



APPLICATION OF THE DIFFERENTIAL SCANNING CALORIMETRY METHOD IN THE STUDY OF THE TOMATO FRUITS DRYING PROCESS

Inha Kuznietsova¹, Valentyna Bandura², Vadym Paziuk¹, Oleksii Tokarchuk², Ihor Kupchuk²

¹*Institute of Engineering Thermophysics of NAS of Ukraine, 2a, Zhelyabova str., UA 03057, Kiev, Ukraine*

²*Vinnytsia National Agrarian University, 3, Sonyachna str., UA 21008, Vinnytsia, Ukraine*

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Vastutav autor: Ihor Kupchuk
Corresponding author:
E-mail: kupchuk.igor@i.ua
Phone: +380 978 173 992

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ABSTRACT. Structural changes in the process of heating fresh fruit, sun-dried fruits and powder obtained from the dried tomato fruits were studied by differential scanning calorimetry method application. The kinetics of the shredded fruits in the dryer proves the prospects for using convective drying, which is performed for 295 minutes. The kinetic coefficients of drying and critical moisture content in the crushed fruits of tomato were determined. The kinetic coefficients were determined by the graphical-analytical method: $a = 0.839$, $\ln(\alpha) = 1.3$ and $\alpha (1 \text{ s}^{-1}) = 0.262$. It was determined that the critical maximum moisture content for drying the shredded fruits of tomatoes is $1.503\% \text{ mm}^{-1}$, after what the process of combustion of vegetable tissue begins. The application of the differential scanning calorimetry (DSC) method allowed the fuller study of the mechanism of drying the fruits of tomato in different condition: fresh, sun-dried and dried. It was determined that the greatest amount of energy is consumed to remove free moisture ($1,993 \text{ J g}^{-1}$) from the fresh tomatoes. At the same time, when being cooled, crystallization in plant tissue occurs with the release of energy in the amount of 0.03922 J g^{-1} . When drying the previously sun-dried tomatoes the process of moisture removal and the partial decomposition of the compounds that are unstable to temperature is completed. At the same time, at the $129.61 \text{ }^\circ\text{C}$ temperature in the powder obtained from the fruits of tomatoes, melting of carbohydrates and other compounds occurred. Thus, this confirms the need to observe the normalized value of the mass fraction of moisture in the powders in the process of their packaging, storage and use. The basic technological system of production of powder from dried fruits of tomatoes is offered.

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Introduction

With the increasing demand for natural products of high biological value, the demand for powders of plant products rises every year. Powders provided by the optimum drying mode, are well stored and are convenient for the use in food production (Petrova, 2013; Khomichak *et al.*, 2019). Among those products the powder obtained from the dried tomato fruits, known as carotene-containing products, take the leading place.

Carotenoids are required for the normal functioning of the organs of vision, cell growth, skin, hair, teeth, and respiratory mucous membranes. (Mukherjee *et al.*, 2011) found that vitamin A has a protective effect against malignant processes. Vitamin A and its derivatives may prevent carcinogenesis of epithelial

tissues, and β -carotene may prevent carcinogenic or ultraviolet skin cancer (290–320 nm). Zhuzha (2013), Shutyuk *et al.* (2016), Gloria *et al.* (2014) and Kuznietsova (2013) confirms the anticancer action of vitamin A and certain carotenoids (quartetin and lycopene).

In the current conditions, the production and creation of new types of food with the use of carotene-containing ingredients are relevant and necessary for the nation's health. The use of lycopene-containing products is also becoming more important. Lycopene is a substance of the carotenoid group, which determines the dietary value and the degree of maturity of the fruit. It is not synthesized in the human body, and consumption of fresh tomatoes or tomato products provides 50–80% of the body needs in the total



consumption of food. Entering the human body, lycopene can enhance protective functions of it, inhibit degenerative processes in the tissues, and reduce the risk of initiation and development of cancer, cardiovascular and other pathologies. According to the Nutrition and Bioactive Substance Consumption Guidelines, the optimal dose of lycopene intake is 5 mg per day and the maximum intake is 10 mg per day. Also, lycopene "blocks" the negative effect of free radicals on the human body and its antioxidant action is three times higher than β -carotene (Gloria *et al.*, 2014). This contributed to the growing interest in lycopene in the medical field, what is reflected in the works of medical scientists, such as (Gloria *et al.*, 2014; Mukherjee *et al.*, 2011) and others. In particular, it was found that the average concentration of lycopene in blood plasma at a healthy person is about $0.5 \mu\text{mol l}^{-1}$, and the maximum level is reached in the period from May to October.

Taken into consideration the importance of the functional capacity of tomato fruits, particular attention is paid to their preservation for a certain period to provide people with the required amount of compounds necessary for the human body and ensure continuous operation of the processing plant. Therefore, it is important to develop and improve technologies for lycopene-containing products processing and their further use in functional food production.

Materials and methods

Tomato fruits of the Popilna variety, which were grown in a subzone of insufficient moisture at the experimental plots of the Institute of Horticulture of the NAAS (Borky village, Kyiv region), were used. The tomato fruits were purified, shredded and dried in a convective TSO-type dryer at the Institute of Technical Thermophysics of the NAS of Ukraine.

The sizes of tomato fragments were selected in a way that provides their uniform drying along with the tray. Also, smaller parts accelerate the drying process which reduces energy consumption.

The raw material was dried down to the constant weight in laboratory automatic dryer. The following methodology was used for the experiment. The temperature was brought to the necessary one, then a container with the material was loaded into the receiver (net basket). The parameters of the thermometer and electronic scale were scanned in equal time intervals and under the constant temperature. The experiment lasted until the difference between the previous and the next scale parameter became unchanging during several tests.

Drying mode parameters: drying agent temperature (air) – $t = 60 \text{ }^\circ\text{C}$, drying agent movement rate – $v = 2.5 \text{ m s}^{-1}$, moisture content – $d = 10 \text{ g kg d.p.}^{-1}$, layer thickness – 15 mm. Drying process parameters can change depending upon the peculiarities of the product that is supplied into convective drying.

The experimental stand (Fig. 1) is a system of the isolated air ducts with the devices for heat treatment and circulation of the heating agent, drying chambers,

measuring circuits and devices for controlling the parameters of the drying process and measuring the values characterizing the drying process of the test material. The stand is equipped with three drying chambers: one horizontal (air blasting model – parallel airflow) and two vertical (expulsion model).

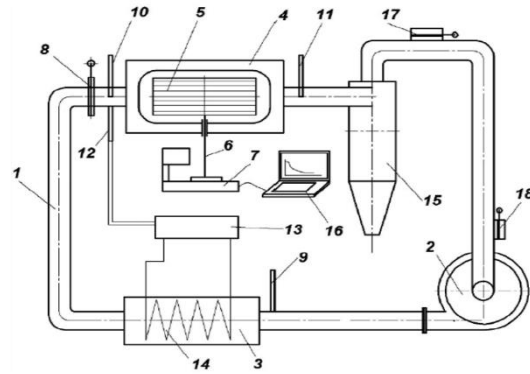


Figure 1. Experimental stand for convective drying process (developed by I. Kuznietsova, V. Paziuk; working principle is explained in the text)

Drying unit (Fig. 1) is thermally insulated circulation metal loop 1, with the airflow generated by fan 2 and flowing consecutively through the electric metal radiator 3 and drying chamber 4, which contacts with the material through the supply of heat and removal of evaporated moisture. Then the waste air moves from the drying chamber through cyclone 15, where caught product particles are removed, to the fan input 2, which provides air circulation in the dryer's circulation loop. The material that is being dried, is placed in a net box 5 (the inner space of the drying chamber), connected with electronic scale 7 through bar 6. The net box is removable. It can be disconnected from the bar and taken out of the drying chamber through a side hatch, locked with a slide glass gate. One can observe the status of the material through this gate during the drying. The consumption and respective heated airspeed in the drying chamber are regulated by gate 8 and controlled by anemometer; air temperatures before radiator t_0 , after radiator t_1 and after drying chamber t_2 are controlled by thermometers 9, 10, 11. The set (target) air temperature t_1 at the chamber input is regulated by electronic contact thermometer 12 through blocking relay 13 which is connected to electric heater 14 of radiator 3. A part of the waste heat agent is removed through a nozzle with gate 17. Fresh air is supplied through the nozzle with gate 18. The mass of the product in the basket is measured on the scale and registered by computer 16 through set time intervals. The experimental error didn't exceed 5% and comprised 2.4%. Based on experimental findings, we calculated current moisture content of the material W and drying speed $\Delta W/\Delta\tau$, built dependency diagrams $W = f(\tau)$ and $\Delta W/\Delta\tau = f(W)$, that is demonstrated on Fig. 2.

The obtained dried tomato fruits with a 7.2% mass fraction of dry matter. The output dried tomato fragments were crushed into powder. A portion of 100 ± 0.1 g of dried tomato fragments was milled in a lab mill. Then the product was weighed, which identified 0.83 g loss. Milled dried tomatoes were bolted through a lab bolter applying a set of 5 bolters. Of the portion of 100.05 g of the product, the mass sample with the particle size of less than 0.2 mm (powder) comprised 98.48 g. Thus, the loss was 1.57 g (1.6%). The plant tissues sample was sealed in a special aluminium capsule and placed in a QDSC-20 Termo Fisher SCIENTIFIC calorimeter measuring unit.

The thermal center of the DSC system consists of two trays: a control tray and a sample tray. The equipment is adjusted to sustain a constant temperature in the trays in the course of the heating process. During DSC measurements the control tray is filled with buffer solution first and then the sample tray is filled with a sample solution. Then they are heated with constant scanning frequency. The heat absorption that takes place during the biomolecule spreading results in the temperature difference (TD) in the trays, which causes temperature gradient in Peltier units with the voltage establishing which is turned into energy and used to control the Peltier unit to bring the TD (temperature difference) to 0°C . The DSC signal is proportional to the heat capacity of constant pressure, which is the derivative of temperature enthalpy.

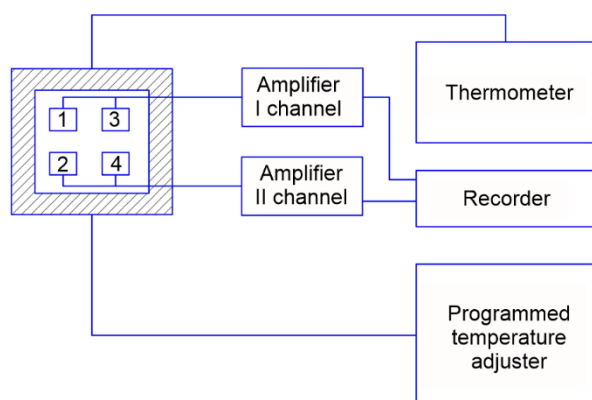


Figure 2. Flowsheet of differentiating scanning calorimeter: 1–4 slots with thermal sensors

The reduction of measurement error was reached by finding the lowest scanning speed for this model of $10^\circ\text{C min}^{-1}$. The planned experimental temperature range was $20\text{--}105^\circ\text{C}$. They are peculiar to convective drying. The range of $105\text{--}250^\circ\text{C}$ was planned for studying the process of pulp biomolecule melting. High precision (to the hundredth) of the temperature and enthalpy calculations during thermal impact on biomolecule was provided through automated data processing of the equipment with the help of STAR[®] software by Mettler Toledo (Switzerland).

Results and Discussion

Thus, the study of the drying process is an important task of the research, which will help to substantiate the physical and chemical processes that occur in plant tissue provided by increasing the temperature in the product.

Kinetics of the crushed fruits in the drier (Fig. 3) shows the prospects for convective drying, which is being performed for 295 minutes (Paziuk *et al.*, 2018, 2019; Khomichak *et al.*, 2019).

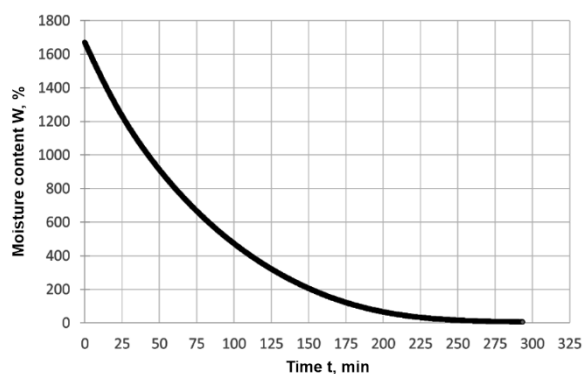


Figure 3. Kinetics of the tomato fruits drying

Regression equation (1) was calculated based on the characteristic curve and according to the expression that describes S-curves of drying plant raw material. The mathematical relation obtained allows describing plant raw material drying curves and can be used to process drying curves under constant temperature.

The kinetics of moisture removal (W , %) from the pulp of tomato fruits is described by the dependence:

$$W = 2897.8 \times e^{-0.389 \times \tau}, \quad (1)$$

where τ – duration of the drying process, min.

The experimental results obtained laid the basis for generalized curves for the studied raw material. They can be used for any temperature modes of drying.

The rate of drying (V , $\% \text{ s}^{-1}$) the crushed tomato fruits is described by the regression equation:

$$V = 2.1083W + 1.6806 \quad (2)$$

Approximation of the experimental data by the linear function made it possible to obtain the following calculated dependence of the internal diffusion coefficient (D) on the temperature (T) for the crushed tomato fruits:

$$D^t = 0.0039D^{293} + 0.0015 \times (T - 293^\circ\text{C}) \quad (3)$$

Determination of the critical humidity, duration and coefficient of drying was carried out by the graphical-analytical method. The results of the studies are presented as a graphical dependence:

$$L_g(W - W_r) = f(\tau), \quad (4)$$

where W – is the running humidity, %; W_r – equilibrium humidity, %; τ – duration of drying, s.

To describe the kinetics of fragmented tomatoes drying under the experimental data and the characteristic curve obtained (Fig. 4) was define kinetic coefficient $\ln(a)$ and coefficient α a slope of a line to an absciss (Khomichak *et al.*, 2019; Kindzera *et al.*, 2014).

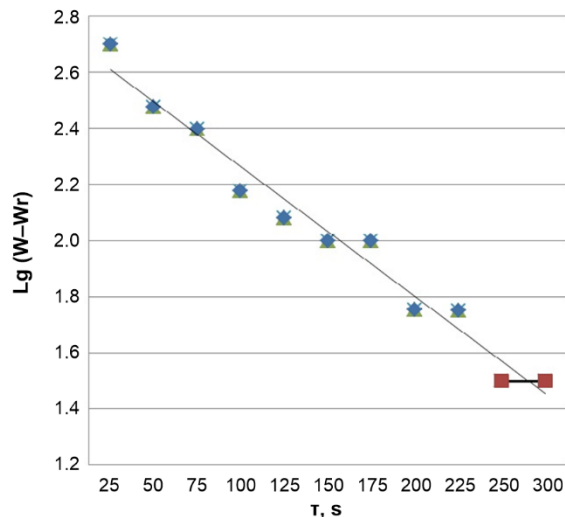


Figure 4. Logarithmic dependence of fragmented tomatoes drying kinetics

Thus, the kinetic coefficients have the values: α (1 m^{-1}) = 0.839, $\ln(a)$ = 1.3, α (1 s^{-1}) = 0.262.

The critical moisture content ($^{\circ}\text{C}$, %) in the crushed tomato fruits will be determined as the square root of the ratio of the kinematic coefficient α to the product of the kinetic coefficient a (1 m^{-1}) and the thickness of the raw material layer. After calculation, it was defined that the critical maximum moisture content for the crushed tomato fruits drying is 1.503% per mm, after what the process of combustion of plant tissue began.

Removal of moisture from the plant tissue is accompanied by destruction of its structure, weakening of intermolecular forces and the hydrogen bonds breaking. The moisture-holding capacity of plant cells depends on the general physiological condition of the plants. Method of the differential scanning calorimetry (DSC) allows studying water transformations in plant tissues under the influence of thermal action. The DSC method for determining the state of water is based on distinguishing the properties of free and bound water. In this case, the bound water is identified as non-freezing water. The bound water does not experience a first-order phase transition when cooled below 0°C . And only free water crystallizes when cooling or heating in the negative temperatures range. Application of the DSC method for the study of the structural properties of food is outlined in the works devoted to the study of stevia leaves (Roik *et al.*, 2015; Kuznietsova, 2014), chocolate, and the like.

The process of drying vegetables takes place at different temperatures (in particular 50°C , $110\text{--}130^{\circ}\text{C}$) depending on the intended purpose of the final product, design and principle of operation of the dryer. The final moisture content of the fruits of vegetables makes up

$6\text{--}10\%$, but drying is possible right up to 2% . The fruits contain both free and bound moisture. Free moisture has the same properties as pure water. The bound moisture is tightly joined to other components of the product and exhibits properties different from those of free moisture. Almost all the moisture in plant products is kept in bound condition but is held by tissues with different strengths.

Corresponding thermograms for tomato fruits when dried fresh, previously sun-dried and powdered are presented. During the initial phase of the substances mixtures, transformation heat is released. Comparison of the DSC-grams (Fig. 5) of the fresh and sun-dried tomato samples shows that the minimum endothermic peaks of the two samples differ.

The tomato thermogram curve (Fig. 5) shows that at the temperature of $20\text{--}97^{\circ}\text{C}$ excess moisture is removed from the tomato fruit, after that the process is stabilized without disturbing the structure of the main components of the fruit. Increasing the temperature to 96.5°C facilitates the opening of pores of the intermolecular space and the rate of the process is limited by the transfer of mass in macropores. Endopeak at the temperature of 97.54°C shows the achievement of the maximum possible removal of moisture from the fruit. In case of the crushed sun-dried tomato fruit (Fig 5, curve 2) two peaks are observed at such temperatures:

- 98.34°C , which causes removal of the free part of moisture and decomposition of tomato fruit compounds which are not resistant to high temperatures;
- 107.29°C , at which some of the bound moisture is removed and then melting of the sun-dried tomato compounds takes place. An acute peak at this temperature indicates crystalline rearrangements, syntheses, or solid-state transitions of relatively pure compounds.

The study of drying the tomato powder shows the smoothness of the thermo-gram curve (Fig. 6), which indicates the even removal of moisture from the powder. That is, during the second temperature treatment, some of the free and capillary moisture is removed from the tomato fruits. Increase in the temperature of heating contributes to the increase of the energy of separation the molecules from the hydrated film surface and the rate of diffusion of moisture in plant tissue macro-pores.

Fig. 4 shows the DSC curve of a sample of tomato powder having one expressed temperature peak at 129.61°C and another at 148.33°C , what indicates the removal of bound moisture from plant cells and partial decomposition of certain compounds which are not resistant to high temperatures.

The aggregated data on the temperature peaks of tomato fruits drying are presented in Table 1, which demonstrates the uniform removal of free moisture from fresh and sun-dried tomatoes and indicates the remains of it in the plant tissue of the fruits after the fresh tomatoes drying. Removal of the adsorbed moisture from the polymolecular and monomolecular layers promotes the increase of the energy of the physical and mechanical bonds of the moisture in the microcapillaries

and the solid phase of the sample, what increases the consumption of energy up to $1,993 \text{ J g}^{-1}$ at the fresh tomato fruit.

In addition, drying fresh tomatoes results in the highest energy consumption the plant tissue structure change.

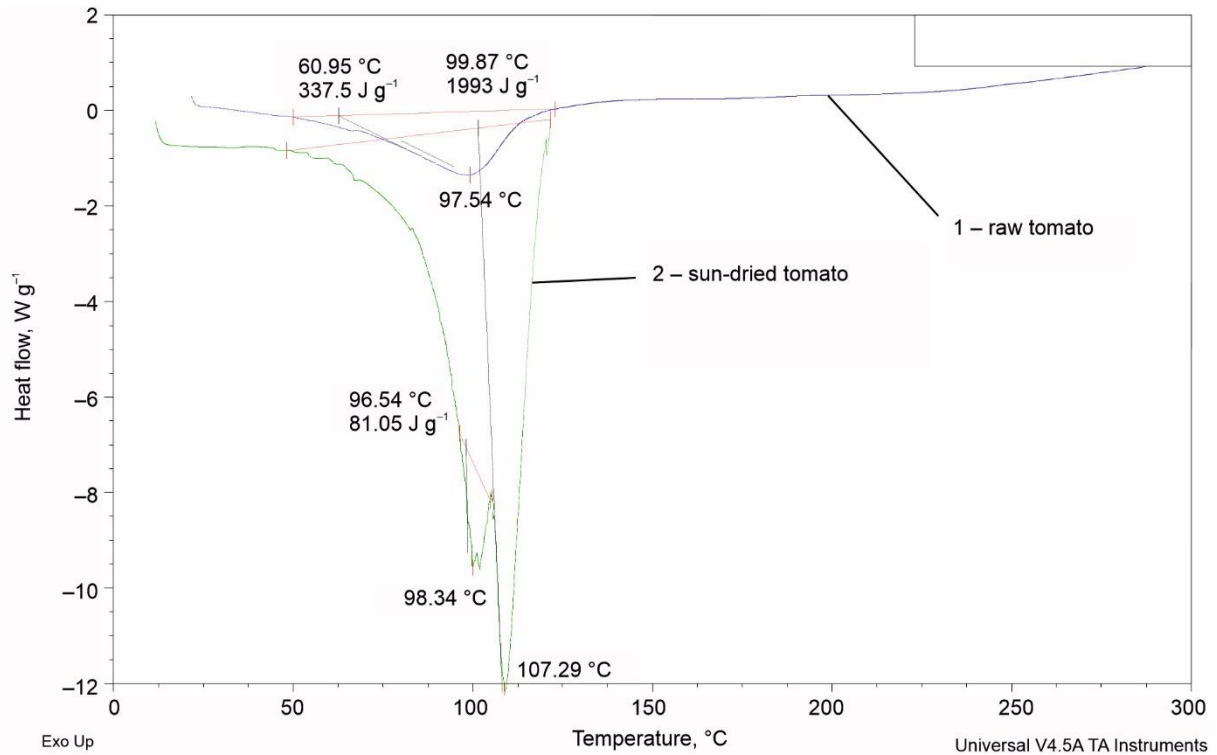


Figure 5. Fresh and sun-dried tomato fruits drying

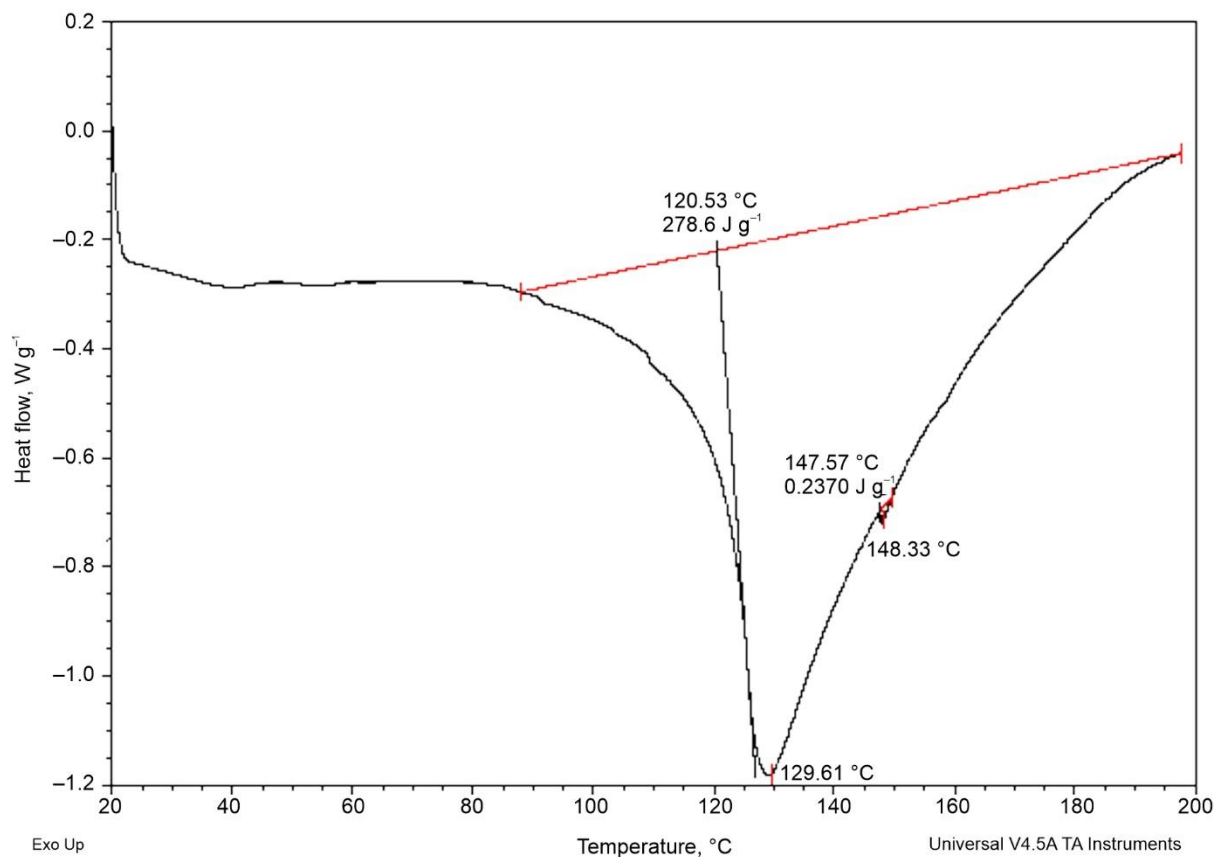


Figure 6. Tomato fruits powder drying

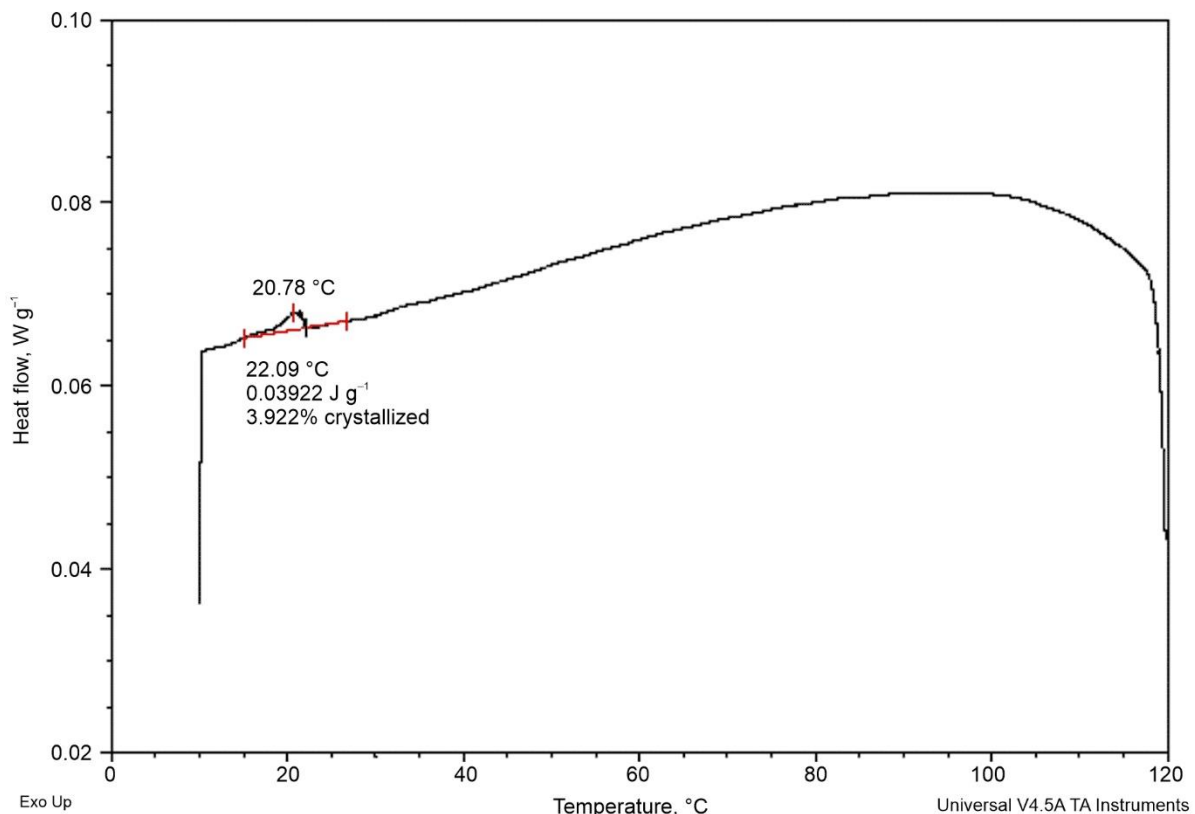
Table 1. Characteristics of the drying process of tomato samples with various dry matter contents

Tomato fruit samples	Temperature of moisture, °C	Melting temperature, °C	Enthalpy, J·g ⁻¹
Fresh	97.54; 99.81	–	1 993
Sun-dried	98.34; 107.29	–	133.5
Powder	–	129.61; 148.33	278.6; 0.237

Part of the capillary moisture is also removed when drying the sun-dried tomato. When drying tomato powder the melting process of certain compounds takes place, which is accompanied by the process of energy

consumption initially at the level of 278.6 J per g of the raw materials, and then a smaller amount of energy – 0.237 J per g, which indicates the plant tissue structure breaks down.

According to the Lavoisier-Laplace law (Pecal *et al.*, 2011), decomposition of a complex compound into simple ones absorbs a certain amount of energy that is consumed to form the same compound. When the dried tomato fruit is cooled (Fig. 7), crystallization of acids occurs in vegetable tissues, what is evidenced by the 20.78 °C temperature peak. At the same time, energy in the amount of 0.03922 J per g was spent for the crystalline structure formation.

**Figure 7.** Cooling of the dried tomato fruit

For industrial applications, it is recommended to use a TSU convective type dryer (Fig. 8), which will provide a dried product of guaranteed quality.

Based on the in-depth research of tomato fruits drying, a basic technological model is submitted (Fig. 9).

Thus, the basic technology for obtaining powder from the fruits of tomatoes involves the following processes:

- receipts of ripe, red fruits of tomatoes for production;
- washing and green mass selection from the fruits;
- shredding to the 5×5×5 mm size particles;
- convective drying under conditions: layer thickness – 15 mm, drying agent temperature (air) – $t = 60\text{ °C}$, drying agent movement rate – $v = 2.5\text{ m s}^{-1}$, moisture content – $d = 10\text{ g kg d.p.}^{-1}$, duration – 225 minutes;
- grinding on a ball mill to a powdered state;
- storage and delivery to consumers.

**Figure 8.** The TSU convective dryer

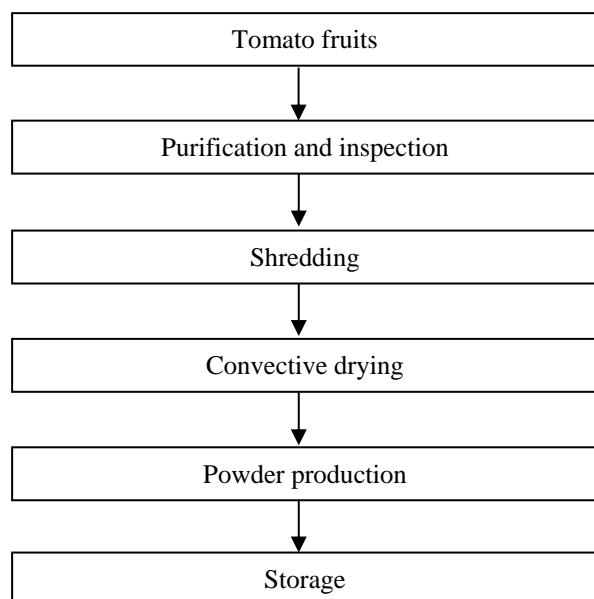


Figure 9. Basic model of the dried tomato fruits powder production

Conclusions

It has been proved that convective drying of shredded tomato fruits is one of the promising ways of producing tomato powder. The values of kinematic coefficients ($\alpha = 0.839$, $\ln(\alpha) = 1.3$, $\alpha(1 \text{ s}^{-1}) = 0.262$) and the critical boundary moisture content (1.503% per mm) were determined.

The application of the DSC method allowed the fuller study of the mechanism of drying the fruits of tomato of different state: fresh, sun-dried and dried. This gives a clear idea of the temperature and energy transformations in tomato fruits with a high content of dry matter during technological operations. It is determined that the most energy is consumed to remove free moisture ($1,993 \text{ J h}^{-1}$) in processing fresh tomato fruit. At the same time, when it is cooled, crystallization occurs in plant tissue with the 0.03922 J g^{-1} energy release.

Further drying of the sun-dried tomato fruits results in the completion of moisture removal and partial decomposition of the compounds that are temperature unstable. At the same time, the $129.61 \text{ }^\circ\text{C}$ temperature causes melting of carbohydrates and other compounds of the powder obtained from tomato fruits. It should be noted that the availability of excess moisture in the product weakens the carbohydrate bonds and accelerates their melting under high temperatures. Thus, this substantiates the need to adhere to the normalized value of the mass fraction of moisture in the powders during their packaging, storage and use.

The basic technological pattern of production of tomato powder is offered.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Author contributions

InK – study conception and design;
 VB, VP, OT, IK – acquisition of data;
 VB, VP – analysis and interpretation of data;
 VP, OT – drafting of the manuscript;
 IK – editing the manuscript;
 InK, VP – critical revision and approval of the final manuscript.

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