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INNOVATIVE FEATURES FOR THE RECOVERY OF PARTIALLY POLYMERIZED HOP OIL

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Abstract

Essential oils are subject to oxidation and polymerization, which changes their organoleptic, physicochemical characteristics and the content of their main components. This makes their further use impossible. The aim of our study was to develop a method for the technological recovery of the essential oil of the Promin hop variety was chosen, as its quality indicators did not meet regulatory requirements. The kinetics of the yield of the recovered oil, changes in the accumulation of terpene compounds, according to the sampling scheme – 15 : 10 : 15 : 20 min. The content of terpene compounds in hop oil obtained by the method of technological recovery was evaluated. There was also established compliance with the regulatory ranges of quality requirements, in particular, 45–75 % myrcene, 4–15 % beta-caryophyllene and 7–35 % humulene. We also confirmed the compliance of organoleptic, physical and chemical quality criteria of the recovered oil with the regulatory requirements. It has been experimentally determined that the rational shelf life of oil after its technological recovery and under anaerobic conditions, at temperature of minus 15 °C, is 9 months.

Keywords: recovery; oil; hops; technology; quality.

ІННОВАЦІЙНІ ОСОБЛИВОСТІ ВІДНОВЛЕННЯ ЧАСТКОВО ПОЛІМЕРИЗОВАНОЇ ОЛІЇ ХМЕЛЮ

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Анотація

Ефірні олії здатні до окиснення та полімеризації, внаслідок чого змінюються їх органолептичні, фізико-хімічні показники та вміст головних компонентів. Це унеможливлює їх подальше використання. Метою нашого дослідження було створення способу технологічного відновлення окисненої частково полімеризованої олії хмелю та встановлення оптимальних термінів зберігання. Для дослідження була вибрана ефірна олія хмелю сорту «Промінь», показники якості якої не відповідали нормативним вимогам. Досліджено кінетику виходу відновленої олії, зміни накопичення терпенових сполук за схемою відбору – 15 : 10 : 15 : 20 хв. Проведено оцінку вмісту терпенових сполук олії хмелю, що отримана способом технологічного відновлення та встановлено відповідність нормативним діапазонам вимог якості, зокрема мірцену, % – 45–75, бета каріофілену, % – 4–15 та гумулену, % 7–35. Аналогічно підтверджено відповідність нормативним вимогам органолептичних, фізико-хімічних критеріїв якості відновленої олії. Експериментально визначено, що раціональний термін зберігання олії після технологічного відновлення за анаеробних умов за температури –15 °С, складає 9 місяців.

Ключові слова: відновлення; олія; хміль; технологія; якість.

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Introduction

The development of society, environmental degradation, and partial shortage of food raw materials encourage scientists to search for new opportunities process food with biologically active components of plant origin under conditions of recovery or recycling of previous production waste. Recovered essential oils, in particular hops, are a promising area for solving this problem.

In accordance with the concept of recycling from food industry waste, the production of bioproducts helps to reduce the negative impact on the environment and increases the economic value of the processing industry as a whole [1].

Any residues or by-products of the processing or food industry are sources of bioactive compounds, for which recovery, purification and further utilization will contribute to the sustainability requirements for new bioactive ingredients [2].

The growing scarcity of natural resources and the increasing instability of waste management, in the context of the world's population growth, emphasize the need to create ways to reuse them. This requires the development of appropriate methodologies for the recovery of compounds or their complexes of interest to industry [3]. A survey of new methods used for the extraction of bioactive compounds from food waste and the selection of a rational one will increase the value of unusable waste and reduce its burden on the planet's ecosystem, thereby adjusting the cost of bioactive compounds [4].

The spectrum of biological activity of essential oils includes antioxidant, antimicrobial, and anti-inflammatory effects. They exhibit pronounced antibacterial and food preservative properties, which is a real potential for the food industry [5]. Hop essential oil is a complex biologically active mixture including several hundred volatile substances in its formulation. These are mainly various mono- and sesquiterpene hydrocarbons and flavoring terpenoids (myrcene, humulene, etc.), which have a proved strong potential against phytopathogenic bacteria and are a potential natural pesticide that has no harmful effects on human beings [6–9]. The major components of hop essential oils, such as monoterpenes and sesquiterpenes, including humulene, bisabolene, caryophyllene, farnesene, and elemental skeletons, are usually determined by estimating the content of volatile compounds by GC [10]. Essential oils, which are a collection of many lipophilic and highly volatile components, are subject to transformation and degradation reactions. Oxidation and polymerization processes can lead to a loss of quality and nutritional properties [11; 12]. In addition, oils are characterized by high instability (sensitivity to light, oxygen, and temperature) and hydrophobic nature, which hinders their solubility in the aqueous phase and creates problems with their processing and storage [13]. Under such conditions, during prolonged storage, the composition of oils changes and its chemical complexity increases even more [14]. Accordingly, the risks of not full, but only partial use of the target product increase.

Therefore, scientists are searching for methodologically rational ways to restore essential oils that have a wide range of biological activity and do not meet regulatory quality requirements.

Previous scientific studies provide a wide range of methods for the production of hop essential oils that take into account most of the properties of the raw material base. Their creativity lies in the evaluation of the effect of various organic oils (extracts) on human microbial pathogens when eluting with certain extractants (methylene chloride, acetone, ethyl acetate, methanol, etc.) [15], or obtaining volatile components of essential oils by industrial super-critical CO_2 – extraction, where isooctene containing hexadecane was used as an extractant [16], or ultrasonic extraction, where the rate of oil release increases due to the collapse of the formed cavitation bubbles. This cavitation effect is largely dependent on the ultrasound frequency and intensity, incubation time, temperature etc. [17].

The traditional method of hop oil extraction is steam distillation, which has an optimal steam flow path for the extraction of essential oils and formulates a multi-objective optimal control problem – to minimize energy consumption and at the same time maximize the extraction yield [18]. It would be a useful tool for predicting the conduct of this process using experimental data and technological parameters when assessing technological priorities for industrial operation [19].

The aim of this research is to develop a method of technological recovery and study the possibility of its application to produce pure hop oil. The quality indicators and content of the major components must comply meet the requirements of regulatory documentation, as well as to determine the rational conditions and terms of its storage.

Experimental

For the research, we used commercially available equipment for the production of essential oils by steam distillation.

Materials and methods. The raw material for the research was waste after steam distillation, namely hop cones with preliminary drying. The product of the reduction was oxidized partially polymerized hop oil, long-term storage, the quality of which did not meet regulatory requirements. For the experiment, we used an installation for the production of essential oil by steam distillation, a steam generator.

Experimental procedure. After steam distillation, hop cones (raw materials) were dried to a moisture content of 12 % and loaded into the tank of the unit for obtaining essential oil by steam distillation. Using fine spraying, a raw material zone of hop cones was created, saturated with oxidized partially polymerized essential oil. Then, according to the standard technology of essential oil extraction, water vapor was passed through the specified zone under a pressure of 0.4–1.0 kg_F/cm^2, the mixture of essential oil and water vapor was condensed, and the essential oil was separated from the condensate by decantation. The filtration was carried out under vacuum through the "F" plate. The proportion of partially polymerized oil to the mass of hop raw material was 1 : 100 (150). To study the kinetics of oil yield and changes in the accumulation of terpene compounds, the oil extraction time was determined to be 15 : 10 : 15 : 20 min, respectively. [20]. The determination of organoleptic and physico-chemical parameters was carried out in accordance with generally accepted methods using appropriate equipment [21]. The study of the content of mono- and sesquiterpenes (myrcene, beta-caryophyllene, humulene) was carried out on a gas chromatograph (Agilent 7890B). The quality stability of the reconstituted hop oil during storage was studied in the same manner, with an interval of 3 months.

Results and discussions

For the study, we used hop oil (basic) obtained from the cones of the bitter Promin hop variety, partially polymerized, by the conventional method of steam distillation. The determination of its organoleptic, physicochemical parameters and the content of biologically active terpene compounds showed a discrepancy in some standardized quality indicators due to its long shelf life.

The research experiment is based on the intensity of molecular interaction with water, which is characterized by the size of the adsorption bond of molecular substances and provides for the possibility of separating essential oils from the material containing essential oils [20].

The study of the kinetics of essential oil extraction has been focused on criteria that are usually based on the creation of a first-order model. This model considers only diffusion in different phases with a few simplified assumptions and provides results that check with experimental data in more than 80 % of the studied cases [22]. Regression models have the ability to predict the output and composition of essential oil for a given length of time for water vapor distillation [23], which are necessary criteria for analyzing the results of the amount of successive oil extraction over time.

Considering that mixtures of sequentially eluted compounds captured at different time intervals during steam distillation will have different profiles of chemical and biological activity [24]. The processing kinetics of oxidized partially polymerized hop oil was studied in terms of percentage yield and determination of the main quality indicators at each stage (according to the research scheme, stages are the time of oil extraction, respectively 15 : 10 : 15 : 20 min).

The study was conducted in two replications with different types of processed hops (bitter and aromatic, but of the same physical form) and their equal ratio with oxidized oil (Fig. 1, Fig. 2).

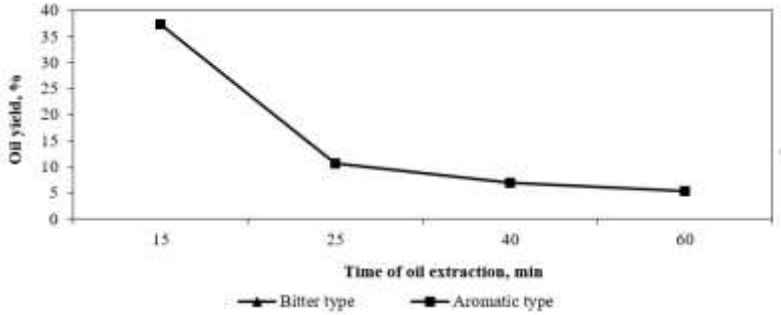

Fig. 1. Hop oil recovery kinetics for different types of processed hops

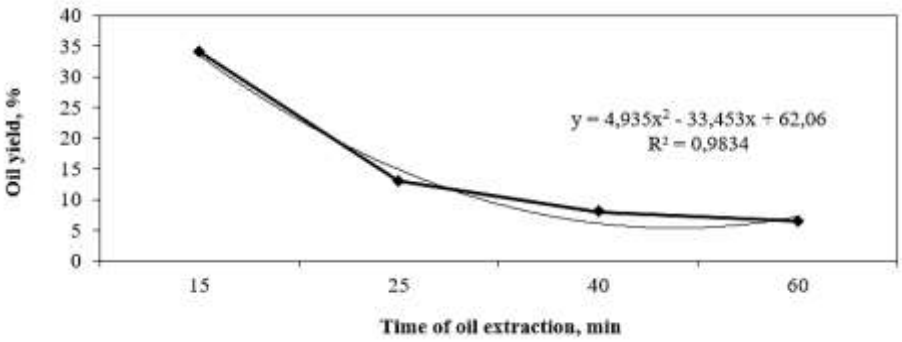

Fig. 2. Average hop oil recovery kinetics for different types of raw materials

The analytical calculations make it possible to approximate the values, determine the trend line, and derive the equation of the function with the optimal approximation reliability value R^2, which characterizes the degree of compliance of the trend model with the original data. The values were approximated for the average values of the recovery kinetics to avoid prioritizing the type of raw material.

The function equation $y = 4.935x^2 – 33.453x + 62.06$, with R^2 0.9834, determines the differential oil output at any time with high reliability of the experimental results. It also allows manufacturers to identify trends in production, composition development and energy consumption depending on the duration of steam distillation [25].

The experimental data confirm that with different types of raw materials (bitter and aromatic) and their ratio (within predefined limits), correlation oscillations occur, but within the error tolerance.

The study of physicochemical parameters was carried out in accordance with the list and requirements of the regulatory document FS 42U-2/303-1125-01. According to the results of experimental studies, the evaluation of these indicators of hop oil after technological recovery showed their full compliance with the requirements of regulatory documents at all stages of hop oil selection (Table 1).

Table 1

The physicochemical values of oil at different stages of production

Indicators	Normative limits	Indicators				
		Oxidized partially polymerized essential oil	stage, min.			
			15	25 (+10)	40 (+15)	60 (+20)
	Physicochemical values					
Density, g/см³	(0.81–0.89)	0.925	0.815	0,817	0.813	0.821
Refractive index (at 20°C)	(1.47–1.49)	1.57	1.485	1.488	1.476	1.483
Acid number, mg KOH/g	not more than 4	6.2	3.1	3,0	3.5	3.8
Ethereal number, mg KOH/g	(20–70)	81.5	57	65	63	55
Solubility	(The presence of opalescence is allowed)	Soluble in ethanol 95 %. Opalescence is observed upon dissolution	Soluble in ethanol 95 %. Opalescence is not observed upon dissolution			

Furthermore, a partial increase in the values (but within the normative limits) of the indicators "density" and "acid number" at the final stage of technological recovery can be explained by an increase in the amount of free acids due to prolonged exposure to elevated temperature (over 100 °C) and humidity in hop oil.

According to the requirements for hop essential oils used in the food industry, the quality criteria for reconstituted oil should include clearly defined indicators: organoleptic, physicochemical and biologically active substances. The content of the latter includes sesquterpene and monoterpene compounds specific to hop oil, characterizing each essential oil of a particular hop variety. The cluster analysis of a wide range of essential oils showed that 47.1 to 89.3 % of hop oils contain myrcene, caryophyllene, humulene [26].

The study of the kinetics of the process of technological recovery, in the context of the study of the content of terpene biologically active substances, at all stages of selection, was based on the experimental values of chromatographic

analysis of hop oil for the main terpenes – myrcene, beta-caryophyllene and humulene.

The polymerized hop oil used for the study did not meet the requirements of regulatory documents in terms of the content of biologically active substances (terpene compounds), namely, it had an excessive content of myrcene 80.09 % (45–75) and a low content of beta-caryophyllene 2.34 % (4–15) and humulene 5.58 % (7–35).

The recovery of hop oil was carried out under the conditions described above.

Experimental data on the content of terpene compounds at all stages of technological recovery are shown in Fig. 3.

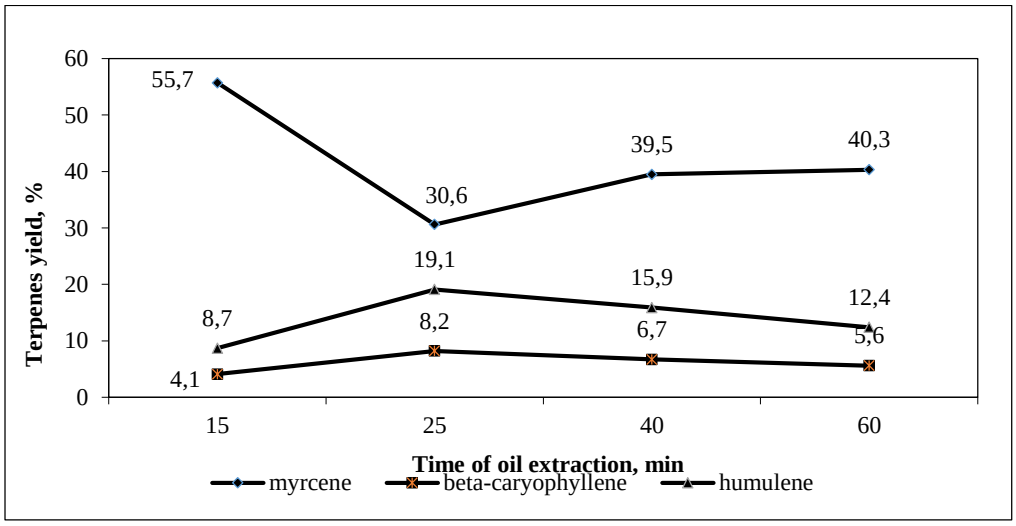

Fig. 3. Terpene yield kinetics

The non-linear yield of terpene compounds may be due to different boiling points of sesqui- and monoterpenes and the time degree of penetration of the agent (steam) into the entire volume of the hop layer.

The experimental data on the quality indicators (organoleptic, physicochemical, and terpene compounds) of the recovered hop essential oil are systematized according to the requirements of regulatory documents and are presented in Table 2. When forming the table, the maximum values of physicochemical parameters and terpene compounds (regardless of the yield period) were used to increase the requirements for the final product.

Table 2

The systematization of experimental data on the quality indicators of oxidized polymerized and reduced hop oils in relation to the requirements of regulatory documents

Indicators	Normative limits	Indicators	
		Oxidized partially polymerized hop oil	Reconstituted hop oil
		Organoleptic indicators	
Color	Transparent liquid of light yellow-green color	Transparent liquid of brown-red color	Transparent liquid of light yellow-green color
Smell	The specific smell of hop cones	Very pungent specific smell of hop cones	The specific smell of hop cones
		Physicochemical indicators	
Density, g/см³	0.81–0.89	0.925	0.821
Refractive index (at 20°C)	1.47–1.49	1.57	1.488
Acid number, mg KOH/g	not more than 4	6,2	3.8
Ethereal number, mg KOH/g	20–70	81.5	65
Solubility		Soluble in ethanol 95 %. Opalescence is observed upon dissolution	Soluble in ethanol 95 %. Opalescence is not observed upon dissolution
		Main terpenes	
Myrcene, %	45–75	80.09	55.7
Beta-caryophyllene, %	4–15	2.34	8.2
Humulene, %	7–35	5.58	19.1

A comprehensive analysis of the organoleptic, physicochemical parameters and content of biologically active components of oxidized partially polymerized hop oil after the process of technological recovery proves their compliance with the requirements of regulatory documents. It also allows us to recommend this product for further use in the food and processing industry.

When producing reconstituted hop oil, the shelf life is set to ensure that all quality and safety parameters are stable and meet regulatory requirements for storage conditions. Subject to certain storage conditions, the shelf life of conventionally produced hop oil is set over a period of 12 months.

Scientists around the world have studied and evaluated changes in hop oil content and its chemical composition over a long storage period. The rational (optimal) storage conditions were determined and then divided into four different groups: anaerobic, aerobic, cold room (4 °C) and room temperature. The best storage conditions were anaerobic conditions at low temperatures [27]. Regarding hop essential oil, the rational storage temperature (minus 15 °C) is determined by the regulatory document FS 42U-2/303-1125-01 and, accordingly, studies of the stability of quality and safety indicators were carried out at the specified temperature regime under anaerobic storage conditions.

Experimental studies of the stability of the quality indicators of oxidized partially polymerized hop oil after the reduction process proved the existence of minor oscillations in the values during the storage of the major biologically active components for 12 months. However, all indicators of terpenes (myrcene, beta-caryophyllene and humulene) were within the normatively permissible limits (Fig. 4).

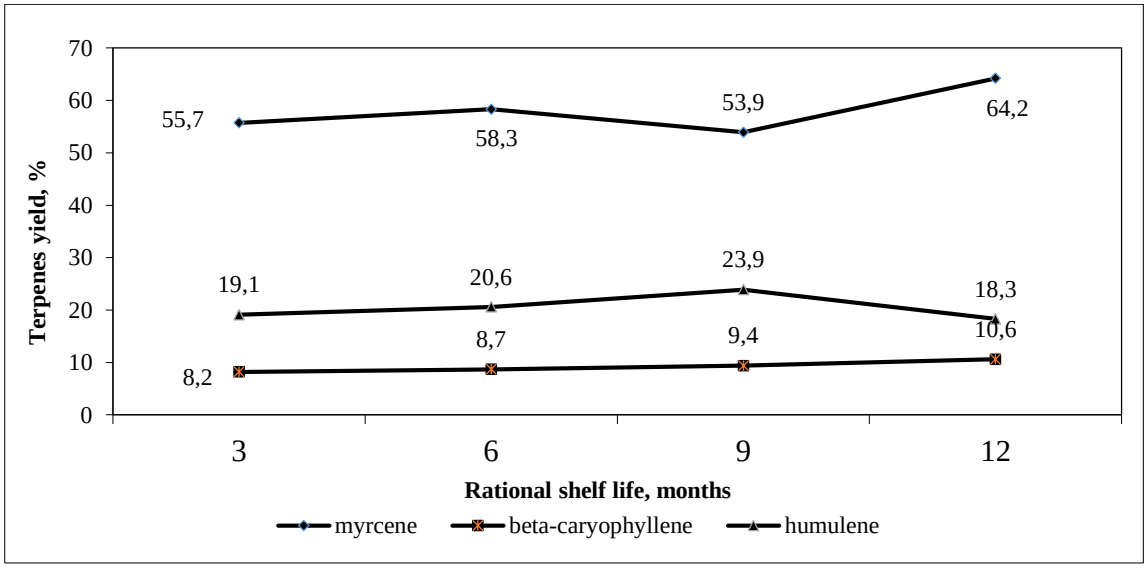

Fig. 4. Stability of terpene compounds

Experimental studies of the stability of the quality indices of oxidized partially polymerized hop oil after the reduction process proved the existence of insignificant fluctuations in the values during the storage of the main biologically active components for 12 months, but all indicators of terpenes (myrcene, beta-caryophyllene and humulene) were within the normatively permissible limits (Fig. 4).

From the above, it is proved that the method of recovery of oxidized partially polymerized oil allows to obtain a final product with quality and safety indicators that meet regulatory requirements. The stability of the recovered oil allows its use within 9 months from the date of receipt, which is 75 % of the standard storage period for oils produced by the classical technology.

Furthermore, the issue of adjusting the requirements for oil storage conditions remains open. It is possible that adjusting the temperature conditions or introducing an additional filtering operation (every 3 months) will have an impact on the stability of quality indicators and will increase the shelf life from 9 to 12 months.

Conclusions

1. The recovery method of oxidized and partially polymerized oil allows to obtain a final product with quality and safety indicators that meet the regulatory requirements for this product.

2. The organoleptic, physicochemical values and the content of the major terpene compounds of the reconstituted hop oil show stability during storage for 9 months.
3. The presented method is proposed for production development and has been tested as a pilot model.

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