Nexo Revista Científica

Vol. 35, No. 03, pp. 771-776/Septiembre 2022

ISSN-E 1995-9516
Universidad Nacional de Ingeniería

http://revistas.uni.edu.ni/index.php/Nexo
https://doi.org/10.5377/nexo.v35i03.15006

New cryoscopic temperature determination technology for plant-based products

Nueva tecnología de determinación de temperatura crioscópica para productos de origen vegetal

Igor Alekseevich Korotkiy*, Evgeniy Nikolaevich Neverov, Elena Valerievna Korotkaya,

Kemerovo State University. Russia.
*Corresponding author E-mail: i.a.korotkiy@mail.ru

(recibido/received: 02-julio-2022; aceptado/accepted: 27-agosto-2022)

ABSTRACT

The determination of cryoscopic temperature is an important parameter in the calculation of low-temperature processing modes of frozen products. The process of rapid freezing is accompanied by temperature changes, therefore, to develop energy-saving and effective methods of preserving and processing fruit and berries, it is necessary to accurately determine some variables that affect the result of freezing. The study aimed to develop a differentiated analysis technique for determining the cryoscopic temperature and the crystallization temperature of the eutectic points of sucrose and glucose solutions. To determine the cryoscopic temperatures in the study, the method of thermal analysis based on the construction of freezing thermograms was used. The study was conducted using berries grown in the Kemerovo region (Russia). As a result of the study, it was found that the cryoscopic temperatures were most influenced by the total (free and bound) moisture content and organic and mineral substances in berry juices. The authors also determined cryoscopic temperatures of different black currant, sea buckthorn, and juneberry varieties. The developed technique will allow for the simulation of freezing processes under various processing conditions.

Keywords: cryoscopic temperature; freezing rate; crystallization process; phase transitions; freezing thermograms.

RESUMEN

La determinación de la temperatura crioscópica es un parámetro importante en el cálculo de los modos de procesamiento a baja temperatura de los productos congelados. El proceso de congelación rápida va acompañado de cambios de temperatura, por lo tanto, para desarrollar métodos efectivos y que ahorren energía para conservar y procesar frutas y bayas, es necesario determinar con precisión algunas variables que afectan el resultado de la congelación. El estudio tuvo como objetivo desarrollar una técnica de análisis diferenciada para determinar la temperatura crioscópica y la temperatura de cristalización de los puntos eutécticos de soluciones de sacarosa y glucosa. Para determinar las temperaturas crioscópicas en estudio se utilizó el método de análisis térmico basado en la construcción de termogramas de congelación. El estudio se realizó con bayas cultivadas en la región de Kemerovo (Rusia). Como resultado del estudio, se encontró que las temperaturas crioscópicas estaban más influenciadas por el contenido de humedad total (libre y unida) y las sustancias orgánicas y minerales en los jugos de bayas. Los autores también determinaron las temperaturas crioscópicas de diferentes variedades de grosella negra, espino amarillo y juneberry. La técnica desarrollada permitirá la simulación de procesos de congelación bajo diversas condiciones de procesamiento.

Palabras claves: temperatura crioscópica; tasa de congelamento; processo de cristalización; transiciones de fase; termogramas de congelamento.

1. INTRODUCTION

In the food industry, freezing of fruit and berries is increasingly used for their subsequent storage for a long time and preservation of useful nutritional elements and organoleptic properties. The daily diet should include various fruit and berries, as they are a source of valuable organic acids, micronutrients, fiber, and antioxidants. The scope of application of frozen berries and fruit is wide, including the preparation of vitamin drinks and cocktails, mousses, yogurts, and fillings for baked and confectionery products. Therefore, the preservation of original properties in frozen fruit and berries is important. The process of rapid freezing is accompanied by temperature changes. Therefore, objective and correct information must be collected for the development of energy-saving and effective methods of preserving and processing fruit and berries (Korotkii et al., 2021; Belyaeva, 2017; Akimov et al., 2020).

The process of freezing fruit and berries is accompanied by a decrease in temperature and crystallization of the substances contained in them. The determination of the cryoscopic temperature (the temperature of the phase transition of a liquid into a solid phase) is an important parameter in the calculation of low-temperature treatment modes (Korotkiy et al., 2021; Korotkii et al., 2022; Semenov et al., 2019; Latkov et al., 2020).

2. MATERIALS AND METHODS

The objects of the study are black currant berries, sea buckthorn fruit, honeysuckle berries, and juneberry fruit grown on the territory of the Kemerovo region. The study used ripe berries with no mechanical damage. The temperatures were determined using thermocouples and a TRM-138 measuring complex which was connected to a computer via an AC-4 adapter. This measuring system made it possible to measure temperatures with high accuracy. The error of this method was 0.05°C. The analysis of the process of crystallization of moisture during the freezing of the berries was carried out by the calorimetric method. The method of thermal analysis was used to determine cryoscopic temperatures, which was based on the construction of freezing thermograms. The berries were put in a conical flask with a volume of 250 milliliters, in the center of which a berry with a thermocouple was placed. Previously, the berries had been cooled to 0 to 1°C, after which the flask was immersed in the refrigerant at a temperature of -25°C. After that, the temperature change in the sample over time was recorded (Denev et al., 2018; Mityurich, Zhidkova, 2015).

3. RESULTS AND DISCUSSION

The analysis of the dependence of the temperature change in the berry sample on time is shown in Figure 1. The temperature curve of the berry freezing process demonstrates a classical dependence represented by three sections. The first section characterizes the cooling that occurs before the cryoscopic temperature is obtained, the second one is quite long, with a slightly varying temperature (the ordinate on the graph corresponds to the cryoscopic temperature), and the third one is the stage of a relatively rapid decrease in the temperature of the berries, which indicates the completion of the freezing process. A further decrease in temperature corresponds to the cooling of the frozen berries (Bogdanov et al., 2019).

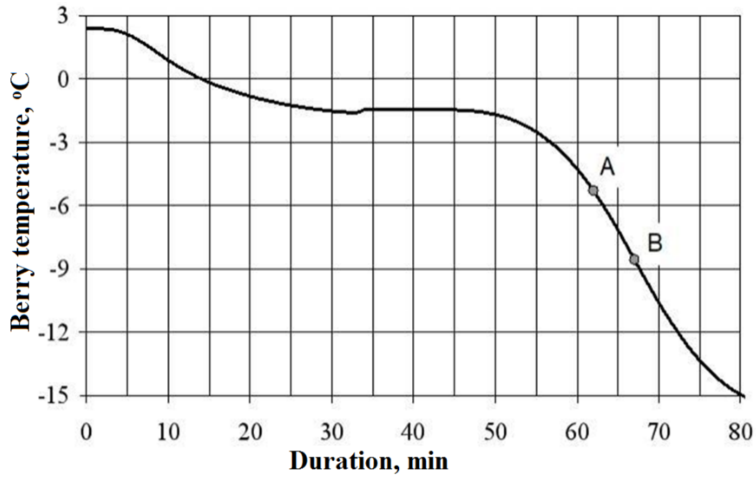

Figure 1. Freezing thermogram for currant berries

For systems in which phase transformations occur, accompanied by heat release or heat absorption, the temperature will not monotonously decrease or increase. To obtain more detailed information about the freezing process and the determination of eutectic temperatures, we will differentiate thermograms twice by time. The first derivative characterizes the dependence of the temperature change rate, i. e. the cooling speed of the berries during freezing (Figure 2).

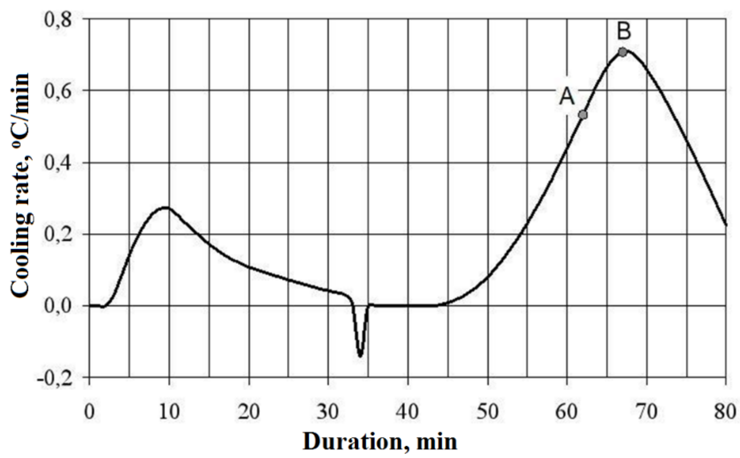

Figure 2. Dependence of the temperature change rate (the cooling speed) for currant berries on time

In Figure 2, in the beginning, the temperature change rate increases quite rapidly, which characterizes the cooling process in berries. Further, we see a prolonged decrease in the temperature change rate and an area with a constant speed, indicating the beginning of water crystallization in the berries, which makes it possible to determine the cryoscopic temperature of ≈ -1.5°C. During the crystallization process, more intense heat release occurs, increasing the temperature change rate. The end of the process shows a decrease in speed and an approximation of the temperature of the berries to the ambient temperature.

The dependence of the temperature change rate (the cooling speed) for currant berries on time determines the curing temperature of the eutectic sucrose solution. This temperature corresponds to the maximum value (point B) in Figure 2. From the comparison of Figures 1 and 2, point B in Figure 2 corresponds to a time of 67 minutes. According to Figure 1, this time interval is a temperature of -8.5°C.

Having analyzed the second derivative of the berry cooling thermogram, the dependence of which is shown in Figure 3, we obtain the dependence of the derivative of the temperature change rate (berry cooling speed) on time.

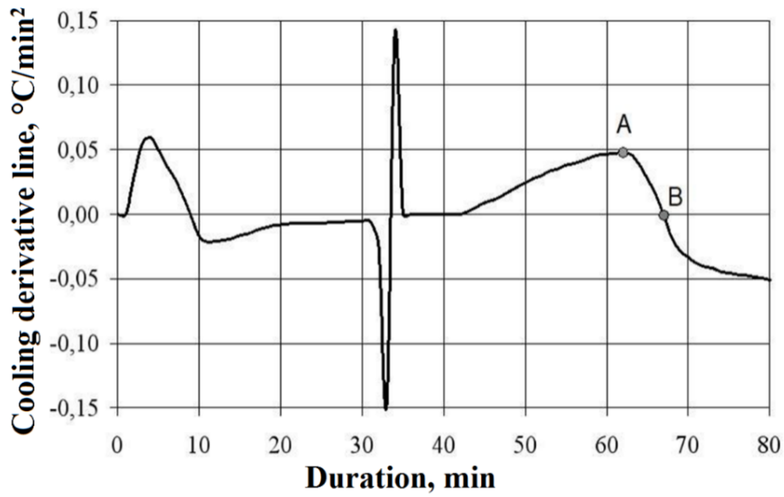

Figure 3. Dependence of the derivative of the temperature change rate (freezing speed) for currant berries on time

The solidification temperature of the eutectic glucose solution corresponds to point A (the temperature at which the complete crystallization of this solution occurs). From the comparison of Figures 1 and 3, this temperature turned out to be -5.3°C, which corresponds to 63 minutes.

Table 1 shows the cryoscopic temperatures for the examined samples according to the proposed method (Rasshchepkin, 2016; Pochitskaya et al., 2019; Mishchuk, 2017; Gribova, Sultaeva, 2013).

Table 1. Crystallization temperatures of the liquid phase of various fruit and berries

Varieties	Cryoscopic temperature, °C	Varieties	Cryoscopic temperature, °C
"Seyanets golubki" black currant	-1.0	"Chuiskaya" sea buckthorn	-1.5
"Pamyat Shukshina" black currant	-1.2	"Dar Katuni" sea buckthorn	-1.7
"Pamyat Lisavenko" black currant	-1.3	"Maslichnaya" sea buckthorn	-2.8
"Chernyi Zhemchug" black currant	-1.4	"Zolotoy pochatok" sea buckthorn	-1.4
"Pushistaya" black currant	-1.5	"Panteleevskaya" sea buckthorn	-1.7
"Krasa Altaya" black currant	-1.6	Honeysuckle (a mixture of varieties)	-2.3
		Juneberry	-4.0

4. CONCLUSION

Cryoscopic temperatures are most influenced by the total (free and bound) moisture content and organic and mineral substances in the juices of berries and fruit.

The cryoscopic temperature of sea buckthorn of the "Maslichnaya" variety turned out to be -2.8°C. This temperature turned out to be lower than that of the presented currant samples, probably due to a lower free water content of 34.8%, which characterizes a higher concentration of sugars in the solution.

Of the fruit and berries considered, the minimum value of cryoscopic temperature was recorded in the juneberries, probably because they contained the least amount of moisture (the proportion of bound moisture was 42.3%, and the proportion of free moisture was 37.7%). Juneberries have a fairly high sugar content (9.4%), which indicates a low cryoscopic temperature. The measured values of cryoscopic temperatures for various varieties of currants were obtained in the temperature range from -1 to -1.6°C.

As a result of the analysis of numerous experiments, a method of differentiated analysis is presented, which allows determining cryoscopic temperatures, as well as crystallization temperatures of eutectic sucrose and glucose solutions. The developed technique will allow simulating freezing processes under various processing conditions.

ACKNOWLEDGMENTS

The work was carried out within the framework of the comprehensive scientific and technical program of the full innovation cycle “Development and implementation of technologies in the field of exploration and production of solid minerals, ensuring industrial safety and bioremediation and creating new products of deep processing from coal raw materials while consistently reducing the environmental load and risks to the life of the population”, government order dated May 11, 2022, N1144-r, measure 13 “Innovative technology for wastewater treatment at open-cast coal mining enterprises”.

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