	-
Raw cane sugar I	Brazil	-	99.67	1344	0.091	50
White cane sugar	Brazil	-	99.46	64	0.055	-
Beet thick juice II	Germany	67.22	94.91	2021	1.188	-
Raw cane sugar II	Brazil	-	99.16	1221	0.101	50
Beet thick juice III	Germany	67.92	94.73	2058	1.268	-
Raw cane sugar III	Brazil	-	99.54	1603	0.090	310
Beet thick juice IV	Germany	68.18	95.54	1509	1.500	-
Raw cane sugar IV	Cuba	-	99.58	2505	0.139	1200

Samples of the homogeneous mass were taken prior to any evaporation. Once a supersaturation level of 1.05 (± 0.01) was achieved seed crystals were added to the syrup. The seed crystals had a color value of 30 IU. Their size range was between 250 and 315 μm . The crystallization process was designed to achieve a final crystal size of 800 μm . Constant supersaturation levels of 1.06 (± 0.01) and 1.10 (± 0.01), respectively, were maintained by well-controlled system pressure and heat supply. The crystallization runs were stopped once a crystal content of 45 to 50 g/100 g was reached. This moment was identified by monitoring the torque of the agitator. It was shown previously that a torque increase by 0.06 Nm is a reliable indication for the increased volume of the dispersed phase. Sucrose crystals were separated from the mother liquor using a centrifuge (3,000 rpm, 1,450 RCF). Samples were taken from the massecuite (slurry) and the run-off syrup

(mother liquor) from the centrifugation. In alignment with industrial practice, washing water was evenly distributed to the mass during centrifugation. This reduced the amount of adhered mother liquor and reduced the risk for agglomeration. The amount of water (343 K) dosed by the self-constructed washing unit was 2.5 g/100 g of massecuite (Schlumbach et al., 2015). The sugar was dried in a fluidized-bed (10 min., $T_{\text{air}}=343$ K) to a residual water content of 0.04 (± 0.01) g per 100 g.

6.2.4 Analysis and data processing

The analysis were carried out according to the analytical methods used in the sugar industry which are published in detail elsewhere (ICUMSA, 2011). Prior to analysis all samples were diluted 1:1 (w/w) with demineralized water using an automatic dilution and dosing system (DDS, Anton Paar, Graz, Austria). The dry substance content (w_{DS}) of the prepared solutions was determined by refractometry (ATR W2 plus, Schmidt & Haensch, Berlin, Germany). The sucrose content (w_S) was determined by polarimetry (Saccharomat NIR W2, Schmidt & Haensch, Berlin, Germany) after clarification with *Carrez*. The purity q is defined as quotient of both values and expressed in %:

$$q = \frac{w_S}{w_{DS}} \cdot 100 \quad (6-1)$$

The method determining the ash content of sugar $C_{ash,s}$ (in % (w/w)) is based on conductivity measurements. It is computed using the conductivity of water, C_w , and of the sample at 293 K, C_I :

$$C_{ash,s} = 6 \cdot 10^{-4} \cdot (C_I - 0.35 C_w) \quad (6-2)$$

The ash content of the syrup $C_{ash,ML}$ (in % (w/w)) is determined according to equation (6-3):

$$C_{ash,ML} = (16.2 + 0.36 \cdot \frac{w_{DS}}{100}) \cdot 10^{-4} \cdot (C_I - C_w) \cdot \frac{5}{S} \quad (6-3)$$

where w_{DS} the dry substance and S the mass of 100 ml sample. The ash transfer factor is defined as the ratio of these values and expressed in %:

$$k_{ash} = \frac{C_{ash,s}}{C_{ash,ML}} \cdot 100\% \quad (6-4)$$

For the photometric color analysis (wavelength at 420 nm) the methods GS1/3-7 and GS2/3-10 were used (ICUMSA, 2011). Using hydrochloric acid or sodium hydroxide solutions the pH-value of all samples, feed syrup, massecuite, run-off syrup, sugar and affinated sugar, was adjusted to 7. According to the method the color value (IU) of a stabilized solution is given by:

$$F_{420} = \frac{10^8 \cdot A_s}{b \cdot w_{DS} \cdot \rho} \quad (6-5)$$

with b the length of the cuvette (1 cm for syrup, 5 cm for dissolved sugar), w_{DS} the dry substance (g/100 g), and ρ (kg m^{-3}) the density.

To eliminate contributions of adhesion to the color values affination was applied to the sugars produced prior to analysis. This is necessary because the centrifugation process, even though

carried out diligently, cannot avoid uncontrollable variation in adhesion of the mother liquor. During the affination procedure the centrifuged and dried sugar crystals were exposed to a saturated sugar solution ($F_{420} < 15$ IU) and stirred for 15 min. The crystals and solution were separated in a laboratory centrifuge at 3,600 rpm (1,000 RCF) prior to a repetition of this procedure with a stirring time of 5 min. The affinated, hence surface cleaned, sugars were dried in a desiccator prior to color and ash analyses.

Particle sizes were determined by sieve analysis (method GS2/9-37). The mean aperture (d_{50}) and coefficient of variation (CV) were calculated according to the Powers Method. The d_{50} value was used to compute the crystal mass growth rate G ($\text{kg m}^{-2} \text{s}^{-1}$) (Bubnik & Kadlec, 1992):

$$G = \frac{3\rho \cdot \alpha}{\beta} \cdot \frac{\Delta d_{50}}{\Delta \tau} \quad (6-6)$$

wherein the crystal shape factor α was set equal to 0.750 for sucrose crystals and Δd_{50} was the difference between the mean aperture sizes of the crystals produced and the seed crystals. According to literature (26) the surface area shape factor β was set to 5.02. The density of sucrose crystals ρ was set to $1,587 \text{ kg m}^{-3}$. The duration of the crystallization process, from seeding to end of process, is indicated as τ (s).

The color transfer factor k_{color} is widely used in the sugar industry to estimate the final color of sugars produced (Chiu & Sloane G.E., 1980). It is defined as the ratio of the color value of the affinated sugar, $F_{420,s}$, and the color value of the feed syrup, $F_{420,ML}(\tau_0)$. It is typically expressed as %-value.

$$k_{color} = \frac{F_{420,s}}{F_{420,ML}(\tau_0)} \cdot 100\% \quad (6-7)$$

This approach is due to its simplicity which is useful for industrial purposes, but ignores some details. For example, is the increase of the concentration of colorants in the mother liquor during the batch crystallization process obviously a function of the amount of crystals produced from a given syrup. This aspect cannot be ignored. To this end, in the study reported here the color value of the mother liquor at the end of the crystallization process $F_{420,ML}(\tau_n)$ was taken into account as well. Based on previous experiments, indicating a linear crystal mass growth, the concentration process of colorants was evaluated. Applying simple mass balances yields that the concentration of the colorants in the mother liquor increases linearly, too (Schlumbach et al., 2015). Consequently, a more realistic color transfer factor k_{color}^* is defined as follows:

$$k_{color}^* = \frac{F_{420,s}}{(F_{420,ML}(\tau_0) + F_{420,ML}(\tau_n)) \cdot \frac{1}{2}} \cdot 100\% \quad (6-8)$$

Applying the same line of thinking equation (6-4) was modified accordingly, to yield equation (6-8):

$$k_{ash}^* = \frac{C_{ash,s}}{(C_{ash,ML}(\tau_0) + C_{ash,ML}(\tau_n)) \cdot \frac{1}{2}} \cdot 100\% \quad (6-9)$$

As pointed above the mother liquor adhering onto sugar crystals is not the main concern of this work since affinated crystals were studied primarily. Nevertheless, the newly introduced modified transfer factors, considering also the concentration process of the colorants, appeared to be applicable also to non-affinated sugars. As mentioned before, three mechanisms – adhesion, liquid inclusion, and co-crystallization – were considered to cause colorant incorporation. Colorants inside the crystal matrix are due liquid inclusions (LIs) and co-crystallization (Co) only. Because affination was applied the absence of any color contribution due to adhesion is assumed:

$$F_{420,s} = F_{LI} + F_{Co} \quad (6-10)$$

Considering equation (6-8) and (6-10) the overall color transfer factors were computed as the sum of the transfer factors for inclusion of mother liquor (k_{LI}^*) and co-crystallization (k_{Co}^*):

$$k_{color}^* = k_{LI}^* + k_{Co}^* \quad (6-11)$$

From equation (6-8), (6-10) and (6-11) it follows that:

$$k_{color}^* = \left(\frac{F_{LI} + F_{Co}}{(F_{420,ML}(\tau_0) + F_{420,ML}(\tau_n)) \cdot \frac{1}{2}} \right) \cdot 100\% \quad (6-12)$$

For affinated sugars ash incorporation was exclusively related to the mechanism of liquid inclusion (Grimsey I.M. & Herrington, 1996; Singh & Delavie H.J., 1974). Consequently, the liquid inclusion transfer factors for ash and colorants are considered identical, ignoring possible colorants adsorption at the inner surface of the liquid filled voids:

$$k_{LI}^* = k_{ash}^* \quad (6-13)$$

Combining equations (6-10), (6-11) and (6-13) the color transfer factor for co-crystallization was derived:

$$k_{Co}^* = k_{color}^* - k_{LI}^* = k_{color}^* - k_{ash}^* \quad (6-14)$$

The emphasis of this work were the transfer factors for the inner color. However, for the evaluation of the color contribution due to adhesion, hence due to syrup adhering to the crystal surface, the color transfer factors of non-affinated and affinated sugars were compared. The color transfer factor for adhesion, k_{Ad}^* , was defined as the differences between the overall color transfer factor of the non-affinated sugar, which is based on the color value of non-affinated sugar, $F_{420,s'}$, and the overall color transfer factor of affinated sugar k_{color}^* :

$$k_{Ad}^* = \frac{F_{420,s'}}{(F_{420,ML}(\tau_0) + F_{420,ML}(\tau_n)) \cdot \frac{1}{2}} \cdot 100\% - k_{color}^* \quad (6-15)$$

6.3 Results and discussion

6.3.1 Influence of feed syrup color value on the transfer of colorants and ash

Various blends according to the scheme shown in Figure 6-3 were composed and processed as described. Earlier work indicated a very good reproducibility of the crystallization runs, so that the different mixed syrups were only crystallized once. It was assumed that the variations in the incorporation of the colorants were the result of compositional changes only and not induced by varying processing conditions as the comparison of the crystal characteristics reveals. The mean values and standard deviations for the mean aperture (d_{50}), coefficients of variation (CV) and crystal mass growth rates are given in Table 6-2. The data, in particular the standard deviations, suggest that processing-induced changes of the color transfer can practically be excluded as cause for the differences observed between different mixtures.

Table 6-2: Mean aperture (d_{50}) and coefficient of variation (CV) from sieve analysis of experiments with blended feed syrups.

Experiments	d_{50} mm	CV %	G kg m ⁻² s ⁻¹
Beet thick juice I & white beet sugar	0.75 (± 0.02)	41.33 (± 2.36)	$2.24 \cdot 10^{-5}$ ($\pm 3.56 \cdot 10^{-6}$)
Raw cane sugar I & white cane sugar	0.77 (± 0.03)	35.06 (± 5.23)	$2.72 \cdot 10^{-5}$ ($\pm 2.54 \cdot 10^{-6}$)

The color transfer factors for liquid inclusion and co-crystallization of pure beet syrups are shown in Figure 6-4. The different syrups crystallized originate from the same thick juice, which was diluted with a synthetic sucrose solution. It was found that the transfer factor for liquid inclusion remained constant for syrups with color values above 800 IU. On further dilution of the juice, syrups with higher purity and lower color values, the transfer factor for liquid inclusion increased. The color transfer for co-crystallization increased systematically with decreasing feed syrup color. Comparing the contribution of both mechanisms to the color value of the sugar it appeared that co-crystallization is the dominant mechanism at less colored feed syrups and the contribution of liquid inclusion increased with more colored starting material. In contrast to the expected results on liquid inclusion the evolution of the co-crystallization effect is surprising. The combination of both processes actually caused the color value for the affinated sugars to only slowly decrease linearly with reduced syrup color.

Data originating from the same experiment based on pure cane material revealed a similar picture (Figure 6-5). In this case the color transfer factor for liquid inclusion remained constant over the whole dilution range. The value determined was actually more than twice as high as for beet material. Similar to the behavior in the beet system the color transfer factor for co-crystallization increased with decreasing feed syrup color value. On dilution of cane syrup with synthetic syrup

it was found as well that the color value of the affinated sugar decreased linearly. In this case, the slope of the affinated sugar color value over syrup color value was approximately 10-times that of the beet system. Our data thus confirm the statement that the color transfer factor is not fully independent on the level of colorants in the syrup (Lionnet & Moodley, 1995).

Additionally, the data revealed that the transfer factor for co-crystallization changed with an almost constant slope irrespective of the origin of the material. Furthermore the data confirmed that co-crystallization is the main color incorporation mechanism for syrups originating from cane (Schlumbach et al., 2017).

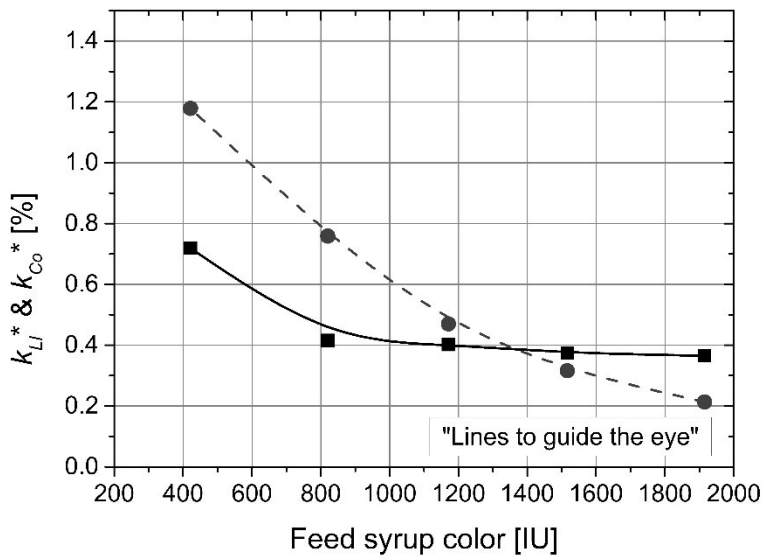


Figure 6-4: Color transfer factors determined at pH 7 for different inclusion transfer mechanisms, liquid inclusion (■) and co-crystallization (●), for beet thick juice diluted with white beet sugar solution.

Looking in detail at the possible mechanism causing the evolution of the transfer factors it appeared easy to explain that the transfer factors for liquid inclusion remain almost constant independent of the dilution. A prerequisite for liquid inclusions to occur is the presence or size of defects (e.g. grooves) on the growing crystal surface. With very consistent processing, see constant growth rates, it is unlikely that significant changes at the growing surface were induced by mildly changing the syrup characteristics. However, there was a significant difference in the respective constant values between beet and cane based syrups. During crystallization of cane more than twice as much liquid material was entrapped. This could be either due to impurities in cane syrups causing more surface defects that evolved to become liquid inclusions of mother liquor, or by nature of the larger impurities that caused the inclusion domain sizes of the liquid inclusions to be bigger.

Considering the evolution of the coloring effects due to co-crystallization it is more complicated to derive a convincing interpretation. Processes that play a role in co-crystallization are the diffusion of material to the interface, adsorption at the interface, and incorporation into the crystal

structure. In how far the latter is related to equilibrium conditions, or driven primarily by kinetic effects remains difficult to elucidate. The fact that the observations made for the cane and beet

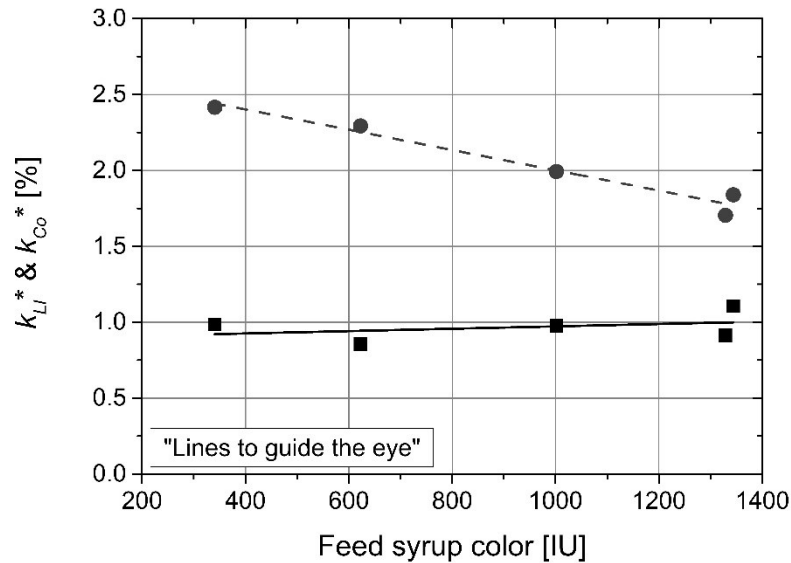


Figure 6-5: Color transfer factors determined at pH 7 for different inclusion transfer mechanisms, liquid inclusion (■) and co-crystallization (●), for raw cane sugar syrup diluted with white cane sugar solution.

system are somewhat contradictory with respect to the level of colorants incorporated by co-crystallization on dilution does not make things simpler. In the cane system dilution of the syrups reduced co-crystallization of colorants. In contrast, in the beet system the dilution resulted in increasing co-crystallization of colorants. Assuming a process of non-specific adsorption at the crystal interface with subsequent occlusion cannot explain these observations. Also the alternative assumption of specific binding at the growth sites and hence a process driven by limited solid solubility of colorants does not allow these observations to be explained convincingly. However, both interpretations allow formulation of a hypothesis with respect to the increased incorporation of cane colorants, either due to higher non-specific adsorption or due to increased solid solubility and/or increased specific adsorption compared to beet colorants, respectively. To unravel these observations is beyond the scope of this manuscript but deserves more detailed attention taking, in particular, also other non-sugar components into account.

Table 6-3: Mean aperture (d_{50}), coefficient of variation (CV) and crystal mass growth rate (G) from sieve analysis of experiments with blended feed syrups.

Experiments	d_{50} mm	CV %	G $\text{kg m}^{-2} \text{s}^{-1}$
Beet thick juice II & Raw cane sugar II	0.77 (± 0.03)	20.59 (± 3.00)	$2.94 \cdot 10^{-5}$ ($\pm 2.71 \cdot 10^{-6}$)
Beet thick juice III & Raw cane sugar III	0.81 (± 0.01)	21.34 (± 1.55)	$5.36 \cdot 10^{-5}$ ($\pm 7.29 \cdot 10^{-6}$)
Beet thick juice VI & Raw cane sugar VI	0.86 (± 0.03)	16.65 (± 1.34)	$5.64 \cdot 10^{-5}$ ($\pm 6.69 \cdot 10^{-6}$)

6.3.2 Influence of raw cane sugar quality on the transfer of colorants in mixed syrups

6.3.2.1 Overall color transfer into affinated sugars

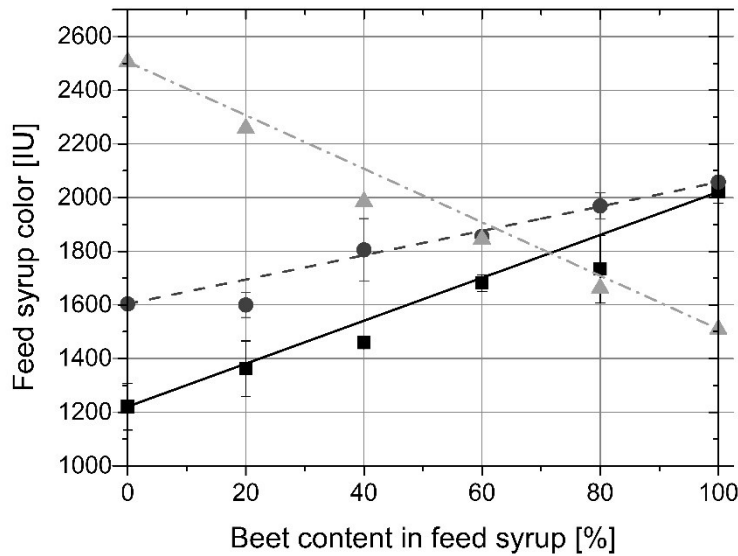


Figure 6-6: Feed syrup color for mixtures of different raw materials. Beet thick juice II & raw cane sugar II (■, full line); beet thick juice III & raw cane sugar III (●, dashed line); beet thick juice IV & raw cane sugar IV (▲, dashed-dotted line).

The influence of raw cane sugar quality on the transfer of colorants in mixed syrups was studied using different raw materials (Table 6-1). The average values and standard deviation (SD) for mean aperture, coefficient of variation and crystal mass growth rate are given in Table 6-3 which reveals that within each raw material combination the variation of mean aperture was small and that the average values varied around the target value of 0.800 mm. The coefficients of variation were below 20% illustrating a narrow particle size distribution and hence a well-controlled crystallization process. The crystal mass growth rates were determined according to Bubnik & Kadlec (1992) (equation (6-6)). For each system a value within the normal range (Lionnet, 1998a; Schlumbach et al., 2015; Schlumbach et al., 2016; Schlumbach et al., 2017) was found and the low SD indicates that process execution was consistent. The reason for the reduced growth rate shown in the top line is the lower ΔT applied in the heating jacket. Consequently, evaporation rates and hence supersaturation and growth rates were reduced. Ongoing research in our laboratory suggests that crystal growth rates only have a modest influence on incorporation the colorants .

The color values of the different feed syrups in the different mixed systems are depicted in Figure 6-6. The figure illustrates that a wide range of different syrups was studied. Regarding the color values for the different mixed feed systems it is not surprising that a linear relation was found.

In order to determine the actual color development of the syrup during the crystallization process it is important to acknowledge that the color value is expressed relative to the amount of dry matter. Formulating the mass balances accordingly the increase of the color value of the syrup was computed as function of the crystal content with equation (6-16). Equation (6-17) provides the concentration factor for a typical crystal content of 0.50 g g^{-1} .

$$C_F = \frac{\frac{w_{CC}(\tau_n)}{(1 - w_{CC}(\tau_n))} + w_{DS,ML}(\tau_n)}{w_{DS,ML}(\tau_n)} \quad (6-16)$$

$$C_F = \frac{\frac{0.50}{(1 - 0.50)} + 0.79}{0.79} = 2.27 \quad (6-17)$$

Assuming that the amount of colorants incorporated into the sucrose crystal was negligible, the color value of the mother liquor at the end of the crystallization was 2.27-fold higher than the color value of the feed syrup. In this case a crystal content of $w_{cc}=0.50 \text{ g g}^{-1}$ and a dry substance level of 0.79 g g^{-1} were used. A parity plot (Figure 6-7) illustrates the good agreement between the calculated and experimental concentration factor of the colorants C_F . The experimental value was computed as quotient of the respective color values of the mother liquor at the end, $F_{420,ML}(\tau_n)$, and begin, $F_{420,ML}(\tau_0)$, of the crystallization process. Apparently, the scattering of the data is relatively high although a reasonably agreement was found. It has to be taken into account that individual accuracies of several experimental values propagate into the concentration factor. Thorough analysis revealed that even minute standard deviations in crystal content or color values can relate to large optical effects in Figure 6-7.

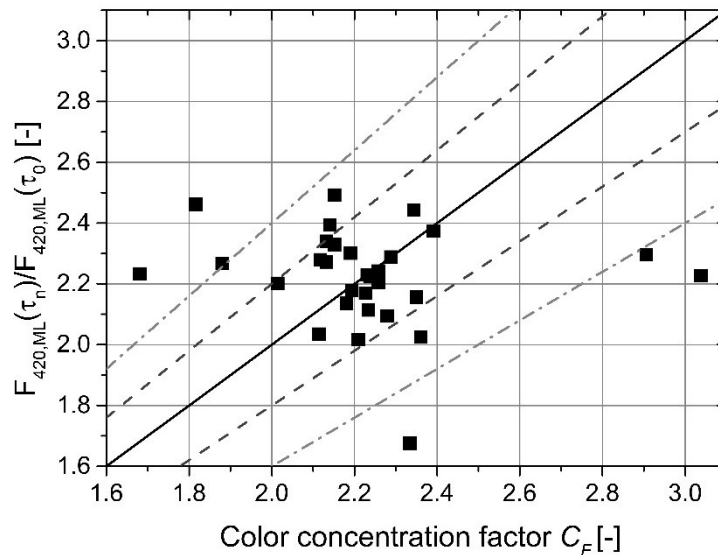


Figure 6-7: Parity plot of relative change of color value from feed syrup to final mother liquor. Quotients of color value from mother liquor at the end $F_{420,ML}(\tau_n)$ to feed syrup color $F_{420,ML}(\tau_0)$ over concentration factor C_F , according to equation (6-16). Lines illustrate the relative deviation from complete consistency: $\pm 10\%$ dashed line; $\pm 20\%$, dashed-dotted line.

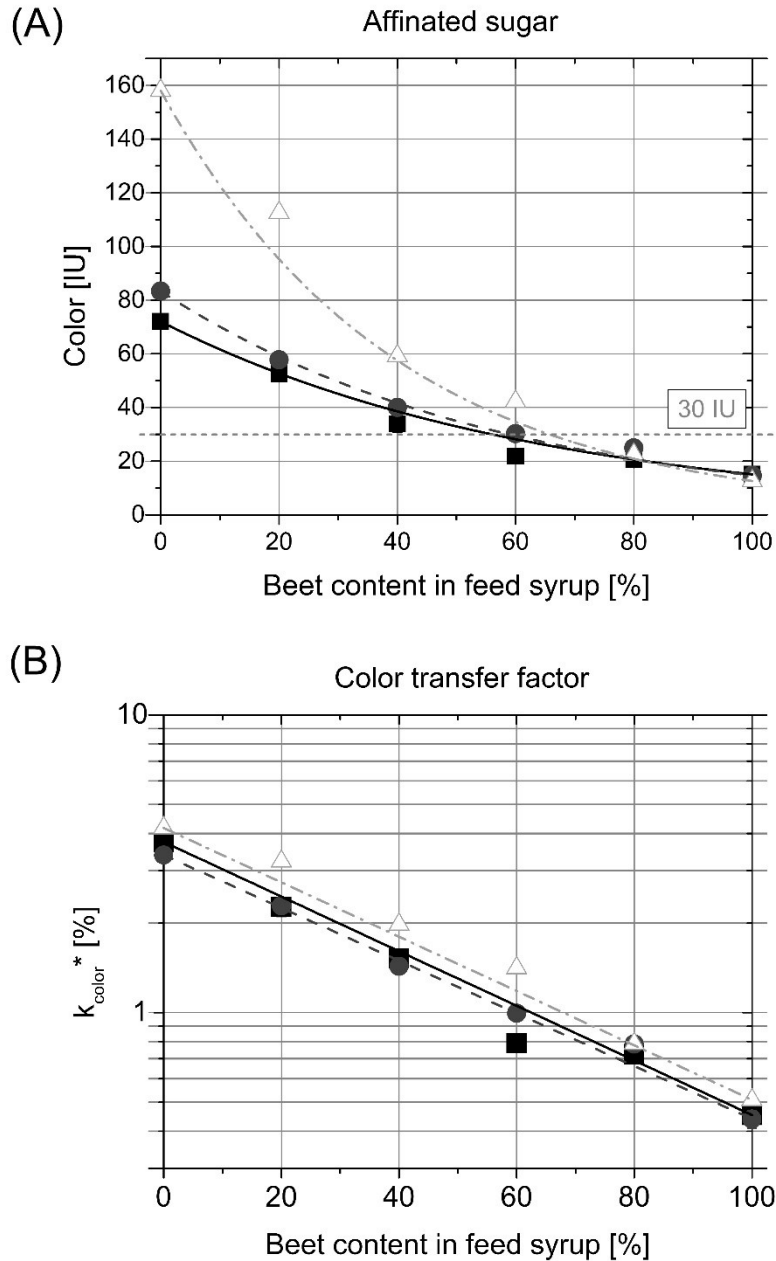


Figure 6-8: Color of affinated sugar (A) and the resulting color transfer factor (B) from crystallization with beet thick juice II & raw cane sugar II (■, full line); beet thick juice III & raw cane sugar III (●, dashed line); beet thick juice IV & raw cane sugar IV (△, dashed-dotted). Lines according to equation (6-18).

The color values of the affinated sugars that were crystallized from the different raw material combinations are shown in Figure 6-8A. For all pure beet syrups the sugar color values are practically identical (14 IU) despite the differences of the color values of the feed syrups of approximately 500 IU. For feed syrups solely containing cane material the color values of the sugar increased from 72 IU to 83 IU and 158 IU. These results confirm cane processing to be more prone to incorporation of colorants compared to beet. The evolution of sugar color values found for the different systems showed the typical behavior identified before (Schlumbach et al., 2017; Schlumbach et al., 2016). Comparing the data with the technical threshold value, 30 IU,

dashed line Figure 6-8A, it is found that raw cane sugars with color values of less than 1600 IU can be admixed safely to beet syrups up to a level of 40 g/100 g. For the raw cane sugar with a much higher color value (2500 IU) the acceptable inclusion levels reduced to around 25 g/100 g. Nevertheless, the systematic data gathered suggest that the earlier recommendations of 20 g/100 g inclusion (Kochergin et al., 2012) is too restrictive.

Transformation of the data in Figure 6-8A into color transfer factors according to equation (6-8) yielded Figure 6-8B. The color transfer factors found for pure syrups are in good agreement with those in the literature (Godshall & Baunsgaard, 2000; Godshall et al., 2002). The evolution of the color values of syrups and sugars in Figure 6-6 and Figure 6-8A, respectively, suggested an exponential increase of the color transfer factor with increasing cane content in the feed syrups. This is line with earlier work (Schlumbach et al., 2017).

The data indicated (Figure 6-8B) also that values of the color transfer factors depended on the specific raw cane sugar used in a mixed system. This is in conflict with the postulate that the color transfer factor is independent of the color load of the feed syrup. Apart from that, the data on raw material characteristics (Table 6-1) reveal that next to different color values also the dextran levels of the used raw cane sugars differed dramatically. These were in material III six-fold and material IV 24-fold higher than in raw cane sugar II. The polysaccharide is an indicator of stale cane or cut-to-crush delay which describes a lag between harvesting and processing (Chen & Chou, 1993; van der Poel, P.W., 2000). The high dextran contents indicate a high microbiological activity (*Leuconostoc mesenteroides*) in the early stages of the sugar production process. Besides microbiological activity enzyme reactions occur as soon as the stalk is damaged until heat

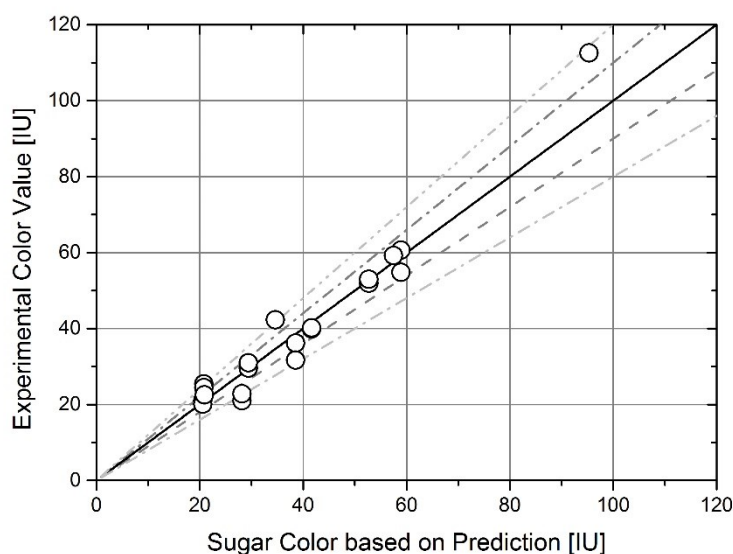


Figure 6-9: Parity plot of sugar color values (\circ). Laboratory analytical data of affinated sugars vs predicted data according to equation (6-18). Lines illustrate the relative deviation: $\pm 10\%$ dashed line; $\pm 20\%$, dashed-dotted line. Color values from sugars of single source syrups are not shown.

treatment deactivates the enzymes (Paton, 1992). During this period also indigenous sugar cane polysaccharides with attached phenolic groups convert to colorant-polysaccharide complexes of high molecular weight which are preferentially incorporated into the sucrose crystal and responsible for high color inclusion levels (Godshall & Baunsgaard, 2000; Godshall et al., 2002; Bourzutschky, 2005; Clarke et al., 1986). Our data hence suggested that the increased presence of polysaccharides in cane material is not only accompanied by elevated levels of colorants but also enhances the transfer of colorants from the syrups into the sugar crystals.

6.3.2.2 Prediction of sugar color values for mixed syrups

As described earlier (Schlumbach et al., 2017; Schlumbach et al., 2016) a useful model-correlation was formulated to predict the color value of sugars produced from blended syrups ($F_{420,s,x}$). The version given in equation (6-18) allows calculation of $F_{420,s,x}$ by solely using sugar color values from pure beet and cane feed syrup crystallization, $F_{420,s,x=1}$ and $F_{420,s,x=0}$, respectively:

$$F_{420,s,x} = F_{420,s,x=0} \cdot \exp(x_{ML,x=1} \cdot \ln(F_{420,s,x=1}/F_{420,s,x=0})) \quad (6-18)$$

where $x_{ML,x}$ is the beet content in feed syrup.

The parity plot (Figure 6-9) illustrates the agreement between the analytical color values for sugars produced from mixed syrups and color values predicted for these sugars based on equation (6-18) using analytical data on the single source juices that constituted the mixed syrup. For color values between 40 and 60 IU very good agreement was found. Once sugar color values below 40 IU were involved the scattering increased. It should be noted that at lower color values small variations in the experimental results lead to substantial relative deviation. Taking the accuracy of the analytical method into account it is fair to conclude that the sugar color values produced from mixed syrups can reliably predicted from the sugar color data of the constituting single source syrups.

6.3.2.3 Contribution of different color transfer mechanisms

It is known that different incorporation mechanisms contribute differently to the total color transfer into sugar crystals. To unravel the total color transfer factor into the contributions of the different incorporation mechanisms, adhesion, liquid inclusion, and co-crystallization is new (Schlumbach et al., 2017). In particular, the specific effect of varying syrup quality, raw cane sugar quality or mixed syrups, is not known. As outlined above the data for liquid inclusions were computed by equation (6-13). The values for co-crystallization were determined as the difference between the transfer factors of affinated sugar and liquid inclusion (equation (6-14)).

Figure 6-10 and Figure 6-11 present the relative color transfer factors for liquid inclusion, co-crystallization and adhesion for the three different mixed systems studied. The color transfer factor representing liquid inclusions was irrespective of the system showing a very clear pattern. The color transfer factor, k_{LI}^* , remained practically constant for all syrups with beet levels above

40 g/100 g independently of the quality of the raw material. For higher cane contents k_{LI}^* increased, depending on the quality of the cane material, to values found for the pure cane system (Figure 6-5). Only for the cane syrup with very high dextran levels was a higher k_{LI}^* found. The color transfer factors accounting for co-crystallization, k_{Co}^* , showed a different behavior. The values increased continuously from 0.13% for pure beet syrups to 2.70% for pure cane syrups. Similarly to the color transfer factors for liquid inclusion it was found that k_{Co}^* was in good

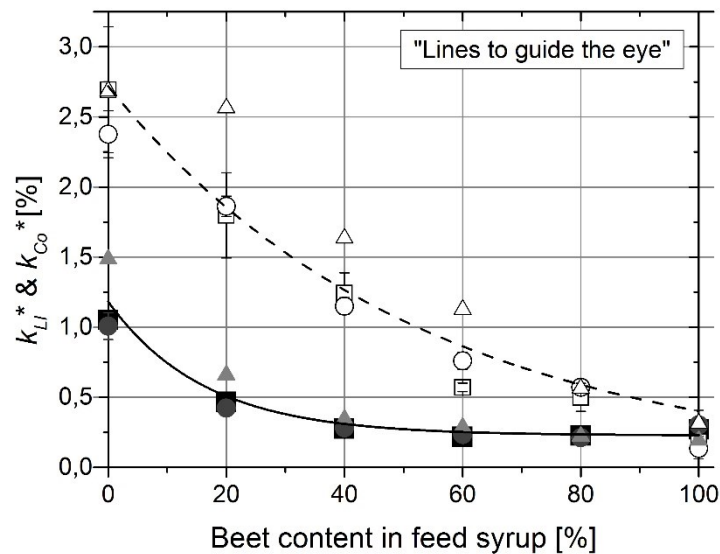


Figure 6-10: Color transfer factors of specific color incorporation mechanisms. Experiments with beet thick juice II & raw cane sugar II (■, □); beet thick juice III & raw cane sugar III (●, ○); beet thick juice IV & raw cane sugar IV (▲, △). Data for liquid inclusions are illustrated in full and co-crystallization in empty symbols.

agreement for the different mixed systems despite the large differences in feed syrup quality. The sugars crystallized from raw cane sugar IV deviated from the other systems with highest incorporation levels. This material, however, contained large amounts of colorants and also high levels of dextran. This deviation is understandable because it is known that dextran can have a profound effect on the crystallization process.

Regarding the dependence of the color transfer factors on compositional changes a clear suppression of color incorporation on mixing is found. Since differences in processing can be excluded as source of variation, the primary cause is seen in the interaction of non-sucrose compounds originating from the different sources, beet and cane. Non-sucrose compounds from cane have a high molecular mass and hence a low diffusivity (Edward, 1970). They typically consist of polysaccharides and contribute directly or indirectly to the color of syrups and crystals. It is believed that their outer sucrose-like structure promotes incorporation. Their increased interaction at the solid-liquid interface (e.g. dextran) (Godshall & Baunsgaard, 2000; Godshall et al., 1987; Godshall et al., 2002; Tu et al., 1977), probably supports co-crystallization into the crystal lattice (Chiu & Sloane G.E., 1980; Lionnet, 1998a; Paton, 1992). In contrast, it is assumed

that the coloring low molecular weight molecules in beet juices have a high diffusivity and show a high affinity to adsorb onto the crystal surface without being incorporated into the lattice. This is related to the relatively low color transfer factors (Schlumbach et al., 2017). Taking into account these differences of colorants of different origin it remains difficult to derive a simple mechanistic hypothesis that explains the observations made. To evaluate comprehensively the interplay of processes like polarization at the interface, diffusion, specific and non-specific adsorption, and incorporation into the crystal lattice it is necessary to delve in more detail into this subject. Activities to better understand this interplay by modelling color incorporation into sugar crystals are actually ongoing.

To evaluate the contribution of adhering mother liquor to the color value, color incorporation due to adhesion, of sugars crystallized from mixed syrups also non-affinated sugars were analyzed. Figure 6-11 depicts color transfer factors for adhesion, k_{Ad}^* , for the three different mixed systems. It was found that the differences between cane and beet material are less pronounced than for the other color incorporation mechanisms. The higher transfer factors found for feed syrups rich in cane possibly just related to higher viscosities caused by elevated levels of polysaccharides. Nonetheless, the data revealed that adhesion contributed significantly to the color values of non-affinated sugars. For beet material this contribution even appeared to be dominant.

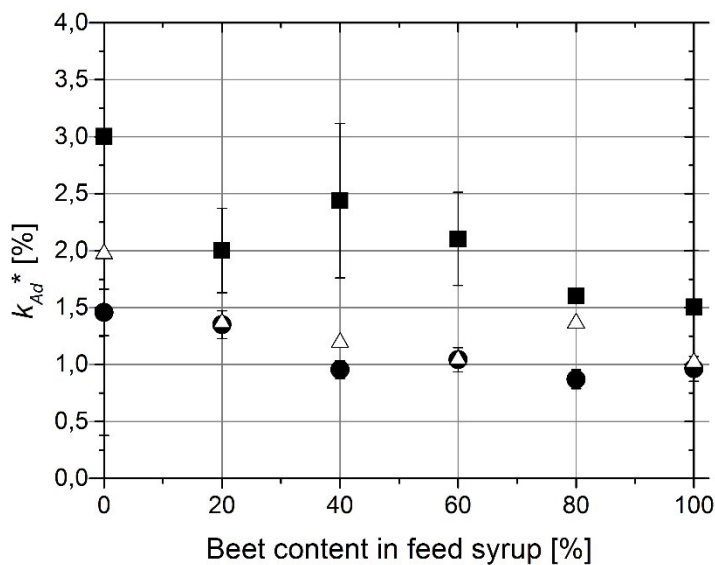


Figure 6-11: Color transfer factors for color values based on adhesion. Experiments with beet thick juice II & raw cane sugar II (■); beet thick juice III & raw cane sugar III (●); beet thick juice IV & raw cane sugar IV (△).

6.4 Conclusion

Previous work (Schlumbach et al., 2017; Schlumbach et al., 2016) in our lab yielded a correlation that allows the prediction of color values of sugars produced from syrups composed of both beet and cane material. The raw materials studied were very similar so that the prediction from the characteristics of the pure raw materials might only be of limited applicability. This manuscript documents the attempt to evaluate the robustness of these earlier findings. Furthermore, the underlying respective contributions of the different mechanisms of color incorporation, namely adhesion, liquid inclusion, and co-crystallization, was looked for. To this end different combinations of beet and cane materials were studied. Assessment of the data gathered proved that the control of the crystallization process was executed such that the differences found could be related to compositional variations according to the experimental design. Because adhesion is difficult to control, predominantly affinated sugars were analyzed and results are for reasons of comparison expressed primarily as color transfer factors. It was found that on reduction of the same colorants mix the transfer factor for liquid inclusion remains practically constant for pure beet and cane syrups. In contrast, the color transfer factors for co-crystallization increased on reduction of the concentration of the colorants, resulting in only limited changes of the color value of the beet sugars produced. For the mixed systems it was found that the formulated framework (Schlumbach et al., 2017; Schlumbach et al., 2016) is also valid for significantly different combinations of syrups, e.g. color value of the feed syrup increasing or decreasing with raw cane sugar addition. The study on the contributions of the different incorporation mechanisms of the colorants revealed that adhesion had a higher transfer factor with increasing concentration of cane material. This was possibly due to increased viscosities caused by elevated levels of polysaccharides. The color incorporation due to liquid inclusion was suppressed strongly by the presence of material with beet origin. Also for the color incorporation based on co-crystallization a systematic pattern emerged irrespective of the combination of raw materials. With increasing concentration of cane material the transfer factors increased significantly. The systematic pattern found for color incorporation due co-crystallization is, however, somewhat disturbed when high levels of dextran are present. In summary, the data gathered confirm the validity of the correlation formulated earlier. The differentiation of color transfer into three separate mechanisms revealed some interesting insights but certainly needs further study prior to any mechanistic interpretation. Finally, it should be noted that the data indicate that the current recommendation, to not include more than 20 g/100 g raw cane sugar into mixed syrups, appears to be too restrictive. Levels of up to 40 g/100 g seem possible. However, it is recommended to take the quality of the actual raw materials into account and hence apply the correlation formulated (Schlumbach et al., 2017; Schlumbach et al., 2016)

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7 THE INFLUENCE OF THE LINEAR GROWTH VELOCITY ON THE PROPERTIES OF SUCROSE CRYSTALS PRODUCED FROM MIXED SYRUPS

Schlumbach, Karl; Schwenkler, Melina; Flöter, Eckhard

TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

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Abstract

The systematic study presented addresses the need to understand the co-crystallization of beet and cane material better. This is important because of the sugar market liberalization in 2017. Here the effect of crystal growth velocity on final sugar quality is investigated. Comparing three different thermal setups, studying different cane and beet mixtures color inclusion into sucrose crystals was analyzed. Within one thermal setup supersaturation was practically constant. Almost exclusively the time necessary to complete the crystallization at 50% solids level changed. Particle size and distribution remained unchanged. Hence, only the growth velocity varied. Growth rate appears to influence color inclusion less than mixing of beet and cane syrups. In cane syrups the relative color inclusion is the highest and most sensitive to growth velocities. Admixing only 33% of beet syrup, already changes this pattern dramatically and the color transfer factor is more than halved. This effect of beet material is most prominent for the mechanism liquid inclusion but also significant for co-crystallization of colorants. This observation is possibly due to the different nature of the colorants originating from beet and cane. The findings provide a framework to optimize the space-time yield under consideration of highest sugar quality to manufacturers.

Practical applications

Co-production of beet and cane is a promising opportunity to increase competitiveness by increasing utilization of equipment in the seasonal sugar industry. To do so reliably, quality parameters have to be met. The main problem to be solved is the control of white sugar color. Since cane and sugar beet deliver different coloring minor components, their interaction and respective inclusion mechanisms need to be understood. The work presented is part of a comprehensive study to elucidate this area of sugar processing that has not been studied yet. Next to the findings on inclusion characteristic and relative contribution of different mechanisms, the conclusions can directly be transferred into practice. The data gathered give a clear guidance to producers that higher inclusion levels of “colored” material, than current conservative practice dictates, can be tolerated due to the mutual suppression mechanism found.

7.1 Introduction

With the end of the Sugar Policy in 2017 the European sugar market is liberalized and competitors from overseas can possibly enter the market. This poses new challenges for the long-established European sugar producers confronted with prices according to the world market. On the other hand, new opportunities arise since possible exports to outside the EU allow for larger production volumes. In the past years the European manufacturers have optimized their production facilities, invested into new equipment or restructured the business to enhance capacities and improve efficiency. However, the beet sugar production is limited to two periods per year, either the fresh-beet or the thick juice campaign. In the remaining time equipment is standing idle and subjected to maintenance. One approach for higher utilization of the factory is the refining of raw cane sugar or the co-production of beet syrup and raw cane sugar. The latter is already adopted by a few factories for several years to prolong the inter-campaign. Obviously, the quality of the respective final product, white sugar, has to meet customers' demands. The most important quality parameters are color and ash values. It is generally acknowledged that an addition of 10 – 20 g/100 g raw cane sugar to beet sugar operations is not jeopardizing high white sugar quality [color values below 30 IU (ICUMSA units)] or robust factory operation (Kochergin et al., 2012). However, various product and process parameters, such as crystal growth rate, nature and concentration of the impurities, are possibly affecting the final product quality (Ferreira et al., 2009; Godshall et al., 2002; Lionnet, 1998b; Mantovani et al., 1986a, 1986b; Rein, 2007; van der Poel, P.W., 2000; Lionnet, 1998a). Much work concerning the processes of impurity inclusions has been reported. It is stated that higher growth rates correlate with higher impurity inclusion levels (Singh & Delavie H.J., 1974; Donovan & Williams J.C., 1992; Lionnet, 1988, 1998a; Guo, 1984). To that end Singh and Delavie (1974) stated that the concentration of salts increases with an increasing crystal growth rate.

In beet and in cane sugar industry it is a widespread practice to predict the final sugar color based on the so-called color transfer factor. This factor is the ratio of the color values of the sugar and the feed syrup. The nomenclature of the transfer factor might be counterintuitive because the scope of the crystallization is the removal of colorants and not the inclusion. According to this, 'partition coefficient' would be the more appropriate term. However, the abovementioned ratio of color values does not fulfil the definition for a partition coefficient, because the characterization of the color value does not provide specific information about the distribution of molecules and hence concentrations of different colorants as described in this work.

Donovan and Williams (1992) showed that color transfer increased by 75% when halving the crystallization time in cane juices. Lionnet (1998a) found similar results. The authors demonstrated that with increasing crystallization rate the rate of color transfer increases linearly. During earlier experiments the same author found a less pronounced influence of the crystallization rate on the color transfer (Lionnet, 1988). Guo (1984) found already earlier that

the inclusion level of impurities correlates linearly with crystal growth rate. In this case a strong dependency was found. Furthermore, the work of Mantovani et al. (1986a) revealed that impurity inclusions occur preferentially in fast growing crystal faces, in either beet or cane processing. Building on this, the level of impurity inclusion of the different crystal faces appeared to depend differently on supersaturation (Saska, 1988). Although extensive research on the influence of crystal growth on impurity inclusion has been performed, the knowledge is limited to either pure beet or pure cane sugar processing, but does not cover co-processed sugars which contain mixed impurities originating from both sources. Profound knowledge of the incorporation mechanisms of impurities is necessary to ensure high quality white sugar and to adapt process parameters accordingly. Three different mechanisms contribute to final sugar color: Adhesion, liquid inclusion and co-crystallization.

Adhesion describes the surface color of the sucrose crystal resulting from mother liquor not completely removed during separation. This contribution is affected by the separation procedure (e.g. centrifugation with washing) and the concentration and the adhesive properties of the colorants in the mother liquor. For beet sugars this contribution accounts typically for 20 – 50% of the final sugar color (Godshall et al., 1991; Shore et al., 1984).

Liquid inclusion refers to droplets of mother liquor which are trapped into crystal voids. This phenomenon occurs when liquid adheres to the rough surface displaying crystal defects such as grooves. Subsequent overgrowing entraps these patches of mother liquor inside the crystal (Grimsey & Herrington, 1994; Mackintosh & White, 1968; Saska, 1988; Vaccari et al., 1990b). Therefore these colorants can only be removed by partial dissolution of the crystal (Mackintosh & White, 1968; Shore et al., 1984), but not by washing processes (e.g. during centrifugation, affination). The amount of liquid inclusions appears to be proportional to the number of surface defects (Grimsey & Herrington, 1994; Singh & Delavie H.J., 1974). Impurities related to ash components, such as *KCl*, are only incorporated by this mechanism. The liquid inclusion is hence a sample of the mother liquor at the moment of inclusion (Grimsey & Herrington, 1994; Grimsey I.M. & Herrington, 1996). Consequently, the ash incorporation into the sugar crystal, which is exclusively due to liquid inclusion, corresponds with incorporation level of other impurities (e.g. colorants) due to liquid inclusions.

Co-crystallization actually refers to the incorporation of the impurities into the crystal lattice (Singh & Delavie H.J., 1974). Thus, especially colorants with a sucrose-like structure are incorporated into the sucrose crystal. Counterintuitively, it is reported that colorants with high molecular weight are preferentially included into the crystal matrix. Different authors suggested that a high concentration at the solid-liquid interface and an apparent sucrose-like structure (Schlumbach et al., 2017) which is a result of cluster formation with sucrose in the mother liquor (Grimsey I.M. & Herrington, 1996) play a role in this process.

These different mechanisms were discussed by various authors but their relative contributions to the final sugar color were not studied yet. In earlier work it was shown that varying raw material

The influence of the linear growth velocity on the properties of sucrose crystals produced from mixed syrups quality influences the color of sugars and results in changes of the relative contribution of the different impurity inclusion mechanisms (Schlumbach et al., 2018). However, the influence of process parameter variation on linear growth rate and hence on color and ash inclusion has not been studied for mixed beet and cane syrups yet. This contribution is aiming to fill this knowledge gap in order to allow the exploration of new raw material combinations in sugar processing in a robust way.

7.2 Material and methods

7.2.1 Crystallizer and ancillary equipment

All evaporative crystallization experiments are conducted in a 0.005 m³ vessel which is described in detail elsewhere (Schlumbach et al., 2015). The process is controlled such that a practically constant supersaturation is maintained. Therefore, constant pressure is ensured by a vacuum pump (PC 3001, Vacuubrand GmbH & Co KG, Wertheim, Germany). The control of the heat transfer media, which flows through the double walls of the vessel, is realized by two thermostats (F32-HD and F12-MC, both Julabo, Seelbach, Germany). The dry substance level of the solution is determined by a process refractometer (iPR 2-3, Schmidt & Haensch GmbH & Co., Berlin, Germany) which is mounted to the bottom of the vessel. For monitoring the temperature during the process a Pt-100 thermo element is submerged into the crystallizing fluid. When a crystal content of 50% is achieved the crystals are separated from the surrounded mother liquor in a temperature-controlled basket centrifuge (DM 2250, Gebr. Heine, Viersen, Germany) with an attached washing unit. The wet sugar is dried in a fluidized-bed (TG 1, Retsch, Haan, Germany) to finally ensure the production of sugar with industrially relevant quality. (Schlumbach et al., 2015)

The experimental set-up is controlled with the help of a self-written program based on LabVIEW (National Instruments Corporation, Munich, Germany). The program records on-line data such as pressure, temperature and refractometric dry substance of the mother liquor.

Additionally, data on mass m , dry substance w_{DS} , purity q , and fluxes of feed, condensate and sample volumes are entered into the system. Based on repeated linear regression of three successive condensate readings the total dry substance level and amount of water present in the system were computed during crystallization strikes. This approach allows the computation of the massecuite dry substance, mother liquor purity, crystal content, and current supersaturation by simple mass balances.

7.2.2 Raw Materials

For ensuring industrial relevance of the work beet thick juice was sourced from a German sugar factory. The raw cane sugar is originating from Brazil. Both materials were supplied by Suiker

Unie. For each experiment, raw cane sugar was dissolved using two parts of solid and one part of demineralized water ($< 2 \mu\text{S/cm}$). The solution was filtered through a stainless-steel mesh (nominal $5 \mu\text{m}$, absolute $8 \mu\text{m}$; TEDRA Dahmen GmbH & Co. KG, Wassenberg, Germany) prior to mixing. The feed syrups were blends of beet thick juice and raw cane sugar solution with the following mass ratios (g/100 g): 100:0, 67:33, 33:67, 0:100. Here, the first number expresses the beet content and the second the cane content. Furthermore, 100 μl of an anti-foaming agent (Struktol SB 2433, Schill + Seilacher 'Struktol' GmbH, Hamburg, Germany) was added into the 5,000 g blend to avoid frothing during evaporation and crystallization. Quality parameters of the feed syrups are listed in Table 7-1.

Table 7-1: Quality parameters of the feed syrup.

Feed syrup composition (beet to cane)	q %	F_{420} IU	C_{ash} %
100:0	94.67 (± 0.50)	5013 (± 352)	1.51 (± 0.07)
67:33	96.32 (± 0.35)	4099 (± 181)	1.12 (± 0.04)
33:67	98.06 (± 0.36)	2964 (± 233)	0.66 (± 0.08)
0:100	99.42 (± 0.32)	1644 (± 90)	0.10 (± 0.01)

7.2.3 Batch crystallization process

Various crystallization strikes were conducted to examine the influence of crystal growth rate on color and ash transfer into the sugar crystal. The general experimental procedure is illustrated in Figure 7-1.

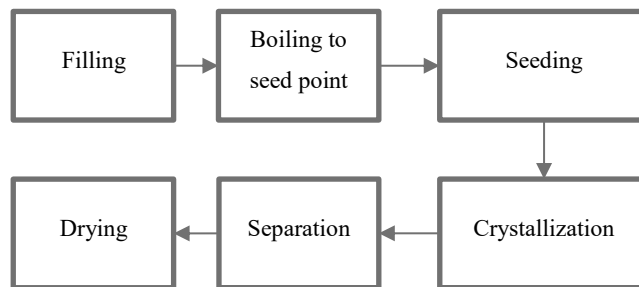


Figure 7-1: General scheme of crystallization experiment.

First the feed syrup (5,000 g) was filled into the vessel and evacuated to a system pressure of 270 mbar (± 1 mbar). The blend was kept homogeneous by means of an agitator (60 rpm) (RZR 2102 control, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany). The temperature of the heating water in the lower jacket was chosen to establish evaporation of the water in the mother liquor. For achieving different crystal growth rates the temperature is set to 361 K, 366 K, and 371 K (± 0.01 K) for each mass ratio. The temperature of the upper jacket was according to standard operation procedure maintained at 343 K (± 0.01 K) to avoid nucleation and sucrose deposition on the wall.

The influence of the linear growth velocity on the properties of sucrose crystals produced from mixed syrups

After adequate stirring and prior to boiling a sample of the homogeneous blend is taken and analyzed. Once a supersaturation of 1.05 was achieved 100 g of seed crystals ($d_{50,0}=0.283$ mm, $F_{420,seed}=20$ IU) were added into the mother liquor to start crystallization. The amount was chosen to achieve an end crystal size of 800 μ m.

Steady heat supply and constant pressure during the process ensured constant supersaturation (± 0.01) during each experimental run. The crystallization strike is finished once the torque of the stirrer increases by a value of 0.06 Nm from the starting value. This increase is caused by higher viscosity of the massecuite due to the disperse phase volume indicating a crystal content of 45 – 50 g/100g.

At this occasion, a sample of the massecuite was taken. Subsequently the sucrose crystals were separated from the mother liquor by centrifugation (1,450 RCF). A sample of the run-off mother liquor was taken before water is spread on the crystal bed surface to remove residues of syrup. The washing water was pre-heated such that no temperature effects are induced during washing. The applied amount of washing water was 2.5 g/100g of the mass of the massecuite. Finally, the wet sugar was dried in a fluidized-bed dryer (TG1, Retsch, Haan, Germany) for 8 minutes with conditioned air at a temperature of 335 K followed by cooling down for 2 minutes to 295 K to yield a residual humidity of 0.04 (± 0.01) g/100 g.

7.2.4 Analytical methods

The analyses were conducted according to standard methods used in the sugar processing industry which are given in detail elsewhere (ICUMSA, 2011). Prior to the laboratory tests all samples were diluted 1:1 (w/w) with demineralized water (<2 μ S/cm).

The dry substance content (w_{DS}) of the prepared solutions was determined by refractometry (ATR-W2 plus, Schmidt & Haensch, Berlin, Germany). The sucrose content (w_S) was analyzed by polarization (Saccharomat NIR W2, Schmidt & Haensch, Berlin, Germany) after clarification with *Carrez* following the ICUMSA Method GS8-2 (ICUMSA, 2011). The proportion of sucrose on dry substance gives the purity q of the samples in %:

$$q = \frac{w_S}{w_{DS}} \cdot 100 \quad (7-1)$$

Simple mass balances allow the determination of the purity, during the process.

The size of the sugar crystals resulting from different crystallization strikes was determined according to ICUMSA Method GS2/9-3 (ICUMSA, 2011). A mechanical shaker (AS 200 Control, Retsch, Haan, Germany) classified the sugar crystals for 7 min. The mean aperture (d_{50}) and coefficient of variation (CV) were calculated according to *Powers* Method (van der Poel, P.W., 2000).

The driving force for the crystallization processes is the supersaturation, respectively the difference between the chemical potential of the current and the saturated state:

$$\frac{\mu - \mu_{sat}}{RT} = \ln \left(\frac{\gamma \cdot c}{\gamma_{sat} \cdot c_{sat}} \right) \quad (7-2)$$

Where μ is the chemical potential, γ is the activity coefficient and c is the molar concentration. The index sat indicates the saturated state. Due to the fact that thermodynamic data are usually unavailable the supersaturation y_{ss} is often computed as the ratio of the concentrations (Myerson, 2001; Mullin, 2001):

$$y_{ss} = \frac{c}{c_{sat}} \quad (7-3)$$

With reference to equation (7-3) it is generally acknowledged in the sugar manufacturing industry that the supersaturation coefficient y_{ss} is described by the quotient of the ratio of the mass fractions of sucrose to water in the given solution ($w_{s,ML}/w_{W,ML}$) to that in a saturated solution ($w_{s,ML}/w_{W,ML}$)_{sat} at the given temperature. For technical, respectively impure solutions a so-called saturation coefficient (y_{sat}) was introduced to compensate the change of sucrose solubility in these solutions:

$$y_{ss} = \frac{c}{c_{sat}} = \frac{(w_{s,ML}/w_{W,ML})}{(w_{s,ML}/w_{W,ML})_{sat}} = \frac{(w_{s,ML}/w_{W,ML})}{y_{sat} \cdot (w_{s,ML}/w_{W,ML})_{sat,p}} \quad (7-4)$$

For this study, the average supersaturation during crystallization was computed. Therefore, the mean values based on mass balance of dry substance and purity throughout the strike were taken into account. For the solubility of pure sucrose solutions, the mean temperature and equation given in Appendix were used. The saturation coefficient (y_{sat}) was determined by empirical correlation to the non-sucrose to water ratio. This approach is based on the work of Rozsa (2000). For the computation of the crystal content (w_{CC}) at the end of the strike three methods are available. On one hand, simple mass balances allow determination of the crystal content from the sugar content (w_s) of the massecuite (MC) and mother liquor (ML):

$$w_{CC} = \frac{w_{s,MC} - w_{s,ML}}{100 - w_{s,ML}} \cdot 100\% \quad (7-5)$$

Data for the sugar contents can either be gathered by lab analyses of the samples ($w_{CC,lab}$) or calculated online by the self-programmed process control unit ($w_{CC,CU}$) based on condensate production and refractive index. Thirdly, the crystal content $w_{CC,color}$ can be computed from experimental color values by rearranging equation (7-6) (Schlumbach et al., 2018):

$$\frac{F_{420,ML,n}}{F_{420,ML,0}} = \frac{\frac{(w_{CC,color})}{(1 - (w_{CC,color}))} + w_{DS,ML}}{w_{DS,ML}} \quad (7-6)$$

With the color of mother liquor $F_{420,ML}$ at end (n) and begin (0) of the strike and the average dry substance of the mother liquor, $w_{DS,ML}$. All data are carefully monitored and appear to be very consistent. This triplicate monitoring ensures that outliers are identified immediately.

The size of the sugar crystals resulting from processing of different mixed syrups was determined according to ICUMSA Method GS2/9-3 (ICUMSA, 2011). Samples of the dried sugars were characterized according to the classes of sieves: 0.180 mm, 0.250 mm, 0.400 mm, 0.630 mm,

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0.710 mm, 0.800 mm, 0.900 mm, and 1.00 mm. From the crystal sizes and the duration of the crystallization strike ($\Delta\tau$) the average crystal mass growth rate G ($\text{kg m}^{-2} \text{s}^{-1}$) was derived (Bubnik & Kadlec, 1992):

$$G = \frac{3\rho \cdot \alpha}{\beta} \cdot \frac{\Delta d_{50}}{\Delta\tau} \quad (7-7)$$

The density of sucrose crystals ρ is $1,587 \text{ kg m}^{-3}$ and Δd_{50} is the difference between the average size of the crystals from seeding and at the end of the process. Here the constants $\alpha = 0.75$ and $\beta = 5.02$ are set according to Bubnik and Kadlec (1992). These values are valid for beet sugar crystals analyzed by sieving. In other studies, it was shown that the shape factors for beet and cane sugar crystals obtained from industrial syrups and refinery liquor, respectively, are almost identical. However, in these studies the particle characterization was done by a different technique. (Bubnik & Kadlec, 1992; Lionnet, 1998a) This implies that the shape factors for beet and cane sugar can be considered equal as well if the particles are characterized by sieving. Based on mass balance a second method for computing crystal growth during the crystallization strike was applied - the linear growth velocity v (m s^{-1}) (Mullin, 2001):

$$v = \frac{\sqrt[3]{m_{Cr,n}} - \sqrt[3]{m_{Cr,0}}}{\sqrt[3]{\alpha \cdot \rho \cdot N \cdot \Delta\tau}} \quad (7-8)$$

Here m_{Cr} is the mass of crystals at end (n) and begin of crystallization (0) strike. The first is calculated by the product of massecuite mass at the end of the strike ($m_{MC,n}$) and averaged crystal content $\overline{w_{CC}}$. The number of crystals, N , is computed by average end crystal size ($d_{50,n}$):

$$N = \frac{m_{Cr,n}}{d_{50,n}^3 \cdot \alpha \cdot \rho} \quad (7-9)$$

Equation (7-8) is simplified by inserting equation (7-9):

$$v = \frac{d_{50,n}}{\Delta\tau} \cdot \left(1 - \sqrt[3]{\frac{m_{Cr,0}}{m_{Cr,n}}} \right) \quad (7-10)$$

Although the separation of crystals and mother liquor is conducted in the same manner an affination process applied to ensure a reproducible quality of the sugar with respect to the adhering mother liquor film. Therefore, the crystals were submerged into a saturated sugar solution made up from refined beet sugar. The crystal dispersion was gently stirred for 15 min and crystals were separated from the solution by the means of a laboratory centrifuge (Sieva-2, Hermle, Wehingen, Germany). The procedure was repeated with 5 min stirring time. Prior to further analysis the sugar was dried in a desiccator.

The ash content $C_{ash,s}$ (in % (w/w)) of the affinated sugar is determined by a method (GS2/3/9-17, ICUMSA (2011)) based on conductivity (In Lab730 and Seven Easy, Mettler Toledo, Gießen, Germany):

$$C_{ash,s} = 6 \cdot 10^{-4} \cdot (C_1 - 0.35 C_w) \quad (7-11)$$

with the conductivity of the sample and water, C_l and C_w respectively, at 293 K.

The ash content of syrup $C_{ash,ML}$ (in % (w/w)) is computed by ICUMSA method GS1/3/4/7/8-13 (ICUMSA, 2011):

$$C_{ash,ML} = (16.2 + 0.36 \cdot \frac{w_{DS}}{100}) \cdot 10^{-4} \cdot (C_1 - C_w) \cdot \frac{5}{S} \quad (7-12)$$

with w_{DS} the dry substance and S the mass of the sample in 100 ml.

The color of the feed syrup, massecuite, run-off syrup and sugar is determined spectrophotometrically (Coloromat, Schmidt & Haensch, Berlin, Germany) using the analytical methods GS1/3-7 and GS2/3-10 (ICUMSA, 2011). The pH-value of all samples was adjusted with hydrochloric acid and/or sodium hydroxide solutions to a value of 7.0. The color value (IU) in solution can be calculated from the absorption (A_s) determined at 420 nm as follows:

$$F_{420} = \frac{10^8 \cdot A_s}{b \cdot w_{DS} \cdot \rho} \quad (7-13)$$

Here b is the length of the cuvette (1 cm for syrup, 10 cm for dissolved sugar), w_{DS} the dry substance content and ρ (kg m⁻³) the density of the investigated solution (ICUMSA, 2011).

The color values of the feed syrup and the sugar allow to calculate the color transfer factor.

$$k_{color} = \frac{F_{420,s}}{F_{420,ML,0}} \cdot 100\% \quad (7-14)$$

This is an easy tool for industrial purposes to predict the final sugar color as a function of the color of the feed syrup.

However, this approach only works if all other relevant parameters remain unchanged. It ignores that the concentration of colorants in the mother liquor is a function of ongoing crystallization and other factors such as growth rate. To take the evolution of color in the mother liquor into account the color value is also determined at the end of the crystallization run $F_{420,ML,n}$. Observations justify to consider the concentration increase of colorants to be linear with time. Consequently, the k_{color}^* which is independent of the final crystal content can be derived:

$$k_{color}^* = \frac{F_{420,s}}{(F_{420,ML,0} + F_{420,ML,n}) \cdot \frac{1}{2}} \cdot 100\% \quad (7-15)$$

Analogous to equation (7-15) the ash transfer factor k_{ash}^* can be calculated with equation (7-11) and (7-12):

$$k_{ash}^* = \frac{C_{ash,s}}{(C_{ash,ML,0} + C_{ash,ML,n}) \cdot \frac{1}{2}} \cdot 100\% \quad (7-16)$$

As mentioned above different mechanisms are responsible for the inclusion of colored compounds. Thus, colorants entrapped inside the crystal structure are either due to the mechanism of liquid inclusions (LIs) or co-crystallization (Co):

$$F_{420,s} = F_{LI} + F_{Co} \quad (7-17)$$

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According to equation (7-15) and (7-17) the color transfer factor is composed of the transfer factors for mother liquor inclusion (k_{LI}^*) and co-crystallization (k_{Co}^*), both determined with respect to the averaged color value of the mother liquor:

$$k_{color}^* = k_{LI}^* + k_{Co}^* = \left(\frac{F_{LI} + F_{Co}}{(F_{420,ML,0} + F_{420,ML,n}) \cdot \frac{1}{2}} \right) \cdot 100\% \quad (7-18)$$

For affinated sugars it is known that ash is solely included into the sugar crystals by liquid inclusions (Grimsey I.M. & Herrington, 1996; Singh & Delavier H.J., 1974). Hence the ash transfer factor and the color transfer factor for liquid inclusions are regarded equal, ignoring possible colorants adsorption at the inner surface of the liquid including voids:

$$k_{LI}^* = k_{ash}^* \quad (7-19)$$

Based on equation (7-18) and (7-19) the color transfer factor due to co-crystallization can be computed by:

$$k_{Co}^* = k_{color}^* - k_{LI}^* = k_{color}^* - k_{ash}^* \quad (7-20)$$

7.3 Results and discussion

7.3.1 Influence of supersaturation on crystal growth velocity

To study the influence of linear growth velocity on final sugar quality crystallization runs of different mixed syrups were performed with different levels of supersaturation. Each crystallization strike was repeated at least once. The raw data of mean aperture, coefficient of variation, and crystallization time are shown in the Appendix (Table 7-2). Figure 7-2 illustrates the computed linear growth velocity as a function of the supersaturation present during the respective crystallization run. The data are grouped in the first place according to the temperature difference between evaporation temperature and temperature of the heating medium, circles indicate constant ΔT . It could be tempting to directly relate the increased driving force (ΔT) for heat transfer to the supersaturation. However, in computing the supersaturation according to equation (7-4) variation within these clusters occurs depending on the composition and level of impurities of the crystallizing solutions. Within each ΔT -cluster solutions with increasing cane content show lower supersaturations and higher growth velocities.

This is the results of different factors such as evaporation rate, dry substance level and purity influencing both supersaturation and growth velocity. It should be noted that although the system pressure was kept constant in all experiments (270.38 mbar, ± 0.19 mbar) the temperature of the syrups increased on average by 0.38 K with an increase of the temperature of the heating medium by 5 K. Consequently, the temperature difference (ΔT) as the driving force for the heat transfer did actually increase by 5 K reduced by the increase of the actual boiling point temperature, 0.38 K on average. Assuming wrongly that the process runs under equilibrium conditions, an

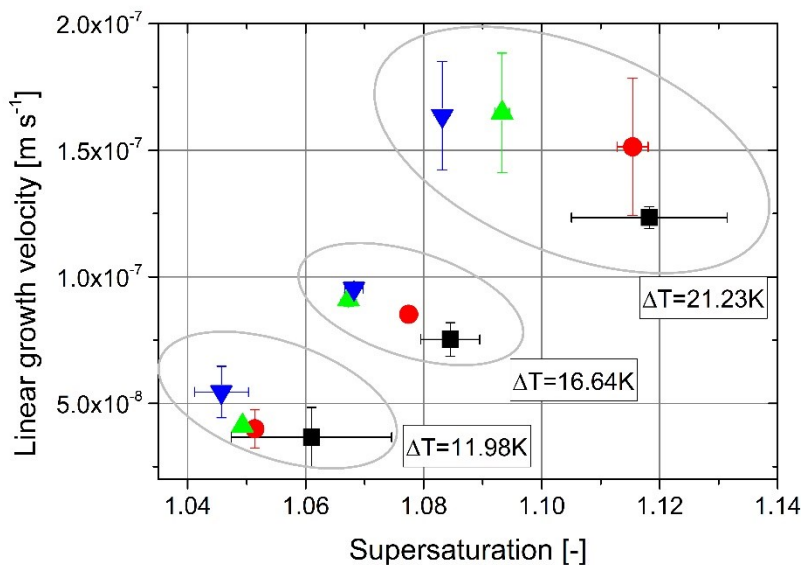


Figure 7-2: Linear growth velocity for different feed syrups (100:0 (■), 67:33 (●), 33:67 (▲), 0:100 (▼)) versus supersaturation. ΔT : Temperature difference heating media and boiling syrup.

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increase in ΔT causes an increased heat transfer into the crystallization vessel. This increased heat flux directly converts into the adequate increased evaporation rates. Maintaining the postulate of equilibrium, this directly converts into increased crystallization rates, ergo growth velocities, liberating additional thermal energy. Even though, in our case the basic logic outlined is still valid, supersaturation factors larger than 1.0 occur because the composition of the mother liquor changes. This is due to kinetic effects, with increasing temperatures of the heating medium, which consequently modulate the direct conversion outlined above. This results in higher dry substance levels of the mother liquor causing increased boiling point temperatures.

For syrups rich in cane the purity is very high (Table 7-1) and it is without saying that the content of non-sucrose compounds which influence sucrose solubility is low. Consequently, the value for the saturation coefficient (γ_{sat} , equation (7-4)) remains practically 1.0. On the other hand, syrups rich in beet contain a larger amount of non-sucrose compounds. Depending on the concentration salting-out effects are reported (Rozsa, 2000; van der Poel, P.W., 2000). This means the sucrose solubility is reduced due to the presence of non-sucrose solutes. Consequently, this causes an increased supersaturation with increasing beet content within experimental sets with the same driving force for heat transfer. Furthermore it is generally acknowledged that with further decreasing purity this effect appears to be inverted so that the growth velocity decreases (van der Poel, P.W., 2000).

Figure 7-3 compares crystal mass growth rate G based on crystal size measurement (equation (7-7)) with the linear growth velocity v based on the change of crystalline mass (equation (7-8)). The trend of both data sets corresponds very well indicating that the crystallization experiments and analysis were performed consistently. Furthermore, this demonstrates that the possible formation of nuclei played a minor role during the crystallization process. However, to further

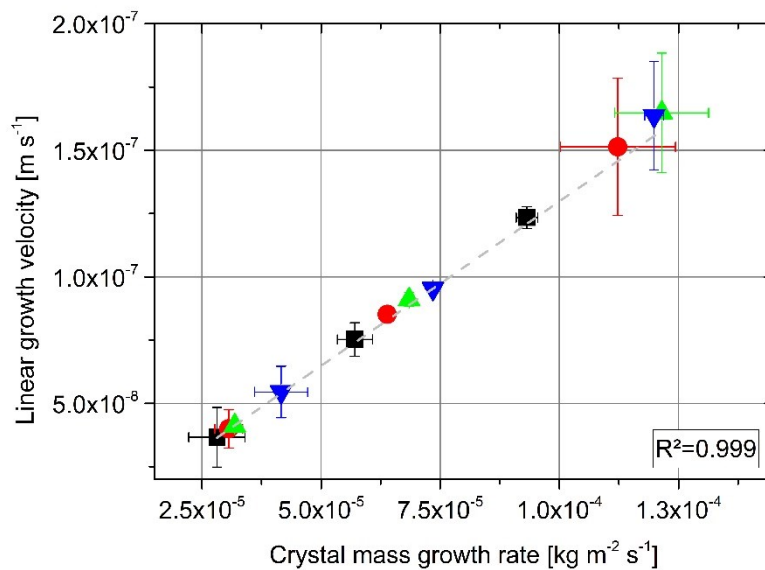


Figure 7-3: Comparison of crystal mass growth rate and linear growth velocity for different compositions of feed syrup: 100:0 (■), 67:33 (●), 33:67 (▲), 0:100 (▼).

address this subject, data on particle size and distribution would need to be taken into account. Since this is not explicit subject of the work reported here, the data based on the measurements of crystalline mass are considered in the following.

7.3.2 Influence of crystal growth rate on particle size and distribution

The study of characteristic particle size data allows to assess the consistency of crystallization process and the influence of growth velocity on size and variation of the crystals. Figure 7-4a depicts the mean apertures (d_{50}) for the different experimental sets. On average, the mean aperture was decreasing slightly with increasing growth velocity for each blend. However, variations are small and the desired mean size of approximately 0.80 mm was achieved satisfactorily. For sugars

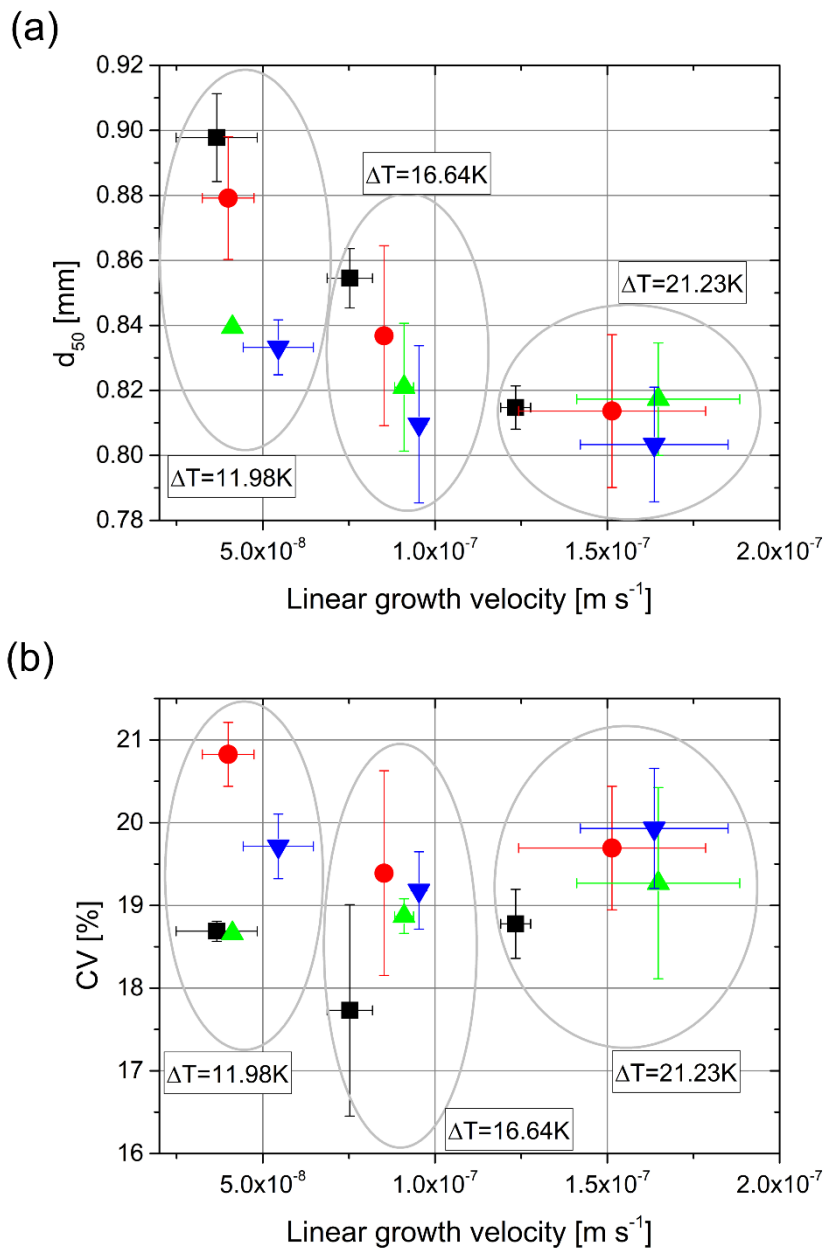


Figure 7-4: Data of particle size analyses from crystallization experiments ((a) mean aperture, (b) coefficient of variation) versus linear growth velocity. Compositions of feed syrups: 100:0 (■), 67:33 (●), 33:67 (▲), 0:100 (▼).

The influence of the linear growth velocity on the properties of sucrose crystals produced from mixed syrups crystallized from blends high in raw cane sugar, thus with higher purity, the particle size appeared to be less sensitive on linear growth rate.

Figure 7-4b illustrates the influence of linear growth velocity on the coefficient of variation (*CV*) ergo particle size distribution. The values spread unsystematically between 17.7 – 20.8%. However, compared to typical sugar crystallization the data indicate a very narrow particle size distribution (van der Poel, P.W., 2000) which is independent from the composition of the feed syrup and growth velocity.

The data gathered for mean crystal size and particle size distribution confirm consistency in crystallization procedure. This is on one hand ensured by maintaining constant heat supply, stirring, and process pressure and on the other hand by equal seed crystal size, quality and quantity. The variation of the duration of crystallization is due to the torque-defined end of process according to the method described. This resulted in final crystal content values fluctuating around the average of 45.36 g/100 g, see Table 7-2. For means of clarity it should be mentioned that each set of data was processed independently. The slight differences in size of particles crystallized applying the same driving force (ΔT) can be explained by inhomogeneities occurring in the crystallizer. With increasing ΔT these inhomogeneities were reduced due to better mixing of the massecuite caused by more intense boiling.

7.3.3 Influence of crystal growth rate on color transfer

To elucidate the influence of growth velocity on color transfer into sucrose, crystals crystallized from syrups of different origin were studied. The relative color inclusion expressed according to equation (7-15) is illustrated in Figure 7-5. The color transfer factor was increasing with increasing cane levels in the blend. Additionally, less pronounced though, the color transfer factors were increasing linearly with increasing linear growth velocity. This effect is most pronounced for syrups solely containing cane material. This indicates that compositional differences, ergo origin of colorants have a much larger influence on color transfer than variation of the growth velocity in the parameter range studied.

In earlier work an exponential model (equation (7-21)) was established to predict final sugar color of mixed syrups from the data of the constituting single source syrups, beet and cane (Schlumbach et al., 2018).

$$F_{420,s,x} = F_{420,s,x=0} \cdot \exp(\ln(F_{420,s,x=1}/F_{420,s,x=0}) \cdot x) \quad (7-21)$$

$$\lambda = \ln\left(\frac{k_{x=1}^*}{k_{x=0}^*}\right) \cdot \frac{1}{100} \quad (7-22)$$

$$k_x^* = k_{x=0}^* \cdot \exp(\lambda x) \quad (7-23)$$

where x is the beet content in the feed syrup.

However, in the previous work crystal growth rates were not considered. Therefore, in this study the intermediate color transfer factors are computed according to the exponential color inclusion model for different linear growth rates. Based on the linear regression parameters from the single

source syrups, λ was computed by equation (7-22) for six different linear growth velocities between $4.00 \cdot 10^{-8}$ and $1.70 \cdot 10^{-7} \text{ m s}^{-1}$. Equation (7-23) allows to compute the color transfer factors for the mixed syrups k_x^* . The results are represented as dotted lines in Figure 7-5. For growth rates similar to those present in the earlier work (Schlumbach et al., 2018) the model describes the data very well. The model overestimates the color transfer factor for increasing growth rates. This increasing deviation appears to be caused by the pronounced dependence of the color inclusion on growth rate for cane syrups. Nevertheless, for practical purposes the correlations can still be considered valuable to determine acceptable inclusion levels of raw cane sugar in mixed syrups. As pointed out earlier it appears to be necessary to discriminate between the different color inclusion mechanisms, liquid inclusions and co-crystallization, in order to get a better grip on color inclusion.

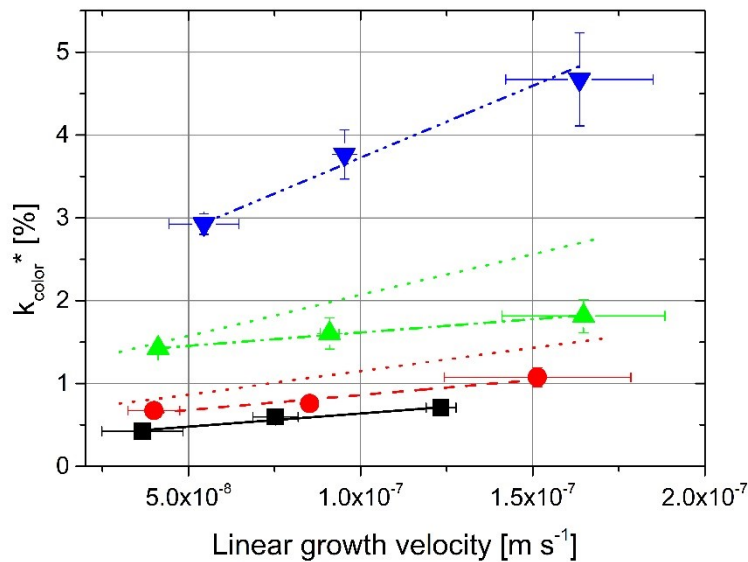


Figure 7-5: Color transfer factors versus linear growth velocity: 100:0 (■, straight line), 67:33 (●, dashed line), 33:67 (▲, dash-dotted line), 0:100 (▼, dash-dot-dotted line). Dotted lines for intermediate compositions predicted based on equation (7-23).

7.3.4 Color transfer mechanisms

Although it is generally acknowledged that different color inclusion mechanisms exist, the separation into their individual contributions to the final sugar color is fairly new. Figure 7-6 and Figure 7-7 depict the data gathered for color transfer by liquid inclusion and co-crystallization for different linear growth velocities. The values for liquid inclusion were derived according to equation (7-19) and the data for co-crystallization were computed by the difference from the transfer factor of affinated sugar and liquid inclusion according to equation (7-20).

Similar to the overall color transfer factor, values increase with increasing cane inclusion levels in the feed syrup and increasing growth rate. As Figure 7-6 reveals all blends studied that contain beet syrup, at least 33%, showed practically no change of the color transfer factor accounting for

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liquid inclusion, it remained between 0.22 and 0.35% throughout all experiments. This is valid for variation of either the composition or the growth velocity. Again, pure cane syrup assumes a distinct position, as the transfer factor for liquid inclusion increased from 0.87 – 1.16% with increasing growth rate. Based on the fact, that the colorants from beet and cane origin are quite different, the observations suggested that the presence of the smaller beet born colorants suppressed the presence of cane born colorants at the growing crystal surface.

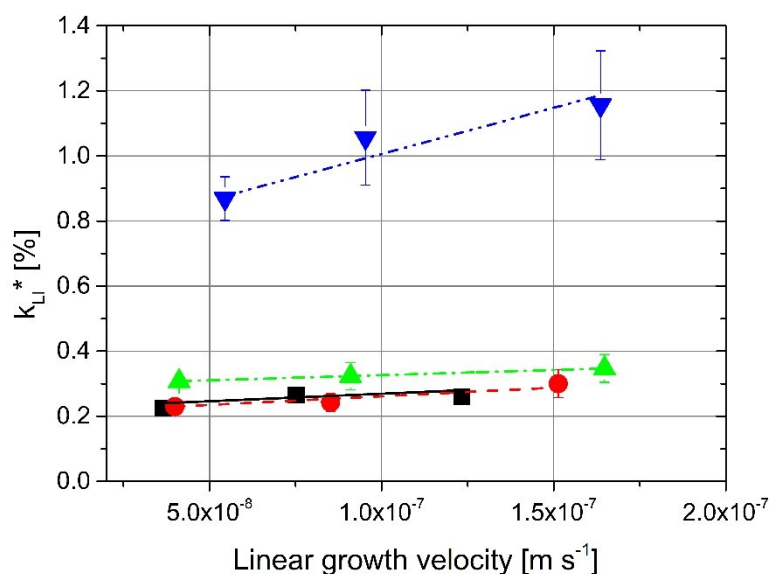


Figure 7-6: Color transfer factors for liquid inclusion versus linear growth velocity. Blends with different compositions: 100:0 (■, straight line), 67:33 (●, dashed line), 33:67 (▲, dash-dotted line), 0:100 (▼, dash-dot-dotted line).

Analyzing the data on color transfer according to co-crystallization a different picture emerged. Already at lower inclusion levels of cane sugar the values of the transfer factor increased continuously with increasing cane inclusion levels in the blend. Again, it was found that the change of color transfer factor with growth rate was practically constant for all blends except for the pure cane syrups. These showed a much more pronounced effect of growth rate. Consequently, sugars with highest cane levels and fastest growth velocities showed the highest relative color inclusion levels for both mechanisms.

The results gathered for the different mechanisms indicate that the relative color transfer depends on both composition and growth rate. Regarding the data for liquid inclusions an interaction between the non-sucrose compounds from different origin was indicated. The non-sucrose molecules originating from cane contain polysaccharides that tend to bind colorants (Godshall & Baunsgaard, 2000). Since their molecular mass is high they have a low diffusion coefficient (Edward, 1970). Their sucrose-like molecular structure promotes interaction at the solid liquid interface which results directly into higher transfer rates according to co-crystallization (Godshall & Baunsgaard, 2000; Godshall et al., 1987; Godshall et al., 2002; Tu et al., 1977). Furthermore, these strong interactions at the interface result in surface defects and hence cause increased

incidents of liquid inclusion. This is in line with earlier observations that irregularities and roughness, combined with repair phenomena on the crystal surfaces at increased growth rates promote liquid inclusions (Vaccari et al., 1990b; Mackintosh & White, 1968). In contrast, non-sucrose compounds from beet origin have a low molecular mass and a higher diffusion coefficient. Despite high diffusion coefficients they have a tendency to adsorb onto solid-liquid interface (Grimsey I.M. & Herrington, 1996; Shore et al., 1984). This leads to the assumption that in co-processed syrups the beet non-sugar compounds adsorb temporarily onto the crystal surface and reduce the contact between cane born colorants and the crystal surface (Schlumbach et al., 2018; Schlumbach et al., 2017). This effect of temporary surface blockage appears to be more effective in reducing color inclusion due to liquid inclusions since the respective transfer factors appear to be fairly independent on growth rate or composition of the mixed syrups.

The presented work documents that the earlier formulated model to predict color inclusion in sugars produced from mixed syrups is not independent on growth rates. With increasing growth rates color transfer factors are overpredicted by the model. This is due to the fact that increased growth rates have profoundly different effects of the colorant inclusion in pure cane syrups and syrups mixed from cane and beet material.

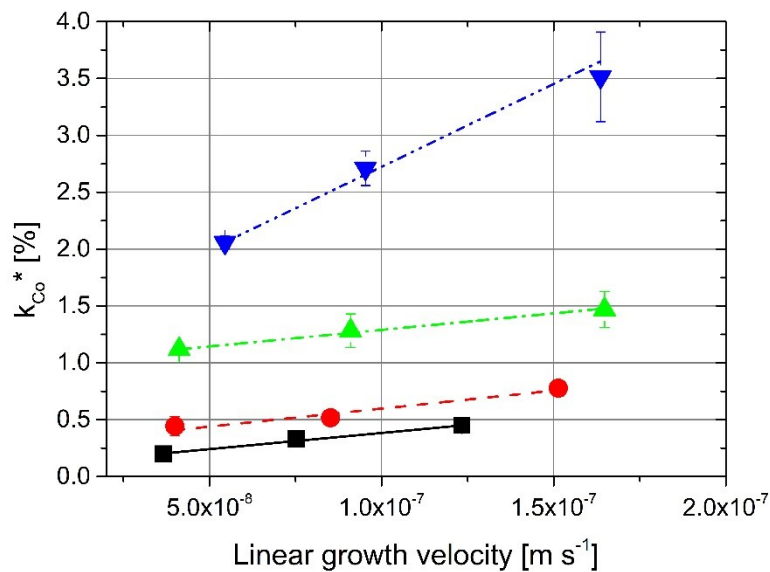


Figure 7-7: Color transfer factors for co-crystallization versus linear growth velocity. Blends with different compositions: (100:0 (■, straight line), 67:33 (●, dashed line), 33:67 (▲, dash-dotted line), 0:100 (▼, dash-dot-dotted line).

7.4 Conclusion

The presented study investigated systematically the influence of varying crystal growth velocity on colorant inclusion into sucrose crystals, crystallized from blended feed syrups containing beet thick juice and dissolved raw cane sugar. Detailed analyses of the crystallization process, the particle size and its distribution were conducted indicating that different temperatures of the heating medium in the crystallizer primarily influenced the time necessary to grow the seed crystals up to the target crystal size. Comparing three different thermal setups and studying different mixtures of cane and beet material the color inclusion into sucrose crystals was analyzed. However, some variation of the supersaturation and growth rate within each set of experiments could not be avoided due to different levels and types of non-sucrose materials in the syrups. It was found that the earlier formulated model to predict color inclusion in mixed syrups based on data on the constituting pure syrups is highly sensitive to growth rates. With increasing linear growth velocities, the model significantly over-predicts the level of colorant inclusion. This is caused by the significant difference of dependency of the colorant inclusion between pure cane syrup and beet containing juices. On further analyses, it appeared that for beet inclusion levels as low as 33% practically no effect of composition or growth rate on colorants inclusion according liquid inclusion was recorded. For the color values related to co-crystallized colorants, there is also a prominent damping effect due to the presence of beet material. For the data sets on both mechanisms, it is found that the change of color transfer factor with growth rate was constant as long as beet material is present in the mixture. The possible explanation that these phenomena relate to differences in diffusivities and surface poisoning due to temporarily adsorption of non-sucrose material originating from beet material needs further verification.

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Appendix

Solubility

According to ICUMSA (2011) the solubility of pure sucrose solution is given by the following formula:

$$w_{S,sat} = 64.447 + 0.8222 \cdot 10^{-2} \cdot T + 1.6169 \cdot 10^{-3} \cdot T^2 - 1.558 \cdot 10^{-5} \cdot T^3 - 4.63 \cdot 10^{-8} \cdot T^4$$

where T is the temperature of the solution.

Saturation Coefficient

Sucrose solubility is varying due to the presence of non-sucrose components. The saturation coefficient y_{sat} is the ratio of sucrose solubility in impure and pure solutions which is independent from solution temperature according to Wiklund's rule (van der Poel, P.W., 2000). It can be computed by the following equation with empirical constants depending on origin of the raw material:

$$y_{sat} = \frac{(w_s/w_w)_{sat,im}}{(w_s/w_w)_{sat,p}} = M \cdot \frac{w_{NS}}{w_w} + B + (1 - B) \cdot \exp(E \cdot w_{NS}/w_w)$$

with the values 0.178, 0.82 and 2.1 for the constants M , B and E for beet syrups and $-6.262 \cdot 10^{-2}$, 0.982 and 2.1 for the constants M , B and E for syrups related to cane, respectively. The saturation coefficient for beet and cane blends was computed linearly with respect to their composition.

Raw data of crystallization experiments

Table 7-2: Raw data of crystallization experiments.

Feed syrup composition (beet to cane)	ΔT	d_{50}	CV	τ
	K	mm	%	s
100:0	11.18	0.884	18.57	19236
100:0	11.59	0.911	18.81	13138
100:0	16.22	0.845	16.45	6589
100:0	16.07	0.864	19.01	7738
100:0	20.41	0.808	18.36	3917
100:0	20.71	0.821	19.19	4213
67:33	11.78	0.898	20.44	15798
67:33	12.07	0.860	21.21	12252
67:33	16.27	0.809	18.15	5857
67:33	16.57	0.864	20.63	6489
67:33	21.18	0.790	18.95	3597
67:33	21.13	0.837	20.44	3172
33:67	12.07	0.839	18.66	12422
33:67	16.85	0.801	18.66	5378
33:67	16.82	0.841	19.08	5806
33:67	21.34	0.800	18.11	3296
33:67	21.53	0.835	20.43	2990
0:100	11.78	0.842	19.32	11026
0:100	12.07	0.825	20.10	8174
0:100	16.27	0.785	19.65	4860
0:100	16.57	0.834	18.71	5342
0:100	21.18	0.786	20.66	3035
0:100	21.13	0.821	19.21	3143

8 THERMAL TREATMENT OF TECHNICAL SUCROSE SOLUTIONS OF BEET AND CANE ORIGIN

Schlumbach, Karl; Tschernich, Jessica; Flöter, Eckhard

TU Berlin, Department of Food Process Engineering, Seestraße 13, 13353 Berlin, Germany

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Abstract

In the production of sugars from mixed syrups containing feedstock from beet and cane origin the non-sugar fraction plays an equally important role as in processing of material from a single source. However, the consequences of the resulting mixed non-sugar fraction on processes such as impurity, mainly colorants, incorporation and chemical reactions have not been studied yet. In this contribution the results of a study elucidating the kinetics of colorants formation in mixed syrups on thermal stress are given. It is found that the relative increase of syrup color values with respect to the starting value behaves quite systematic for wide range of mixed syrups. In all syrups the color values increase linearly with exposure time. The rate of increase is the highest for beet syrups. The generation rate increases with temperature in line with Arrhenius' law. Different to earlier work no promoting effect of increased dry matter contents could be found. Furthermore, a model, assuming a first order reaction, to predict the color generation in mixed syrups based on the information of the pure syrups was formulated. This model is in essence generating data that match the experimental data within the range of the accuracy of the color determination method. In conclusion the data suggest that there is no excess color generation on thermal stress due mixing of the non-sugar materials from different sources.

8.1 Introduction

With the abolishment of the EU sugar quota on 30 September 2017 the sugar market is liberalized. The amount of sugar produced in the European Union is not limited anymore. In addition, WTO regulations do not limit sugar export. Thus, sugar manufacturers are forced to enhance the utilization of their factories. So far, the perishable nature of sugar beet limits the beet campaign to 90 – 130 days in Europe. In many factories sugar is crystallized from stored thick juice in the so-called “inter-campaign”. Due to competitive pressure in respect to manufacturing costs, one can imagine that this inter-campaign-period could be extended due to co-processing of imported cane raw sugar. This could be done either by adding the cane raw sugar to the thick juice or by refining the cane raw sugar in a separate campaign. The co-processing of beet thick juice and raw cane sugar, ergo the combination of both raw materials can be attractive for manufacturers depending on the factory design and the economical conditions to increase factory utilization. Before applying co-processing, different challenges need to be overcome in order to achieve a final product within the quality requirements. Firstly, the color transfer factors in the crystallization stage depend on the source of the raw material, e.g. color transfer during crystallization is high for cane and low for beet syrups. In earlier studies (Schlumbach et al., 2016; Schlumbach et al., 2017) it was shown that in sugar crystallization from mixed syrups a high-quality sugar (with a color value lower than 30 IU) can be obtained when starting with a syrup of up to 40 g cane raw sugar solution per 100 g feed syrup. This is explained by mutual suppression of the inclusion of the colorants originating from the different raw materials. Additionally, color

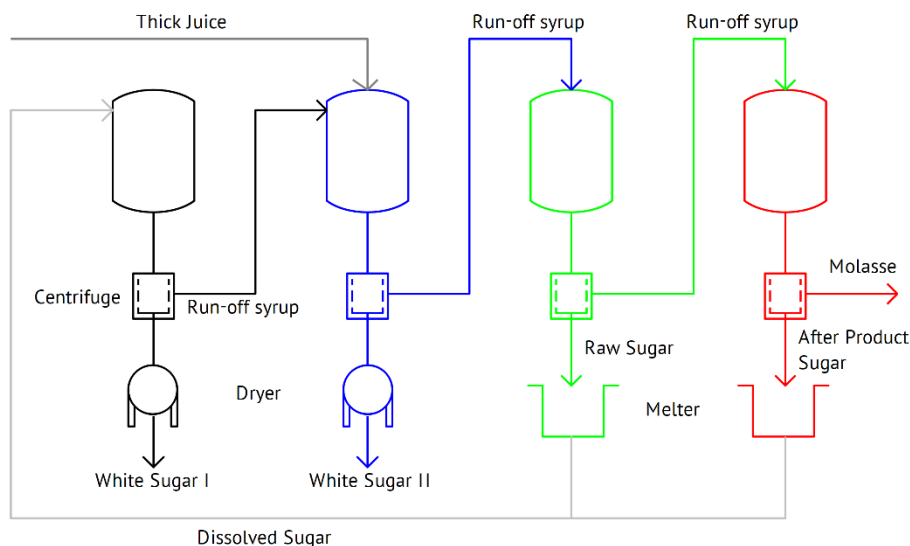


Figure 8-1: Simplified four-product crystallization scheme.

formation due to the components specific to cane or beet raw material needs to be considered. Since beet thick juice contains amino acids and cane raw sugar comprises reducing sugars (e.g. glucose), *Maillard* reactions are promoted when combining the two raw materials. Beet thick

juice and raw cane sugar contain different color compounds which have been formed in process steps before they are blended.

In Figure 8-1 a simplified four-product crystallization scheme is shown. The thermal exposure of sucrose and non-sucrose compounds (e.g. colorants and precursors) increases downstream due to enhanced retention times. The crystallization times of white sugar I and II, raw sugar and after product are about 2, 4 – 6 and 8 – 48 hours, respectively (Asadi, 2007; van der Poel, P.W., 2000). In total, syrups can be under thermal treatment for up to 45 – 80 hours (van der Poel, P.W., 2000), because the process is designed with several refluxes to increase the quantity and quality of white sugar. It was shown that 80% (IU) of the coloring matter substances in molasses were formed in the sugar house, ergo the crystallization process (Hangyal & Paradi, 1984). Thus, special attention should be paid to color formation during this process step.

Color formation is influenced by different factors, in particular by temperature and process time (Witte & Cronewitz, 1988). Imming et al. (1994) confirmed an exponential increase of the color value with temperature and a linear dependency on process time for synthetic beet syrups.

An excessive thermal treatment of sucrose results in its hydrolysis into glucose and fructose, i.e. invert sugars, which are precursors of color compounds. For beet syrups, the color value increase during evaporation depends linearly on the content of the invert sugar in the thick juice. If invert sugar is absent, there is no color formation because the invert sugar first needs to be formed by sucrose hydrolysis (Imming et al., 1994).

Furthermore, Imming et al. (1994) reported that the syrup color formation rate increases linearly with amino acid concentration. The reactions are limited by the low content of invert sugar, so that an excess of amino acids does not result in excessive color formation. Furthermore it was shown that color formation reaction rates increase exponentially with increasing pH value (Imming et al., 1994). Furthermore, it is generally acknowledged that an increased dry substance content (80 – 90 g/100 g) favor *Maillard* reactions (Heitz, 1995).

For sugar manufacturers, it is essential to sustain the quality of the produced sugar also when producing from mixed cane and beet syrups. Therefore, color development in the sugar house when applying co-production need to be understood. To our knowledge, there are only studies on color formation during sugar production from either cane or beet but not from co-processed syrups. Due to the fact that 80% (IU) of colorants in molasses are formed in the sugar house, it is of highest interest to formulate a model which gives the color value of the syrups after thermal treatment based on initial color value, mixing ratio, temperature, process time and dry substance level of the blend.

In this work, the influence of process temperatures and time on color formation in blended white sugar feed (standard liquor A) and its run-off syrups (standard liquor B) were studied. Therefore, syrups of different amounts of cane and/or beet raw material were heated at three different temperatures (348 K, 358 K and 368 K) for 24 h and their color value was determined. Based on experimental data on color formation of either cane or beet raw material, a simple model was

formulated which allows to predict the color value after thermal treatment of blend consisting of different amounts of raw material. The predictions are verified by the experimental data obtained in this work.

8.2 Materials and methods

8.2.1 Raw materials and sample preparation

Beet thick juice supplied by a sugar factory in Germany and cane raw sugar by a producer in Brazil. The beet thick juice was stored for month at 280 K in a refrigerator cell before experiments were conducted. Cane raw sugar solutions were prepared by dissolving 67 g/100 g of cane raw sugar and 33 g/100 g of demineralized water ($< 2 \mu\text{S/cm}$). Subsequently, the solution was filtered through a mesh (nominal 5 μm , absolute 8 μm ; TEDRA Dahmen GmbH & Co. KG, Wassenberg, Germany) to remove insoluble particles. Standard liquor A samples were prepared by mixing beet thick juice and aqueous raw cane sugar solution in different ratios. Before the experiments were done the pH values of these syrups were determined and are given together with the quality parameter in Table 8-1. The analytical methods used to determine these values are described in 8.2.4.

Table 8-1: Mean dry substance content, purity, color value, pH-value and glucose and fructose content of standard liquor A.

Beet content	Cane content	Dry substance content	Purity	Color value	pH-value at 298 K	Glucose content	Fructose content
% (w/w)	% (w/w)	g/100 g	%	IU	-	g/kg	g/kg
100	0	67.41	94.57	1946	8.29	0.310	0.037
80	20	67.43	95.78	1896	8.23	0.307	0.089
60	40	67.25	95.68	1621	8.09	0.315	0.208
40	60	67.23	96.25	1595	7.93	0.325	0.260
20	80	67.13	97.55	1473	7.71	0.321	0.374
0	100	67.05	98.53	1066	6.29	0.316	0.455

In addition, experiments with standard liquor B were conducted. These syrups (run-off syrups) were collected after crystallization experiments which are described in detail elsewhere (Schlumbach et al., 2017). For the crystallization experiments, the beet thick juice and raw cane sugar were supplied from German and Brazilian sugar factories, respectively. The beet thick juice was stored 2 month at 280 K in refrigerator cell before crystallization experiments were conducted. After crystallization, the run-off syrups, ergo standard liquor B, were stored in sealable jars at 255 K in a freezer until they were used for this work. Prior to the experiments the syrups were defrosted in a shaking water bath (SW 23, Julabo, Seelbach, Germany) at 348 K for 30 min and then diluted to a dry substance content 75.5 g/100 g ($\pm 1 \text{ g/100 g}$) to ensure dissolution of all

crystals. The pH values of these solutions were then determined, which are given with other quality parameter in Table 8-2.

Table 8-2: Mean dry substance content, purity, color value, pH-value and glucose and fructose content of standard liquor B.

Beet content	Cane content	Dry substance content	Purity	Color value	pH-value at 298 K	Glucose content	Fructose content
% (w/w)	% (w/w)	g/100 g	%	IU	-	g/kg	g/kg
100	0	74.50	89.10	4621	8.65	0.595	0.289
80	20	75.84	91.04	4332	8.44	0.646	0.328
60	40	74.52	92.70	3622	8.29	0.808	0.607
40	60	76.40	94.05	3563	7.88	0.808	0.809
20	80	75.15	95.55	3189	7.13	0.941	0.970
0	100	75.98	98.27	2686	6.08	1.558	1.830

8.2.2 Experimental setup

The thermal treatment experiments were conducted in sealed vessels (volume around $3.75 \cdot 10^{-4} \text{ m}^3$). The schematic set-up is shown in Figure 8-2. The vessels were placed in an oil bath which was positioned on a magnetic stirrer hot plate (MR Hei-End, Heidolph, Schwabach, Germany). This device controlled and monitored the temperature of the solution by means of an external Pt 100 which was submerged into the solution. For monitoring the pH-value during the experiment, a pH-meter (Seven Excellence, Mettler Toledo, Gießen, Germany) and a pH-electrode (Inlab Routine Pro, Mettler Toledo, Gießen, Germany) were used. Therefore, the pH-electrode was submerged into the solution. The pH and temperature data were recorded with the

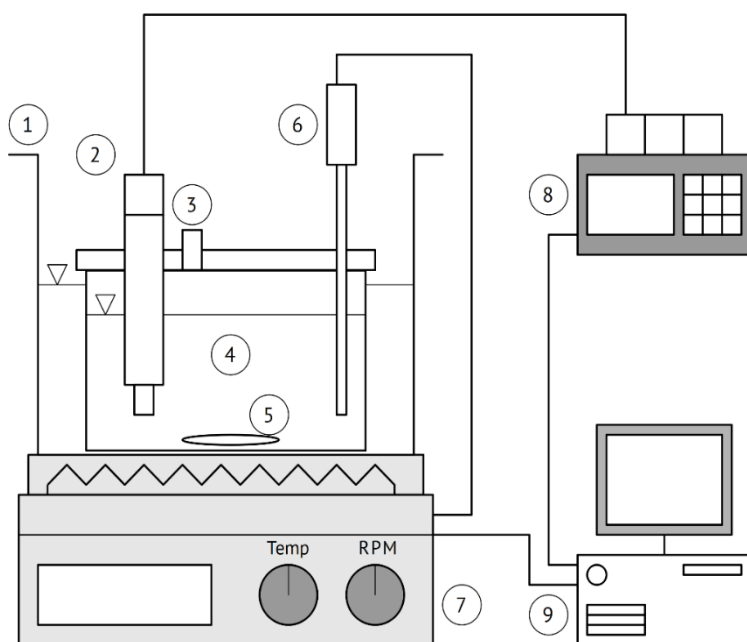


Figure 8-2: Schematic illustration of experimental setup: 1 – oil bath, 2 – pH-electrode, 3 – plug (sealable opening), 4 – vessel, 5 – magnetic stirrer, 6 – Pt-100, 7 – magnetic stirrer hot plate, 8 – pH-meter, 9 – computer unit.

help of a computer unit. Sampling of material was conducted through a sealable opening in the lid of the vessel.

8.2.3 Experimental procedure

The vessel was filled with 0.25 l of the respective prepared solutions and placed in the oil bath. The solution was kept homogenous by means of a magnetic stirrer (100 min^{-1} , $\pm 1\%$). For achieving different color formation and sucrose hydrolysis rates, the temperature for the solutions was set to 348 K, 358 K or 368 K ($\pm 1 \text{ K}$) for each blend, respectively. The actual experiment started when the desired treatment temperature was reached. The time of treatment for each experiment was 24 h. Samples of standard liquor A were taken after 0 h, 1.5 h, 3 h, 4.5 h, 6 h, 16 h and 24 h, respectively. The standard liquor B sampling occurred after 0 h, 2 h, 4 h, 6 h, 16 h and 24 h, respectively. For sampling in general, the plug in the lid of the vessel was removed (3 in Figure 8-2) and 30 ml of solution were removed by means of a syringe (Perfusor 50 ml, Braun, Melsungen, Germany).

8.2.4 Methods

The methods to determine the dry substance content, sucrose content and color value were performed according to ICUMSA methods (ICUMSA, 2011). Prior to analysis samples were diluted 1:1 (m/m) with demineralized water ($< 2 \mu\text{S/cm}$) to decrease the concentration of colored compounds to allow the determination by polarimetry.

The dry substance content (w_{DS}) of the diluted samples was determined based on the refractive index (ATR-W2 plus, Schmidt & Haensch, Berlin, Germany). For the determination of the sucrose content (w_S), the samples were clarified with Carrez solutions according to ICUMSA method GS8-2 (ICUMSA, 2011) to remove colloids and suspended solids. The clarified solution was analysed subsequently by polarimetry (Saccharomat NIR W2, Schmidt & Haensch, Berlin, Germany). The color value (F) of the samples was analyzed according to ICUMSA method GS1/3-7 (ICUMSA, 2011). The prediluted samples were diluted again with the same proportion of demineralized water ($< 2 \mu\text{S/cm}$) to ensure an absorption value between 0.080 – 0.800 E. The pH value was adjusted to 7.0 by means of hydrochloric acid solution and sodium hydroxide solution. Subsequently, the samples were filtered through a $0.45 \mu\text{m}$ membrane filter (CHROMAFIL, Machery-Nagel, Düren, Germany) to remove suspended solids. The filtered solution was analyzed in a spectrophotometer at a wavelength of 420 nm (SPEKOL 1300, Analytic Jena, Jena, Germany). The relative increase of color value during thermal treatment (RCI) in % is calculated as follows:

$$RCI(T, \tau_i, x_j) = \frac{F_{420}(T, \tau_i, x_j) - F_{420}(\tau_0, x_j)}{F_{420}(\tau_0, x_j)} \cdot 100 \quad (8-1)$$

With the times τ_0 and τ_i , at the beginning (0) and at various times (i) of the procedure, temperature T , and the beet content in the syrup x_j (m/m). It should be noted that at τ_0 the color value only depends on the mixing ratio. The glucose and fructose contents were analyzed according to ICUMSA method GS8/4/6-4 (2007) (ICUMSA, 2011).

8.3 Results and discussion

8.3.1 Color formation

8.3.1.1 Influence of treatment time

Various blends of standard liquor A and standard liquor B were processed as described above to investigate the effect of treatment time, temperature and mixing ratio on colorants formation. Figure 8-3 shows the color values of standard liquor A blends and B blends in dependence of treatment time at 368 K. For pure standard liquors A and B from beet sources, the values increase linearly within 24 h from 2,000 IU to nearly 8,000 IU and from 4,600 IU to 15,500 IU for A and B-syrup, respectively. The linear behavior with time during thermal treatment was already outlined by Imming et al. (1994) who did experiments with syrups solely from a beet source. For pure cane syrups, the color value increases linearly, too, from 1,400 – 2,100 IU and from 2,700 – 4,600 IU for standard liquor A and B, respectively.

Regarding the results from both experimental sets, the formation of colorants is more pronounced for syrups from beet source. Hence, for mixed syrups the color value is increasing with increasing beet content. With the results presented here the statement of linear color dependency on time can

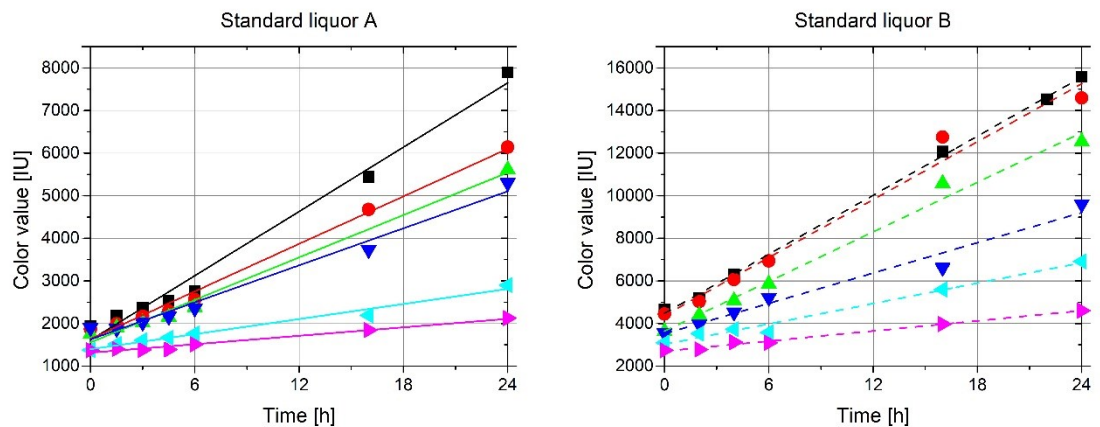


Figure 8-3: Color values of thermal treated (368 K) standard liquor A (solid lines) and B (dashed lines) with the following beet to cane ratios: 100:0 (■), 80:20 (●), 60:40 (▲), 40:60 (▼), 20:80 (◄), 0:100 (►).

be confirmed and can be further extended to cane and mixed syrups. The color value difference of the treated syrups from 100 g/100 g beet and from 100 g/100 g cane raw sugar can be explained based on the purity of the raw material (see Table 8-1 and Table 8-2) and the nature of colorants. The increased amount of impurities in beet syrups corresponds with higher color formation rates. New reactants such as glucose and fructose are continuously formed during the process due to sucrose hydrolysis at high temperatures and long treatment time. Both components take part in color formation reactions such as *Maillard*-reactions, caramelization and alkaline degradation of hexoses.

In case of cane syrups, the impurities in the syrup predominantly consist of colorants, such as caramels and indigenous sugar cane polysaccharides, color precursors like invert sugar and other nonsugars such as dextran and starch. Analysis of the cane raw material showed that the content of amino acids to be so low that it can be neglected (van der Poel, P.W., 2000; Chen & Chou, 1993). This is further supported by the fact that the *Maillard* reactions do not occur during thermal treatment of these syrups. In Table 8-1 and Table 8-2 it can be seen that the pH-value of the cane raw syrups is 6.29 and 6.08, respectively. At these pH-values, color formation due to alkaline degradation of hexoses does not occur. Other likely color formation reactions during thermal treatment are polymerization (oxidation, condensation, dehydration reactions) of melanins, caramels and polysaccharide-colorant complexes which were already formed during the sugarcane processing. Due to the increased polymerization degree, colored compounds appear to become darker so that with increasing time the color values increase (Bourzutschky, 2005; Coca, 2004).

Even though it is not known exactly which colorants are formed, the linear dependency of the color value on time indicates that the color formation might be described by a quasi-chemical approach in which rather the color value than concentrations of colorants are mixed. The color formation is then described by a zero-order reaction with the quasi-chemical rate or apparent reaction rate, k_{RCI} , determined by:

$$k_{RCI}(T, x_j) = \frac{d[RCI(T, \tau_i, x_j)]}{d\tau} \quad (8-2)$$

8.3.1.2 Influence of temperature

Figure 8-4 illustrates the influence of temperature on the color value of the syrup. Here the data of a blend with a mixing ration of 80:20 (m:m) is shown as an exemple. The blends with other mixing ratios show qualitatively the same behavior. For the standard liquors A and B, again a linear increase of the relative color value with the processing time was found at all investigated

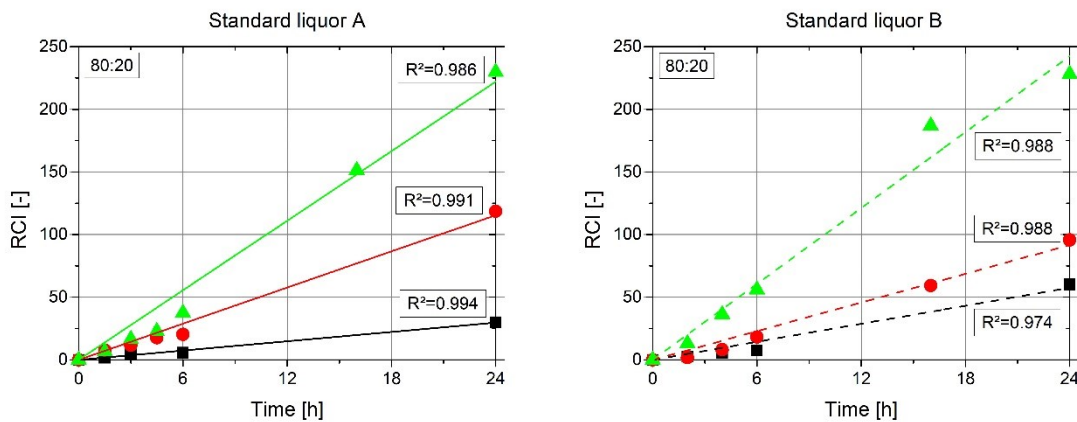


Figure 8-4: Relative color value increase of standard liquor A (left) and B (right) shown for a blend with 80:20 (m:m) mixing ratio at different temperatures: 348 K (■), 358 K (●), 368 K (▲). Blends with other mixing ratios show qualitatively the same behavior.

temperatures. As expected the color value increase is stronger for higher temperatures than for lower temperatures. The color value increase for both syrups is comparable. With the given data the temperature dependence of the apparent reaction rate k_{RCI} is determined and can be described by an *Arrhenius*-type equation).

$$k_{RCI}(T, x_j) = A_{Arr}(x_j) \cdot \exp\left(\frac{-B_{Arr}(x_j)}{T}\right) \quad (8-3)$$

With the rate constant (k_{RCI}), the absolute temperature (T), the pre-exponential factor (A_{Arr}) and the *Arrhenius*-type-constant B_{Arr} .

After reformulation of equation (8-3), the logarithm of the relative rate of color value formation can be described by a function of the reciprocal temperature:

$$\ln(k_{RCI}(T, x_j)) = -B_{Arr}(x_j) \cdot \left(\frac{1}{T}\right) + \ln(A_{Arr}(x_j)) \quad (8-4)$$

The data according to equation (8-4) are shown in Figure 8-5. On a logarithmic scale the reaction rates decrease linearly with the reciprocal temperature. This means that the apparent reaction rate describing the color formation in blended syrups obeys the *Arrhenius* relation which is also supported by the coefficients of determination (Table 8-3). This is in agreement with studies from Imming et al. (1994) and Heitz (1995) on color formation in beet syrups.

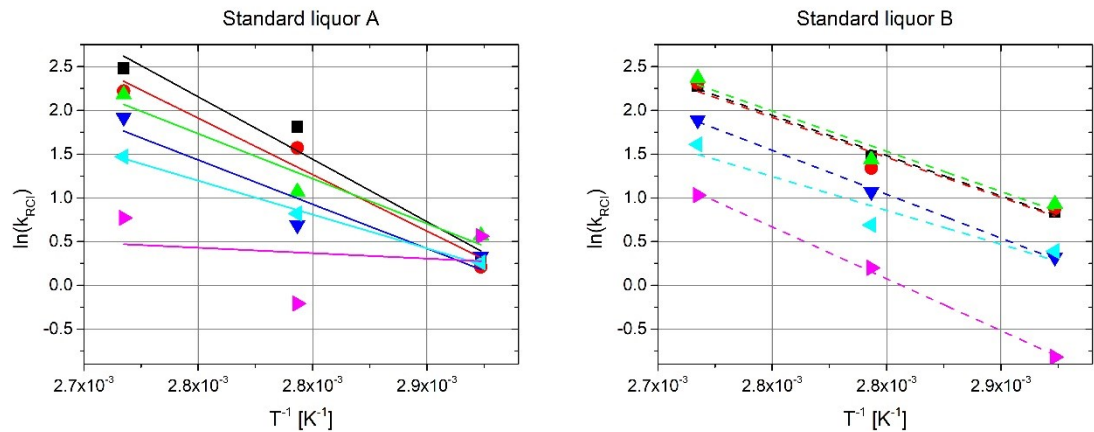


Figure 8-5: Apparent reaction rate (k_{RCI}) versus T^{-1} for standard liquor A (left) and B (right) according to the following beet to cane ratios: 100:0 (■), 80:20 (●), 60:40 (▲), 40:60 (▼), 20:80 (◄), 0:100 (►). Lines according to equation (8-4).

Table 8-3: Coefficients of determination (R^2) from the fits in Figure 8-5.

Beet to cane ratio	Standard liquor A	Standard liquor B
	R^2	R^2
100:0	0.914	0.984
80:20	0.932	0.905
60:40	0.895	0.934
40:60	0.800	0.997
20:80	0.993	0.824
0:100	Line to guide the eye	0.966

8.3.1.3 Influence of mixing ratio and dry substance level

The influence of syrup composition and dry substance content which is in average 67.3 g/100 g and 75.4 g/100 g for the mixtures of standard liquors A and B, respectively, is discussed using the apparent chemical reaction rate (k_{RCI}) at 348 K, 358 K and 368 K (Figure 8-6).

For both standard liquors, k_{RCI} increases with increasing temperature and increasing beet content in the blend. An exception was observed for standard liquors A at 348 K, where the apparent reaction rate scatters around a mean value of 1.6 h⁻¹ with standard liquor composition. It is assumed that the deviations are within the inaccuracy of the determination.

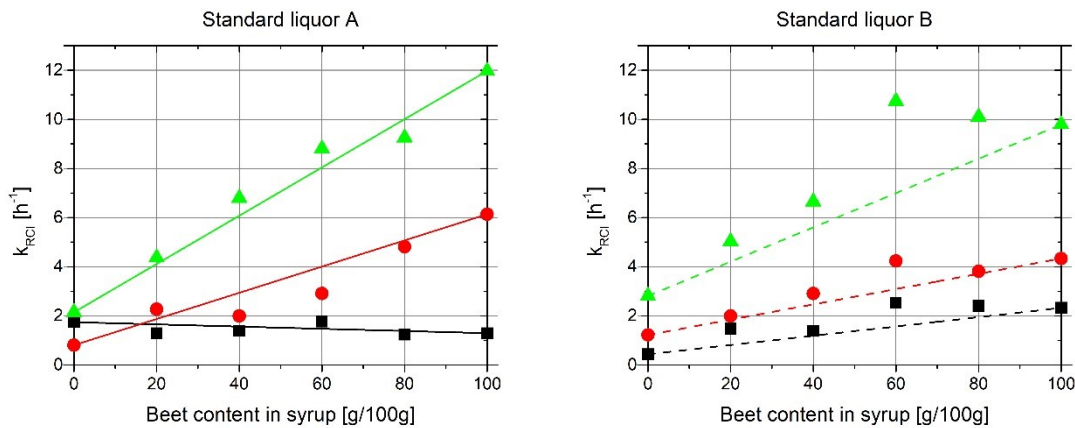


Figure 8-6: Apparent reaction rate for A (left) and B-syrup (right) at 348 K (■), 358 K (●), 368 K (▲). Lines drawn connect data points from syrups solely from beet and cane source, respectively.

Regarding the different blends, it is remarkable that k_{RCI} for pure cane syrups is below 3 h⁻¹ for all temperatures. For syrups consisting solely of beet raw material k_{RCI} is increasing with increasing temperature. However, the data reveal that there are no significant and systematic differences in the relative color value increase between standard liquor A and B of similar mixing ratio and temperature. The assumption that the color value increase during thermal treatment is increased by higher dry substance levels (80 – 90 g/100 g) (Heitz, 1995) could not be confirmed by the experimental data. Color formation for standard liquors A and B is nearly equal although the dry substance content of standard liquor B is higher (see Table 8-1 and Table 8-2). However, the experimental data is in agreement with the work from Imming et al. (1994) who worked with beet syrups in a similar dry substance range of 70 – 80 g/100 g.

Additionally, standard liquors A and B did not only differ in their dry substance levels, but also in their initial color value (see Table 8-1 and Table 8-2). Thus, the data show that k_{RCI} of syrups with similar mixing ratio is independent of the initial syrup color values.

The following conclusions can be drawn from the findings:

- Color value increases linearly with treatment time which allows to use a quasi-chemical approach and a so-called apparent reaction rate k_{RCI} .
- k_{RCI} of each blend increases exponentially with temperature.

- k_{RCI} is independent of dry substance content (between 67.3 g/100 g and 75.4 g/100 g) ergo A and B-syrup.
- k_{RCI} is independent of the initial syrup color value.

8.3.2 Model for prediction of color formation in mixed syrups

A model forecasting the color value of syrups containing beet and cane syrups has been formulated based on color values of single source syrups. Variables of the model are the mixing ratio of the syrups, length of the treatment time and temperature. The experimental data of the mixed standard liquors A and B are used to verify the model.

From previous work it is known that color value of a mixed syrup is a linear combination of the color values of the single source juices (Schlumbach et al., 2016; Schlumbach et al., 2017). Thus, the initial color value of the mixed syrups is calculated by the mixing ratio of the beet, x_j , in the blend:

$$F_{420}(\tau_0, x_j) = F_{420}(\tau_0, x_j = 1) \cdot x_j + F_{420}(\tau_0, x_j = 0) \cdot (1 - x_j) \quad (8-5)$$

Additionally, it was found that the color value of the single source syrups increased linearly with time so that final syrup color can be calculated by reformulation of equation (8-1):

$$F_{420}(T, \tau_i, x_j) = F_{420}(\tau_0, x_j) \cdot \frac{RCI(T, \tau_i, x_j) + 100}{100} \quad (8-6)$$

The relative color increase is described by the apparent reaction rate (k_{RCI}) and time τ_i (see equation (8-2)):

$$RCI(T, \tau_i, x_j) = k_{RCI}(T, x_j) \cdot \tau_i \quad (8-7)$$

The combination of equation (8-6) and (8-7) results in:

$$F_{420}(T, \tau_i, x_j) = F_{420}(\tau_0, x_j) \cdot \frac{k_{RCI}(T, x_j) \cdot \tau_i + 100}{100} \quad (8-8)$$

The apparent reaction rate depends exponentially on T^l which is described by an *Arrhenius* type equation (8-3). For the model it was assumed the factors A_{Arr} and B_{Arr} depend on the mixing ratio:

$$A_{Arr}(x_j) = \exp\left(x_j \cdot \ln(A_{Arr}(x_j = 1)) + (1 - x_j) \cdot \ln(A_{Arr}(x_j = 0))\right) \quad (8-9)$$

$$B_{Arr}(x_j) = x_j \cdot B_{Arr}(x_j = 1) + (1 - x_j) \cdot B_{Arr}(x_j = 0) \quad (8-10)$$

Equations (8-9) and (8-10) are described by means of the raw material constants A_{Arr} and B_{Arr} (see Table 8-4) and the mixing ratio. In Figure 8-7 the constants $A_{Arr}(x_j)$ and $B_{Arr}(x_j)$ of various mixing ratios of mixed standard liquors A and B obtained by actually fitting the equation to the individual experimental data sets are given and compared to the A_{Arr} and B_{Arr} values obtained from the above given linear relationships.

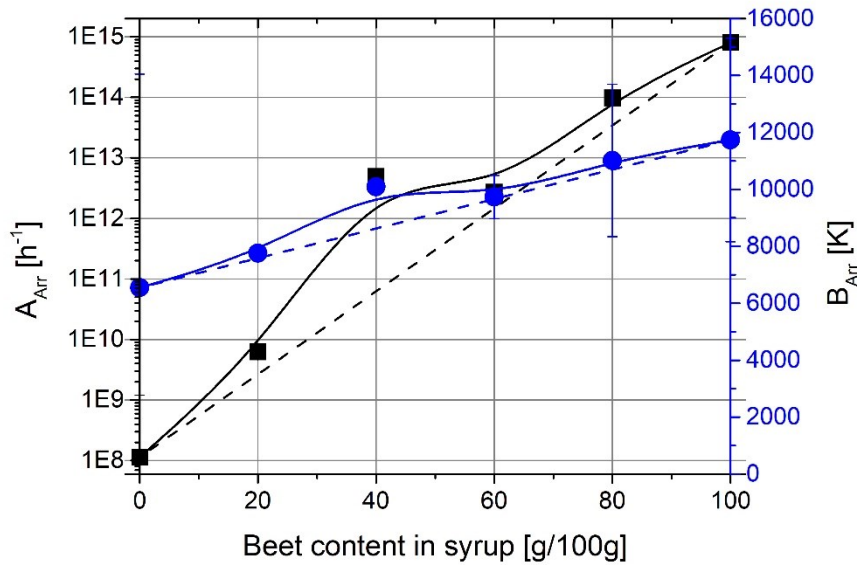


Figure 8-7: Constants A_{Arr} (■) and B_{Arr} (●) as a function of feed syrup composition. Points and full lines derived for single data sets (mixtures). Dashed lines predicted according to equation (8-9) and (8-10).

Table 8-4: Averaged values of pre-exponential factor, $A_{Arr}(x_j)$, and the Arrhenius-type-constant, $B_{Arr}(x_j)$ from syrups solely consisting of beet ($x_j=1$) and cane ($x_j=0$) material.

x_j	$A_{Arr}(x_j)$ in % h ⁻¹	$B_{Arr}(x_j)$ in K
1	$8.05 \cdot 10^{14}$	$1.17 \cdot 10^4$
0	$1.14 \cdot 10^8$	$6.55 \cdot 10^3$

Except for the mixing ratio of 40% beet, the simple linear relationship formulated represents the experimental data very good. From the data obtained in this work it cannot be said if the deviation from the linear relationship is arbitrary or caused by the fact that the color formation reactions interfere with each other.

Finally, equations (8-3) – (8-10) are combined to predict the color value of thermally treated syrups in dependence of mixing ratio x_j , temperature T and treatment time τ_i .

In Figure 8-8 the experimental data for color values of thermal treated syrups versus predicted color values according to the model are given. The parity plot indicates a good agreement between the experimental and predicted color values. For mixed standard liquors A and B, it is found that 77.3% and 73.5% of the values show a relative deviation of less than 10%, respectively. For 50.4% of the A and 49.0% of the B standard liquors, the relative deviation of predicted values from experimental values is less than 5%. The highest agreements are found for syrups with 60 g of beet material/100 g. The greatest deviations are observed for a beet content of 40 g/100 g. Thus, the predictive power for standard liquors A and B is comparable. The averaged relative deviations are 6.7% and 6.9% for standard liquors A and B, respectively. It should be noted that the deviation of the predicted values from the experimental data is in the same order of magnitude as the

repeatability of the well-established experimental color analysis method, namely by around 5% (ICUMSA, 2011). The formulated quite simple color value prediction model for sugar syrups gives agreeable predictions for the color values of thermally treated beet and raw sugar single source syrups as well as of mixtures of both single source syrups.

However, the results of the parity plot indicate that competitive and/or synergistic color formation reactions might occur in blended syrups in particular for longer treatment times. The presented study and model should be regarded as a starting point for a more detailed investigation of color formation reactions in blended beet and cane syrups.

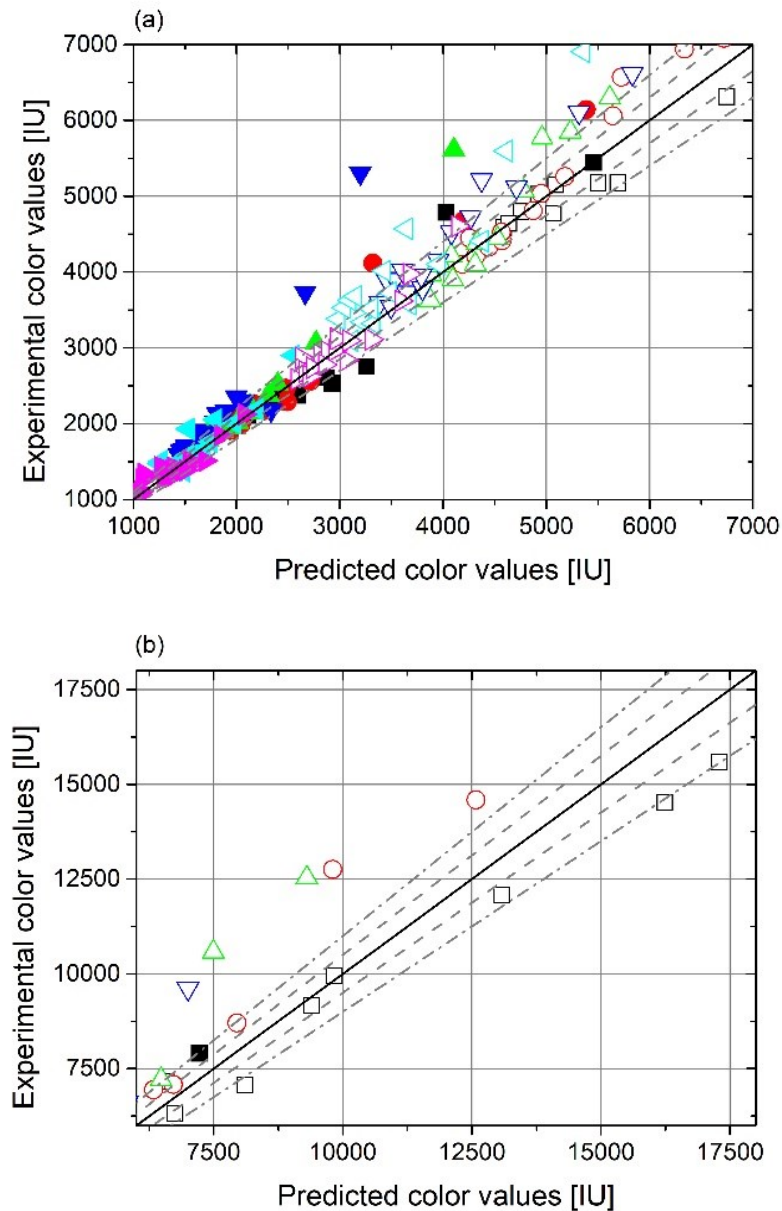


Figure 8-8: Parity plot of standard liquors A (full symbols) and B (open symbols) color values in the range of 1,000 – 7,000 IU (a), and 6,000 – 18,000 IU (b). Experimental data versus predicted data according to equation (8-5) for the following beet to cane ratios: 100:0 (■, □), 80:20 (●, ○), 60:40 (▲, △), 40:60 (▼, ▽), 20:80 (◄, ►), 0:100 (▷, ◂). Lines illustrate the relative deviation: $\pm 5\%$ dashed line; $\pm 10\%$, dashed-dotted line.

8.4 Conclusion

Co-production of beet thick juice and raw cane sugar is a promising opportunity to deal with the challenges of EU market liberalization and decreasing sugar prizes. The study reported here deals with the formation of colorants during thermal treatment in mixed syrups originating from beet and cane. Especially, the question how color formation behaves in syrups of different sources was of key interest. Studies on color formation in highly concentrated beet syrups were already done before (Imming et al., 1994). However, studies regarding mixed syrups have not been reported previously. Color formation during thermal treatment of syrups consisting of different combinations of beet thick juice and raw cane sugar was studied. Therefore, syrups of different purity and dry substance contents were analyzed at different temperatures to prove the influence of initial syrup color value, temperature, time and dry substance content.

The data gathered for cane and mixed syrups confirmed earlier findings for beet syrups that color formation is a reaction of zero order. Comparison of data from mixed standard liquors A and B syrups revealed that color formation is independent of starting color value and dry substance content. The comparison of the data at different temperatures showed that the apparent reaction rate shows an *Arrhenius* dependency on the temperature.

The formulated framework to predict sugar color value of thermally treated syrups as function of temperature, time, composition and initial color values of the single source syrups, revealed a good agreement with the experimental data. The accuracy of the predicted values is within the accuracy of the experimental color determination method.

The results for mixed syrups are novel findings which certainly need further investigation regarding the transformation of constituents (e.g. sucrose, invert sugar and amino acids) and a mechanistic explanation of color formation reactions. Further analysis of beet thick juice, raw cane sugar and the occurring color formation reactions are recommended so that the model can be improved. Additionally, detailed investigations have to verify the model at higher and lower temperatures and for longer treatment times. The model has to be fed with more data to enhance its accuracy. Nevertheless, the model provides a simple tool for manufacturers to forecast color development in a factory when using syrup blends. The combination of the model presented and the model previously established to predict sugar color values provides a comprehensive tool to simulate the sugar production processes and to optimize process parameters to meet customers' demands (Schlumbach et al., 2017; Schlumbach et al., 2016).

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9 METHODS AND ERROR ANALYSIS

9.1 Introduction

The focus of this thesis was the crystallization of beet thick juice and cane sugar syrup blends. In particular, the effects of different process and product parameters on final crystal quality were analyzed. In this context, sugar color, particle size and particle size distribution were the most important quality parameters to assess the effects of the raw material and process parameters. Before the final product could be analyzed, different process steps were conducted (Figure 9-1): First, a blend of beet thick juice and dissolved raw cane sugar was produced. The mixture was filled into the crystallization vessel and boiled at low

pressure conditions (270 mbar) from undersaturated into supersaturated state. When the supersaturation level for seeding was achieved, sieved seed crystals were introduced into the vessel and boiling was continued. Crystal growth and water evaporation occurred simultaneously. The crystallization strike was stopped at a crystal content of around 50 g/100 g. Subsequently, the massecuite was separated into sugar crystals and mother liquor via centrifugation. To assist the removal of mother liquor from the crystals' surface, washing water (2.5% on mass of massecuite) was distributed evenly onto the crystals during the separation process. Afterwards, the wet sugar was dried in a fluidized-bed. The crystallization plant and process are described in detail elsewhere (Chapter 3).

In earlier work, it was shown that the crystallization process carried out on our plant is well controlled and sugar produced is of industrially relevant quality. However, to assess the significance and accuracy of the final data the whole process and the analytical methods have to be considered as sources of errors. Therefore, this chapter focuses especially on the post crystallization process (separation and drying), affination and laboratory analyses – color determination (F_{420}) and sieve analysis (particle size (d_{50}) and particle size distribution (CV)).

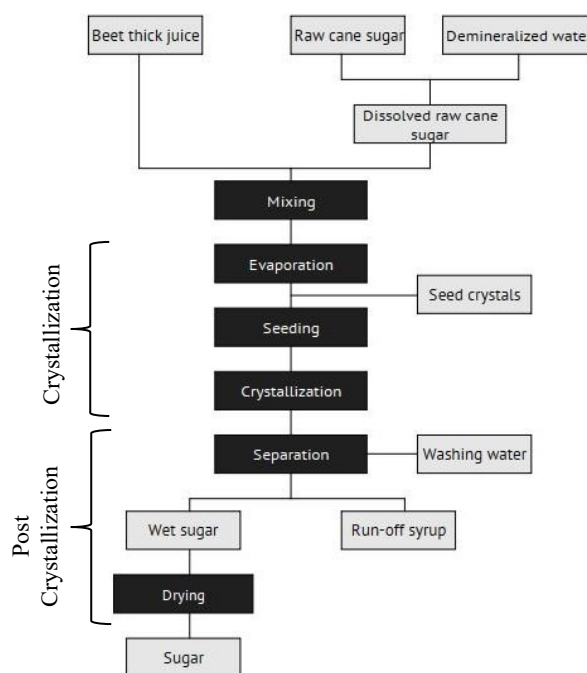


Figure 9-1: Scheme of crystallization and post crystallization process.

Different experimental sets (Figure 9-2 to Figure 9-4) were executed to investigate the reproducibility and repeatability of post crystallization, affination and analytical methods. There is no uniform definition of repeatability and reproducibility. Within this work, the repeatability indicates the variation of data points gathered under consistent conditions by a single instrument and person utilizing only one sample. The reproducibility is the accuracy of data gathered from different experiments which were performed under consistent conditions but at different days or by different individuals.

Special focus is given to the color determination method, which is described in detail in section 9.2.3. The method utilizes the proportionality of light absorbancy to dry substance and density which allows to determine the color of sugars and syrups at different dry substance levels. This approach is investigated in detail, because in this thesis color value determination was performed at different dry substance levels.

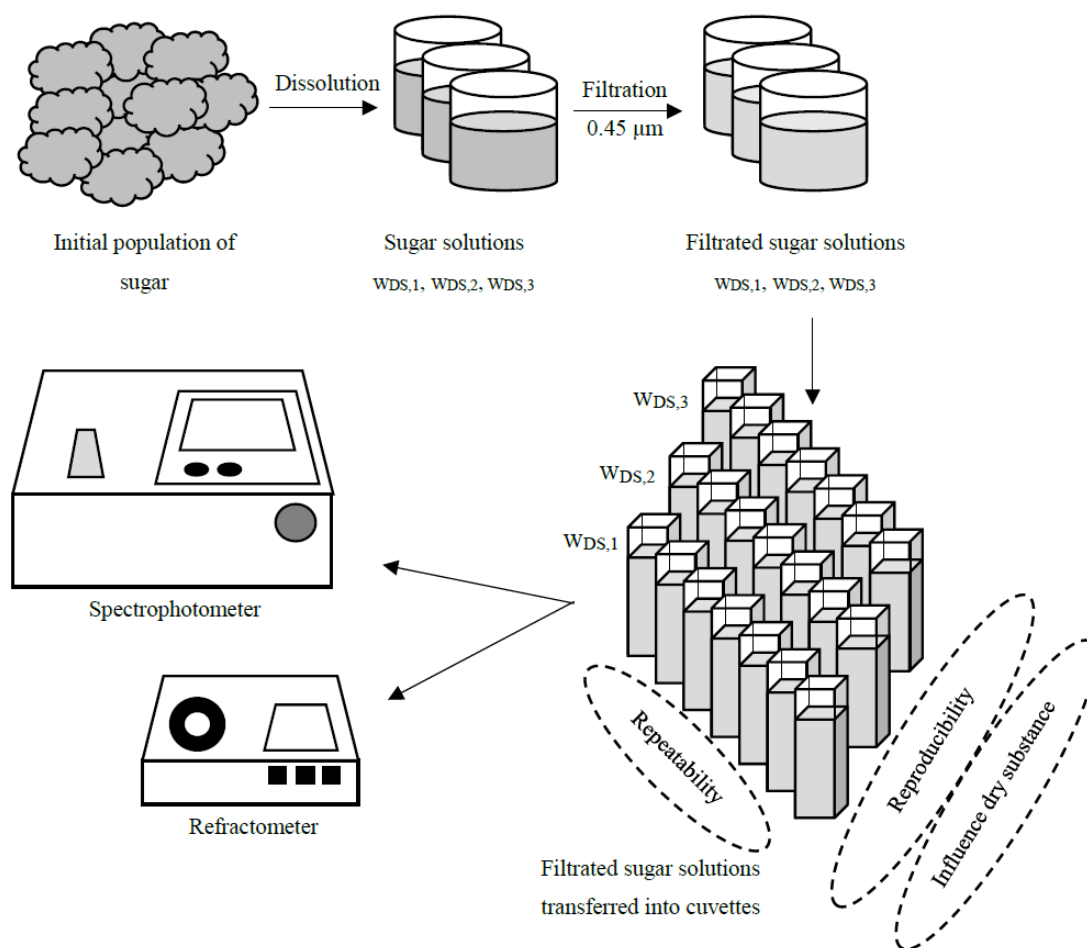


Figure 9-2: Experimental design for the investigation of repeatability and reproducibility of the color determination method and of the influence of dry substance on color value.

Additionally, the mean color values, standard deviations and relative standard deviations of mixed syrup, massecuite, run-off syrup, sugar and affinated sugar are given to evaluate the reproducibility of the whole process. The crystallization experiments were conducted in duplicate. The mean particle size and distribution of the crystallized sugars are stated, too.

9.2 Materials and methods

9.2.1 Materials

Sugars and syrups used for this work were supplied by German sugar factories. Specific properties of the materials used are given in the experimental approaches and specific methods are described in the following sections. The chemicals and materials utilized for color analysis are listed in Table 9-1. The devices used for the color determination method and their accuracies are represented in Table 9-1.

Table 9-1: Materials used for color analyses.

Materials	Distributor
CHROMAFIL® membrane filters GF/PET 0.45 µm	Machery-Nagel GmbH & Co. KG, Düren, Germany
Hydrochloric acid solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
Sodium hydroxide solution (0.1 mol l ⁻¹ , 1 mol l ⁻¹)	Bernd Kraft, Duisburg, Germany
10 mm UV-cuvette (612-5685)	VWR International, Darmstadt, Germany
50 mm glass cuvette 100-OS (634-9017)	VWR International, Darmstadt, Germany
1000 mm glass cuvette 100-OS	VWR International, Darmstadt, Germany

Table 9-2: Devices used for analyses and their accuracy.

Device	Labelling	Manufacturer	Accuracy
pH meter	Seven Excellence	Mettler Toledo, Gießen, Germany	n/a
pH electrode	Inlab Routine Pro	Mettler Toledo, Gießen, Germany	± 0.25
Refractometer	ATR	Schmidt & Haensch GmbH, Berlin, Germany	± 0.05 g/100 g
Spectrophotometer	NANOCOLOR UV/VIS	Machery-Nagel GmbH & Co. KG, Düren, Germany	± 0.005; ± 1% from > 0.500
Balance	LC 6200 S	Sartorius, Göttingen, Germany	± 0.02 g

9.2.2 Experimental approaches

Different experimental designs were applied to assess accuracy and significance of the processes and methods conducted in this thesis. The different approaches are illustrated and explained in the following sections.

9.2.2.1 Experimental approach 1

The experimental approach in Figure 9-2 was designed to investigate the repeatability and reproducibility of the color determination method as well as the influence of dry substance on color value. Therefore, sugar crystallized by TU Berlin was dissolved in demineralized water (< 2 µS cm⁻¹) to achieve three sugar solutions with different dry substance levels. Subsequently,

these solutions were processed according to ICUMSA color determination method (see 9.2.2.4). For each solution, absorption and dry substance level was analyzed seven times.

9.2.2.2 Experimental approach 2

The process steps which follow crystallization are centrifugation and drying. For the evaluation of the reproducibility of these post crystallization processes, the experiments illustrated in Figure 9-3 were performed. The massecuite used in these experiments is produced synthetically and not by crystallization to exclude deviations in sugar color, size and size distribution which might otherwise be caused by the crystallization process. Additionally, to minimize variations in the system, the experiments were conducted at ambient temperature. It goes without saying that the removal of mother liquor from crystal surface during crystallization is improved at increased temperatures due to decreased viscosity of the solution. However, minimal variances in temperature during this process can cause crystal dissolution or growth. To assess the reproducibility of the post crystallization process steps it was indispensable to perform these experiments with minimal risk of crystal growth or dissolution. The removal of all of the thick juice was of minor importance compared to the assessment of the reproducibility of the post crystallization process.

Materials used for this study were chosen to ensure industrial relevance. Beet sugar and thick juice were sourced from German sugar factories. The white beet sugar and the thick juice had color values of 32.3 IU (± 3.5 IU, determined in duplicate) and 2,012 IU, respectively. The beet thick juice had a dry substance level of 67.22 g/100 g and a purity of 94.91%. The initial thick juice used was in an undersaturated state at ambient temperature. To avoid crystal dissolution during the evaluation of the post crystallization process steps, the thick juice had to be transferred into the saturated state. Therefore, white sugar was added in excess to the undersaturated thick juice and blended for four hours. Subsequently, the saturated solution was separated from the sugar crystals by means of a basket centrifuge (Sieva 2, Hermle, Wehingen, Germany).

The post crystallization steps start with the preparation of massecuite. Therefore, 750 g of white sugar (32.3 IU) and 750 g of saturated thick juice were blended for 15 min by means of a stirrer (60 rpm). Then the well-mixed solution was separated in a basket centrifuge (DM2250, Gebr. Heine, Viersen, Germany). Therefore, the massecuite was filled into the centrifuge and the basket was accelerated to a G-force (RFC) of 1,450. After one minute 75 ml of water were sprayed onto the crystals' surface by means of a self-constructed washing unit. This should ensure that the residual syrup film on the sugar surface is displaced. The total centrifuging time was two minutes. Finally, sugar was dried in a fluidized-bed dryer, designed by TU Berlin, for 10 min with conditioned air (343 K). The design of the centrifuge and fluidized-bed dryer are described in detail elsewhere (Chapter 3).

To evaluate the reproducibility of the post crystallization process, the experiments were performed six times and color analyzes were conducted in duplicate according to ICUMSA method GS2/3-10 (ICUMSA, 2011). Additionally, reproducibility of color analyses was investigated. Therefore, one of the post crystallized sugar samples was analyzed seven times instead of in duplicate.

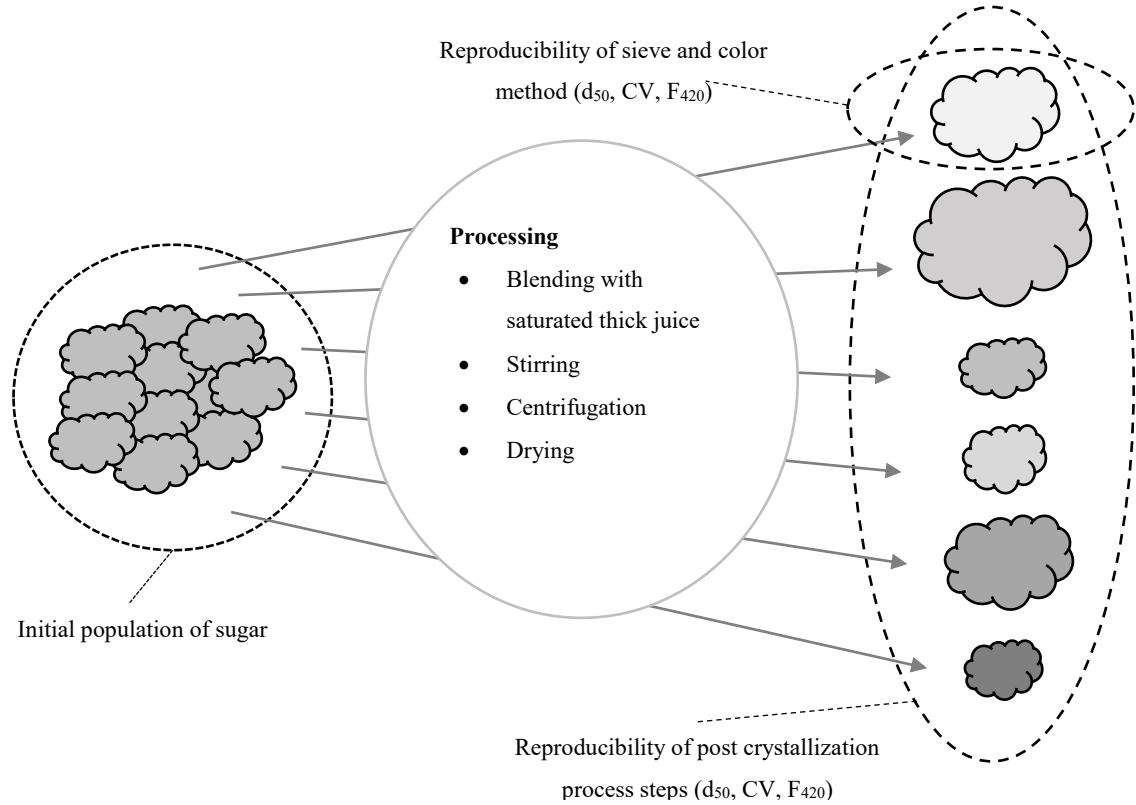


Figure 9-3: Experimental design of testing the reproducibility of the post crystallization process and of the color determination method.

9.2.2.3 Experimental approach 3

To investigate the influence of dry substance level and colorant concentration on color value, beet thick juice ($F_{420} = 4,722$ IU ($\pm 2.9\%$), $w_{DS} = 71$ g/100 g ($\pm 1.3\%$), $q = 94.6\%$ ($\pm 0.5\%$)) was diluted with white refined sugar (27 IU $\pm 5.0\%$) and demineralized water (< 2 μ S/cm) in different ratios. Therefore, in a first step, the sugar was dissolved in the demineralized water. Then the beet thick juice was added and the solution was mixed thoroughly (Figure 9-4). Table 9-3 illustrates the composition of each sample. Subsequently, the solutions were analyzed according to the ICUMSA color determination method GS1/3-7 described in section 9.2.3.

Table 9-3: Composition of samples for experimental approach 3.

Water content (g/ 100 g)		Sugar (g/ 100 g)				
		10	20	30	40	50
Thick juice content (g/ 100 g)	0	90	80	70	60	50
	1	89	79	69	59	49
	2	88	78	68	58	48
	3	87	77	67	57	47
	4	86	76	66	56	46
	5	85	75	65	55	45

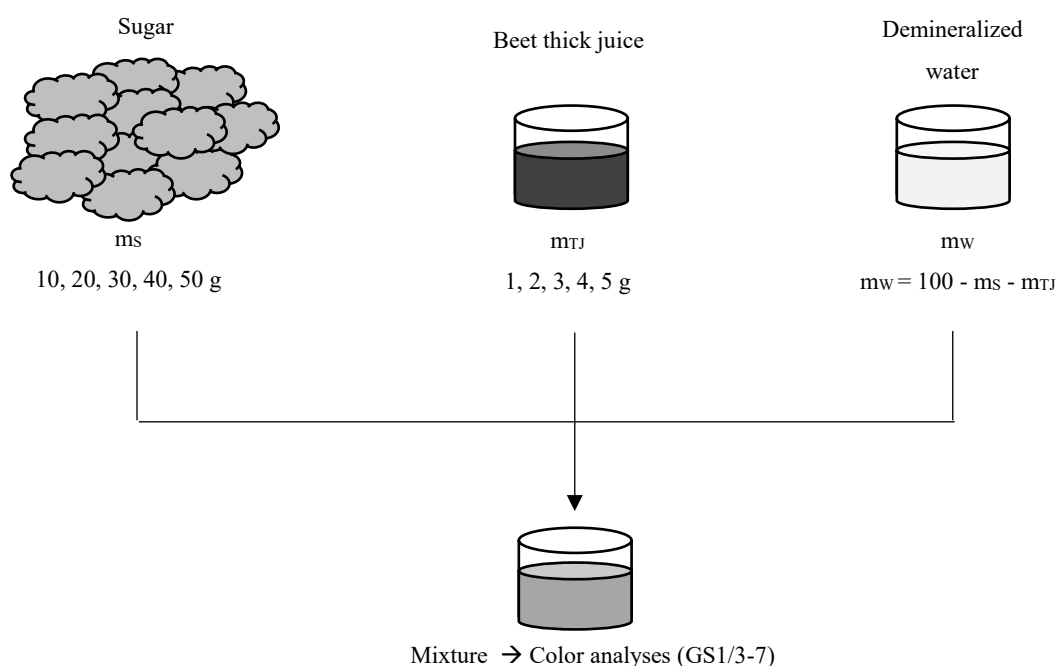


Figure 9-4: Experimental design to prove the influence of colorant concentration and dry substance level on color value.

9.2.2.4 Experimental approach 4

For investigating the reproducibility of the affination process, TU Berlin crystallized sugar was divided into six samples. For the affination process, a saturated sugar solution was made with industrial refined white beet sugar with a color value of less than 30 IU. Then, the saturated sugar solution was added to the above-mentioned samples (50%:50% (w/w)). The suspension was stirred for 15 min and 5 min. In the following step, the affinated sugar was separated from the solution by means of a centrifuge (Sieva 2, Hermle, Wehingen, Germany) at 3,600 rpm. This procedure was repeated twice. Subsequently, color values were analyzed according to ICUMSA method GS2/3-10.

9.2.3 Color analysis

Color of sugars and sugar solutions was determined by the methods GS2/3-10 and GS1/3-7, respectively (ICUMSA, 2011). In the following, method GS1/3-7 is explained exemplary. It is typically used for colored syrups, raw sugars, affined sugars and higher color plantation white sugars. The method is based on the transmittance ergo the absorbance (extinction) of the tested solution. The absorbance, A_s , is the negative decadic logarithm of the ratio between transmittance of the solution, $T_{solution}$, and the solvent, T_{sov} :

$$A_s = -\log\left(\frac{T_{solution}}{T_{sov}}\right) \quad (9-1)$$

Sugars are dissolved in demineralized water and solutions are diluted with demineralized water. The pH-value of the resulting solution is adjusted to a value of 7.0. Therefore, hydrochloric acid solution and sodium hydroxide solution are used. Subsequently, the sample is filtered through a 0.45 μm syringe filter and the absorbance is measured at a wavelength of 420 nm. Final extinction should be between 0.080 and 0.800 to ensure representative results by staying within the range of the linear relation between colorant concentration and extinction. Otherwise, samples would have to be diluted. The proportionality of absorption to dry substance and density allows to conduct the method at various dry substance levels. Thus, the refractometric dry substance (w_{DS}) of the sample needs to be determined. ICUMSA color (F_{420}) can be computed as follows:

$$F_{420} = \frac{10^8 \cdot A_s}{w_{DS} \cdot \rho \cdot b} \quad (9-2)$$

where b is the length of the cuvette (1 cm for syrups, 5 or 10 cm for sugars), and ρ is the density of the solution. The density of the sucrose solution can be computed using the dry substance of the solution:

$$\rho = 0.998 + 3.86 \cdot 10^{-3} \cdot w_{DS} + 1.28 \cdot 10^{-5} \cdot w_{DS}^2 + 6.11 \cdot 10^{-8} \cdot w_{DS}^3 - 1.68 \cdot 10^{-10} \cdot w_{DS}^4 - 4.63 \cdot 10^{-13} \cdot w_{DS}^5 \quad (9-3)$$

In Table 9-1 and Table 9-2 materials and devices used for the color analyses are listed.

The methods GS2/3-10 and GS1/3-7 are actually quite similar. The only difference is the pH adjustment in method GS1/3-7 which is necessary for sugars and solutions with color values above 50 IU. This is due to the pH sensitivity of the colorants. For sugars with color values below 50 IU, colorant concentration is low and pH variations do not affect absorption ergo color value to a great extent (ICUMSA, 2004). The proportionality of adsorption to dry substance and density allows to carry out the analysis at different dry substance levels. However, for this thesis the relationship was investigated, as described in the previous sections.

9.2.4 Determination of particle size and distribution

For assessing the influence of the post crystallization steps on particle size and distribution, sieve analyses were performed according to ICUMSA method GS2/9-37 (2007) (ICUMSA, 2011). This method is suitable for granular sugars with a loss of drying of less than 0.025 g/100 g and should not be applied to powdered sugars. Sieves used for this method are of woven stainless-steel with defined mesh sizes. A set of sieves is chosen such that no more than 30% of the sugar sample retains on any sieve. The clean and dry sieves are weighed and sorted by size before the sieving procedure starts. Then a weighed sample (approximately 100 g) of the sugar is placed on the top sieve. The sieving shaker segregates the sugar into fractions by vibrations. After sieving, each sieve is weighed again and the difference to the unladen weight yields the retained fraction weight of the sugar. The sum of the fractions has to be ± 0.6 g of the initial sample weight. Otherwise the procedure should be repeated.

With the data gathered, mean aperture (d_{50}) and coefficient of variation (CV) are determined by Powers method. Therefore, Gaussian distribution of the sugar fractions is assumed. The retained cumulative weights (%) are plotted versus the sieve aperture on a linear scale. A straight line is drawn through the points. The mean aperture d_{50} can be received by reading the sieve aperture at 50% retained cumulative weight. For computing the coefficient of variation CV the apertures at 16% (d_{16}) and 84% (d_{84}) retained weight are noted. Then the CV is calculated as follows:

$$CV = \left(\frac{d_{16} - d_{84}}{2} \right) \cdot \frac{100\%}{d_{50}} \quad (9-4)$$

For the experiments conducted in this chapter each sugar was analysed with the following classes of sieves: 0.900 mm, 0.800 mm, 0.710 mm, 0.630 mm, 0.500 mm, 0.400 mm, 0.250 mm and 0.180 mm (Retsch Technology GmbH, Haan, Germany). The mechanical shaker (AS 200, Retsch Technology GmbH, Haan, Germany) fractioned the sucrose crystals for 10 min applying a shaking amplitude of 1.00 mm.

9.3 Results and discussion

9.3.1 Repeatability of the color determination method

To evaluate the repeatability of spectrophotometric color determination, sugar solutions of three different dry substance levels were analyzed seven times each. In Table 9-4, results for repeatability of dry substance, density, absorption and color value are displayed. The three samples had mean dry substance levels of 30.11 g/100 g, 35.27 g/100 g and 40.28 g/100 g. The relative standard deviations vary between 0.06 – 0.08%. The accuracy of the device is given with 0.05 g/100 g. For the samples investigated, this results in a relative standard deviation of 0.17%, 0.14% and 0.12% with increasing dry substance level. Hence, deviations caused by the user are smaller than deviations caused by the refractometer.

The density of the solution is computed applying the dry substance level of the solution (equation (9-3)). The resulting relative standard deviation is 0.01% for all of the samples. Thus, the deviation in density caused by the dry substance level is negligible.

The absorption of the samples was measured with a spectrophotometer. The absolute standard deviation determined here is in line with the photometric accuracy of the device (± 0.005 for the observed range). Hence, the errors caused by the user do not exceed the errors caused by the device.

Table 9-4: Results for repeatability of the color determination method.

		w_{DS,1}			w_{DS,2}			w_{DS,3}		
	Unit	Mean	SD	Rel. SD	Mean	SD	Rel. SD	Mean	SD	Rel. SD
w_{DS}	g/100 g	30.11	0.02	0.06%	35.27	0.03	0.08%	40.28	0.03	0.07%
ρ	kg/m ³	1127.46	0.09	0.01%	1152.58	0.13	0.01%	1177.85	0.14	0.01%
A_s	-	0.171	0.002	1.34%	0.209	0.005	2.23%	0.247	0.005	1.84%
F₄₂₀	IU	100.6	1.3	1.30%	102.9	2.2	2.10%	103.9	1.7	1.70%

The error analyses of the single variables of the color determination method showed that the relative standard deviations caused by the user are smaller than the ones caused by the devices. To compute the maximum error, the total differential is formulated. Therefore, the equation to calculate the color value is differentiated in dependency of the variables ($F_{420}(w_{DS}, \rho, A_s)$) – dry substance, density and absorption:

$$\Delta F_{420} = \left| \frac{\partial F_{420}}{\partial w_{DS}} \right| \Delta w_{DS} + \left| \frac{\partial F_{420}}{\partial \rho} \right| \Delta \rho + \left| \frac{\partial F_{420}}{\partial A_s} \right| \Delta A_s \quad (9-5)$$

$$\Delta F_{420} = \frac{10^8 \cdot A_s}{w_{DS}^2 \cdot \rho \cdot b} \Delta w_{DS} + \frac{10^8 \cdot A_s}{w_{DS} \cdot \rho^2 \cdot b} \Delta \rho + \frac{10^8}{w_{DS} \cdot \rho \cdot b} \Delta A_s \quad (9-6)$$

Via reformulation, the previous equation results in the maximum relative error:

$$\Delta F_{420} = \frac{1}{w_{DS}} \left(\frac{10^8 \cdot A_s}{w_{DS} \cdot \rho \cdot b} \right) \Delta w_{DS} + \frac{1}{\rho} \left(\frac{10^8 \cdot A_s}{w_{DS} \cdot \rho \cdot b} \right) \Delta \rho + \frac{1}{A_s} \left(\frac{10^8 \cdot A_s}{w_{DS} \cdot \rho \cdot b} \right) \Delta A_s \quad (9-7)$$

$$\Delta F_{420} = \frac{\Delta w_{DS}}{w_{DS}} (F_{420} (w_{DS}, \rho, A_s)) + \frac{\Delta \rho}{\rho} (F_{420} (w_{DS}, \rho, A_s)) + \frac{\Delta A_s}{A_s} (F_{420} (w_{DS}, \rho, A_s)) \quad (9-8)$$

$$\frac{\Delta F_{420}}{F_{420} (w_{DS}, \rho, A_s)} = \frac{\Delta w_{DS}}{w_{DS}} + \frac{\Delta \rho}{\rho} + \frac{\Delta A_s}{A_s} \quad (9-9)$$

From equation (9-9) follows that the relative error of the color determination method is the sum of the relative errors of the variables. Therefore, the maximum relative standard deviations of dry substance, density and purity (Table 9-4) are inserted into equation (9-9):

$$\frac{\Delta F_{420}}{F_{420} (w_{DS}, \rho, A_s)} = 0.08\% + 0.01\% + 2.34\% = 2.43\% \quad (9-10)$$

The color values of the samples vary between 100.6 IU and 103.9 IU with relative standard deviations of 1.3 – 2.1%. The distribution of the determined values is thus very narrow. The relative deviations are lower than the maximum relative error (equation (9-10)).

It can be concluded that the repeatability of the color determination method is very high. The errors occurring caused by the laboratory staff are lower than the variations of the devices. The errors introduced by the refractometer can practically be neglected. The standard deviation observed for the spectrophotometer is in line with the specifications given by the manufacturer. Finally, the maximum relative error for the repeatability of the color determination method is 2.43%. The repeatability observed is valid for sugars and syrups.

9.3.2 Reproducibility of the color determination method

The data of the experimental approaches 1 and 2 are used to determine the reproducibility of the color determination method. The box-plots in Figure 9-5 illustrate the results of experimental approach 1. For the three solutions of different dry substance level the mean values are 100.6 IU, 102.9 IU and 103.9 IU with relative standard deviations of 1.3%, 2.1% and 1.7%, respectively. In order to determine the reproducibility, the mean value and the relative standard deviation of the complete data set were computed. The resulting values are 102.5 IU and 2.3%, respectively. In ICUMSA Proceedings (2004) the relative reproducibility standard deviations for sugars in color ranges of 92 – 121 IU and 84 – 128 IU are given with 6.7% and 10.5%, respectively. The results from those collaborative investigations (ICUMSA, 2004) scatter 3 – 4.5-fold more than the data of this work. However, the reproducibility from the collaborative ICUMSA tests is computed by comparing data from 12 different labs. Data gathered in the work presented here were only produced in one lab. To enhance the comparability the reproducibility data of this work should

thus be compared to repeatability instead of reproducibility data from ICUMSA Proceedings (2004). The repeatability relative standard deviations are given with 2.3% and 6.1% for sugars in color ranges of 92 – 121 IU and 84 – 128 IU, respectively (ICUMSA, 2004). The reproducibility determined for this work is hence in line with the minimum scatter of the collaborative ICUMSA tests (2004).

In addition to the above, one sugar population from the post crystallization experiment (approach 2) was analyzed seven times to evaluate the method of sugar color determination in another color range. Figure 9-6 illustrates the data in a box-plot. The mean value is 34.1 IU (± 1.8 IU) with a relative reproducibility standard deviation of 5.3%. In ICUMSA Proceedings (2004) the repeatability relative standard deviations, which are equivalent to the reproducibility standard deviation in this work as outlined above, for sugars in a color range of 26 – 33 IU, 23 – 31 IU and 28 – 37 IU are given with 3.2%, 6.0% and 6.4%, respectively. This results in an average value of 5.2%, which is perfectly in line with the reproducibility error observed in this work (5.4%).

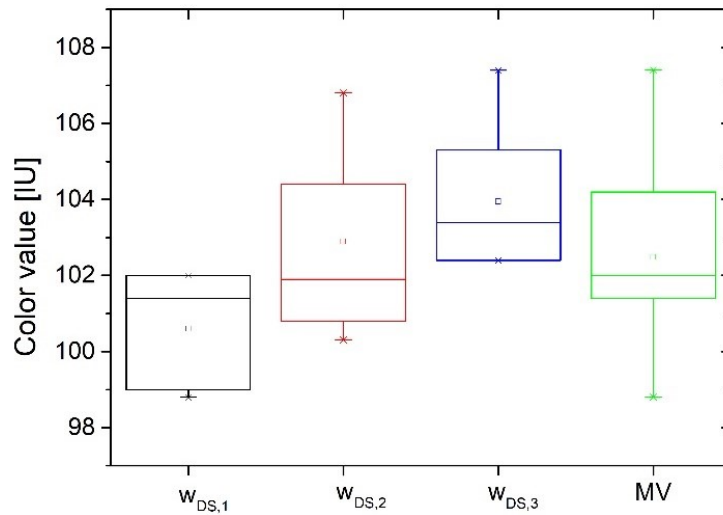


Figure 9-5: Data from experimental approach 1 ($W_{DS,1}$; $W_{DS,2}$; $W_{DS,3}$) and their mean value (MV), used for reproducibility evaluation of the color determination method.

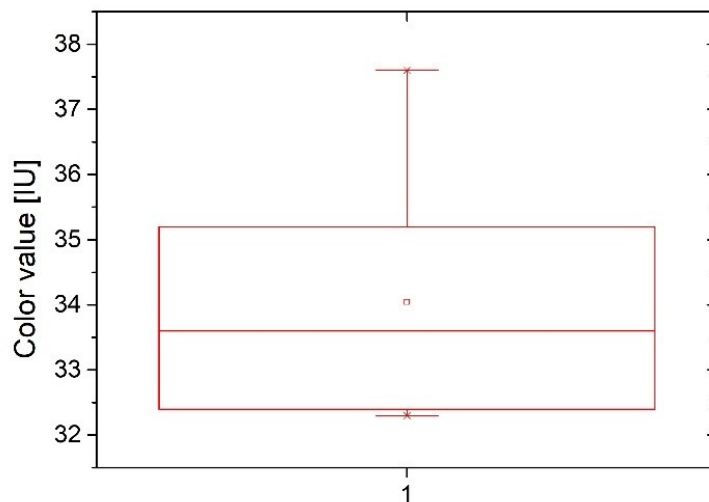


Figure 9-6: Data from experimental approach 2, used for reproducibility evaluation of the color determination method.

9.3.3 Reproducibility of sieve analysis

In order to determine the reproducibility of sieve analyses regarding average size (d_{50}) of sugar crystals and size distribution (CV), one sugar population from the post crystallization experiment (approach 2) was analyzed seven times. The data sets are illustrated in box-plots (Figure 9-7 and Figure 9-8). Regarding the average size, a mean value of 0.512 mm and a standard deviation of 0.005 mm were determined. This yields a relative reproducibility standard deviation of 1.0%. Regarding the coefficient of variation, the mean value is 29.8% and the standard deviation is 0.2%. This results in a relative reproducibility standard deviation of 0.7%.

The relative standard deviations for both, mean aperture and coefficient of variation, are very low. This allows the statement that sieve analysis gives results of very high accuracy.

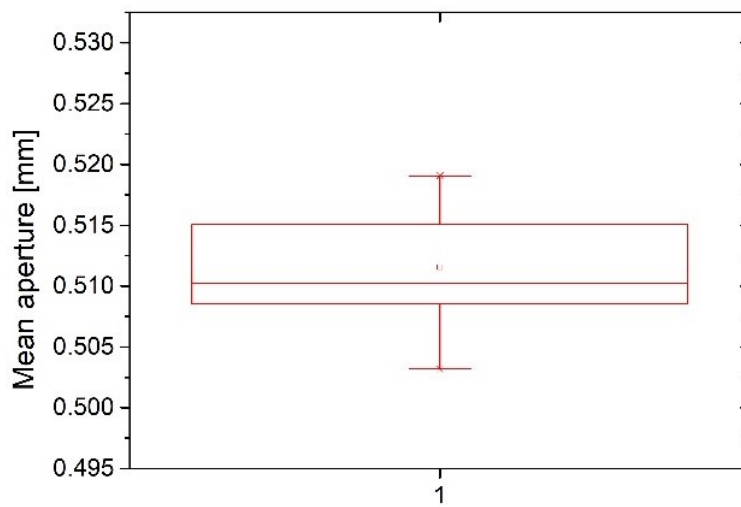


Figure 9-7: Mean aperture data from experimental approach 2, used for reproducibility evaluation of sieve analysis.

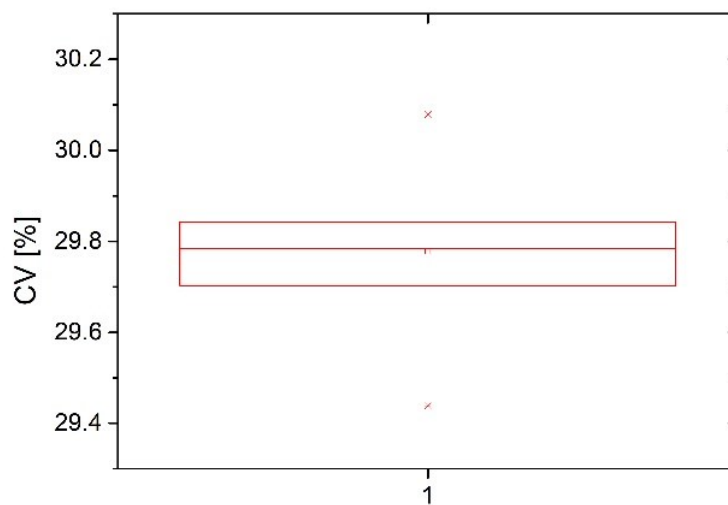


Figure 9-8: Coefficient of variation data from experimental approach 2, used for reproducibility evaluation of sieve analysis.

9.3.4 Reproducibility of the post crystallization process

Sugar is separated from mother liquor after crystallization in a centrifuge and dried subsequently in a fluidized-bed. Variations in these process steps might change sugar characteristics such as color value, particle size and distribution. The knowledge of the reproducibility of these process steps is necessary to discuss crystallization results according to different process or product parameters. Post crystallization steps are conducted in a most consistent manner. The results of the post crystallization experiments regarding color value, mean aperture and coefficient of variation are discussed in the following two sections.

9.3.4.1 Color value

The color value data of six independently conducted post crystallization strikes are illustrated in Figure 9-9. Values from sample number 1 (sevenfold analysis) scatter distinctively compared to the other samples (duplicate analysis). The mean values of the data gathered are between 34.1 and 36.7 IU with relative standard deviations of 0.2 – 5.4%. Since the values from sample number 1 scatter the most the relative standard deviation is distinctively higher than for the other samples. However, the scattering of sample number 1 is still in line with literature data and the color determination method has been proven to be reproducible (9.3.2). Differences between the results of the six strikes can thus be ascribed to the influence of the post crystallization process. In order to determine the reproducibility of the post crystallization process the mean color values of all of the six strikes are compared, resulting in an average mean color value of 35.0 IU and an average relative standard deviation of 2.7%. Unfortunately, literature does not provide any data related to reproducibility of centrifugation and drying processes. Nevertheless, based on a standard deviation of 2.7%, the reproducibility can be considered as very high. Regarding the relative standard deviations, the reproducibility of the post crystallization process is comparable to the

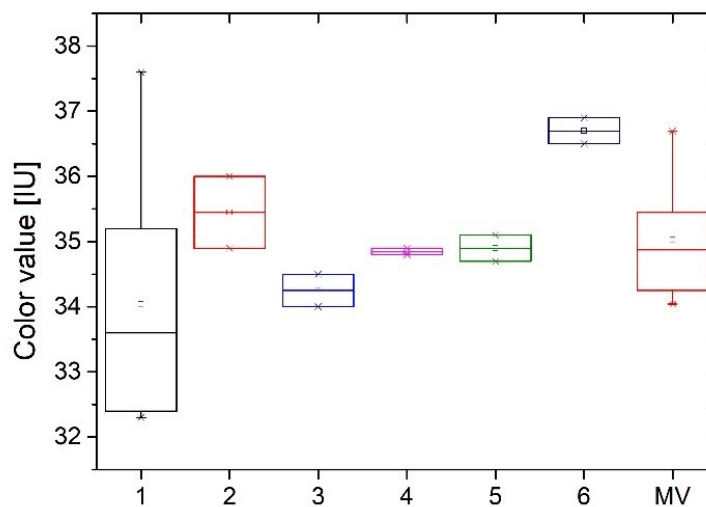


Figure 9-9: Reproducibility data of the post crystallization process according to sugar color, with number of experiment (1 – 6) and mean value of all experiments (*MV*).

reproducibility of the color determination method itself. It can be concluded that the post crystallization process conducted in this work is very reliable and yields in reproducible results.

9.3.4.2 Sieve analysis

The reproducibility of the post crystallization process concerning particle size (d_{50}) and distribution (CV) are illustrated in Figure 9-10 and Figure 9-11. The data of sample number 1 (sevenfold analysis) have been discussed above regarding reproducibility of the sieve analysis method. For the other samples sieve analysis was conducted in duplicate. The average values of mean aperture and coefficient of variation are 0.512 – 0.541 mm and 26.52 – 29.78%, respectively. For both characteristics, sample number 1 differs significantly from the other samples. Comparing those other samples, it can be said that the mean values of average particle size and coefficient of variation do not deviate significantly. The scatter of the data of each sample can be regarded as narrow. For evaluating the reproducibility of the post crystallization process the values of all of the six data sets are compared. The average value of the mean aperture is 0.532 mm ($\pm 2.03\%$), the average value of the coefficient of variation is 27.88% ($\pm 3.77\%$). If sample number 1 is regarded as an outlier, the relative standard deviations decrease to 0.70% and 1.99% for d_{50} and CV , respectively. It can be stated, that reproducibility of the post crystallization process according to mean aperture and coefficient of variation is very good.

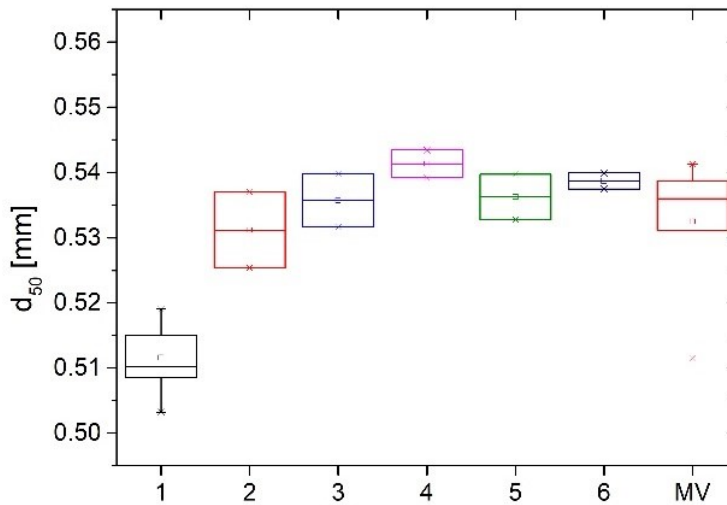


Figure 9-10: Mean aperture (d_{50}) data used for evaluating the reproducibility of the post crystallization process, with number of experiment (1 – 6) and mean value of all experiments (MV).

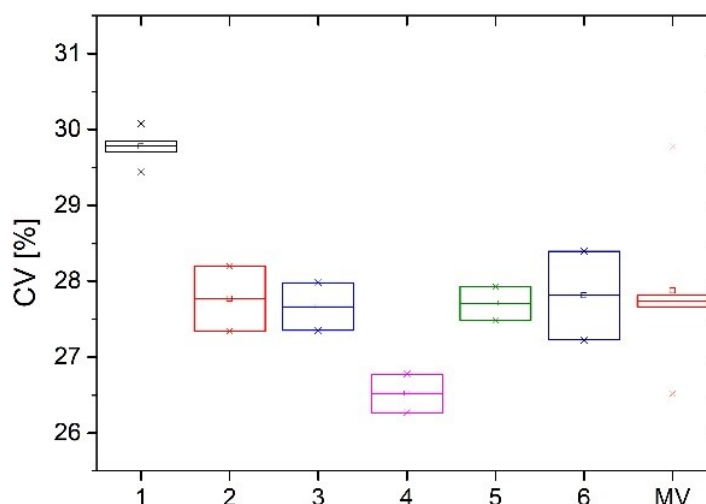


Figure 9-11: Coefficient of variation (*CV*) data used for evaluating the reproducibility of the post crystallization process, with number of experiment (1 – 6) and mean value of all experiments (*MV*).

9.3.5 Influence of the post crystallization process on the color value

In order to investigate the efficiency of the washing process in the centrifuge, the initial sugar color value is compared with the sugar color after the post crystallization process according to experimental approach 2. The results are illustrated in Figure 9-12. For post crystallized sugar, data from all six experiments were used. The values from initial sugar and post crystallized sugar average at 32.4 IU (± 3.5 IU) and 34.7 IU (± 1.4 IU), respectively. Although this difference is almost negligible, it is supposed that the residual film of mother liquor on the sucrose crystal surface might not always be removed completely during the washing process. Color values of syrups present in the different experiments of this work obviously varied so that the thick juice used here, $F_{420} = 2,012$ IU, can only yield indicative results. Even though the residual mother liquor film on the sucrose crystal surface could have influenced the color value of sugars differently it appears that the washing in the centrifuge is quite effective. After all, the increase of color value corresponds to only approximately 0.1% of adhering material and the analysis presented here was performed at low temperatures promoting adhesion. Anyhow, variations or errors in the washing process could result in a residual film of different thickness which potentially falsifies results further. Hence, for assessing color inclusion properties of crystallization experiments conducted in this thesis, sugars were affinated after crystallization processes to ensure that remaining mother liquor was removed completely.

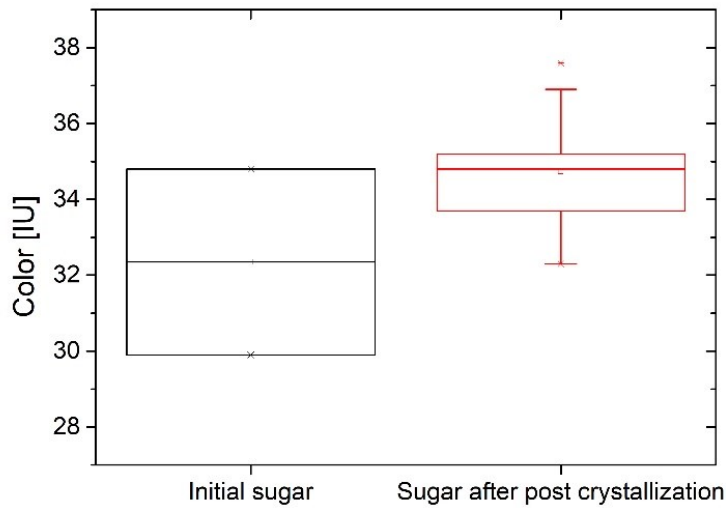


Figure 9-12: Box-plot of color values from initial sugar and post crystallized sugar.

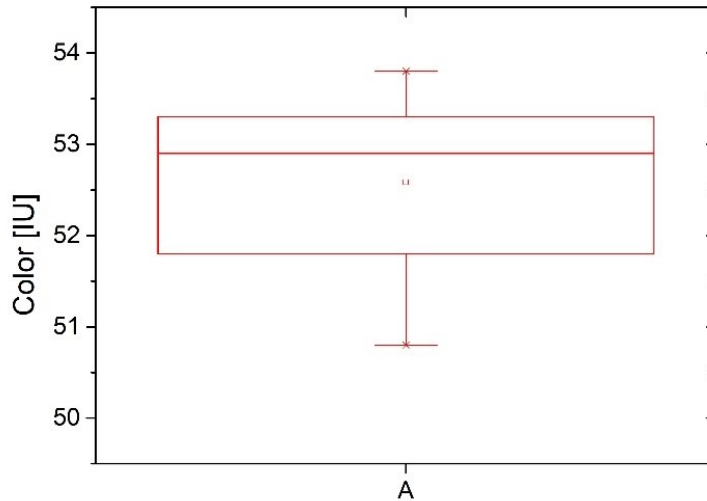


Figure 9-13: Results from experimental approach 4 illustrated in a box-plot.

9.3.6 Reproducibility of affination process

Affination process was conducted in this thesis to quantify the removal of colorants and ash components from the crystals' surface. Furthermore, the affination process ensured that variations during separation and washing processes did not falsify colorant inclusion results due to residual syrup on the crystal surface. Experiments in this section were performed to verify reproducibility of the affination process. The results are illustrated in Figure 9-13. The color values after affination (experimental approach 4) average between 50.8 IU and 53.8 IU resulting in a mean value of 52.6 IU and a relative standard deviation of 1.9%. The results indicate a very high reproducibility of the affination process conducted. This can be concluded in particular taking into account the repeatability and reproducibility of color determination method itself.

9.3.7 Influence of non-sugar concentration and dry substance level on color value

In this thesis, sugar is crystallized from blended syrups of beet and cane material with different color values and non-sucrose contents. It is generally acknowledged that different dry substance levels of the test solution are acceptable, as long as the measured absorption is in the desired range of 0.080 – 0.800. Thus, this section discusses the influence of dry substance content and non-sucrose level on final color value.

9.3.7.1 Influence of non-sugar concentration on color value

The influence of non-sugar concentration on color value was investigated in experimental approach 3. The graph in Figure 9-14 reveals a linear relation between the color value and the ratio of non-sugar to dry substance ($R^2 = 0.999$). This suggests, that if two or more different colored syrups are blended, the resulting syrup color value is a linear combination of the constituents. Additionally, regarding the non-sugar and dry substance level area investigated, absorption behaves proportionally, and no artefacts or drifts of absorption can be observed. Consequently, it can be stated that the color determination method used is suitable for (blended) syrups and sugars – measured as dissolved sugar – in the investigated absorption area (0.080 – 0.800).

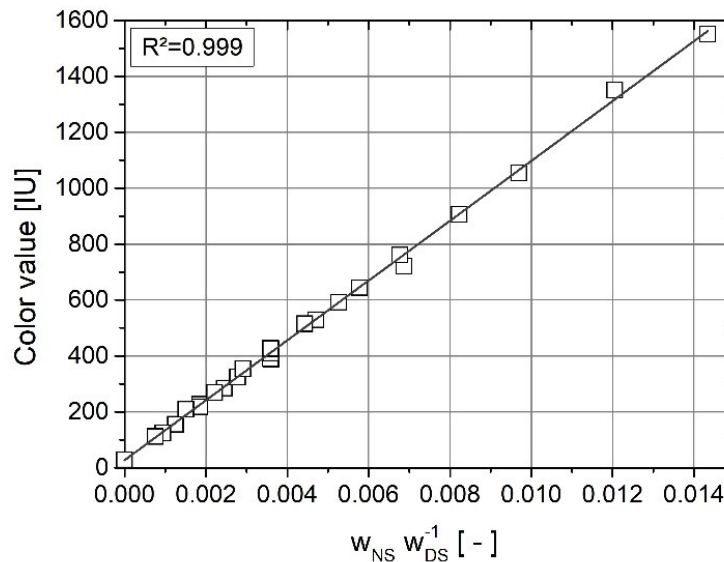


Figure 9-14: Color value versus non-sucrose to dry substance content.

9.3.7.2 Influence of dry substance on color value

Figure 9-15 illustrates the color value versus the dry substance content of different syrups and dissolved sugars of experimental approaches 1 and 3 which have identical ratios of non-sucrose to dry substance level. To ensure absorption in the desired range of 0.080 – 0.800, an adequate cuvette length was chosen for each sample. For sample set 1 (■) color value increases from 388 IU

to 427 IU with increasing dry substance level. For another syrup (▲) and for both sugars (□, ▼), the data reveal similar behavior. The data shown indicate that there is a systematic influence of the dry substance level of the actual solution subjected to the measurement on the resulting color value determined.

Table 9-5 depicts the mean color values and relative standard deviations of the samples of the experimental approaches. The relative standard deviations are between 1.7 % and 5.0% averaging at 3.6%. Additionally, the table demonstrates data from ICUMSA Proceedings (2004) in equivalent color ranges to the samples from the experimental approaches presented here. The relative standard deviations from ICUMSA Proceedings vary between 2.2 – 6.1% averaging at 4.1%. It should be noted that these standard deviations were drawn from repeatability data, ergo the deviations caused by a single instrument and/or person under equal conditions. It can be assumed that these color determinations were conducted at approximately constant dry substance levels. Overall, the relative standard deviations of both data sets, experimental approach presented here and ICUMSA samples, are in the same range. Considering this in combination with section 9.2.3, it can be concluded that the general practice to allow for limited variation of the dry substance level in the measurement sample appears tolerable. However, for improved accuracies it is recommendable to standardize the procedure to eliminate the systematic deviations caused by variation of these background values. However, with respect to the data within this thesis, differences in color values originating from different dry substance levels are considered insignificant.

Table 9-5: Mean color values and relative standard deviations of different syrups and sugars determined at various dry substance levels from different experimental approaches (1, 3) compared with samples of equivalent color ranges from collaborative ICUMSA tests (ICUMSA, 2004).

Experimental approaches			ICUMSA samples	
Sample Set No.	MV (IU)	Rel. SD	Color range (IU)	Rel. SD
1 (■)	407.9	4.4%	286 – 359	2.2%
			447 – 555	5.1%
2 (●)	222.5	2.8%	133 – 188	4.1%
			162 – 208	2.4%
3 (▲)	741.9	3.7%	447 – 616	5.0%
4 (▼)	27.0	5.0%	25 – 31	6.0%
			26 – 33	3.3%
5 (□)	102.5	2.3%	92 – 121	2.3%
			84 – 128	6.1%
Mean	n/a	3.6%	n/a	4.1%

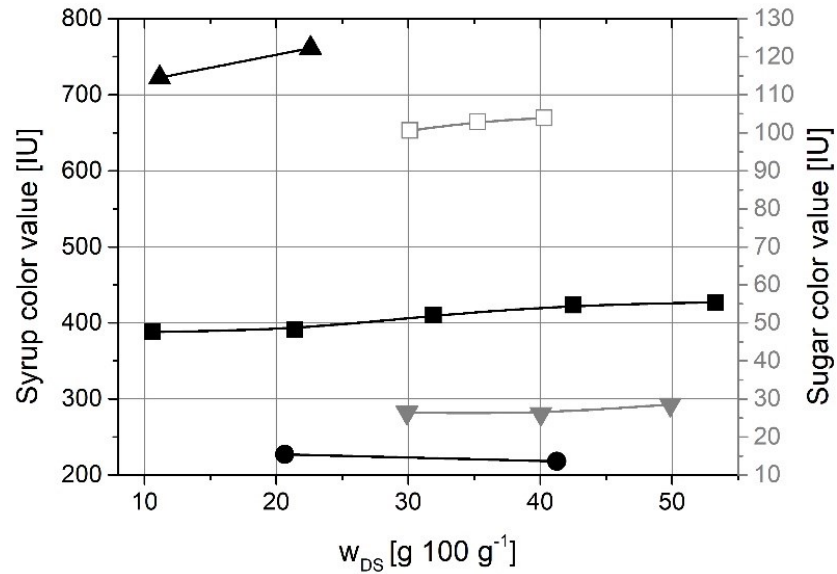


Figure 9-15: Color value versus dry substance content of different syrups (■, ●, ▲) and sugars (□, ▼) from experimental approach 1 (open symbols) and 3 (full symbols).

9.3.8 Reproducibility of experiments

Crystallization experiments (see Figure 9-1) performed in this thesis were conducted in a most consistent manner to prevent variations due to execution. Additionally, most experiments were performed in duplicate to prove the accuracy of the experiments. In the following two sections the accuracy of the data of the crystallization experiments are discussed.

9.3.8.1 Color value

The mean color values and the relative standard deviations for feed syrups, run-off syrups, sugars and affinated sugars of crystallization experiments are shown in Table 9-6. In Figure 9-16 the data points from Table 9-6 are illustrated in box-plots. Feed syrups were the result of mixing beet thick

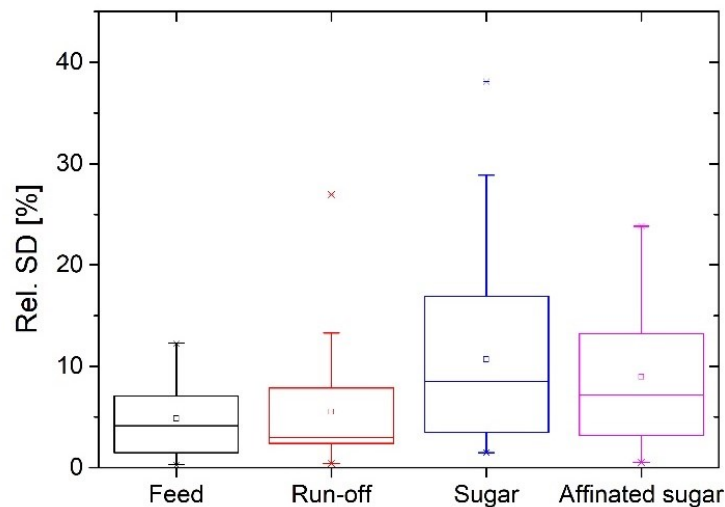


Figure 9-16: Data used for evaluating the reproducibility of the crystallization process according to color values of feed syrup, run-off syrup, sugar and affinated sugar.

juice and dissolved raw cane sugar in a certain ratio. For feed syrups the relative standard deviation of the color values scatters between 0.29% and 12.29% averaging at 4.9% ($\pm 3.6\%$).

Table 9-6: Mean color values and their relative standard deviations of crystallization experiments performed in duplicate.

Sample No.	Feed		Run-off		Sugar		Affinated sugar	
	MV (IU)	Rel. SD	MV (IU)	Rel. SD	MV (IU)	Rel. SD	MV (IU)	Rel. SD
1	2021	2.92%	4623	2.39%	65	28.87%	15	6.59%
2	1733	10.30%	3960	13.27%	66	7.20%	21	3.26%
3	1681	2.64%	3870	0.40%	80	15.00%	22	5.96%
4	1459	0.77%	3037	26.98%	87	2.52%	34	9.38%
5	1362	10.72%	3289	8.17%	99	5.30%	52	1.44%
6	1221	10.07%	2644	6.39%	128	38.11%	72	3.48%
7	2058	1.19%	4620	2.27%	47	3.50%	15	10.89%
8	1969	3.50%	4393	5.23%	53	8.74%	25	2.79%
9	1856	0.48%	4225	1.17%	62	4.16%	30	3.16%
10	1805	9.13%	3794	2.87%	67	1.68%	40	0.50%
11	1599	4.14%	3451	2.64%	92	2.29%	58	7.12%
12	1604	1.08%	3326	1.66%	119	5.53%	83	2.24%
13	5016	12.29%	12090	13.28%	136	16.92%	37	23.82%
14	4909	5.28%	10888	7.86%	145	20.29%	47	3.18%
15	5114	7.06%	11086	8.44%	193	18.14%	57	12.01%
16	1594	1.47%	3396	2.41%	128	3.06%	73	7.16%
17	1731	4.40%	3179	3.43%	140	17.60%	92	7.38%
18	1608	6.67%	3072	3.76%	157	1.48%	109	16.82%
19	2738	0.29%	6133	4.90%	157	10.36%	71	13.20%
20	3056	5.29%	6441	2.66%	177	9.04%	86	19.05%
21	4124	6.46%	8474	2.58%	117	7.38%	42	19.47%
22	3961	3.20%	8639	1.21%	156	10.11%	48	15.40%
23	4212	2.55%	9477	3.00%	188	8.51%	73	12.02%
MV	n/a	4.9 %	n/a	5.5 %	n/a	10.7 %	n/a	9.0%
SD	n/a	3.6 %	n/a	5.9 %	n/a	9.3 %	n/a	6.5%

Different errors might occur during the mixing process and color analyses, such as inhomogeneities in the raw materials, inaccurate ratio of the raw materials in the mixture, inhomogeneities in the mixture and errors during execution of the color determination method. None of these errors was examined in detail except for the repeatability and reproducibility of the color determination method (9.3.1, 9.3.2). However, the reproducibility was only determined for sugars which have lower color values than syrups. In ICUMSA Proceedings (2004), reproducibility of syrup color analyses was analyzed by comparing data from different labs. To a certain degree, this is comparable to the work presented here in which mixed syrups of duplicate experiments were produced and analyzed at different days. In ICUMSA Proceedings (2004) the

deviation regarding reproducibility is stated to be 5.09% and 4.92% for syrup color values of around 2,500 IU and 4,500 IU. Thus, the average relative standard deviation of feed syrup color values found is in line with the reproducibility of the color determination method itself examined by ICUMSA Proceedings (2004).

The accuracy of feed syrup color values is found again in products later on in the process (e.g. run-off syrup, sugar, affinated sugar). However, the extent of these deviations is smaller for sugars than for run-off syrups because the final sugar color value is only 1 to 10% of the initial feed syrup color value. In contrast, run-off syrup is the concentrate of the feed syrup after the crystallization. Its relative standard deviation scatters between 0.40% and 26.98% with an average value of 5.5% and a standard deviation of 5.9%. It should be noted that one of the data points is certainly an outlier – origin of deviation not identified – (26.98%) which is disturbing the dataset. Without this data point, the average relative standard deviations of run-off syrup and feed syrup would be found in the same range. It can be concluded that the reproducibility of both feed and run-off syrup color value is very high.

The end product of crystallization and post crystallization process is sugar. Regarding the color value, its average relative standard deviation scatters between 1.48% and 38.11% with an average value of 10.7% ($\pm 9.2\%$). As can be seen in Table 9-6 the scattering of color values is increased compared to the data of the syrups. In addition to the possible errors already mentioned before, the reason for deviating sugar color values after the centrifugation process is that increased quantities of high colored run-off syrup might remain on crystals' surface which leads to an increased color value. Therefore, the affination process is performed to remove the residual syrup film from the sugar surface.

For affinated sugar, the average relative standard deviation of the color value scatters between 0.50% and 23.82% with an average value of 9.0% ($\pm 6.5\%$). It is noticeable that especially the relative standard deviations of samples 13 – 23, which were derived from only one experimental design, are increased compared to the other samples. Several reasons for these high standard deviations regarding the color determination method could be excluded such as an incorrect spectrophotometer (results not published). The beet thick juice used, however, showed higher color values which might be a reason for increased scattering of colorant inclusion.

9.3.8.2 Particle size and distribution

Sieve analysis was performed to assess the crystallization process considering particle size and distribution. It also allows to determine the influence of raw material and process parameters on particle characteristics. In Table 9-7 the average mean apertures and the average coefficients of variations from crystallization experiments gathered for this thesis are listed along with their relative standard deviations. Figure 9-17 and Figure 9-18 illustrate the data points from Table 9-7 in a box-plot. For mean aperture, the relative standard deviations scatter between 0.01% and 4.68% averaging at 2.2% ($\pm 1.5\%$). The data reveal that deviations of mean aperture are small for the crystallization experiments performed. It shows that experiments were well controlled and highly reproducible. For the coefficient of variation, the relative standard deviation varies between 0.18% and 10.19% averaging at 3.4% ($\pm 2.8\%$). For sieve analyses it is noticeable, similar to for color determination, that the relative standard deviations for samples 13 – 23, which were derived from only one experimental design, are increased compared to the other samples. The combination of color determination and sieve analysis data reveals that reproducibility of crystallization processes of samples 13 – 23 is lower compared to the other experiments. The reason might be lower quality of the beet thick juice used.

Regarding the combined duplicate data it can be stated that the reproducibility of the crystallization process is high since the actual variation of duplicate processes is in the same range as the reproducibility of the analysis itself.

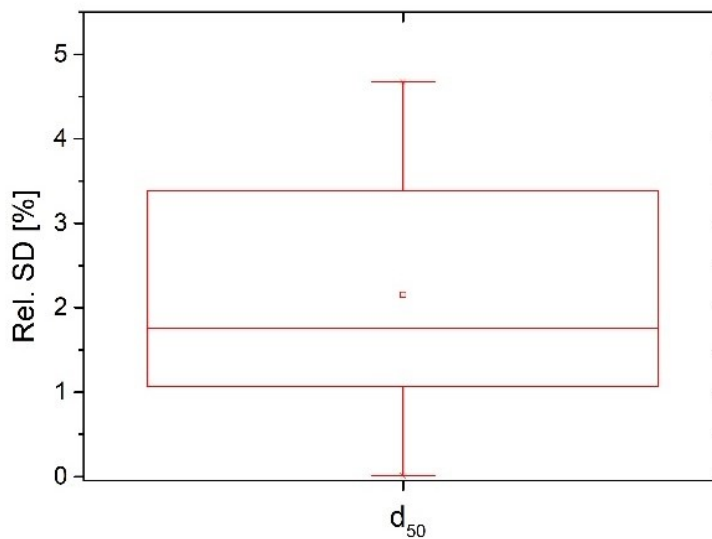


Figure 9-17: Mean aperture (d_{50}) data for evaluating the reproducibility of experimental crystallization processes.

Table 9-7: Average mean aperture and coefficient of variation from sugars of crystallization experiments performed in duplicate.

Sample No.	Mean aperture		Coefficient of variation	
	d ₅₀ (mm)	Rel. SD	CV (%)	Rel. SD
1	0.74	1.13%	27.12	1.74%
2	0.75	1.68%	18.75	0.86%
3	0.80	3.58%	20.06	4.63%
4	0.80	0.40%	19.93	0.71%
5	0.76	0.48%	18.87	0.18%
6	0.80	4.21%	18.79	1.38%
7	0.82	1.07%	20.29	1.56%
8	0.82	0.17%	20.40	0.92%
9	0.81	0.16%	24.52	1.72%
10	0.82	1.76%	20.22	2.44%
11	0.82	0.01%	21.43	3.81%
12	0.80	3.08%	21.15	4.46%
13	0.90	2.13%	18.69	0.92%
14	0.85	1.51%	17.73	10.19%
15	0.81	1.15%	18.78	3.14%
16	0.83	1.44%	19.71	2.80%
17	0.81	4.22%	19.18	3.45%
18	0.80	3.10%	19.93	5.15%
19	0.82	3.39%	18.87	1.55%
20	0.82	2.99%	19.27	8.49%
21	0.88	3.03%	20.83	2.63%
22	0.84	4.68%	19.39	9.02%
23	0.81	4.08%	19.69	5.36%
MV	n/a	2.2 %	n/a	3.4 %
SD	n/a	1.5 %	n/a	2.8 %

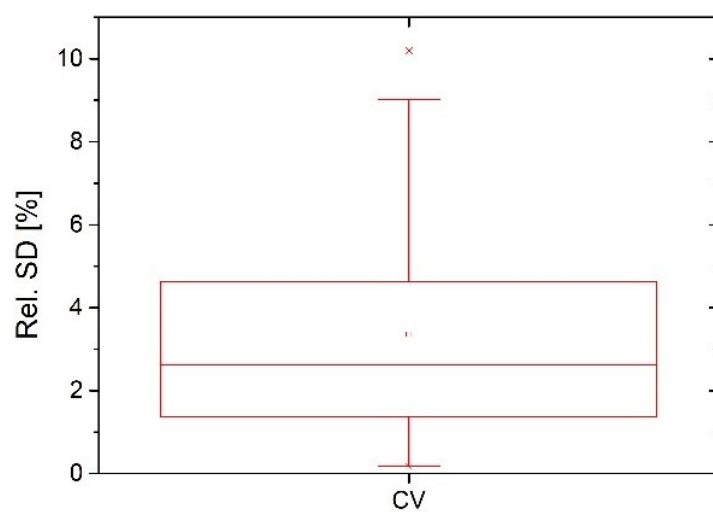


Figure 9-18: Coefficient of variation (*CV*) data for evaluating the reproducibility of experimental crystallization processes.

9.4 Conclusion

Sugar crystallization from sucrose solutions was studied systematically in this thesis. In order to evaluate the significance of the results, error analyses of the methods applied were conducted. Additionally, reproducibility of crystallization experiments performed in duplicate regarding color value, particle size and distribution was discussed.

The determination of the color value is central to this work and the most frequently used method throughout this thesis. Thus, special focus was given to this analysis. Table 9-8 depicts the repeatability and reproducibility of the color determination method. The results show that repeatability and reproducibility of the method are very high. Additionally, the accuracy achieved in the TU Berlin laboratory is in line with or even higher than the industrial standard. Furthermore, experiments revealed that regarding sugar color values the reliability of the post crystallization processes, separation and drying, is very high (2.7%), too. However, it was found that the process applied does not completely remove syrup from the crystals' surface. In this thesis syrups with different adhesion properties and color values were used. In order to eliminate the influence of varying residual surface films on the crystals' surface the affination process was applied. The reproducibility of the affination process was found to be better than for the post crystallization processes (1.9% versus 2.7%). Affination hence appeared to be an appropriate measure to increase accuracy of sugar color value determination. Furthermore, it was verified that color values of mixed syrup are a linear combination of the color values of the juices blended with each other. The assumption that the color determination method is also applicable at different dry substance levels, given the absorption of the tested solution is between 0.080 – 0.800, could be confirmed. The maximum error for color determination is obviously a combination of the relative standard deviations determined for the process steps applied. Comparing the maximum error with the relative deviations of syrups and sugars from crystallization experiments, it can be stated that the crystallization experiments were in line with the maximum error of the methods applied. The data presented allow to conclude that results considering color values in this thesis are significant.

Table 9-8: Standard deviations of processes and methods regarding color value.

		Post crystallization	Affination	Color determination method		Max. error	Crystallization experiments
		Reprod.	Reprod.	Repeat.	Reprod.	Sum	Reprod.
Feed syrup		n/a	n/a	2.43%	5.4%	7.83%	4.9%
Run-off syrup		n/a	n/a	2.43%	5.4%	7.83%	5.5%
Sugar	100 IU	2.7%	n/a	2.43%	5.4%	10.53%	10.7%
Affinated	30 IU	n/a	1.9%	2.43%	2.3%	6.63%	9.0%
sugar	100 IU	n/a	1.9%	2.43%	5.4%	9.73%	

Conclusion

Regarding the reproducibility of particle size and distribution, error analyses on sieve analysis and post crystallization processes were performed and compared to deviations of particle characteristics from duplicate crystallization experiments. For the sieve analysis method, the relative standard deviations of mean aperture (1.0%) and coefficient of variation (0.7%) were found to be very low. For post crystallization processes the relative standard deviations of these characteristic data, d_{50} and CV , were 2.03% and 3.77%, respectively. For crystallization experiments the relative standard deviations of mean aperture and coefficient of variation were 2.2% and 3.4%, respectively. This indicates that also regarding particle size characterization the methods applied are suitable for the studies performed and the crystallization experiments conducted did not introduce significant additional variation of results.

In conclusion, this critical evaluation reveals that on the one hand the analytical methods applied are appropriate for the purpose of this thesis. On the other hand, it shows that the processes applied to prepare the samples were designed and executed so diligently that their contribution to the uncertainty of the results could be kept minimal. The reproducibility of crystallization experiments regarding color value and particle size characteristics is very high rendering the results presented in this thesis significant.

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10 CONCLUSION

The field of co-production achieves increased interest by European sugar manufacturers due to the end of the EU Sugar Policy. In general sugar manufacturers with easy access to beet and cane raw materials or intermediate products, such as beet thick juice or raw cane sugar, are possible benefactors of improved understanding in the domain of processing of mixed syrups. Additionally, in emerging countries investments made into the sugar industry are increasing and manufacturers are open for innovations to satisfy the national demand of sugar. For these groups, co-production offers a promising opportunity to enhance factory utilization and improve their efficiency. Although co-production was already performed irregularly in several countries since decades, practically no data exist on crystallization of mixed syrups, originating from beet and cane material. The differences of the sucrose containing streams are obviously not manifested in the sucrose itself but in the accompanying non-sucrose material. Since in this context components that have coloring effects are most important, this thesis studied systematically the inclusion of colored components into sucrose crystals dependent on raw material and process parameters. Because the colorants in mixed syrups originating from beet and cane sources are different in their nature, their interactions play a key role that had not been studied.

The analytical methods used throughout this work, especially color value determination and particle size characterization, were refined and evaluated carefully. Benchmarking with industrial data safeguarded the industrial relevance of the work. Additionally, the crystallization process and post crystallization processes were validated in detail. It was found that all process steps, crystallization, centrifugation and drying are conducted such that produced sugars are comparable to those in the industrial practice. Due to the fact, that the process from mixing feed material to the evaluation of the affinated sugars involves several steps building on each other, each process and method, e.g. affination, color determination and sieving, had to be performed with great care to ensure best reproducibility of final determinations.

Before first experiments were conducted, the behavior of color inclusion factor for mixed syrups was derived from single source syrups. However, the crystallization experiments showed that neither the approach of linear combination of color transfer factors nor of sugar color values represent the actual color inclusion satisfactory. Instead, an exponential increase of color inclusion was found with increasing cane content. It is indicated that colorants from both sources mutually suppress their inclusion into the crystal. The explanation is that colorants from beet are significantly smaller in molecular size and hence have a higher diffusivity. In contrast, cane colorants are sucrose-like complexes with a low diffusivity but a high preference for inclusion.

Hence, beet colorants poison the sucrose surface without being incorporated which inhibits cane colorants to be included. An exponential model for color prediction was formulated.

A more detailed theoretical approach of the color inclusion mechanism revealed that final crystal content, ergo run-off syrup color influences color inclusion. Since colorants concentrate during the crystallization process dependent on the crystal content, color transfer factors have to be adjusted with the run-off syrup color value to achieve an average color transfer factor.

The exponential correlation of color transfer as a function of cane level was confirmed for different qualities of beet and cane material. The experiments were designed such that different combinations of syrups, e.g. color value of the feed syrup either increasing or decreasing with raw cane sugar addition, were used. Thus, the results underline the general validity of the exponential behavior found. The formulated model for the color value prediction solely by the color values of the single source syrups is also valid for syrups of different quality. The previously formulated rule of thumb that a level of 20 g/100 g raw cane sugar does not lead to unpredictable problems during processing appears to be too restrictive. The data reveal that a cane level up to 40 g/ 100 g results in high quality white sugar with color values below 30 IU. However, it was found that a high dextran content in the syrup promotes colorant inclusion.

In this study, it was the first time that the relative contributions of the different inclusion mechanisms, adsorption, liquid inclusion and co-crystallization to sugar color were differentiated. A detailed consideration of the different mechanisms revealed that they are dependent on the mixing ratio. Adsorption was increased linearly with increasing cane content in the mixture. However, colorants on the surface are strongly influenced by a combination of washing process and adsorption properties which might result in misinterpretation of the results. Thus, it should be noted that analyses were primarily conducted on affinated sugar ergo focusing on the inner color. The incorporation based on liquid inclusions was suppressed strongly by the presence of compounds from beet origin. Inclusion due to co-crystallization is increasing systematically as a function of cane content. Additionally, the mechanism of co-crystallization was promoted significantly due to the presence of dextran in the syrup.

Another important parameter influencing color transfer is the growth rate. Therefore, a systematic study of blended syrups was performed. The temperature of the heating media was varied to influence the evaporation rate and hence the supersaturation in the system. This consequently resulted in different times the crystals needed to grow to the target size. The results revealed that color inclusion increases linearly with increasing growth velocity. The previously established model for color prediction overestimates the color value with increasing growth rates. Regarding the specific inclusion mechanism, it should be noted that color transfer due to liquid inclusion is influenced minimally by increasing growth rates if beet material is in the blend. For co-crystallization increased beet levels have a damping effect on color inclusion, too.

Additionally, to the effects observed according to color inclusion between non-sucrose components from different sources, it is necessary to evaluate effects regarding color formation

due to heat exposure during the process. For this purpose, color formation of mixed syrups due to different thermal treatments was determined. It was found that color formation increases linearly with time and exponentially with increasing temperature according to the Arrhenius-equation. A model to predict the color formation in mixed syrups was formulated. Based on limited data from the constituting pure syrups the prediction for different time-temperature combinations matches experimental data very well.

The present thesis demonstrates detailed the principles of color inclusion for sugars produced from mixed syrups. The work provides a comprehensive framework for manufacturers and researchers to apply co-production. However, this study revealed new questions which will feed further research regarding this topic. Questions concerning color transfer and the respective inclusion mechanisms are of highest interest to predict and model sugar color satisfactory with respect to syrup color, crystal content and color formation during the process. Additionally, color formation and chemical reactions during thermal treatment of mixed syrups depended on pH-value, time and temperature should be investigated in more detail. The research on the topic of colorants inclusion into sugars produced from mixed syrups not only benefits sugar producers using co-processing because the insights gained are of general interest for sugar producers since the colorants load of sugars is a key quality parameter.