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Molasses as a by-product of sugar crystallization and a perspective raw material

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Abstract

The aim of C sugar operation in a sugar factory is a high quality C sugar for effective follow-up refining, minimizing sugar in molasses together with low energy consumption. On the other hand, biotechnology – ethanol fuel production – can change these targets: either sugar in molasses is increased for fermentation processing (higher sugar content) or C sugar operation is excluded from the sugar technology at all so that the refinery process can be simplified. To optimize the effect of cooling crystallization, a new static model was developed. The model involves balance equations for a horizontal crystallizer or for a part of vertical crystallizer of C-sugar operation and takes in account the balance of the sucrose ratio in liquid and solid phase. An addition of mixing media, such as syrup or water, into the crystallizer has been also considered. Molasses is applied in many food or non-food processes because of high content of nitrogenous compounds, carbohydrates and its sweet taste. Molasses is traditionally used in fermentation technologies to produce ethanol and for production of animal feed. The further potential applications are given.

Key-words: C-sugar operation; sugar crystallization; molasses; molasses utilization

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Nomenclature

Symbols and units:

a	($m^2.kg^{-1}$)	Specific surface area
A	(m^2)	Interfacial surface area
b,m	(1)	Constants in the Polish test
Gr	(1)	Grut number; Gr = Nc/W
Gr_e	(1)	Standard (effective) Grut number of molasses
H_0	(1)	Herzfeld number (ratio P/W), sucrose solubility in water at given temperature
H_1	(1)	Herzfeld number (ratio P/W); solubility in water containing non sugars
Kn	(1)	Coefficient of saturation; $Kn = H_1/ H_0$
Kp	(1)	Coefficient of supersaturation; $Kp = (P/W)/H_1$
L	(mm)	Average crystal length
$\dot{m}$	(t/h)	Mass flow rate
m_j	(t)	Weight content of a crystallizer j
Nc	(% wt.)	Nonsugar content; Nc = S - P
OK	(%)	Crystal content
P	(% wt.)	Sugar content, polarization
Q	(%)	Purity (sugar content in dry substance); Q = 100.P/S
r_s	(%)	Addition ratio (flow rate of added water or syrup/flow rate of the massecuite)
S	(% wt.)	Dry substance content
S_{eC}	(% wt.)	Dry substance content after optimized syrup addition
t	(°C)	Temperature
T	(K)	Absolute temperature
W	(% wt.)	Water content, W = 100 – S
x	(1)	Formal molar fraction of dry substance
κ	-	Constant in Wagnerowski equation
μ	(Pa.s)	Dynamic viscosity
τ	(h)	Time
v	($g.m^2.min^{-1}$)	Crystallization rate

Indexes:	
C	C massecuite
CK	Crystals in C massecuite
j	Stage of a vertical crystallizer or a part of horizontal crystallizer in C sugar operation
mix	Massecuite after mixing with water or syrup
ML	Mother liquor
n	Saturated solution
od	Output (input into centrifuges)
real	Measured value

1. Introduction

The aim of C sugar (after product) operation in a sugar factory is a production of high quality C sugar for effective follow-up refining, minimizing sugar in molasses together with low energy consumption. The C sugar operation involves vacuum evaporating crystallization of C massecuite, desugarizing during retention time in cooling crystallizers, centrifugation to separate molasses from C sugar and following affination of C sugar.

However, an implementation of some biotechnologies, like bio-ethanol production, can affect above mentioned targets of traditional sugar technology: either the sugar content in molasses needs to be increased for fermentation process, or C sugar operation is excluded from the sugar technology at all (Fig. 1). That is why the refinery process can be simplified.

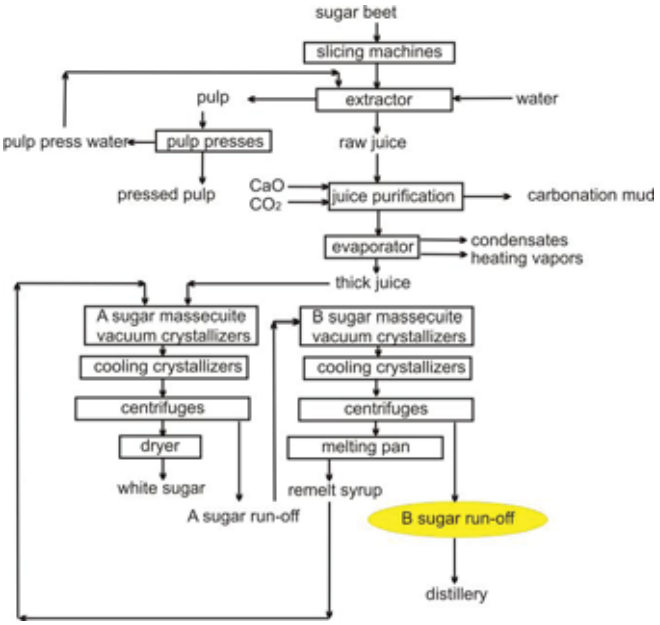

Fig. 1. Simplified scheme of the sugar technology completed with fermentation

Similarly, the aims of subsequent chromatography for molasses desugarization can be affected as well. One of the outputs from a chromatography separation is a product of higher purity and desired colour, therefore it is not always necessary to increase non-sugars content in molasses (in other words, it is more effective to process molasses of higher purity).

The sugar residue in molasses could be, apart from the sugar beet quality, also affected by all technological steps during sugar production, especially by improper technology design and control of individual operations. Minimizing sugar content in molasses requires:

- steady flow of C massecuite into a battery of cooling crystallizers and its uniform quality (homogenous size of crystals, purity and dry substance),
- suitable supersaturation in cooling crystallizers by adjusting temperature in cooling crystallizers,
- lower viscosity of mother liquor for high quality centrifugation of C massecuite.

2. Influence of vacuum evaporating crystallization on C sugar operation

Modern batch evaporating crystallizers are equipped with forced circulation of C massecuite and most of old-type crystallizers has been modernized by additional stirrers. More intensive circulation enables higher energy efficiency, reduces formation of conglomerates and improves the uniformity of crystals. Continuous evaporating crystallizers provide steady flow of massecuite into the C sugar operational unit thus increase the standard quality.

Most common mistakes during evaporating crystallization of C massecuite are improper seeding, too low or too high massecuite purity, unsatisfactory cleaning of an empty crystallizer with steam (sugar crystals remaining on the crystallizer's bottom can result in two different fractions of seed in C magma), incorrect setting of the computer system and also unprofessional work of the operational and laboratory staff. The purity of C massecuite affects crystal content and also following desugarizing [1]. Operating control of the end of evaporating crystallization e.g. by viscometers enables discharging at correct dry substance content.

3. Viscosity adjustment in C sugar operational unit

Magma entering the cooling crystallizers, where follow-up crystallization process is carried on, needs to be of optimal supersaturation and consistency. This is provided both by temperature control and dilution using dilution media.

If dry solid content of the massecuite is too high the consistency considerably increases in C sugar operation during the following desugarizing, which causes a loss of the Newtonian character and flow disturbances. On the other hand, if highly diluted, every 1 kg of extra water absorbs approximately 3 kg of sugar at the temperature 45 – 50 ºC.

So called mixers equipped with in-line viscometers are used to adjust proper dry solid content of the massecuite. This way the uniformity of the product entering the C sugar operation is ensured. Recommended value of dry solid content of the massecuite entering the C sugar operation is 92 – 93 % [1]. This number was obtained from data evaluation of several C sugar operational units.

4. Temperature profile during cooling crystallization of C massecuite

Crystallization rate can be controlled by temperature which affects coefficient of supersaturation. It also has a significant influence on the viscosity of mother liquor, and therefore the consistency of the massecuite. Cooling in a cascade of horizontal mixers is usually uncontrolled.

Horizontal continuous crystallizers equipped with heating and cooling elements enables full temperature control of C massecuite desugarizing. Thus these crystallizers are divided into independent individual sections where heating or cooling is realized.

The final temperature of the magma before centrifugation should be around 50 °C. An important parameter for desugarizing is the retention time which is related to the cooling rate in the crystallizer battery. Suitable cooling rate of the massecuite depends on supersaturation, Grut number, purity of the massecuite, temperature, viscosity of the mother liquor, crystal content, and viscosity of the massecuite.

5. Separation of molasses

Continuous or discontinuous centrifuges are used for separation of C magma. The main advantages of discontinuous centrifuges are lower crystal transfer into molasses, lower abrasion of screens and higher adaptability with regard to changing quality of massecuite [2]. On the other hand, continuous centrifuges are quiet, they enable to process massecuite of lower quality and have constant load of the electrical grid.

An important parameter for good separation is heating of the magma before centrifugation, since the reduced viscosity of mother liquor leads to better separation of crystalline and liquid phases. Therefore, it is suitable to use screens with perforations of 40 μm and high open area (10 %) to ensure smooth passage of molasses through the screen [3].

6. Model for C sugar (after product) operation

To optimize the effect of cooling crystallization, a new static model was developed. The model involves balance equations for every stage (section) of C-sugar operation (see Fig. 2) and takes in account the balance of the sucrose ratio in liquid and solid phase. An addition of mixing media, such as syrup or water, into the crystallizer has been also considered.

A parameter $Gr = Nc/W$ is of high importance for C sugar operation. Sucrose solubility in water is expressed by Herzfeld number H_0 (kg sucrose/kg water). Sucrose solubility in water containing non sugars (H_1; kg sucrose/kg water) varies from the one in clean water. The ratio of H_1 to H_0 is called a coefficient of saturation Kn:

$$H_1 = Kn \,.\, H_0. \tag{1}$$

In areas of higher Gr, there is a linear dependence of Kn on Gr:

$$Kn = m.Gr + b \tag{2}$$

In case of C sugar desugarizing in cooling crystallizers, the coefficient of supersaturation of mother liquor in the massecuite Kp is calculated according to:

$$Kp = \frac{P_{ML}}{W_{ML}.(m + b.Gr_{ML}).H_0} \tag{3}$$

The standard (effective) Grut number of molasses Gr_e (i.e. Grut number to obtain normal purity of molasses) is calculated according to Wagnerowski [4]:

$$Gr_e = \frac{b.(1-0{,}01.Q_n)}{0{,}01.Q_n.(m+\frac{1}{Kp_{od}.H_{0,od}})-m} \quad (4)$$

where Kp_{od} (1) is a coefficient of supersaturation of output massecuite (value of 1.07 is considered).

An optimal dry substance content of massecuite for given Grut number depends on purity quotient, due to the relation:

$$S_{eC} = \frac{100.Gr_e}{1+Gr_e-Q_C/100} \quad (5)$$

This formula is valid for every operational stage in the crystallizer battery. The amount of added syrup can be optimised according to calculated S_{eCmixj} value, on the basis of the difference between the optimal and calculated dry substance content:

$$\Delta S_j = S_{Cmixj} - S_{eCmixj}. \quad (6)$$

Viscosity of mother liquor after mixing medium addition at the temperature t (°C), likewise the viscosity of the saturated solution μ (Pa.s), is approximated according to Kaganov [5] using the equation:

$$\log \mu = x.[2440/(t_{ML} + 68) - 6.68\,] - 2.7 \quad (7)$$

where t_{ML} (ºC) is a temperature of massecuite and x is a formal molar fraction of dry substances defined as:

$$x = \frac{S_{ML}}{1900-18.S_{ML}} \quad (8)$$

where S_{ML} (%) is dry substance content in mother liquor.

The crystallization rate v_j (g/(m^2.min)) in a stage j is calculated according to the formula suggested by Wagnerowski [4,6]:

$$v_j = \kappa.H_{0,j}.Kn_j.\ (Kp_j - 1).T_j/[0{,}25(\mu_{ML,j} + \mu_{n,j})^2], \quad (9)$$

where κ is constant, $\mu_{ML,j}$ is viscosity of mother liquor (Pa.s), $\mu_{n,j}$ is viscosity of saturated solution at the crystal's face (Pa.s) and T_j is thermodynamic temperature (K).

Weight increase of crystal mass $\Delta\dot{m}_j$ (t/h) in a stage j is calculated:

$$\Delta\dot{m}_j = 0{,}001.v_j.A_j, \quad (10)$$

where A_j (m^2) is interfacial surface area of crystals in the massecuite, which depends on specific surface area a_j (m^2/kg) and mass flow rate of crystals in the massecuite:

$$A_j = a_j.\dot{m}_{Cmixj}.\tau_j, \quad (11)$$

where τ_j (min) is time delay in the stage j determined by:

$$\tau_j = m_j / \dot{m}_{Cmixj}, \quad (12)$$

where m_j (t) is the weight content of a crystallizer j.

The specific surface area *a* of crystals in the input massecuite depends on average length according to the following equation [7]:

$$a = 4{,}21.10^3/L \qquad (13)$$

where *L* (mm) is an average length of crystals entering the C sugar operation, therefore:

$$a_j = 4{,}21.10^3.\frac{\left(\frac{\dot{m}_{CKj}}{\dot{m}_{CK0}}\right)^{2/3}}{L}, \qquad (14)$$

where $\dot{m}_{CK0}$ (t/h) is mass flow rate of crystals entering into the C sugar operation.

The input parameters of this model are:

- coefficients *m, b* from the Polish test [8] - see equation (2),
- temperatures measured in individual stages of cooling crystallization including the outlet temperature,
- dry substance contents and purities of massecuites and mother liquors in individual crystallizers (S_{jreal}, Q_{jreal}).
- temperatures, purities and dry substance contents of added media (syrup, water), their possible inputs into crystallization stages,
- average length of crystals entering into the C sugar operation,
- weight contents of individual crystallizers.

The optimisation of individual crystallizers is calculated (Fig. 2).

The optimising parameter for every stage to describe the current state is a parameter:

$(S_{Cmixj} - S_{jreal})^2 + (Q_{Cmixj} - Q_{jreal})^2$,

Simultaneously, the sum of these parameters for the whole system is tested. This computation provides both the real data of syrup (or water) addition into individual sections and also specifies the constant κ.

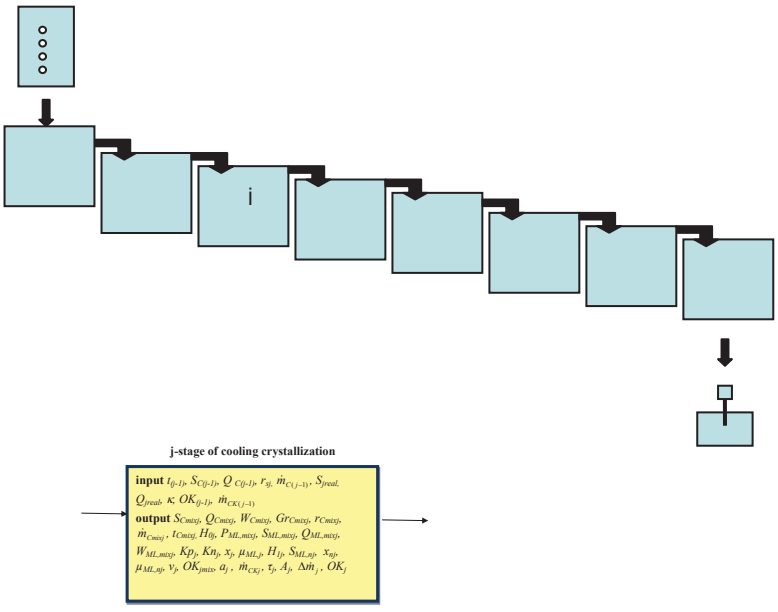

Fig. 2. The model of the crystallization process

The model was verified practically in three Czech sugar factories.

8. Molasses utilisation

Molasses is applied in many food or non-food processes because of high content of nitrogenous compounds, carbohydrates and its sweet taste. Molasses is traditionally used in fermentation technologies to produce ethanol and for production of animal feed. Sweet taste of molasses is applied also in bait treatments to capture free-ranging animals [9] or in multinutritional pellets for the control of parasites for animals [10].

Ethanol obtained by molasses fermentation is used for food purposes. Nowadays, the production of ethanol fuel and ETBE (ethyl-tert butyl ether) is gaining an attention [11]. Fermentation treatment of molasses to produce baker´s yeast or proteins is also tightly connected with ethanol production.

Other applications of molasses are:

a) partial or complete decomposition of molasses using SMB chromatography [12],
b) substrate for enzymes or co-enzymes bio-production,
c) for production of amino acids and their salts, nitrogen-free organic acids and betaine using isolation or fermentation techniques,
d) carbon source for biological metal-leaching, biodegradation of pollutants in waste waters, e.g. biotreatment of trinitrotoluene, carbofuran and xenobiotic compounds, or remediation of contaminated soil [13,14],
e) biosurfactant and bioemulsifiers production,
f) ephedrine production [15],
g) molasses-based material for de-icing of roads,
h) binder of catalyst granules [16],
i) production of biogas in sugar plant's waste water treatment [17], biohydrogen [18] and butanol fuel [19] for energetic purposes,
j) carbon source for denitrification of waste waters [20],
k) material for liquefaction of lignite where a mixture of ground lignite and molasses is treated at 350 – 425 °C in a nitrogen atmosphere [21],
l) substrate for biopolymers production, e.g. bacteria *Ralstonia eutropha* is known as a microorganism for production of polyhydroxybutyrates,
m) part of fermentation medium for feather degradation [22],
n) antibiotics and vitamins production, especially vitamin B12 [23],
o) aceton-butanol fermentation [24],
p) manufacture of fatty acid esters[25],
q) production of microalgae for food and energetic purposes in a molasses-containing medium,
r) part of microbial agent for disease and pest control in leafy vegetable [26],
s) glycerine production [27].

9. Conclusion

Molasses is mainly used in fermentation technologies to produce ethanol (nowadays as ethanol fuel production) or in agriculture as feed. It can also be applied as a raw material in further biotechnologies, as a source of nitrogen compounds (e.g. amino acids, betain), as an activator for microbial elimination of toxic products from waste water or soil, or as an additive in veterinary products, and many others.

In the traditional sugar technology where no ethanol fuel production is implemented, the recoverable sugar content in molasses should be minimal. Therefore, the paper presents a mathematical model of crystallization to optimise the C sugar operation. The described model has been verified practically in three Czech sugar factories.

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