DEVELOPMENT OF LOW TEMPERATURE TRAP FOR CAPTURING VALUABLE BIOLOGICAL ACTIVE MATERIALS

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Abstract. Producers and processors of agricultural raw materials are faced with the task of increasing the competitiveness of their products and added value. One of the solutions to these problems is to increase the depth of processing raw materials by agricultural producers or primary processors to obtain valuable products with high added value that are in demand in the markets for the production of final products (in pharmaceuticals, perfume and cosmetics industry, ready-made food production, etc.). In the process of obtaining valuable products of agricultural raw materials there is a need for low-temperature condensation and/or low-temperature adsorption of useful products or intermediate technological substances. Low temperature refrigerated vapour traps with an operating temperature range of -70 ºC to -110 ºC and below are used for such process operations. In many technological applications, these traps are used in combination with vacuum processes, e.g. in the deposition of vacuum distillation products, which predetermines the requirements for hermetic tightness of the flowing part of such a trap. In recent years, in connection with the struggle to reduce emissions of gases that destroy the ozone layer and contribute to the greenhouse effect, the EU has banned the use of the cheapest and most efficient refrigerants, e.g. R13, which allows to obtain temperatures of about -100 ºC using single-stage refrigeration machines. Modern refrigerants on the market, having an order of magnitude higher price, require 2-3 times higher design pressure from the equipment and have a lower cycle efficiency. In this regard, the creation of a low-temperature trap is a complex engineering task associated not only with the design of a multi-stage refrigeration machine, but also with the creation of a control system for the cascades of the refrigeration machine and vacuum pumping equipment, ensuring the safe and reliable operation of the trap and the achievement of the desired low temperature range during its long-term operation. SIA Cryogenic and vacuum systems have created a prototype of this low-temperature trap and is working on creating of processing complexes, included such traps for industrial quantities of processed biomaterials. The article highlights our engineering approaches, calculations and experience in creating a prototype of a low-temperature trap.

Keywords: ultralow temperature refrigeration, vapour trap.

1. Application of cooled vapour traps in processing of agricultural and biological active materials

In the processing of biological active materials in many cases there is a requirement for low-temperature condensation and/or adsorption of process products.

Solvents like dichloromethane, ethyl acetate, acetone and ethanol are used in processes of extraction of caffeine from coffee or tea [1; 2]. In rose oil extraction diethyl ether and ethanol are used [3; 4]. For such cases of liquid extraction, modern technology exists to collect the solvent for reuse with minimal loss, and to effectively purify the gas used to transport the extraction products from residual solvent vapour for release to the atmosphere or supply it to a vacuum pump or compressor for reuse. This is a method of refrigerated condensation or cryocondensation. After precipitation or separation of the main substance, the solvent (usually in the vapour phase with a flow of transport gas) is directed to a refrigerated vapour trap, where it condenses, and is then collected and sent back to the extractor. E.g. on the website "Energy and Environmental Information System for the Flemish Region" [5] data is available on the required temperatures and efficiency of solvent capture using this method, Table 1.

Table 1

Operating temperature of the trap and its efficiency for capturing some types of solvents [5]

Component	Condenser temperature, ºC	End concentration, mg·nm^{-3}
Acetone	-86	< 150
Dichloromethane	-95	< 20
MEK	-75	< 150
Methanol	-60	< 150
Toluene	-65	< 100

Currently, the leading R&D Companies such as MIRAI Intex, Refolution GmbH and HOF Sonderanlagenbau GmbH, base themselves on refrigerated vapour traps to create innovative industrial systems for renewable use of organic solvents in the biological and pharmaceutical industries [6].

In quite a few cases equipment for recycling of solvents in processing of biological active materials uses pneumatic or vacuum transportation. The atmosphere in such machines is formed as a result of evaporation of water and volatile organic compounds contained in biological active materials. Upon entering vacuum pumps and compressors, such an atmosphere causes oil degradation and subsequent coking of stressed seals, so vapour and organic compounds must be removed before entering the vacuum pump or compressor. Instead of complex and replaceable filter systems, a refrigerated vapour trap is a viable alternative. The high efficiency of the cryocondensation method for removing volatile organic compounds during the purification of gas and steam-gas mixtures is described, e.g. in paper [7].

Another use of refrigerated traps is to obtain useful substances condensed at a given low temperature from vapour mixtures. This method is used, for example, by the Wet chemistry & colloids group of the University of Padua to create biomimetic dopamine-based polymers based on bioengineered zinc oxide nanoparticles derived from plant materials for drug delivery to damaged cells of the body [8]. The same method is used by SIA Cryogenic and vacuum systems in the development of machines for the extraction of volatile organic compounds from agricultural raw materials.

2. Problem of low temperature refrigeration

Until 2009, designing refrigeration machines to ensure operating temperatures of the traps did not present a significant technical problem. Utilizing as the base R-13 (Chlorotrifluoromethane) or R-13B1 (Bromotrifluoromethane) refrigerant it was possible to design rather simple and cheap single-cascade refrigeration units, which could provide cooling temperatures up to -150 ºC (R-13B1) or up to -170 ºC (R-13) in a typical vapour-compression cycle. Both refrigerants were fire and explosion-proof and had no harmful effect on humans. Their only drawback was their high ozone destroying and hydrocarbon potential. For this reason, in accordance with [9], both of these refrigerants were prohibited for use in the EU countries. At the same time, no retrofits were proposed to replace these refrigerants in low-temperature installations without making changes to the design of the equipment.

The new commercially available refrigerant R-23 (Trifluoromethane), R-116 (Hexafluoroethane) and R-508 (mix of R-23 and R-116) fail to solve the issue.

First, from a formal point of view, their use is forbidden according to [10] as of 1 January 2020, with a provision temporarily allowing their employment in “Stationary refrigeration equipment ... intended for application designed to cool products to temperatures below -50 ºC” (i.e. they cannot be used from a formal point of view in mobile, process and laboratory equipment).

Secondly, the cost of new refrigerants is an order of magnitude higher than the cost of R-13, e.g. China and Russia, which have not stopped, but expanded the production of R-13, on their websites sell R13 at a price of about 67-68 Euros per kilogram, while on the websites of the suppliers of refrigerants in Latvia and Lithuania there is only refrigerant R508 with the price of 600-650 Euro per kilogram, i.e. 10 times more expensive. Also, in our experience, it was not possible to order any of new refrigerants from any supplier with a delivery time of less than 16 weeks.

Thirdly, the thermophysical characteristics of new refrigerants are such that to achieve equal cooling performance it is necessary to increase the system charging pressure by 15-25 bar, and the required compression ratio for a single-stage machine is more than 1:50, which is practically not feasible, and therefore requires either the use of a 2-x -- 3-x stage compressor, or the creation of at least a 2-cascade machine with a low-temperature circuit designed for a static pressure of about 60-70 bar and a dynamic pressure of low-temperature refrigerant at start of about 100-110 bar.

Thus, creating a competitive (compared to Chinese products) low-temperature refrigerated vapour trap is currently a complex engineering and economic task.

3. Implemented approach to creating a low-temperature trap

To ensure the competitiveness of the product being created, we had to find a cheaper low-temperature refrigerant with better thermophysical characteristics. One of the search directions was hydrocarbon gases. The successful experience that has led many companies to replace HFC

(Hydro(chloro)fluorocarbons) refrigerants R-404A/R-407A/R-407B/R-407C etc., with HC (Hydrocarbon) R-600/R600a/R-601/R-601a (Butane, Isobutane, Pentane and Isopentane) has given us possible research directions. These turned out to be the hydrocarbon gases Ethene (Ethylene) and Ethane. Although ethylene is produced by many EU chemical plants, e.g. in Lithuania and Poland, it is almost impossible to order it in small quantities. We managed to order ethane and persuaded SIA Baltic Refrigeration Group to get it pumped into small cylinders and delivered to Latvia.

The authors apologize that the small size of the paper does not allow the calculation method applied to be presented in a full and detailed manner. Therefore, the key ideas and expressions applied in the calculation of the developed refrigerated vapour trap are presented below.

The functional purpose of the created trap is to collect valuable biochemical raw materials contained in the vapour-gas mixture entering the trap as a result of primary drying of agricultural products. Therefore, the design of the trap should provide the following requirements: - reduction of the vapour-gas mixture flow velocity to increase the time of gas contact with cold surface before evacuation, - sufficient surface area for condensation of biological active materials, - sufficient area for precipitation and crystallisation of water vapour for its separation from biological active materials, - possibility of draining the obtained valuable raw materials (volatile essential oils, aromatic alcohols, organic acids, etc.) before ice melting, - possibility of draining water after ice melting, - possibility of disassembly, washing and disinfection of all elements of the trap, - repeated cyclic operation under vacuum conditions in the flow part, - minimal heat losses with the possibility of stable mechanical fastening and removal of the load from the refrigerant pipelines, - the presence of sensors for measuring the temperature of condensing surfaces of the flow part of the trap.

The target for the development of the prototype was the condensation or precipitation of 7 kg of water vapour and/or product within 48 hours.

The total thermal load on the trap in stationary mode, H_S, was determined as:

$$H_S = \Delta E_{VR} + \Delta E_{VPC} + \Delta E_{IR} + H_{IL} + H_{BL}, \quad (1)$$

where ΔE_{VR}– enthalpy of vapour refrigerating, J;
ΔE_{VPC} – enthalpy of vapour phase change, J;
ΔE_{IR} – enthalpy of ice refrigeration, J;
H_{IL} – thermal insulation losses, J;
H_{BL} – thermal bridge losses, J.

The heat input from the flowing air can be neglected as the process takes place at pressures of the order of 1-5 mbar, with an air partial pressure of 0.001-0.01 mbar.

For the calculation, the worst case in terms of energy consumption was used, when the entire mass of the deposited product is water vapour entering the trap at a temperature of + 40 ºC. The heat loss conditions were assumed to be the worst case: trap temperature -100 ºC, ambient air temperature + 40 ºC. The structural basis of the trap was a stainless steel cylinder with an outer diameter of 163 mm, a length of 350 mm, with a bottom and a lid, mounted on thin-walled stainless steel supports. The enthalpy of vapour cooling was calculated as:

$$\Delta E_{VR} = c_v \cdot m \cdot \Delta T_v, \quad (2)$$

where c_v – specific heat capacity of vapour, equal to 1996 J/(kg·K);
m – vapour mass, taken as 7 kg;
ΔT_v – temperature difference between the vapour input temperature and ice formation temperature, K.

Enthalpy of the phase change is calculated as:

$$\Delta E_{VPC} = s_f \cdot m, \quad (3)$$

where s_f – specific heat of ice fusion, J.

Enthalpy of ice refrigeration was calculated as:

$$\Delta E_{IR} = c_I \cdot m \cdot \Delta T_I, \quad (4)$$

where c_I – specific heat capacity of ice, equal to 2093 J·(kg·K)$^{-1}$;

ΔT_I – temperature difference between the ice formation temperature and trap operation temperature, K.

Heat losses through thermal insulation were calculated as:

$$H_{IL} = k_i \cdot \Delta T_t \cdot \frac{A}{d} \cdot t \,, \tag{5}$$

where k_i – thermal conductivity of polyurethane foam insulation, taken as 0.03 W/(m·K);
ΔT_t – temperature difference between the trap wall and the machine environment, K;
A – trap outer surface area, m^2;
d – thermal insulation thickness, m;
t – trap operation time, s.

The calculation of heat losses through thermal bridges (support and pipelines) was made in accordance with (5), but there were taken the thermal conductivity of stainless steel, area of supports and pipelines and the length of supports and pipelines until fastening with the instrument frame.

The calculation was made using Scilab 2024.0.0 software.

As a result, we obtain the total refrigeration energy H_S value equal to 8.493 MJ, what, taken into consideration given trap operation time 48 hours, gives the value of needed refrigeration power Pr in Watts:

$$Pr = \frac{H_S}{t} \,. \tag{6}$$

Thus, we obtain the refrigeration power value 49.15 W, which with the power reserve factor 20% gives app. 60 W.

The refrigeration trap is cooled by a spiral heat exchanger, at the inlet of which liquid ethane enters from a capillary tube, which is expanding in the heat exchanger. Due to the phase transition of ethane, external heat is absorbed.

Since the total temperature difference between the surface of the trap and the environment is 140 ºC, for the development of the refrigeration machine, a two-cascade scheme was taken as a basis, in which 1 cascade provides cooling of the plate heat exchanger, into which after pre-cooling in the air-cooled heat exchanger, 2 – cascade compressor supplies compressed ethane. A schematic diagram of such two-cascade refrigeration machine for cooling the trap is shown in Fig. 1.

In order to determine the parameters of the elements of the refrigeration machine cooling the trap, it is necessary to calculate the mass and volume flow rate of ethane, providing sufficient energy extraction under different conditions of intermediate cooling of ethane in the first cascade heat exchanger. For this purpose, it is necessary to analyze the diagram of ethane states in the coordinate axes temperature T and entropy S [11], Fig. 2, at different temperatures of the supplied liquid ethane and to choose the optimum ratio of operating temperatures of 1 and 2 cascade of the refrigerating machine from the point of view of minimizing the required power of the ethane compressor 2 to decrease ethane heating. Further, the values of enthalpies of transitions of the refrigerating machine working cycle are specified according to the tables given in [11].

As a result of the analysis, the following values of the characteristics of the operating points of the evaporation zone of the ethane circuit were selected: evaporation occurs at a temperature of -100 ºC and a pressure of 52.4 kPa [11] (suction pressure of the compressor 2 of the low-temperature cascade), while the maximum ambient temperature is assumed to be + 40 ºC. Under such conditions, taking into account the need for subcooling of the liquid ethane cooling heat exchanger, the optimum temperature distribution between the first and second cascades corresponds to a total enthalpy change of 350.6 $kJ \cdot kg^{-1}$ during ethane boiling, then the required ethane mass flow rate is 0.171 $g \cdot s^{-1}$.

Under these conditions, the optimum temperature of liquid ethane injected into the evaporator will be -40 ºC. The required liquid pressure for the required enthalpy change at boiling is 830 kPa, which corresponds to an uncooled gas temperature of about + 60 ºC [11]. Taking into account the subcooling heat losses in the plate heat exchanger, the required evaporation temperature of refrigerant 1 (high-temperature) cascade is -45 ºC. Then at selection for cooling of 1 cascade of R-410A refrigerant, possessing the maximum thermodynamic efficiency from currently authorized refrigerants, the boiling

pressure (suction pressure) will make 152 kPa, at necessary refrigerating power of about 0.14 kW, the mass flow rate of the refrigerant will make 1.52 $g \cdot s^{-1}$, and the discharge pressure will make 2140 kPa. Thermodynamic properties of R-410A refrigerant are given in [12]. At the same time, the compression ratio in both stages is less than 20, which makes it possible to use conventional refrigeration piston compressors without any special modification.

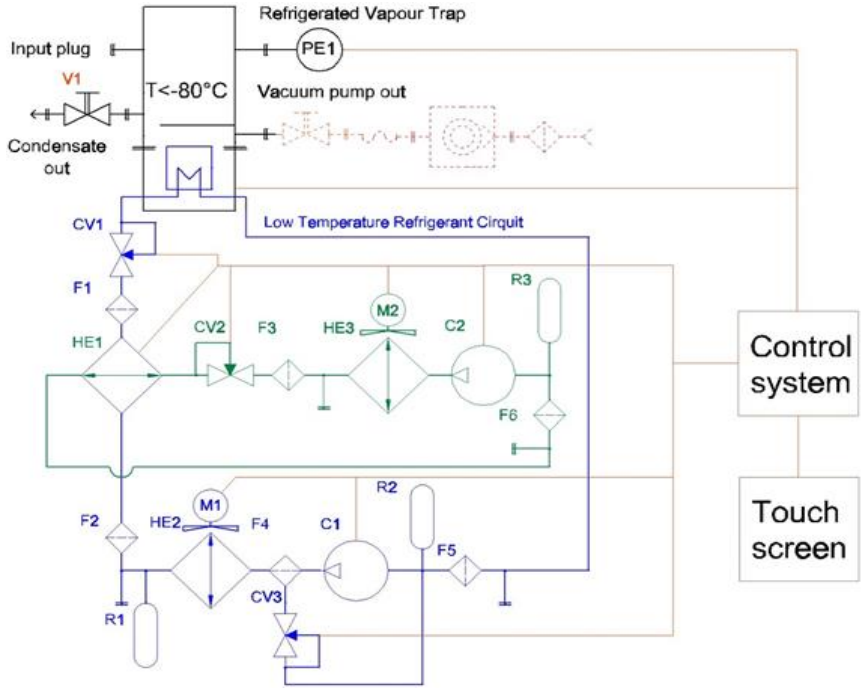

Fig. 1. **2-cascade refrigeration machine diagram**: green – 1 (high temperature cascade); blue – 2 (low temperature cascade); orange – control and auxiliary (vacuum) circuits; PE – vacuum transducer; V1 – condensate draining valve; CV1 – adjustable hydraulic resistance of the 1 cascade; F1 – refrigerant liquid filter; HE1 – between the cascade plate heat exchanger; F2, F3, F4, F5, F6 – refrigerant gas filters; R1, R2, R3 – receivers; CV2 - adjustable hydraulic resistance of the 2 cascade; HE2, HE3 - air-cooled heat exchangers, CV3 – oil returning valve; M1, M2 – heat exchanger fan motors; C1 – 2 cascade compressor; C2 – 1 cascade compressor

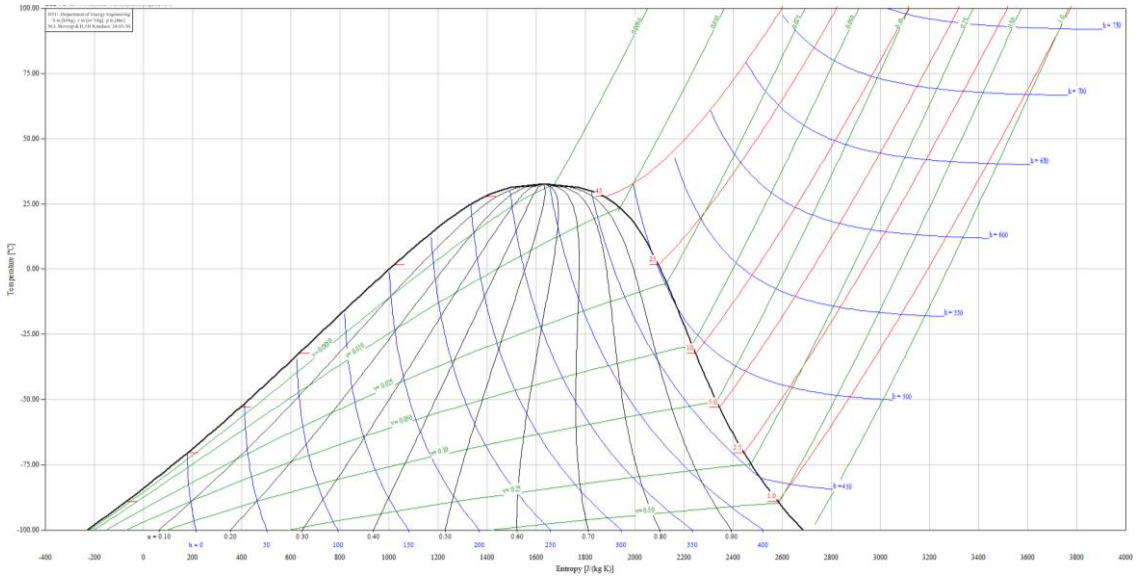

Fig. 2. **T, S diagram of ethane [11]**

The required pressure drops between the suction and discharge lines are provided by hydraulic resistances – capillary tubes of a given length. The length of the capillary tubes was calculated by solving the adopted Darcy-Weisbach equation [13]:

$$\Delta P = \frac{\rho \cdot u_0^2}{2} \cdot \left(\lambda \cdot \frac{l}{d} + \xi \right) , \quad (7)$$

where ΔP– pressure drop in the capillary, kPa;
ρ – density of the liquid, kg/m^3;
l – capillary pipe length, m;
d – capillary pipe diameter, m;
λ – linear coefficient of hydraulic resistance;
ξ – hydraulic resistance coefficient of capillary pipe entrance.

Approaches to the calculation of the hydraulic resistance coefficient and it values for different conditions are also shown in [13]. The Blasius dependence was used:

$$\lambda = \frac{0.3164}{Re^{0.25}} , \quad (8)$$

where Re – Reynolds number.

The method used for calculating the hydraulic resistance coefficient of capillary pipe entrance, ξ, is given in [14].

As a result of the calculations, the following values were obtained: the internal diameter of the capillary tube of the 1st cascade is 1.2 mm, the length of the capillary tube is 1920 mm and the internal diameter of the capillary tube of the 2nd cascade is 0.67 mm with a length of 3270 mm.

4. Results and discussion

Based on these calculations, design documentation was developed, which was used to produce a prototype of a low-temperature cooled vapour trap for the collection of valuable biological raw materials. The appearance of the open trap during installation is shown in Fig. 3:

Fig. 3. **Vapour trap with opened lid**

The trap was mounted on a common frame together with a two-stage refrigeration machine and a vacuum chamber. The vacuum pump was mounted separately. The external view of the assembled unit is shown in Fig. 4.

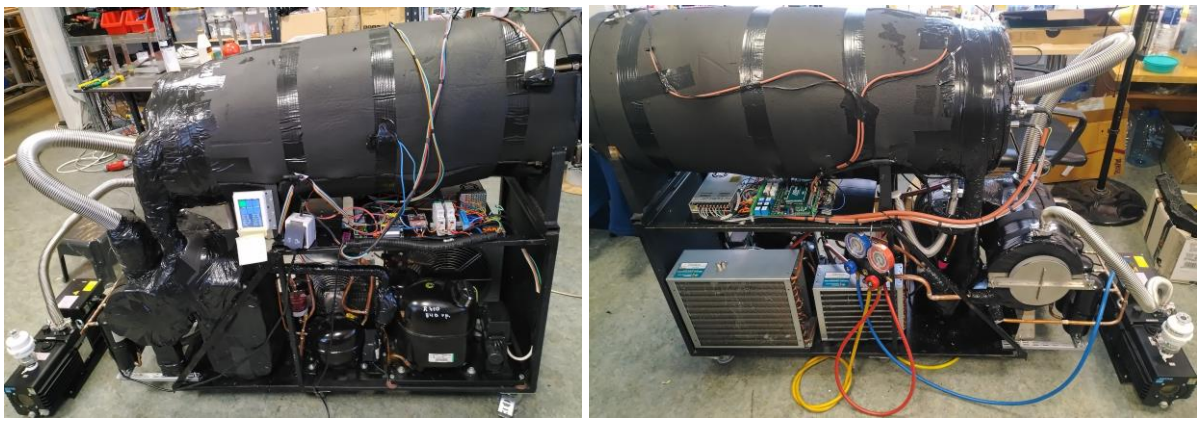

Fig. 4. **Assembled machine for vacuum cold condensing**

Tests of the whole device with a cooled vapour trap were carried out. During the tests, the design modes and characteristics of the developed two-stage refrigeration machine and the cooled vapour trap were confirmed. A photograph of the control system datalogger screen with temperature readings at the test points of the whole system is shown in Figure 5. The point eT4 shows the surface temperature of the refrigerated trap at -100 ºC.

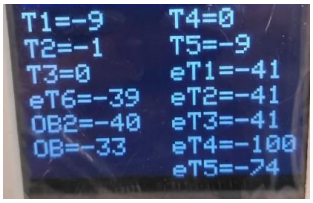

Fig. 5. **Thermal sensor reading during the test, refrigerated trap temperature is -100 ºC**

The tests showed the stability of the plant operation and repeatability of the results within 1-4 days of switching on with repeated cycles.

As a result of the prototype development it became possible to estimate the price of the industrial refrigerated vapour trap with operational temperature -120° C for 200 kg of captured biological active materials, which at the moment is about 192 000 Euro.

Conclusions

1. The possibility to create a two-cascade refrigeration machine using ordinary refrigeration compressors and other ordinary refrigeration equipment (not designed for high pressure) and mass-produced HFC refrigerant in the first cascade (R-410A) and HC refrigerant (ethane) in the second cascade has been experimentally proved. This machine provided long-term and stable cooling of the vapour trap to -100 ºC at a given heat load (-107 ºC was obtained in some experiments).
2. The correctness of the developed method of calculation of cooled traps and two-cascade refrigerating machines has been experimentally confirmed.
3. The developed calculation method, design and technological solutions allowed to significantly reduce the self-cost of the trap, compared to the machines with high pressure compressors. The economy is such that it can compete even with low-temperature traps produced in PRC, while achieving a lower temperature. Also the developed technical solutions can be scaled up to large machines, which will be competitive in performance with large industrial traps produced by German and US companies that use liquid nitrogen, but will have a significantly lower price and operating costs.
4. The new machines allow Latvian agricultural producers to increase the added value by creating valuable products, which are raw materials for biological additives, perfumes, cosmetics and pharmacology.

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Author contributions

Conceptualization, project administration and funding acquisition Kravchenko S. and N., formal analysis, methodology, Kravchenko S., Kuleshov N., software, Kravchenko A., validation, Panova D., Laptinov I., Kravchenko S., Kuleshov N., investigation, Kravchenko S, N and A, Kuleshov N., Laptinov I., Panova D., original draft preparation, review, editing, Kravchenko S. and N., Kuleshov N. All authors have read and agreed to the published version of the manuscript.

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