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INVESTIGATION OF PROPERTIES OF SUNFLOWER AND RAPESEED OILS OBTAINED BY THE SOXHLET AND MICROWAVE EXTRACTION METHODS

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ABSTRACT. The main purpose of the study was to evaluate the possibility of replacing hexane, which is traditionally used for the extraction of vegetable oils, with ethanol as a safer solvent when extracting oil from sunflower meals and rapeseed in the microwave field. Thus, the influence of the solvent type on physicochemical characteristics of oil and the low-fat meal was studied. The main indicators of the composition and quality of sunflower and rapeseed extraction oil were studied. The quality of oil and ways of its use in food products are mostly determined by its fatty acid composition. Analysis of the fatty acid composition of the oil was performed by the method of gas chromatography using a column HP-88 100 m* 0.25 mm*0.20 μm. The possibility of using oil in food was established by conducting pilot laboratory studies and investigating changes in physicochemical parameters during storage. The extraction by the Soxhlet method (hexane as a solvent) was compared with the method of extraction of raw materials in a microwave field (ethyl alcohol as a solvent). Studies of physicochemical parameters indicate the degree of oil oxidation (determination of peroxide and anisidine values). The peroxide value is an indicator of the content of primary oxidation products. The peroxide value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 5.0 (½O mmol) kg^{-1}. The peroxide value of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 3.8 (½O mmol) kg^{-1}. The anisidine value is an indicator of the content of aldehydes in vegetable oils (secondary oxidation products). The anisidine value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 0.3 s.u. The anisidine value of oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 0.2 s.u. Comparing the data of peroxide and anisidine values, it can be argued that the oil obtained by extraction of raw materials in a microwave field (ethyl alcohol as a solvent) had the best indicators. The acid value is one of the main qualitative indicators that characterize the degree of oil freshness. The acid value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 3.1 (mg KOH) g^{-1}. The acid number of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 2.1 (mg KOH) g^{-1}. A comparison of the acid values of oils extracted from the raw material by different extraction methods shows that the oil obtained by the method of extraction of raw materials in a microwave field using ethyl alcohol as a solvent has the best acid value. Studies have shown that the oil, which was obtained by extraction of raw materials in a microwave field using ethyl alcohol as a solvent, had the best resistance to oxidation during storage (three months).

Introduction

Ukraine holds the leading position in the world's gross yield of sunflowers. The bulk of sunflower seeds is processed into oil, fodder cake and meal. According to the results of 2020, Ukraine remained the leader in the production and export of sunflower oil on the world market. In 2020, for the second time, the export of sunflower oil from Ukraine reached a record high of 6.9 million tons exceeding by 12% the 2019 record of 6.1 million tons (National Research Center, Institute of Agrarian Economics). Therefore, the development and implementation of up-to-date technologies for processing oilseeds, including sunflower seeds, remain relevant.

The increasing manufactured load on the environment and the threat of depletion of non-renewable natural resources caused the need to create and implement resource-saving energy-efficient and environmentally friendly production technologies. Improvement of the production of various products based on innovative methods of technological processes is a prerequisite for the development of the modern industry. One of the problems to be solved by innovative methods and technologies is the maximum extraction of useful products from raw materials. All vegetable oils are composed of fats (triglycerides) by 99–99.5% and have a high caloric content – 9 kcal g^{-1} of product. However, the value of vegetable oils is not limited to this only. In the 1930^{th,} it was found that vegetable oils contained substances necessary for human life, which could not be produced in the body. These compounds are fatty acids with two or more unsaturated bonds in the molecule, namely linoleic acid (18 carbon atoms and 2 double bonds) and linolenic acid (18 carbon atoms and 3 double bonds), which are called essential.

Nowadays, the most common methods of oil extraction are the method of mechanical pressing of raw materials and oil extraction with solvents (Beloborodov, 1966). At the present stage of the development of science and technology, the potential of microwave technology to increase the efficiency of many traditional industries and obtain products with new, better consumer qualities deserve recognition.

Formulation of the problem

A great experience has been gained in the use of microwave technologies in various industries to intensify the production process. However, in our opinion, there is very little research on the extraction of sunflower seeds with ethyl alcohol, and there is no reliable data on microwave extraction modes, or properties of the extracts obtained, which does not allow us to create appropriate technology and develop a microwave device for obtaining substances. These circumstances have determined the relevance of scientific research on the extraction of crude oil with solvents in the microwave field**.**

New methods are being developed since traditional ones have various disadvantages, e.g. they are more energy and time consuming, provide lower yields and are less environmentally friendly (Sharma *et al*, 2019). Physical methods of oil extraction allow for extracting only about 80% of the oil available in the oil material; therefore, another technology must be used to extract the remaining 20% (Puertolas *et al*, 2016). Extraction with a solvent has become widespread due to the simplicity and economy of the process (Mwaurah *et al*, 2020). Solvents are usually hexane and n-hexane, as they give the highest yield (95%) (Tan *et al.*, 2016). In particular, n-hexane is preferred due to its properties such as simple extraction, low latent heat of vaporization (330 kJ kg^{-1}), narrow boiling range (63–69 °C), high solubility and non-polarity. Unfortunately, the use of these solvents poses problems for health, safety and the environment, and therefore, despite their high efficiency of extraction, their use is not only harmful and toxic but also leads to air pollution (Konopka *et al*, 2016; Kumar *et al*, 2017). In addition, although it is approved for the food industry by the European Commission and the Food and Drug Administration (FDA), hexane is still considered and classified as hazardous and not the best for some international organizations (Castejón *et al*, 2018). However, the extraction of vegetable oil consumes large amounts of hexane, and therefore there is a need to study environmentally friendly technologies.

The oil is extracted from the raw material by pressing under the action of compressive external forces created in the press. This method ensures the extraction of high-quality oil, however, when pressed, about 8–14% of the oil remains in the cake (Ionescu *et al*, 2013). Extraction with a solvent allows the oil to be removed, leaving only 0.5–0.7% of oil in the meal (Topare *et al*, 2011) and can be used for raw materials having low oil content, as well as for the final extraction of oil from the cake after pressing. Some works present the results of the use of both pure solvents and mixtures (Hussain *et al*, 2018). Oil extraction provides maximum degrease of vegetable raw materials and is carried out by mass transfer. Mass transfer during the extraction of oil from particles of pre-crushed vegetable raw materials is the process of mass transfer on the surface of the particles and diffusion inside (Bandura *et al.*, 2021). Recently, research into new methods of extracting oil from raw materials, such as microwave extraction, has become widespread (Grasso *et al*, 2012).

Microwave-assisted extraction (MAE) is a new method, which can reduce the extraction time and solvent consumption. The study (Taghvaei *et al.*, 2014) aimed to evaluate the influence of MAE on oxidative stability and physicochemical properties of cottonseed oil. It was found that optimal conditions for extraction were as follows: irradiation time of 3.57 min; moisture content in cotton seeds of 14% and the ratio between cotton seeds and a solvent of 1:4, which resulted in the extraction efficiency of 32.6%, total phenolic content of 46 parts per million, 0.7% of free fatty acids, peroxide value of 0.2.

Replacement of toxic organic solvents from fossil sources with nontoxic ones of biorenewable origin in

large-scale processes has been the subject of research (Ferreira *et al*, 2022). Although ethanol has been currently investigated as a hexane substitute for vegetable oil extraction, most studies are conducted on a laboratory scale and in batch assays. Initial parameters of a continuous and countercurrent extractor that indicates the technical possibility of a large-scale operation are still scarce. Here, a continuous extractor composed of fixed bed columns connected in series (resembling the so-called simulated moving bed extractor) for soybean oil extraction with anhydrous ethanol was experimentally reproduced by a multiple-batch solid-liquid extraction system. After a 5-stage extraction, the residual oil in the solid phase was 0.17% with a 99.2% extraction yield, confirming that ethanol was capable to exhaust the solid matrix with a reasonable extraction yield. Although the minimum solvent-to-feed ratio (S:F) for ethanol (S:F = 2.62:1) was higher than that for hexane (S:F = 0.36:1), benefits to food safety, reduction in handling danger, and less environmental impact reinforce ethanol as a safe and promising solvent for the extraction of vegetable oils in continuous equipment.

It is assumed that extracts from plant raw materials obtained using the influence of microwave electromagnetic field, acquire qualitatively new biochemical and biological properties in comparison with analogues obtained by traditional extraction methods. Bandura *et al* (2018) investigated the possibilities of reducing the duration of the extraction process of soybean and rapeseed, obtaining a higher yield of the target component, and increasing the number of valuable components (tocopherols) in the finished product. It was found that in the microwave intensifier, compared to the classical method of extraction, the extraction time of soybean and rapeseed is reduced to 70% and the yield of the target component increases by 30%.

Intensification of the technological processes in the production of vegetable oils is a topical scientific and practical task. It is assumed that extracts from the plant raw materials obtained by exposure to the electromagnetic microwave field possess qualitatively new biochemical and biological properties in comparison with similar extracts obtained utilizing the conventional extraction methods. The article deals with the possibility to reduce the duration of the extraction process of the soybean and canola seeds, achieving a great output of the target component, to increase the number of valuable components (tocopherols) in the finished product. It has been established that in the microwave intensifier, in contrast to the classic method of extraction, the extraction time of the soybean and canola seeds is reduced to 70%, but the output of the target component increases within the limits of 30%.

The ethanolic extraction of oil from sunflower collets was studied and compared with previous data, where hexane was used as an extraction solvent (Baümler *et al*, 2016). First, the extractive power of ethanol was determined by Soxhlet. It gave a higher yield of extracted material, and which content of soluble hexane components (oil phase) was similar to that obtained with n-hexane. When ethanol was used as the solvent, 70% less crystallizable waxes and at least 38% more tocopherols and phospholipids were extracted. In addition, ethanol showed great ability to extract sugar, mainly raffinose and sucrose, extracting over 75% of the initial sugar content. Then, the kinetics of ethanolic extraction was studied at 50 and 60 °C in a batch reactor. At equilibrium conditions, it was observed that extraction could be limited by the solubility of the extractable material. Oil effective diffusivities were 9.94×10^{-10} at 50 °C and 3.11×10^{-9} m^2 s^{-1} at 60 °C. From the point of view of the quality of the obtained products, this work demonstrated the feasibility of using ethanol as an alternative solvent to hexane in the oil extraction from sunflower collets.

The influence of ethyl alcohol concentration, temperature and productivity of sprinkling the material with an extraction agent on its oleaginous condition as well as on the output and fractional makeup of the extractive matters is evaluated in the research. It is determined that the productivity of sprinkling is the most influential factor within the investigated limits. Hydromodulus 1:1.7 with the use of refillable miscella of single sprinkling is achieved. Residual oleaginous condition of oilcake equals 0.6–0.9% (Matiukhov, Hladkyi, 2013).

A comparison of the extraction of cake obtained from sunflower seeds with different organic solvents was performed (Matiukhov, Hladkyi, 2013). It was found that ethanol extracts extractives from sunflower meal more slowly than petroleum and diethyl ethers. The latter extract extractives at almost the same speed. Sources cited in the paper argued that the best extractant for oil is absolute ethanol at near-boiling temperature; it also denatures protein to a lesser extent, but extracts phenolic compounds slightly worse than rectified ethanol (Matiukhov, Hladkyi, 2013). Burdo *et al* (2018) emphasize that the most important problems of human development (energy, ecology, food) are typical for the food industry, and their solution is related to finding new approaches to the thermal processing of raw materials. Prospects of electrical technologies of targeted energy supply for individual elements of food raw materials utilizing microwave processing are substantiated. Hypotheses of energy-efficient processes of dehydration, extraction and inactivation of microorganisms are formulated.

In this paper, we emphasize that the most important problems in human development (energy, ecology, food) are typical of the food-production sector, and their solutions are connected with the search for fundamentally new approaches to the thermal processing of raw materials. The prospects of electrotechnologies of targeted energy delivery for single elements of food raw materials are substantiated. Hypotheses for energy-efficient processes of dehydration, extraction, and inactivation of microorganisms are formulated.

Microwave extraction is a popular extraction method that has high productivity and extraction efficiency

compared to other traditional methods. Microwave radiation interacts with the dipoles available in the sample matrix, causing them to oscillate in response to changing electromagnetic fields. Oscillation or rotation of dipoles during motion leads to the friction of molecules, which is converted into heat and transferred into the material due to thermal conductivity. In addition to dipoles from the solvent used in the extraction process, this heat leads to the formation of water vapour and electroporation effects that destroy the cell wall of oilseeds and enhance the efficient extraction of intracellular metabolites (Mwaurah *et al*, 2020).

Microwave radiation is a non-contact source of energy that provides efficient heating, minimum temperature gradient and selective heating if necessary (Burdo *et al*, 2016a). Therefore, the extraction time is significantly reduced (from 10 to 15 minutes), a smaller volume of solvent is used, both polar and non-polar solvents are contained, the extract yield is increased, and excellent sensory characteristics are achieved, *i.e.* colour, odour and aroma in products (Balasubramanian *et al*, 2011; Picó, 2013).

During the processes of the extraction of the plant cell, walls complicate diffusion processes that prevent the removal of target components (Edwards *et al*, 1997). However, when using a microwave field, the yield of extractives increases significantly, as stated in the scientific works of Western (Chemat, Cravotto, 2013, Flórez *et al*, 2015; Tewari *et al*, 2015), Asian (Bhuyan *et al*, 2015;Chan *et al*, 2015; Pan *et al*, 2003), and domestic scientists (Lebovka, Vorobiev, 2012; Burdo *et al*, 2016a; Burdo *et al*, 2018). Therefore, it can be concluded that the rupture of the cell membrane and the release of target components require not only the intensification of the molecule movement but also a significant increase in pressure.

As for the product quality and yield, microwave radiation allows direct binding of molecules by selective absorption; thus, it leads to high-quality products compared to traditional methods of heating and extraction (Khan, Rathod, 2018). The higher the power of the microwave field is, the faster the molecules move, and the higher the temperature and reaction rate is. On the other hand, low power increases the time required to reach the phase transition temperature (Zhang *et al*, 2018).

When using microwave extraction, non-polar solvents show the poor synergy between the solvent and microwave radiation due to their low dielectric penetrability. In addition, the mechanism of microwave heating is based on the rotation of molecules or dipoles in combination with ionic conductivity. For these reasons, polar solvents are best for microwave extraction because they have a high dielectric constant, absorb more microwave radiation, and promote conductivity. Moreover, polar solvents have shown better results than non-polar solvents in most cases (Khan, Rathod, 2018). Ethanol has excellent microwave absorption properties, while commonly used hexane is transparent to microwave radiation.

The main purpose of the study is to evaluate the possibility of replacing hexane, which is traditionally used for the extraction of vegetable oils, with a safer solvent, *i.e.* ethanol, when extracting oil from sunflower meal and rapeseed in the microwave field.

Materials and Methods

Sunflower seeds were taken from a consignment of seeds received at Vinnytsia Oil and Fat Plant. The moisture content of sunflower seeds was determined according to the standard (SSTU, State Standard of Ukraine). Sunflower seeds were processed by pressing by the technology of sunflower oil production approved by the enterprise. Samples of cake left after pressing were taken for further research of the extraction process. Rapeseed of the 'Champion' variety harvested in 2021 was used. Seed moisture content was determined according to the current standard (GOST 10856-96).

Hexane as an extractive solvent was obtained from Antecom LLC (Ukraine). Ethyl alcohol was obtained from the manufacturer, namely the State Enterprise SpirtLux (Ukraine).

Research methods are based on thermophysical analysis of the structure of the material and solvent. During the experimental research, there was used control and measuring equipment, and modern techniques and devices, including the authors' developments. Excel software packages were used for analytical research.

Laboratory equipment that was used included the laboratory sieve, thermostat TC-80 M2, thermometer TL-2K, electronic scales PS 750/c/1 RADWAG®, desiccators, tanks, flasks, boxes, drying cabinet SPT-200, drying cabinet 2B-151, analytical scales of the AS 310X series, an experimental stand of microwave action (developed by Odessa National Technological University), Agilent 8890 gas chromatograph (distributed by ALSI-Chrome (USA).

Soxhlet extraction was performed by GOST 10857-64. In this method, we weighed (40 g) of crushed sunflower meal (or crushed rapeseed) and transferred to a Soxhlet apparatus. The extraction was completed in 22–24 hours at a maximum temperature of 50–68.7 °C (boiling point of n-hexane). After the extraction process, the solvent residue was removed at 50 °C and reduced pressure using a rotary evaporator (Heidolph, Germany). For the further reduction of the amount of solvent, the extracted oil was transferred to a thermostat TC-80 M2 (Ukraine) at a temperature of 50 °C until a constant mass. The resulting oil was weighed and the oil yield was calculated.

The same experiments were performed with a solvent of ethyl alcohol. The extraction was completed in 22–24 hours at a maximum temperature of 50.0–78.3 °C (boiling point of ethyl alcohol). The determination was performed in triplicate for each solvent.

A microwave oven manufactured by Samsung (Korea, output power 425 W with a frequency of 2450 MHz) and a refrigerator connected to it were used

(Fig. 1). For each cycle of the experiment, 40 g of sunflower meal (or crushed rapeseed) was weighed and added solvent (n-hexane or ethyl alcohol) in a ratio of cake and solvent 1:3 in each cycle of experiments. The sunflower seeds or rapeseed were drained, then with solvent, it was placed in a glass flask and processed in the electromagnetic field for 10 to 20 minutes. Next, the kinetics of the process was investigated.

The main elements of the experimental microwave stand were a chamber in which a microwave field was created thanks to a magnetron, as well as a container in which the process of extraction of research objects took place: sunflower seed cake and winter rape of 'Champion' variety.

The principle of operation of the experimental stand was as follows: the extraction process took place in the container with the product under the action of a microwave field in chamber 1. Vapours of the extractant entered the reflux condenser 2, condensed and flew back into the reaction vessel with the test sample and solvent. Miscela was collected by syringe for further study of the oil concentration.

The extraction was completed in 10–20 minutes. For further reduction of the amount of a solvent, the extracted oil was transferred to a thermostat TC-80 M2 (Ukraine) at a temperature of 50 °C until a constant mass. The resulting oil was weighed and the oil yield was calculated.

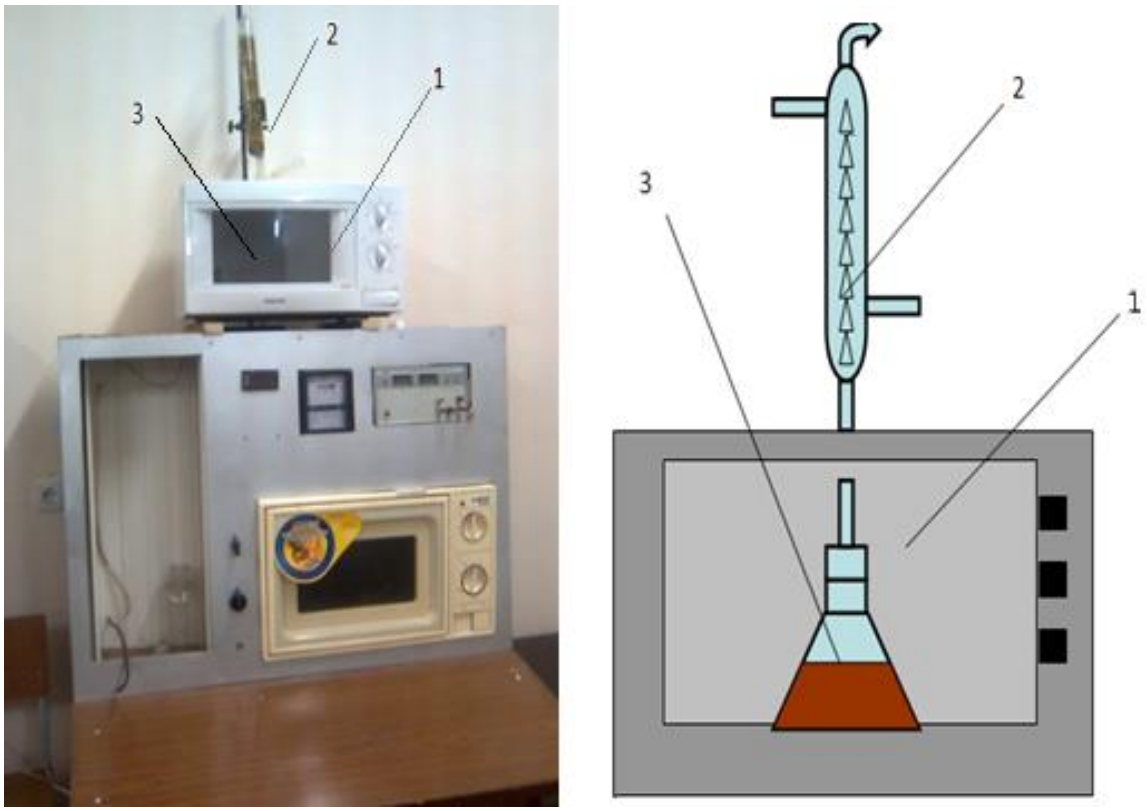

Figure 1. Photo and scheme of the experimental installation for oil extraction in a microwave field

To obtain a control sample (sunflower and rapeseed oil), there were used oils obtained at Vinnytsia Oil and Fat Plant using the current technology (extraction in a carousel extractor, hexane was used as solvent).

Analysis of the fatty acid composition of the oil was performed by the method of gas chromatography using a column of HP-88 100 m * 0.25 mm * 0.20 μm. The possibility of using oil in food was established by conducting pilot laboratory studies and studying changes in physical and chemical parameters during storage for three months.

Methodology of statistical processing of experimental data included the evaluations of observational errors in experimental results. Random errors was deleted from study results. In research was used verified measurement equipment and measurement errors was taking into account in results analyzing. The studies were repeated three times and mathematically processed using Microsoft Excel 2007 to ensure the accuracy of the results. The statistical error did not exceed 5% (with a 95% confidence level).

Results

Non-polar aliphatic hydrocarbons are used in classical oil extraction technologies due to their highest efficiency among solvents. It is known that the activation of reacting molecules is possible by heating substances, by releasing energy during the reaction, as well as by the absorption of radiation quanta by reagents (radioactive, light, electromagnetic, *etc.*), by ultrasound or electric discharge and even by hitting the bulb wall. An electromagnetic field was used to activate the molecules, which set the particles in motion. The forming particle layer promotes turbulence of the flow

and efficient mixing of the reaction mass. The turbulence of the flow and the action of the electromagnetic field leads to changes in the mass transfer coefficient, the energy of initial connections and the speed of the process.

In the study of the extraction process without the influence of a microwave field, only under the action of temperature, hexane as a solvent is much more effective than ethyl alcohol (Fig. 2). Where No. 1 is for rapeseed + ethyl alcohol 0.5 mm fraction of the whole grain under 50 °C and No. 1 is for rapeseed + hexane 0.5 mm fraction of the whole grain under 50 °C.

Due to the use of the microwave field as an intensifying effect, the study was conducted with polar ethyl alcohol, the intensity of removal of which under the action of microwave radiation increased to the efficiency of hexane (Fig. 3), where No. 1 – results without the influence of a microwave field (hydro module 1:3) and No. 2 are results under the influence of a microwave field (hydro module 1:3).

The study of physicochemical parameters of sunflower extraction oil obtained by the Soxhlet method and extraction oil under the influence of microwave field was carried out by conventional methods of analysis set out in relevant standards and manuals on techno-chemical control of production and methods described in the State Standards of Ukraine (Table 1). Table 1 are shown shows the methods of sunflower oil testing.

Table 1. Methods of sunflower oil research

Indicator	Principle of the research method
A sampling of oil and preparation for analysis	According to SSTU 4349:2004
Mass fraction of moisture and volatile substances, %	According to SSTU ISO 662:2004
Mass fraction of non-fatty impurities,%	According to SSTU ISO 663-2003
Acid value, (mg KOH) g^{-1}	According to SSTU 4350:2004
Peroxide value, (½O mmol) kg^{-1}	According to SSTU 3960-2001
Mass fraction of phosphorus-containing substances in terms of stearooleolecithin,%	According to GOST 7824
Flashpoint, °C	According to GOST 9287
Anisidine value	According to SSTU ISO 6885 – 2002
Fatty acid composition of oil	According to SSTU ISO 5508-2001. Analysis of methyl esters of fatty acid by the method of gas chromatography

We conducted a study of sunflower extraction oil obtained by the Soxhlet method and extraction oil obtained under the influence of a microwave field. The results are shown in Table 2.

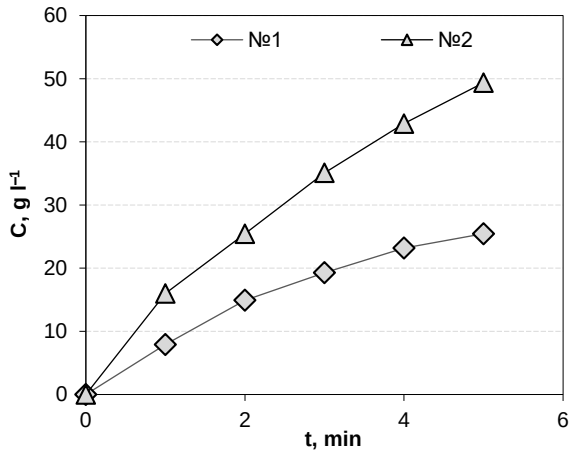

Figure 2. Dependence of concentration on time in the process of oil extraction with different solvents

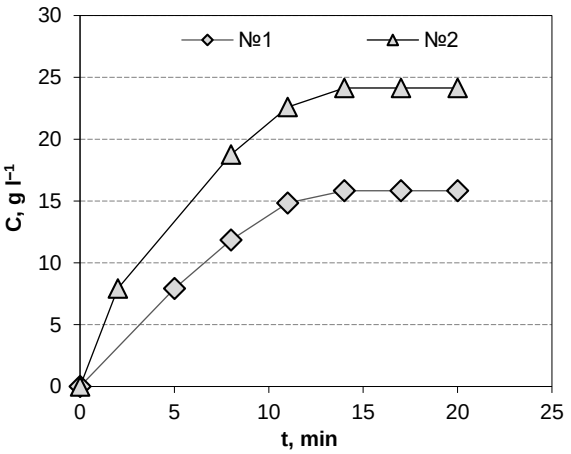

Figure 3. Dependence of concentration on time in the process of oil extraction with alcohol from rapeseed at a boiling point of a solvent of 78.3 °C

Table *2.* Physicochemical parameters of sunflower extraction oil obtained after extraction with solvents: hexane (samples No. 1, No. 3) and alcohol (samples No. 2, No. 4).

Indicator	Soxhlet method		Under the influence of a microwave field	
	Hexane as a solvent	Ethyl alcohol as a solvent	Hexane as a solvent	Ethyl alcohol as a solvent
Experimental sample	No. 1	No. 2	No. 3	No. 4
Mass fraction of moisture and volatile substances,%	0.18	0.17	0.19	0.16
Mass fraction of non-fatty impurities,%	0.05	0.04	0.05	0.03
Acid value, (mg KOH) g^{-1}	3.1	2.5	2.8	2.1
Peroxide value, (½O mmol) kg^{-1}	5.0	4.8	4.3	3.8
Mass fraction of phosphorus-containing substances in terms of stearooleolecithin,%	0.45	0.41	0.43	0.38
Anisidine value, s.u.	0.3	0.25	0.28	0.2
Flash point, °C	226	227	226	225

The studies of physicochemical parameters indicate the degree of oxidation of the oil (determination of the peroxide and anisidine values).

The peroxide value is an indicator of the content of primary oxidation products. The peroxide value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 5.0 (½O mmol) kg^{-1}. The peroxide value of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 3.8 (½O mmol) kg^{-1}.

The anisidine value is an indicator of the content of aldehydes in vegetable oils (secondary oxidation products). The anisidine value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 0.3 s.u. The anisidine number of oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 0.2 s.u.

Comparing the data of the peroxide and anisidine values, it can be argued that the best indicators were found in the oil obtained by the method of extraction of raw materials in a microwave field (ethyl alcohol as a solvent).

Studies have shown that oil, which is obtained by the method of extraction of raw materials in a microwave field using ethyl alcohol as a solvent, has the best resistance to oxidation during storage (3 months).

Chromatograms of the fatty acid composition of extraction oil are shown in the next results: No. 1 – sunflower, sample No. 1; No. 2 – sunflower, sample No. 2; No. 3 – sunflower, sample No. 3; No. 4 – sunflower, sample No. 4; No 5 – rapeseed oil; sample No. 1. It should be noted that the main guarantee of the nutritional value of oil is the fatty acid composition. Together with the generally accepted indicators of oil, we studied the fatty acid composition of sunflower extraction oil. The Agilent 8890 gas chromatograph (distributed by ALSI-Chrome (USA) was used to determine the fatty acid composition of the oil. The results are shown in Tables 3–6.

Table 3 Fatty acid composition of sunflower extraction oil (sample No. 1)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass fraction of fatty acid (% to the sum of fatty acids)
$C_{6:0}$	Capronic acid	0.069
$C_{14:0}$	Myristic acid	0.067
$C_{16:0}$	Palmitic acid	6.491
$C_{16:1}$	Palmitoleic acid	0.089
$C_{18:0}$	Stearic acid	3.687
$C_{18:1}$	Oleic acid	28.366
$C_{18:2}$	Linoleic acid	59.233
$C_{20:0}$	Arachic acid	0.212
$C_{20:1}$	Eicosanoic acid	0.113
$C_{18:3}$	Linolenic acid	0.161
$C_{21:0}$	Heneicosylic acid	0.184
$C_{22:0}$	Behenic acid	0.694
$C_{24:0}$	Lignoceric acid	0.167

In accordance with SSTU 4492-2017, fatty acids of sunflower oil should mainly include the following fatty acids: myristic acid (up to 0.2%), palmitic acid (from 5.0 to 7.6%), palmiticoleic acid (up to 0.3%), stearic acid (from 2.7 to 6.5%), oleic acid (from 14.0 to 39.4%), linoleic acid (from 48.3 to 74.0%), linolenic acid (up to 0.3%), arachic acid (from 0.1 to 0.5%), gondoic acid (up to 0.3%), behenic acid (from 0.3 to 1.5%), and lignoceric acid (up to 0.5 %).

Table 4. Fatty acid composition of sunflower extraction oil (sample No. 2)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass fraction of fatty acid (% to the sum of fatty acids)
$C_{16:0}$	Palmitic acid	6.871
$C_{16:1}$	Palmiticoleic acid	0.085
$C_{17:0}$	Margaric acid	0.061
$C_{18:0}$	Stearic acid	3.699
$C_{18:1}$	Oleic acid	25.836
$C_{18:2}$	Linoleic acid	59.535
$C_{20:0}$	Arachic acid	0.677
$C_{20:1}$	Eicosanoic acid	0.298
$C_{18:3}$	Linolenic acid	0.215
$C_{21:0}$	Heneicosylic acid	0.151
$C_{22:0}$	Behenic acid	0.822

Table 5. Fatty acid composition of sunflower extraction oil (sample No. 3)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass fraction of fatty acid (% to the sum of fatty acids)
$C_{14:0}$	Myristic acid	0.081
$C_{16:0}$	Palmitic acid	6.877
$C_{16:1}$	Palmiticoleic acid	0.113
$C_{18:0}$	Stearic acid	3.270
$C_{18:1}$	Oleic acid	30.090
$C_{18:2}$	Linoleic acid	57.415
$C_{18:3}$	Linolenic acid	0.248
$C_{20:1}$	Gondoic acid	0.095
$C_{24:0}$	Lignoceric acid	0.206

Table 6. Fatty acid composition of sunflower extraction oil (sample No. 4)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass fraction of fatty acid (% to the sum of fatty acids)
$C_{6:0}$	Capronic acid	0.189
$C_{8:0}$	Caprylic acid	0.053
$C_{14:0}$	Myristic acid	0.082
$C_{16:0}$	Palmitic acid	7.184
$C_{16:1}$	Palmiticoleic acid	0.174
$C_{17:0}$	Margaricoleic acid	0.407
$C_{17:1}$	Margaric acid	0.190
$C_{18:0}$	Stearic acid	3.532
$C_{18:1}$	Oleic acid	26.436
$C_{18:2}$	Linoleic acid	57.121
$C_{20:0}$	Arachic acid	0.186
$C_{20:3}$	Mead acid	0.671

Thus, having conducted laboratory studies, it can be stated that sunflower extraction oil obtained by the method of extraction of raw materials in a microwave field meets the requirements of SSTU 4492-2017.

The authors set the task to study organoleptic and physicochemical parameters of sunflower meals after these processes.

Table 7 shows the methods of research for sunflower meals. These methods are used in modern Ukrainian productions since the 1980-s and are validated for most of them.

The results of the study of sunflower meals obtained after oil extraction by the methods of extraction in the Soxhlet apparatus and microwave field are shown in

Table 8. Hexane as a solvent in traditional extraction methods, and as a Soxhlet apparatus, demonstrate better results.

Thus, the obtained sunflower meal meets the requirements of SSTU 4638: 2006 "Sunflower meal. Specifications".

There was also conducted the study on the fatty acid composition of rapeseed oil obtained by the method extraction of rapeseed meal in a microwave field with hexane and ethyl alcohol as solvents by SSTU 8175: 2015 "Rapeseed oil. Specifications".

Table 7. Methods of research of sunflower meal

Indicator	The principle of the research method
A sampling of meal and preparation of samples for analysis	According to GOST 13979.0-86
Colour, odour, amount of dark spots and trifles	According to GOST 13979.4-68
Mass fraction of moisture and volatile substances,%	According to GOST 13979.1-68
Mass fraction of fat and extractives,%	According to GOST 13979.2-94
Mass fraction of crude protein,%	According to GOST 13496.4
Mass fraction of crude fibre,%	According to GOST 13496.2

Table 8. Organoleptic and physicochemical parameters of sunflower meal were obtained after extraction with hexane (No. 1, No. 3) and alcohol (No. 2, No. 4), respectively

Indicator	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
Appearance	homogeneous bulk mass	homogeneous bulk mass	homogeneous bulk mass	bulk mass, available small beeps
Colour	grey	grey	grey	grey
Odour	Inherent in sunflower meal without odour			
Mass fraction of moisture and volatile substances,%	8.3	8.1	7.9	7.5
Mass fraction of fat and extractives,%	1.49	1.5	1.5	1.47
Mass fraction of crude protein,%	36.5	36.9	36.7	36.8
Mass fraction of crude fibre in terms of absolutely dry matter,%	25.4	25.5	25.1	25.6

Table 9. Fatty acid composition of rapeseed oil (sample No. 1, hexane as a solvent)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass of fatty acid (% to the sum of fatty acids)
$C_{16:0}$	Palmitic acid	7.53
$C_{16:1}$	Palmiticoleic acid	0.141
$C_{18:0}$	Stearic acid	3.154
$C_{18:1}$	Oleic acid	27.655
$C_{18:2}$	Linoleic acid	60.078
$C_{18:3}$	Linolenic acid	0.157
$C_{20:0}$	Arachic acid	0.220
$C_{20:1}$	Gondoic acid	0.115
$C_{22:0}$	Behenic acid	0.463
$C_{22:1}$	Erucic acid	0.483

Table 10. Fatty acid composition of rapeseed oil (sample No. 2, ethyl alcohol as a solvent)

Reference designation of acid	Name of acid according to trivial nomenclature	Mass fraction of fatty acid (% to the sum of fatty acids)
$C_{14:0}$	Myristic acid	0.1
$C_{16:0}$	Palmitic acid	7.3
$C_{16:1}$	Palmiticoleic acid	0.16
$C_{18:0}$	Stearic acid	2.98
$C_{18:1}$	Oleic acid	28.79
$C_{18:2}$	Linoleic acid	58.56
$C_{18:3}$	Linolenic acid	0.23
$C_{20:0}$	Arachic acid	0.19
$C_{20:1}$	Gondoic acid	0.16
$C_{22:0}$	Behenic acid	0.48
$C_{22:1}$	Erucic acid	0.5

After comparing, the results assumed that with microwave influence we obtain a higher concentration of major fatty acids in samples. This means that the quality of oil samples is improved. All the studies show that microwave technology is a powerful tool for the implementation of food nanoenergy technologies (Burdo *et al*, 2016b). Compared to traditional technologies, they will significantly increase the concentration of biologically active substances and reduce the processing time, creating technologies for processing food raw materials that fully meet modern requirements for resource and energy efficiency, environmental safety and market economy.

Thus, the use of microwave technologies in the oil and fat industry is a new and promising scientific approach to the improvement of traditional processes of extraction of crude oil and production of finished products.

Discussion

Analyzing the obtained results, one can trace the influence of the choice of solvent and the product treatment method. The extraction by the Soxhlet method (hexane as a solvent) was compared with the method of extraction of raw materials in a microwave field (ethyl alcohol as a solvent) shown in Figure 2 and Figure 3. The studies of physicochemical parameters indicate the degree of oxidation of the oil (determination of peroxide and anisidine values).

The peroxide value is an indicator of the content of primary oxidation products. The peroxide value of the oil obtained by Soxhlet extraction (hexane as a solvent) was 5.0 (½O mmol) kg^{-1}. The peroxide value of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 3.8 (½O mmol) kg^{-1}.

The anisidine value is an indicator of the content of aldehydes in vegetable oils (secondary oxidation products). The anisidine value of the oil obtained by Soxhlet extraction (hexane as a solvent) was 0.3 s.u. The anisidine value of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 0.2 s.u.

Comparing the data of peroxide and anisidine values, it can be argued that the best indicators were found in the oil obtained by the method of extraction of raw

materials in a microwave field (ethyl alcohol as a solvent).

The acid value is one of the main qualitative indicators that characterize the degree of oil freshness.

The acid value of the oil obtained by the method of Soxhlet extraction (hexane as a solvent) was 3.1 (mg KOH) g^{-1}. The acid value of the oil obtained by extraction in a microwave field (ethyl alcohol as a solvent) was 2.1 (mg KOH) g^{-1}. That let us say that obtained in microwave field oils have better oxidation resistance.

A comparison of the acid values of oils extracted from the raw material by different extraction methods shows that the oil obtained by the method of extraction of raw materials in a microwave field using ethyl alcohol as a solvent has the best acid value. Accordingly, the obtained results make it possible to recommend the microwave method for implementation in the production of vegetable oils with ethyl solvents. The next step is the patenting of this method and the development of technological conditions for the production of vegetable oils. Since a more detailed study of the effect of a microwave field on the product is required. The microbiological and technological studies of the finished product obtained using new technology are necessary.

The given in the revived studies of the use of the microwave field for the intensification of extraction processes are confirmed by the results of this work. The discrepancy for some target components is because they are insoluble in Ethyl alcohol, which in turn is a polar solvent. The choice of polar solvents is justified for microwave devices by the dipole shift effect. Thus, if the main target component in the extraction is those fatty acids that are insoluble in alcohol, combined or other methods of extraction should be considered.

Study on the microwave field influence has been carried out by authors for more than 20 years. As a result of research on the efficiency of using a microwave field in drying processes, PhD and doctoral thesis was published by the authors: Extraction of coffee in a microwave continuous operation (Levtrinskaya Y., 2017, PhD), Scientific and Practical Substantiation of Energy Efficient Technologies for Oilseed Raw Material Processing based on Mechanical and Electromagnetic Intensifiers (Bandura V., 2021, Sc.Doct.), Scientific and technical foundations for creating energy-efficient equipment for improving the quality of vegetable oils (Osadchuk P., 2021, Sc.Doct.). With the use of fundamental research in the field of studying the effect of a microwave field, innovative equipment is being created, as shown in the publications of the authors (Burdo *et al*, 2020). The principles of directional energy action and microwave exposure at the product capillary level are used in extraction to intensify and increase the energy efficiency of processes. The main difference of this study is a deeper study of the use of various solvents for the extraction of oils. Obtained results deepen the understanding of the expediency of using a microwave field for various "solid-liquid" systems and further introducing these technologies into production.

This study correlates with research by Ferreira *et al.* (2022), Burdo *et al.* (2018), and Baümler (2016), which assume that extracts from plant raw materials in which the solvent is ethanol and obtained using a microwave field, acquire qualitatively new biochemical and biological properties compared to analogues obtained by traditional methods of extraction with hexane. Since ethanol is non-toxic and safe but extracts extractives more slowly than n-hexane, it is advisable to perform the extraction in a microwave field. The physicochemical parameters of extraction of sunflower oil obtained by the method of extraction in a microwave field (solvent – ethyl alcohol) have the best indicators in terms of peroxide and anisidine numbers. A comparison of the acid numbers of oils extracted from the raw material by different extraction methods shows that the oil obtained by the method of extraction in a microwave field using ethyl alcohol as a solvent has the best acid value.

Conclusion

The results of the study showed that the use of microwave leads to the increase in the efficiency of the process of oil extraction, oil density, oxidative stability, oil color and meal protein. Based on the results obtained in our studies, we can say that the use of microwave extraction with ethyl alcohol as a polar solvent was effective for improving the quality properties of the extracted oil.

The studies have shown that oil, which is obtained by extraction of raw materials in a microwave field using ethyl alcohol as a solvent, has the best resistance to oxidation during storage (3 months). The use of a microwave field in the process of extracting oil raw materials with ethyl alcohol as a polar solvent leads to a gradient-free wave supply of electromagnetic energy to polar molecules. Due to dipole shift effect, a powerful diffusion flow is forming. The extracted oils obtained from the raw material with electromagnetic intensification has the richest complex of components and better quality, than the same samples obtained in thermal methods only.

Conflict of interest

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

Author contributions

VB, LF, YL – study conception and design;
VB, LF – acquisition of data;
YL, PO – analysis and interpretation of data;
AP – drafting of the manuscript;
VB, PO – critical revision and approval of the final manuscript.

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