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VEGETABLE OILS – RAW MATERIALS FOR PRODUCING BIODIESEL

Abstract. *This paper presents the results of a study of the physical and chemical properties of samples of vegetable oils (sunflower, rapeseed, olive). It has been shown that the viscosity of oils varies from 41.4 to 61.7 cSt at a temperature of 40 ° C for olive and sunflower oils, respectively. The acid numbers of the oil samples were also determined, it was found that the lowest indicator is characteristic of sunflower oil. Pour points of oils also range from -3 to -16 ° C for olive and sunflower oils, respectively. Using the method of IR spectroscopy, functional groups in the composition of samples of vegetable oils were studied and it was shown that the composition of oils contains carbonyl and hydroxyl functional groups, indicating the presence of carboxylic acids. Based on studies of the physical and chemical properties of vegetable oils, it was found that sunflower, olive and rapeseed oils can serve as raw materials for the synthesis of biofuels based on them, since they contain free fatty acids. To obtain biodiesel fuel based on vegetable oils, it is planned to use the transesterification method in the presence of various catalysts (alkaline, acidic, and complex).*

Keywords: *biodiesel fuel, vegetable oils, sunflower oil, rapeseed oil, olive oil, IR spectrum, iodine value.*

Introduction. Currently the global energy policy is based on two fundamental principles - economic rationality and sustainability, the main goal of which is to significantly reduce greenhouse gas emissions, enhance the diversification of initial energy sources, economical and efficient use of resources.

Transport is in the highest demand for energy, accounting for over 40% of the total energy volume. Therefore, there is a need to minimize the use of fossil fuel resources and pay attention to renewable resources such as waste oil to produce cheaper and biodegradable fuels [1].

Biodiesel is a clean, renewable and degradable fuel that has the ability to reduce the greenhouse effect and acid rain with low emissions of carbon monoxide, unburned

hydrocarbons, polycyclic aromatic hydrocarbons and particulate matter [2]. It is known that this fuel can be produced as a result of the transformation of green plants by esterification [3] or transesterification reactions with edible and non-edible oils [4].

In this work, the possibility of producing biodiesel using sunflower, rapeseed and olive oils as raw materials is considered, and the study of their physical and chemical composition and characteristics is the purpose of this work.

Materials and methods. For the study, 3 samples of oils were selected: sunflower seeds, rapeseed and olive oil.

Determination of the density of oil samples was carried out using a hydrometer in accordance with GOST 3900. The essence of the method is to immerse the hydrometer in vegetable oil and take readings on the hydrometer scale.

Studies of the viscosity of oils were carried out in accordance with GOST 33-2000 (ISO 3104-94), the purpose of which is to measure with a calibrated glass viscometer the expiration time, in seconds, of a certain volume of the test liquid under the influence of gravity at a constant temperature. The kinematic viscosity is the product of the measured flow time and the constant viscometer.

To determine the acid number of test samples vegetable oils performed according to GOST P 52110-2003 «Vegetable oils. Methods for determining the acid number».

The infrared spectra of the products of the radiation-chemical modification were recorded at a temperature of 20 ° C on an FTIR-8400S device from Shimadzu.

Results and discussion. The main characteristics of vegetable oil samples are presented in table 1.

Table 1 – Characteristics of raw materials

Description of characteristics	sunflower oil	olive oil	rapeseed oil
Density, kg / m ³	921	918	915
Viscosity, cSt at 40 ° C	61,7	41,4	49,1
Acid number, mg KOH / g	0,44	0,57	0,48
Pour point, ° C	-16	-3	-12

It is known that one of the important signs of the quality of sunflower oil is the acid number, which serves as an indicator of the content of free fatty acids in it and their accumulation. For the test samples of oil value of the acid number from 0.44 to 0.57 was observed, which classifies it as high-class.

The process of producing biodiesel based on vegetable oils can be considered as a reaction of their transesterification with methanol / ethanol with the formation of a mixture of esters of higher aliphatic acids. In this regard, of particular interest is the contents of fatty acids in the original samples of vegetable oils, for determining which was drawn by IR spectroscopy.

Experimental IR spectra of oil samples are shown in Figures 1-3.

The IR spectrum of vegetable oil samples (Figure 1-3), which differs in its raw material in the region of $700\text{-}3000\text{ cm}^{-1}$, contains absorption bands at $2850\text{-}2900\text{ cm}^{-1}$, characteristic of deformation vibrations of C-H bonds of methyl and methylene groups. The absorption bands in the range of $1460\text{-}1370\text{ cm}^{-1}$ are due to CH_2 and CH_3 groups of both long paraffin chains and alkyl substituents in the rings.

Intense absorption bands in the region $1000\text{ - }1300\text{ cm}^{-1}$ characterize the presence of unbranched paraffin chains in hydrocarbons. The presence of a peak of rather high intensity in the region of 700 cm^{-1} , which is an analytical band of vegetable oil, is noted [5].

The presence of vibrations of carboxylic acid groups in the studied oils is associated with absorption bands caused by stretching vibrations of C – O bonds (frequency 1750 cm^{-1}) with bending vibrations of OH groups (frequencies $2950\text{-}2800\text{ cm}^{-1}$), which indicates a high content of oils of fatty carboxylic acids.

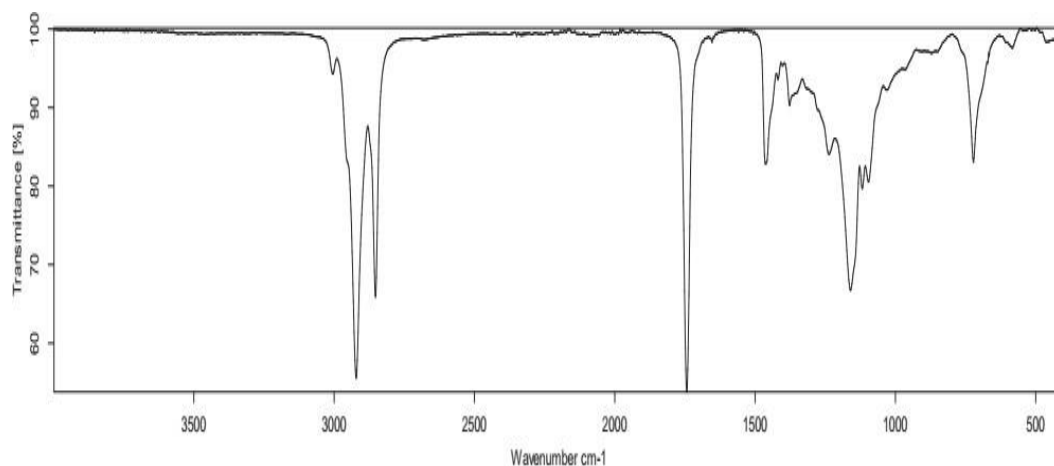


Figure 1 – IR - spectra of a sample of sunflower oil

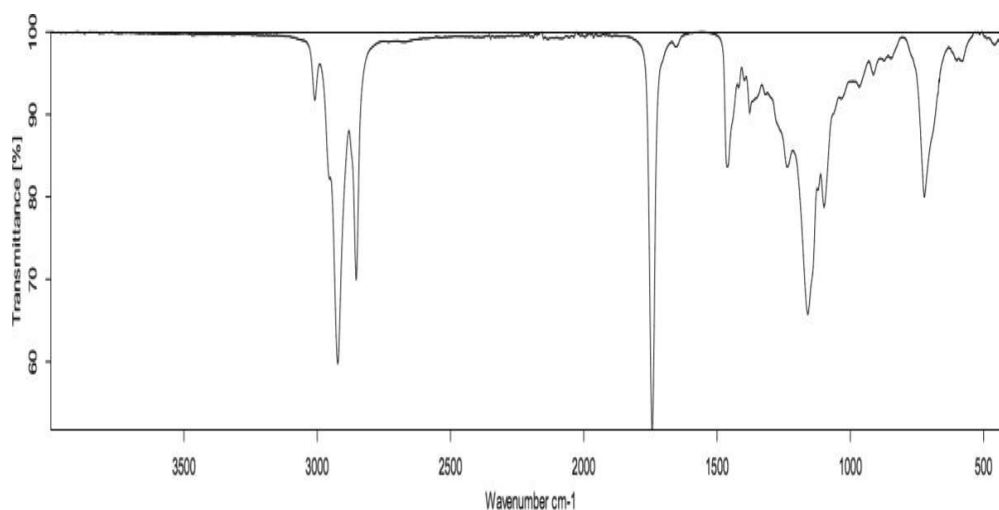


Figure 2 – IR - spectra of a sample of olive oil

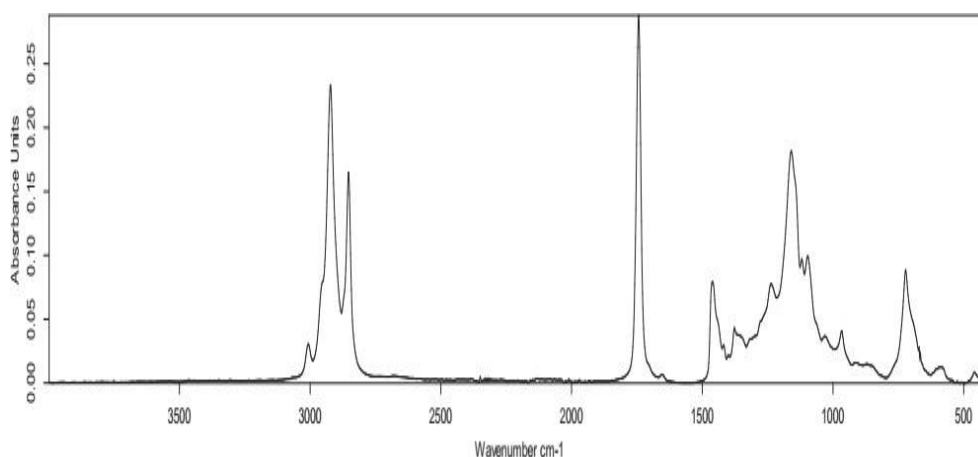


Figure 3 – IR - spectra of a sample of rapeseed oil

In the paper [6] in an analytical bands in the IR spectra is proposed to use oil absorption band at 900 cm^{-1} , which is formed by the stretching vibration of C-C bonds between carbon CH_2 -groups and carbon atoms belonging to the unsaturated bonds. It is known that the spectral composition of vegetable oils is determined by the presence of lipid molecules containing fatty acids. In this connection, they are in second analytical absorption band range can be considered 3000 cm^{-1} , characteristic stretching vibrations of CH-unsaturated fatty acid portions of chains. A change in the degree of unsaturation of these chains is naturally reflected in the intensity of these bands, which makes it possible to use them to estimate the relative content of unsaturated acids in vegetable oils.

The results of evaluating the refractive index (n_D) and iodine number (ID), which summarize the unsaturation of fatty acids and fat-soluble compounds in the oil are presented in the graph (Figure 4).

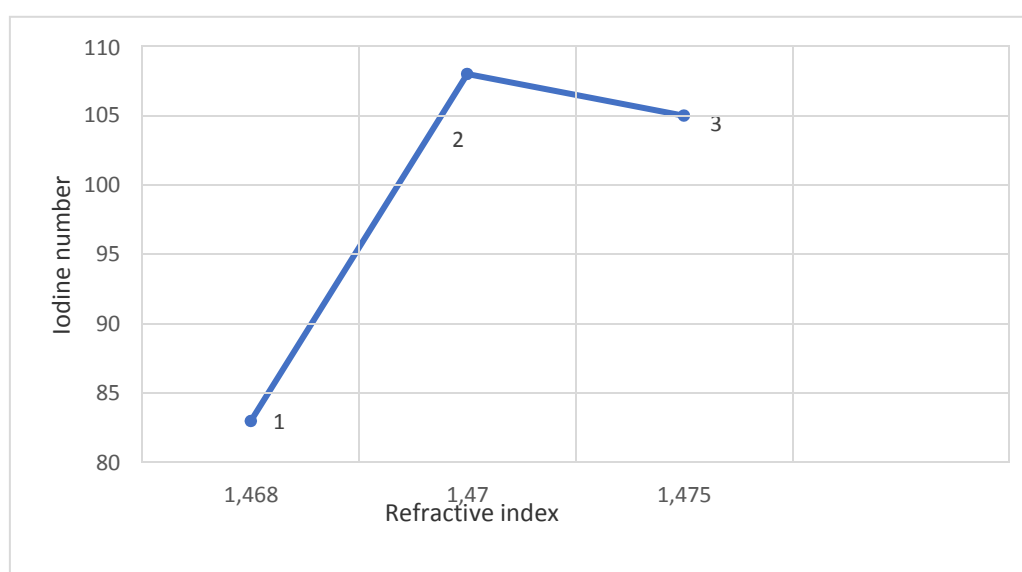


Figure 4 – Results of refractometric analysis of an experimental series of vegetable oils:
1 – olive oil, 2 – sunflower oil, 3 – rapeseed oil

The observed noticeable differences in the ratio of the refractive index and iodine number of vegetable oil samples demonstrate rather high refractive indices and iodine numbers for sunflower and rapeseed oils, which makes it possible to adequately assess the increase in the content of C = C bonds in the composition of triglyceride fatty acids with an increase in their unsaturation [7-10].

Conclusion. Thus, the chemical composition, physical and physicochemical indicators of the original and used sunflower vegetable oil have been investigated and high prospects have been revealed for their use with affordable and cheap raw materials for the production of fatty esters and alcohols. It is known in Kazakhstan the greatest demand is for sunflower and rapeseed oil, while in the world – palm and soybean, which implies the development of the topic of obtaining biodiesel directly from palm and soybean oils. Based on the results obtained, the article reveals that sunflower and rapeseed oils are not inferior to the rest in terms of their physical and chemical characteristics and composition, and they can be used as raw materials for the production of biodiesel fuel.

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ӨСІМДІК МАЙЛАР – БИОДИЗЕЛЬ ӨНДІРУГЕ АРНАЛҒАН ШИКІЗАТ МАТЕРИАЛДАРЫ

Аңдатпа. Бұл жұмыста өсімдік майлары үлгілерінің (күнбағыс, рапс, зәйтүн) физикалық-химиялық қасиеттерін зерттеу нәтижелері келтірілген. Зәйтүн және күнбағыс майлары үшін 40 ° С температурада майлардың тұтқырлығы сәйкесінше 41,4-тен 61,7 сСт-ға дейін өзгеретіні көрсетілген. Май сынамаларының қышқылдық саны да анықталды, ең төменгі көрсеткіш күнбағыс майына тән екендігі анықталды. Майдың құйылу нүктелері сәйкесінше зәйтүн және күнбағыс майлары үшін -3-тен -16 ° С-қа дейін болады. ИҚ-спектроскопия әдісін қолдана отырып, өсімдік майлары сынамаларының құрамындағы функционалды топтар зерттелді және майлардың құрамында карбон қышқылдарының бар екендігін көрсететін карбонил және гидроксил функционалды топтары бар екендігі көрсетілді. Өсімдік майларының физикалық-химиялық қасиеттерін зерттеу негізінде күнбағыс, зәйтүн және рапс майлары олардың негізінде биоотын синтезі үшін шикізат бола алады, өйткені құрамында бос май қышқылдары бар екендігі анықталды. Өсімдік майлары негізінде биодизель отынын алу үшін әр түрлі катализаторлардың қатысуымен трансэтерификация әдісін қолдану жоспарланған (сілтілі, қышқылдық және кешендік).

Түйін сөздер: биодизель отыны, өсімдік майлары, күнбағыс майы, рапс майы, зәйтүн майы, ИҚ спектрі, йод құндылығы.

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РАСТИТЕЛЬНЫЕ МАСЛА – СЫРЬЕ ДЛЯ ПОЛУЧЕНИЯ БИОДИЗЕЛЯ

Аннотация. В данной работе представлены результаты исследования физико-химических свойств образцов растительных масел (подсолнечное, рапсовое, оливковое). Показано, что вязкость масел варьируется от 41,4 до 61,7 сСт при температуре 40 °С для оливкового и подсолнечного масел, соответственно. Также определены кислотные числа образцов масел, выявлено, что наиболее низким показателем характеризуется подсолнечное масло. Температуры застывания масел также находятся в пределах от -3 до -16 °С для оливкового и подсолнечного масел соответственно. С привлечением метода ИК-спектроскопии исследованы функциональные группы в составе образцов растительных масел и было показано, что в составе масел присутствует карбонильная и гидроксильная функциональные группы, указывающие на наличие карбоновых кислот. На основании исследований физико-химических свойств растительных масел было установлено, что подсолнечное, оливковое и рапсовое масла могут служить сырьем для синтеза на их основе биотоплив, так как содержат свободные жирные кислоты. Для получения биодизельного топлива на основе растительных масел планируется применить метод переэтерификации в присутствии различных катализаторов (щелочных, кислотных, а также комплексных).

Ключевые слова: биодизельное топливо, растительные масла, подсолнечное масло, рапсовое масло, оливковое масло, ИК-спектр, йодное число.