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SELECTIVE CRYSTALLIZATION OF MALTOSE BY ISOPROPANOL AND ACETONE FROM GLUCOSE–MALTOSE SYRUPS

DOI: 10.7904/2068–4738–VII(14)–120

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Abstract. The solvability of glucose and maltose in water–based isopropanol and acetone has been studied. It has been revealed that with increase of organic solvent fraction the solvability of maltose in comparison with glucose sharply decreases. When the mass fraction of water in mixed solvent is less than 0.3, the difference in solvability of glucose and maltose in water–based acetone is significantly higher than their difference in water–based isopropanol. The obtained data served as the basis for the study of crystallization process of glucose and maltose mixtures of different compositions from water–organic solvents. It has been found that the highest efficiency of maltose crystallization from acetone and isopropanol is achieved during crystallization of the mixture containing 75 % of maltose and 25 % of glucose in case of twelve–fold exceedance by the volume of added organic solvent over the volume of water contained in initial syrup. The use of acetone gives a higher total efficiency of separation process, while the use of isopropanol gives a higher optimal content of dry substances (two times and more) in glucose–maltose syrup.
Keyword*:* acetone, crystallization, maltose, glucose, isopropanol, syrup.

Introduction

Maltose and glucose as independent chemical substances are widely used in various sectors of food, medical and chemical industry.

Maltose, for example, is irreplaceable in such bio–technological processes, as bread baking and preparation of fermented beverages (beer, ethyl alcohol), while glucose is an indispensable component of intravenous injections and many medicinal preparations, the mother substance for ascorbic acid (vitamin C) synthesis.

The specified sugars are also the most common components of microbiological nutrient media.

Glucose–maltose syrup is a final product of the deep hydrolysis of starch.

The ratio of maltose and glucose in these syrups depends on their application targets and is mainly defined by a set of specific ferments used in the process flow. Existing methods of maltose production e.g. Patent US 4595418 A, 17.06.1986. Zenichi Yoshino, Sanwa Kosan Kabushiki Kaisha. Production of powdery maltose; Patent US 5141859 A, 25.08.1992. Masahiro Niimi, Yukari Hariu, Koichi Kataura, Yoshibumi Ishii, Kazuaki Kato. Manufacturing method of high purity maltose and its reduced product) consist in successive enzymatic conversion of starch into oligosaccharides and maltose.

At this, high requirements are imposed on the quality of original stock and selectivity of enzyme preparations in order to obtain a solution with at least 90 % of maltose.

Besides, to divide a saccharified solution into a fraction containing highly purified maltose (90–98 % of the weight of sugars) with its further crystallization, and a fraction of oligosaccharides, chromatographic equipment is applied the maintenance of which requires highly qualified personnel and considerable material inputs [CAUNII *et al.*, 2015, BUTNARIU *et al.*, 2014].

It is necessary to note that nowadays the Russian Federation produces high–maltose syrups in the form of molasses, while individual mixture components, such as glucose and maltose, are not manufactured.

One of the reasons for this is the absence of the technique for separating such mixtures into chemical components.

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Non–applicability of foreign techniques of maltose and glucose production is conditioned by the peculiarities of original stock: objectively, wheat and potato starch are more difficult to hydrolyze than corn starch [BUTNARIU *et al.*, 2016]. Besides, produced ferments have low action selectiveness.

The purpose of the conducted research is modification of the process of maltose and glucose production from starch–bearing raw material with the help of selective crystallization method.

The essence of the proposed modification of the universally accepted technology of starch converting into maltose and glucose consists in the scientific substantiation of the stage of effective separation of glucose and maltose with the help of the proposed by the author innovative method of selective crystallization of maltose from glucose–maltose syrups in presence of organic solvents—isopropanol and acetone.

Conventional re–crystallization of glucose–maltose mixtures from water solutions fails to separate the specified sugars, as glucose and maltose have practically equal solvability at a wide range of temperatures [YALKOWSKY and HE, 2003, MONTAÑÉS *et al.*, 2009].

Material and methods

The solvability of carbohydrates was measured at a temperature of 25 C (298 K) by titration binary mixtures (water solutions of carbohydrates) of different compositions by the third component (organic solvent) up to the turbidity of the solution [VOROBEV, 1975, KONYUKHOV and POPOV, 2002].

Glucose and maltose content in liquid and crystalline phases was measured by the high–performance liquid chromatography.

Results and discussion

The research found that notwithstanding the close solvability of glucose and maltose in water–organic solvents with a high content of water (more than 50 mass percents), with increase of the organic solvent (isopropanol and acetone) share the solvability of maltose in comparison with glucose sharply decreases (Figure 1, Figure 2, Figure 3).

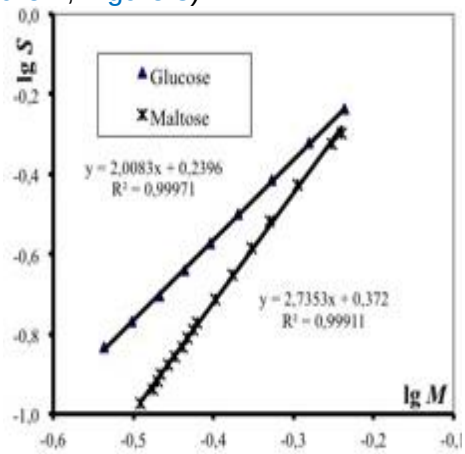

Figure 1. Solvability of glucose and maltose in water–based isopropanol

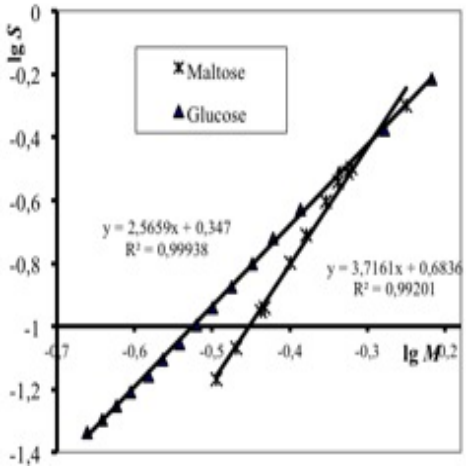

Figure 2. Solvability of glucose and maltose in water–based acetone

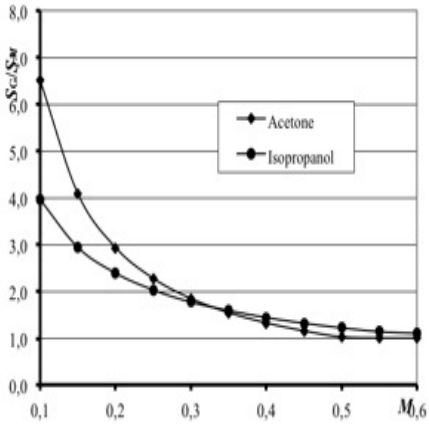

Figure 3. Dependence of the ratio of glucose (S_G) and maltose (S_M) solvability in water–based acetone and isopropanol on the mass fraction of water (M) and maltose

From (Figure 3) it is evident that when the mass fraction of water in the mixed solvent *M* is less than 0.3, the difference in solvability of glucose and maltose in water–based acetone is significantly higher than the difference in their solvability in water–based isopropanol, which indicates a higher efficiency of the sugars separation in the first case

However, this conclusion is correct if not to take into account possible influence of glucose and maltose on each others' solvability, as it was found out earlier in the analysis of joint solvability of glucose and fructose [DANILCHUK, 2012a].

This work presents the results of the study of crystallization process of glucose and maltose mixtures with different compositions from water–organic solvents at a temperature of 25 C.

Three compositions with the relative glucose content f_0 25, 50 and 75 %, the rest being maltose, were studied.

The ratio of organic solvent and water ω varied from 2 to 12.

It was experimentally shown that in all cases the composition of saturated solutions (massecuite liquid) corresponded to solubility equations [DANILCHUK and SIDORENKO, 2013] of glucose S_G and maltose S_M in a water–organic solvent with the content of water *C* in water–based isopropanol:

$$S_G = 1.74C^{2.01},\ S_M = 2.36M^{2.74},$$

in water–based acetone:

$$S_G = 2.22C^{2.57},\ S_M = 4.83M^{3.72}.$$

Such correspondence indicates the independence of carbohydrates' solvability, i.e. the absence of chemical interaction of glucose and maltose during a solution process.

This permits to execute the calculations of the process complete material balance presented in (Figure 4, Figure 5) and (Tables 1, 2, 3, 4), where DS is the mass fraction of dry substances in the initial syrup, f_1, f_2 are the mass fractions of glucose with respect to DS in massecuite liquid and crystals, respectively, d_1 is the mass fraction of carbohydrates that diffluenced into a liquid phase, *E* is the integral value of the efficiency of glucose and maltose separation calculated by formula [DANILCHUK, 2012a]:

$$E = \frac{(f_1 - f_0)d_1}{f_0(1 - f_0)}.$$

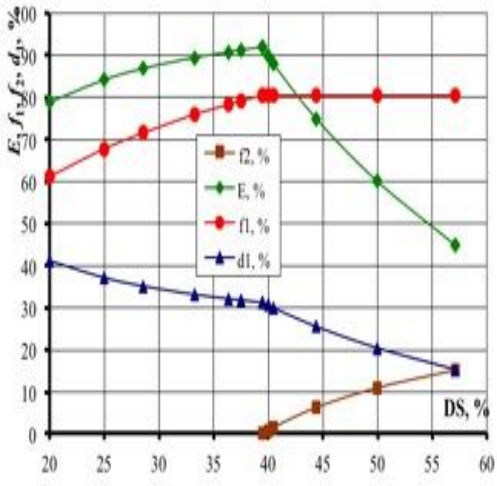

Figure 4. Parameters of glucose–maltose mixtures crystallization from water–based isopropanol for ω = 12 at f_0 = 25%

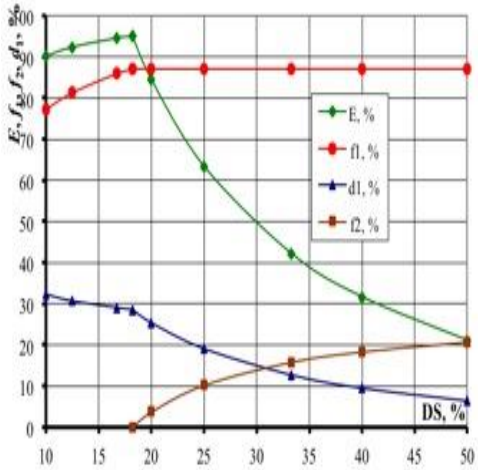

Figure 5. Parameters of glucose–maltose mixtures crystallization from water–based acetone for ω=12 at f_0=25 %

As shown in (Figure 4, Figure 5) drawn for the case of f_0 = 25 % and the ratio of the volume of added organic solvent to the volume of water contained in the initial syrup, ω = 12, dependence of efficiency and other crystallization parameters on the content of DS in syrup has a complex character.

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2016, VII(14)

Table 1.
Maximum efficiency *E* and extreme values DS, f_1, d_1 of glucose–maltose mixture crystallization (f_0 = 25 %) in water–based isopropanol

ω	2	4	6	8	10	12
max. *E*, %	77.3	83.9	87.2	89.3	90.9	91.8
opt. DS, %	72.8	62.3	54.5	48.4	43.5	39.5
f_1, %	59.5	67.5	72.4	75.9	78.4	80.3
d_1, %	42.0	37.0	34.5	32.9	31.9	31.1

With increase of DS dissolved in a fixed volume of water with formation of syrup at the specified ratio ω, the maximum efficiency (max. *E*) is achieved in case when the concentration of glucose in the obtained mixture is equal to the maximum possible concentration for the given composition of binary solvent.

Table 2.
Maximum efficiency *E* and extreme values DS, f_1, d_1 of glucose–maltose mixture crystallization (f_0 = 50 %) in water–based isopropanol

ω	2	4	6	8	10	12
max. *E*, %	31.9	51.8	61.8	68.3	72.5	75.5
opt. DS, %	57.3	45.3	37.5	31.9	27.8	24.6
f_1, %	59.5	67.5	72.4	75.9	78.4	80.3
d_1, %	84.0	74.0	69.0	65.9	63.8	62.3

Thus, in the extreme point (opt. DS), upon the achievement of massecuite syrup saturation with glucose, its content in precipitated crystal fraction is equal to zero (f_2 = 0), i.e. when DS is below the optimum value, the crystal phase consists of pure maltose, and when DS is above the optimum value, the crystal phase contains both carbohydrates, which causes a sharp decrease of efficiency *E* and gives a change of *E*(DS) graphic chart.

After saturation of the mixture with glucose, the composition of massecuite syrup does not change, while the content of glucose in the crystals increases.

Table 3.
Maximum efficiency *E* and extreme values DS, f_1, d_1 of glucose–maltose mixture crystallization (f_0 =25 %) in water–based acetone

ω	2	4	6	8	10	12
max. *E*, %	75.6	85.9	90.3	92.7	94.1	95.1
opt. DS, %	66.7	48.6	36.4	28.1	22.3	18.2
f_1, %	57.8	70.3	77.4	81.9	85.0	87.3
d_1, %	43.3	35.6	32.3	30.5	29.4	28.6

Upon comparison of (Figure 4) and (Figure 5), it is obvious that efficiency of glucose–maltose crystallization and concentration of glucose in massecuite syrup is substantially higher in presence of acetone than in presence of isopropanol. In the first case, with ω = 12, the efficiency reaches the value *E* = 95.1 %, and f_1 = 87.3 %; the same parameters were achieved during separation of glucose–fructose syrups by selective crystallization method in presence of isopropanol for a mixture of carbohydrates containing 25 % of fructose and 75 % of glucose [DANILCHUK, 2012b].

Table 4.
Maximum efficiency *E* and extreme values DS, f_1, d_1 of glucose–maltose mixture crystallization (f_0 = 50 %) in water–based acetone

ω	2	4	6	8	10	12
max. *E*, %	26.9	57.8	70.8	78.0	82.4	85.4
opt. DS, %	50.1	32.1	22.2	16.3	12.5	10.0
f_1, %	57.8	70.3	77.4	81.9	85.0	87.3
d_1, %	86.5	71.1	64.6	61.0	58.8	57.3

The (Table 1, 2, 3, 4) present the maximum values of efficiency *E* achievable and corresponding extreme parameters of DS, f_1, d_1 with fixed ratios ω = 2, 4, 6, 8, 10 and 12.

Data for the mixture containing 75 % of glucose and 25 % of maltose (f_0 = 75 %) are not specified, as in this case the selective crystallization method is not efficient.

Crystallization efficiency of a composition with f_0 = 50 % in cases of acetone and isopropanol application is significantly lower than crystallization efficiency of a high–maltose mixture containing 75 % of maltose and 25 % of glucose (f_0 = 25 %).

Decrease in the amount of organic solvent added to the initial syrup of carbohydrates' mixture brings about a sharp decrease in the total efficiency of the process of glucose and maltose separation.

Conclusions

The analysis of the results of the study permits to recommend the selective crystallization method for effective separation of glucose–maltose mixtures with a high content of maltose into a maltose crystal phase and high–glucose massecuite liquid, which can be further converted into crystal glucose.

Thus, the use of this method makes it technologically possible to separate initial glucose–maltose mixtures into pure components.

For practical implementation of the method, as organic solvents, both acetone and isopropanol can be used.

The use of acetone gives a higher total efficiency of the separation process, while the use of isopropanol has another important technological advantage, namely, a higher (two or three times) optimal content of DS in glucose–maltose syrup, that is, in the latter case, significantly less organic solvent is used for crystallization per unit of processed sugars' weight.

It is optimal to use the developed method for processing of high–maltose syrups with glucose content less than 30 % easily obtained by starch hydrolysis, which usually represent a final product of starch–dextrose production in the Russian Federation and other countries.

Acknowledgements

This work was supported by the RF President grant No. MD–3576.2015.4.

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Received: May 27, 2016
Article in Press: October 26, 2016
Accepted: Last modified on: November 20, 2016