

INFLUENCE OF EXTRACTION CONDITIONS ON QUALITATIVE
COMPOSITION OF VEGETABLE OILS

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Abstract. The influence of the production conditions for rapeseed and soybean oils obtained by extraction in the system “solid – liquid” on the qualitative composition of the obtained vegetable oils has been studied. The main chemical values (acid value, iodine value, ester value, saponification value) and optical properties (refractometric refractive index and UV-Vis spectroscopy) for rapeseed and soybean oils obtained by extraction using methylene chloride as a solvent from different plant raw materials (grade of grinding is 0.2, 0.5 and 1.0 mm) and mixtures of crushed grain fractions have been determined. It has been shown that the grade of grinding of the raw material affects the quality of the obtained product.

Keywords: extraction, solid-liquid system, vegetable raw materials, rapeseed oil, soybean oil, qualitative analysis, refractometry, UV-Vis spectroscopy.

1. Introduction

Oil raw materials are traditionally one of the key export goods of Ukraine, in particular due to their wide use in various industries. The last few decades the technologies have been actively developing for the use of vegetable oils not only in food, pharmacology, paint, and other industries, but also for the manufacture of alternative environmental fuels [1, 2]. Soybean, palm, and rapeseed occupy the leading positions in terms of vegetable oil use [3]. The development of new more efficient technologies and equipment is one of the important tasks for supporting the industry.

Basically, industrial extraction of oils from vegetable raw materials is realized by pressing and extraction. The conditions of extraction are selected individually for each type of raw material and target component, by selecting the optimal technological

parameters to achieve maximum ultimate efficiency while minimizing energy and cost [4]. The extraction method is widely used in world industry due to the high efficiency of extraction of oils not only from raw materials with a high content of the target component, but also from those where the concentration of the latter does not exceed 5 %. For comparison, an alternative method of extracting oils by pressing cannot be used for this type of raw material [5, 6].

The technical design and operating conditions of the extraction process are determined by the properties of the selected extractant. Criteria for extraction suitability are primarily selective ability – the ability to selectively dissolve the target component, the type and nature of the solvent (polar, non-polar), physical and chemical parameters, and inertness to raw materials. Also, an important parameter for the implementation of mass transfer is the ability to penetrate the solvent to the location of the target component. Comparative experimental studies have shown that polar solvents are more effective in dissolving vegetable oils [7]. Methylene chloride is among the most effective solvents due to its polarity parameters and low boiling point, which determine the main advantages over other solvents in terms of improving the energy efficiency of the process [8, 9].

Along with increasing the quantitative indicators of extraction, it is necessary to investigate in detail the qualitative parameters of the obtained target component, both to determine the influence of the extractant nature on the chemical state of oils and to further plan the purification stages according to technological requirements [10].

Along with the correct selection of the solvent, there are several other intensifying parameters. In particular, an important role in the efficiency of the dissolution process is played by the state of the raw material – moisture, grain shape (for grain products), the grade of grinding, the presence of by-products (grain shells), and others. Due to the fact that the extraction of oil from vegetable raw materials includes both intra-molecular transfer of components to the contact surface and external diffusion from the phase contact surface to the bulk of the solvent, there is information about the influence of grinding on the extraction efficiency and on the path of movement of the target component in the grain. The

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obtained data indicate a direct effect of grinding on the intensification of the target component extraction [11].

It is known that the intensification of the extraction process affects the quantitative indicators of the obtained oil, but it is not entirely clear whether the method and conditions of extraction depend on the qualitative characteristics of the obtained oils. It is also important to control the quality and chemical composition of the extracted oil. The main indicators that determine the properties and quality of oil are chemical values (iodine, acid, ester values, saponification value, refractive index and specific gravity).

Chemical values are needed to characterize the chemical composition of the oil and to compare it with data for oils obtained from other facilities or existing standards. Thus, the iodine value (IV) is the most important chemical indicator of fats and vegetable oils, its value is judged by the predominance of saturated or unsaturated fatty acids in vegetable oil. Acid value (AV) characterizes the content in one gram of vegetable oils of free fatty acids. Ester value (EV) indicates the amount of alkali used for complete saponification of esters in oil. Saponification value (SV) is the amount of potassium hydroxide required to neutralize both free and bound fatty acids contained in 1 g of oil.

At the same time, the optical and spectral properties of the obtained oils are important, because due to them the qualitative composition of oils can be identified, the purity of the substance can be established, and its concentration in solution can be determined.

2. Experimental

Extraction of vegetable oil was carried out in a Soxhlet apparatus, the detailed scheme of the laboratory installation is shown in Fig. 1.

Rapeseed and soybean seeds grown on local farms (Lviv region, Ukraine) were used as experimental raw materials. The plant raw material was pre-milled and distributed using sieve into fractions with different particle sizes of 0.2 mm, 0.5 mm, 1.0 mm, and the average crushed mixture.

The separated crushed seed fractions before the extraction process were dried to the humidity of 2–5 % by pre-holding the samples in an oven at the temperature of 373–383 K for 1 h. For pre-drying a crushed rapeseed or soybean oil was taken in excess of ≈ 80 –100 %.

The initial ratio of solid to solvent was $\approx 1:10$, as for the experiment 32 g of crushed vegetable raw materials and 320 ml of extractant were used [12].

Each fraction in a cylindrical cartridge made of thick filter paper was placed in the Soxhlet apparatus (Fig. 1), which was connected to a flask with solvent and

equipped with a reflux condenser. During boiling, the extractant forms vapors which moved up and condensed in the refrigerator. The refrigerator allows all condensed steam draining into the chamber with the cartridge. The chamber containing the solid crushed material was slowly filled with solvent. Some of the oil dissolved in the extractant. When the Soxhlet chamber was filled, it was automatically emptied when the solvent was returned to the flask. The cycle was repeated periodically throughout the experiment.

Methylene chloride, which is one of the most effective polar solvents [13], was used as a solvent in the extraction process. The extraction process was carried out under the boiling temperature of the solvent (≈ 312.6 K) for 8 h. The time of the first solvent overflow from the chamber of the Soxhlet apparatus was considered as the beginning of the experiment. Next, sampling was performed every 2 hours and further determination of the oil concentration was performed by separating the solvent by evaporation at the temperature higher than 10–20 K from its boiling point. At the end of the experiment, the solvent was distilled off, the extract was concentrated, the residue of which was evaporated in an oven. The final mass was calculated by product yield. To maintain the solvent balance in the system, an appropriate amount of pure solvent was added to the reaction flask each time after sampling. In this way, the volume of solvent remained constant and the oil content in the flask decreased. Therefore, when calculating the oil concentration, corrections were made to change the concentration.

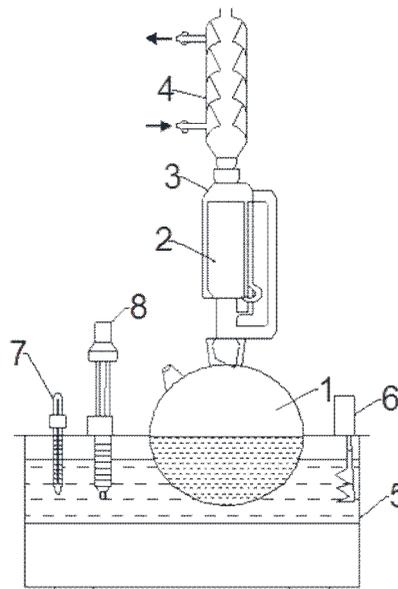


Fig. 1. Scheme of the laboratory installation: 1 – round-bottomed flask; 2 – cartridge with crushed seeds; 3 – extractor; 4 – backflow condenser; 5 – thermostat (flask heater); 6 – tan; 7 – control thermometer; 8 – contact thermometer

LTHS-500 electric flask heaters were used in the experiments to increase the stability and heating efficiency of the Soxhlet apparatus.

The chemical values (acid value, iodine value, ester value, saponification value) of the obtained oils were determined according to the methods described in [14-16].

To determine the optical and spectral properties of the obtained products, the methods of refractometry and UV-Vis spectroscopy were used.

The refractive index n_d^{20} for the obtained oil samples was measured on an Abbe refractometer, model Kruss AR4. The refractive index serves as a criterion for establishing the purity of the substance and determining its concentration in solution. On the other hand, the refractive index can also be used to identify the substance. The refractive index of the oil was determined according to [17]: a drop of oil was applied to the prism of the refractometer using a molten glass tube without touching it. After that, the prism was closed, and the image sharpness and optimal illumination was set. Turning the compensator made the blurred spectral boundary clear. Next, the refractometer was adjusted so that the intersection was located at the junction of light and shadow. Data were obtained on a refractive index scale.

Data of the ultraviolet spectroscopy (UV-Vis), which is a simple, stable, and cost-effective method [18] in comparison with chromatography, were obtained on a spectrophotometer ULAB 108UV, operating in the range

of 190–1100 nm. Absorbance spectra on the spectrophotometer were measured using quartz cells.

3. Results and Discussion

In the course of previously conducted experimental studies [12], under the conditions described above, a certain visual difference was found in the samples of rapeseed and soybean oils obtained from fractions of different diameters. In view of this, analytical, optical, and spectral studies of experimental samples were carried out in order to establish the influence of the production method on the qualitative characteristics of the obtained vegetable oil. Also, to determine the qualitative characteristics of the extracted oils, the chemical values of the obtained product – acid value, iodine value, ester value, *etc.* were determined according to the methods described in [14-16].

The results of determination of chemical values of rapeseed and soybean oils obtained from different fractions by extraction with methylene chloride are given in Table 1 and Table 2, respectively. There is also additional comparison of the obtained values with the requirements for the corresponding crude unrefined oils according to the standards of Ukraine, taking into account the absence of purification of the obtained products in the laboratory conditions.

Table 1

Chemical values of rapeseed oil obtained from fractions of different grinding

Parameter	The size of the initial fraction of raw materials				Standards (DSTU 46.072:2003), unrefined grade II
	0.2 mm	0.5 mm	1 mm	mixture	
Density, kg/m ³	1.22	0.98	0.98	0.9	0.911-0.921
IV	65.86	82.46	59.96	122.72	94-106
AV	6.4	4.58	1.71	4.96	≤ 6
EV	156.36	183.31	190.41	205.2	–
SV	162.76	187.89	192.13	210.17	165–180

Note: extractant is methylene chloride

Table 2

Chemical values of soybean oil obtained from fractions of different grinding

Parameter	The size of the initial fraction of raw materials				Standards (DSTU 4534:2006), unrefined
	0.2 mm	0.5 mm	1 mm	mixture	
Density, kg/m ³	0.91	0.92	0.94	0.91	0.922-0.934
IV	124.33	94.73	95.51	119.87	≤ 100
AV	6.39	4.37	2.86	3.94	≤ 4
EV	196.06	179.62	148.47	204.97	–
SV	202.45	183.99	151.33	208.90	186–195

Note: extractant is methylene chloride

A comparative analysis of the determined values of the obtained vegetable oils shows that there is a certain influence of the grade of grinding of the raw material on the quality of the product, because the chemical values of the samples were changed (Tables 1, 2).

It should be noted that in the process of extraction of rapeseed samples, oils with a density slightly higher than the corresponding indicator of unrefined rapeseed oil according to the standards were obtained. Also, compared to this state standard, the extracted oil from the fractions of 0.2 mm, 0.5 mm and 1.0 mm contains a reduced number of unsaturated bonds in the molecules of substances, which shows the IV (Table 1).

At the same time, in the case of rapeseed oil, there is increasing in the AV index with decreasing of the size of the initial raw material fraction, which indicates increasing in the amount of free fatty acids in the extracted oil samples. Also, with decreasing of the raw material size, there is decreasing of the ester value, although these indicators are not normalized for the rapeseed oil (Table 1).

Comparative analysis of chemical values for soybean oil, as well as for rapeseed one, showed the effect of grinding the seeds of raw materials on the quality of the obtained products. According to the obtained values, given in Table 2, all samples of extracted oil have approximate density values to the mentioned standard of Ukraine for soybean oil (Table 2).

The indicators of IV, AV, EV, and SV for the obtained samples of soybean oil increase with decreasing grade of grinding of raw materials (Table 2).

Thus, having conducted a comparative analysis of the chemical values of the obtained samples of rapeseed and soybean oils, we can conclude that the grade of grinding of the raw material affects the quality of the extracted vegetable oil.

Due to the fact that the oil samples obtained by extraction of different fractions had differences in their color, the optical properties of the obtained vegetable oils were additionally studied using the following methods: refractometry (determination of refractive index) and ultraviolet spectroscopy (obtaining transmission spectra).

The refractive index n_d^{20} was measured on an Abbe refractometer as described in the Experimental

section [19]. It is known [20] that the refractive index for rapeseed oil is in the range close to 1.470–1.474, and for soybean – in the range of 1.471–1.475. The results of measuring the refractive index of the obtained oils are given in Table 3.

The obtained refractive indices are close to the reference data [19, 20], although the differences in the experimental results indicate the optical differences of the obtained oils. However, refractometry data cannot be conclusive evidence of differences in qualitative composition.

To clarify and compare the differences, the data of ultraviolet spectroscopy (UV-Vis) of the investigated oils were obtained, as described in the Experimental section. The results of studies of the obtained oil samples from fractions of different grinding on a spectrophotometer are presented in Figs. 2 and 3. Measurements were performed in quartz cells with the path length of 10 mm, without additional dilution of samples with solvent. Samples of oils without dilution were measured in the wavelength range of 220–800 nm.

Fig. 2 shows the data of ultraviolet spectroscopy (UV-Vis) of the obtained samples of rapeseed oil, Fig. 3 – for soybean oil samples.

The obtained spectra of oils are characteristic and do not differ from the UV spectra of pure vegetable oils [21, 22]. The absorbance bands corresponding to the main characteristic components of vegetable oil – higher unsaturated fatty acids – are in the range of 260–460 nm. According to [23] in this range there is the absorbance of higher oxygen-containing compounds of monounsaturated triglycerides. Absorbance in the range of 670–700 nm refers to chlorophyll impurities in oils.

Analysis of the obtained results of ultraviolet spectrometry of the studied samples of rapeseed oil (Fig. 2) showed some differences in the visible region of the spectrum (380–750 nm), which is confirmed by refractometric analysis (Table 3). However, we note that in the ultraviolet region (220–380 nm) changes are almost absent.

As for the distribution of the spectra of rapeseed oil obtained from different crushed fractions, we see the following distribution in the row (Fig. 2):

$$1.0 \text{ mm} > \text{mixture} > 0.5 \text{ mm} > 0.2 \text{ mm}$$

Table 3

Refractive indices of oil samples obtained from fractions of different grinding

Oil	Refractive index			
	0.2 mm	0.5 mm	1 mm	mixture
Rapeseed oil	1.4689	1.4720	1.4726	1.4719
Soybean oil	1.4765	1.4753	1.4787	1.4761

Note: extractant is methylene chloride

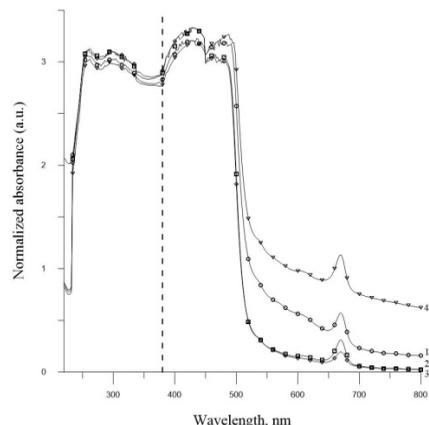


Fig. 2. Normalized UV-vis absorption spectra of test samples of rapeseed oil obtained from different fractions of crushed seeds: mixture (1); 0.5 mm (2); 0.2 mm (3) and 1.0 mm (4)

It should be noted that this series closely correlates with the previously obtained data of refractometric analysis for samples of rapeseed oil (Table 3).

Thus, the spectrum of rapeseed oil obtained from a mixture of crushed fractions is close to the average value (0.5 mm), because the initial size of rapeseed grain is not much larger than the largest investigated fraction (1.5–2 mm), and the mixture contains particles of different size – both close to the size of the grain, and close to the smallest particles.

As for the distribution of spectra obtained from soybean oil samples (Fig. 3), the distribution of spectra is as following:

$$1.0 \text{ mm} > 0.5 \text{ mm} > \text{mixture} > 0.2 \text{ mm}$$

In this case, obviously, the mixture of crushed soybeans contained smaller particles, although the overall picture correlates with the results obtained from different samples of rapeseed oil (Fig. 2).

4. Conclusions

We can conclude that the grinding of vegetable raw materials – rapeseed and soybean oils – has an impact on the qualitative composition of the obtained vegetable oil, in particular on the compounds identified in the visible region of the spectrum (380–750 nm). Since there are almost no changes in the ultraviolet region (220–380 nm), this may indicate that the main components of vegetable oils – higher unsaturated fatty acids and their compounds – are extracted in virtually the same volume, regardless of the grinding method.

The explanation of the nature of changing in the qualitative composition, obviously, refers to the mechanism of extraction in the system “solid – liquid”, different degrees of penetration of the solvent and

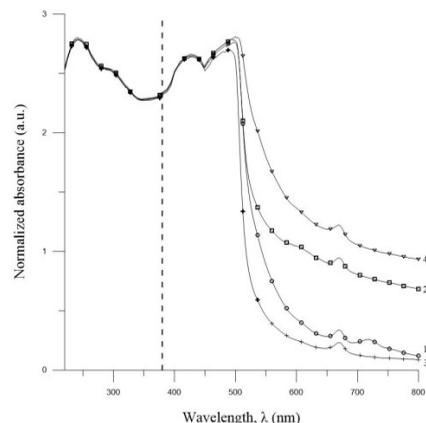


Fig. 3. Normalized UV-vis absorption spectra of test samples of soybean oil obtained from different fractions of crushed seeds: mixture (1); 0.5 mm (2); 0.2 mm (3) and 1.0 mm (4)

solubility of the raw material. The question of significance of the differences in the oils composition requires additional investigations – it is advisable to conduct a study of additional purification of the obtained oils and compare the quality characteristics of the obtained products, as well as to perform spectral studies in the infrared spectrum to compare changes in functional groups of obtained oil samples.

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ВПЛИВ УМОВ ЕКСТРАКЦІЇ НА ЯКІСНИЙ СКЛАД РОСЛИННИХ ОЛІЙ

Анотація. Досліджено вплив умов одержання ріпакової та соєвої олій методом екстракції у системі «тверде тіло – рідина» на якісний склад одержаних рослинних масел. Визначено основні хімічні константи (кислотне число, йодне число, естерне число, число омилення) та оптичні властивості (рефрактометричний показник заломлення та UV-Vis-спектри) для ріпакової та соєвої олій, одержаних екстракцією, при використанні хлористого метилену як розчинника із вихідної рослинної сировини різного ступеня подрібнення (0,2; 0,5 і 1,0 мм) та суміші подрібнених зернових фракцій. Показано, що ступінь подрібнення вихідної сировини впливає на якісний склад одержаного продукту.

Ключові слова: екстракція, система тверде тіло – рідина, рослинна сировина, ріпакова олія, соєва олія, якісний аналіз, рефрактометрія, UV-Vis спектрографія.