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THE ASSESSMENT OF SUSTAINABILITY INDICATORS FOR TRIGLYCERIDES TRANSESTERIFICATION WITH ALCOHOLS CATALYZED BY ION EXCHANGE RESINS

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The research was aimed at determining the dependences of sustainability indicators on the parameters of the sunflower oil transesterification with ethyl, propyl, and butyl alcohol catalyzed by anion exchange resin AV-17-8 with OH^- ions or cation exchange resin KU-2-8 with H^+ or immobilized Zn^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} ions. Such sustainability indicators as the E-factor, atomic efficiency, mass intensity and mass productivity, reaction mass efficiency, stoichiometric factor, etc., have been determined. We established that sustainability indicators of transesterification catalyzed by ion exchange resins depend on the yield of higher fatty acid esters that can be achieved by immobilized metal ions. The unreacted alcohol regeneration significantly reduces the E-factor value and increases the reaction mass efficiency. During the sunflower oil ethanolysis, the minimum E-factor value is achieved at the ethyl alcohol:triglyceride molar ratio corresponding to the maximum yield of higher fatty acid esters. The reaction mass efficiency calculated without considering the unreacted alcohol regeneration is one of the criteria for determining its regeneration expediency. The sustainability indicators are the additional criteria for selecting optimal conditions of the sunflower oil transesterification with aliphatic alcohols catalyzed by ion exchange resins. The calculated sustainability indicators indicate that the investigated ion exchange resins as heterogeneous transesterification catalysts provide a high yield of higher fatty acid esters. Using the researched catalysts ensures a low E-factor, making the process environmentally friendly.

Keywords: transesterification, sunflower oil, alcohol, ion exchange resin, sustainability indicator.

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Introduction

Methyl, ethyl, propyl, and butyl esters of higher fatty acids are used as biofuel, raw materials for synthesizing fatty alcohols, surface-active substances, and plasticizers for paints, varnishes, and polymers, etc. Triglyceride transesterification is the process of green chemistry and green engineering. It is primarily due to the possibility of obtaining methyl esters of higher fatty acids used as diesel fuel, but also due to the use of renewable raw materials. It is important not only to reduce the waste amount, but also to ensure the efficient use of raw materials for the transesterification process. These requirements are achieved primarily by using effective transesterification catalysts.

Both basic and acidic homogeneous and heterogeneous catalysts are used for triglyceride transesterification with alcohols [1]. The raw materials for transesterification processes are purified or refined oil (rapeseed, soybean, sunflower, palm, etc.), crude or waste cooking oil, microalgae oil, and animal fats [1]. Methyl alcohol is the most widely used among alcohols, although other lower aliphatic alcohols, such as ethyl [2], butyl alcohol [3], etc., are widely used.

Today, the only manufacturing method of higher fatty acids esters implemented in the industry is triglyceride transesterification with methyl alcohol catalyzed by potassium or sodium hydroxide or alcoholate [4]. These catalysts provide a high yield of methyl esters of higher fatty acids under sufficiently mild conditions. For example, the rapeseed oil or a sunflower and corn oil mixture transesterification with methyl alcohol at 1 wt.% catalyst content of potassium hydroxide, the alcohol:triglyceride molar ratio of 6:1, a temperature of 60^0C, and a stirring speed of the reaction mixture of 300 rpm provides a methyl esters yield of more than 96.5% [5].

Despite the indicated advantages of using basic homogeneous catalysts, triglyceride transesterification by alcohols implemented in the industry has several disadvantages. Foremost, it requires expensive refined oil and anhydrous alcohol to avoid triglyceride saponification and neutralizing of free fatty acids to form soap. The specified side reactions significantly complicate the products' separation and worsen the process's environmental friendliness.

Currently, two methods are used to process crude or waste cooking oil. The first method is the two-stage oil transesterification process. At the first stage, the esterification of oils with a high acid value, and therefore with a high acid content, is carried out in the acid catalysts presence. At the second stage, triglyceride transesterification is carried out in the presence of potassium or sodium hydroxide or alcoholate as a homogeneous basic catalyst [6].

The previous esterification reduces free fatty acid content by 99% in raw oil materials [7]. The reaction catalyzed by 2% sulfuric acid as the homogeneous catalyst is carried out with water separation to achieve high fatty acids conversion. The reaction temperature is 70^0C, and the methyl alcohol: triglyceride molar ratio is 6:1. This method's disadvantages of crude or waste cooking oil transesterification are neutralizing the acid catalyst, and washing and drying the reaction mixture after the esterification. Along with increasing the process duration and equipment metal intensity, these additional operations also cause the formation of waste and wastewater additional amount.

Heterogeneous acid catalysts can also be used at the first stage of the two-stage process in the used or crude oil processing. For example, KU-2-8 cation exchange resin is an effective esterification catalyst [8]. The use of a heterogeneous catalyst excludes its neutralizing and washing step before the second stage of the transesterification process, significantly simplifying the process and reducing the amount of wastewater.

The heterogeneous basic and acid catalysts are used in the second method of higher fatty acid ester obtaining. Here, the transesterification process occurs in one stage. The use of heterogeneous catalysts has significant advantages compared to homogeneous catalysts, such as the catalyst separation from the reaction mixture, the absence of their neutralizing, and the catalyst reusing.

In particular, the use of Amberlyst A26 (OH) as a heterogeneous base catalyst for of jatropha oil transesterification with ethyl alcohol at a temperature of 55^0C, the ethyl alcohol:oil molar ratio of 35:1, and the catalyst amount of 15% provides the yield of higher fatty acids ethyl esters of 36.31% in 540 min [2]. Amberlyst 45, as a heterogeneous acid catalyst, makes it possible to use raw oil materials with acid content corresponding to the acid value of 2.5 mg KOH/g and alcohols with a water content of up to 10–20% [9]. The catalyst provides the yield of higher fatty acid esters of 80 and 84% by methanolysis and ethanolysis, respectively. By sunflower oil transesterification with ethyl or 1-butyl alcohol catalyzed by solid metal oxides, such as nickel (II) oxide or zinc oxide, the triglyceride conversion is over 97% [10–12]. The cation exchange resin KU-2-8 with H^+ or immobilized metal ions are effective catalysts for the sunflower oil transesterification with ethyl, 1-propyl, 2-propyl, and 1-butyl alcohols [13]. The catalysts provides the triglyceride conversion of 90.6% (KU-2-8) by ethanolysis, 97.6% and 99.7% (KU-2-8/Sn^{2+} and KU-2-8/Ni^{2+}, respectively) by propanolysis, and 79.1% (KU-2-8/Ni^{2+}) by butanolysis. The advantages of the heterogeneous catalysts are the possibility of their separation from the reaction mixture by filtration and the almost complete absence of wastewater and waste.

Green chemistry processes are important for the chemical industry [14–16]. Sustainability indicators are widely used for the quantitative assessment of the environmental efficiency of technological processes, including transesterification [16]. The conditions of the transesterification process significantly affect the sustainability indicators.

Therefore, it is important to research the conditions influence of the oils transesterification with alcohols catalyzed by ion-exchange resins as heterogeneous catalysts on the sustainability indicators and evaluate the efficiency of these catalysts from the viewpoint of these indicators.

The research was aimed at studying the conditions influence of the sunflower oil transesterification with C_2–C_4 alcohols catalyzed by ion exchange resins on sustainability indicators.

Experimental

The sunflower oil (according to the state standard DSTU 4492:2017), ethyl alcohol (according to the state standard DSTU 4221:2003), 1-propyl alcohol (reagent grade), and 1-butyl alcohol (reagent grade) were used as raw materials. Before use, ethyl alcohol was dehydrated over calcined magnesium sulfate to a water content of no more than 0.05 vol.%. Anion exchange resin AV-17-8 with OH^- ions, cation exchange resin KU-2-8 with H^+ or immobilized Zn^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} ions were used as transesterification catalysts. The sunflower oil transesterification with aliphatic alcohols and the reaction product analysis were carried out using the methods described elsewhere [13]. The saponification number of sunflower oil was 201±2 mg KOH/g. It correspond the average molar mass of acids as triglyceride component of 279±2 g/mol. The average molar mass of sunflower oil calculated from these data was 876±6 g/mol. The acid value of sunflower oil was 0.50±0.02 mg KOH/g [12].

We used the sustainability indicators given in ref. [16] to characterize the sunflower oil transesterification with aliphatic alcohols from the viewpoint of the process environmental efficiency. Since ion-exchange resins, which can be easily separated from the reaction products by filtration, were used as a catalyst, the catalyst can be reused [17]. So the catalyst's mass was not considered in the calculations. In addition, it was also taken into account that since the reaction products after the catalyst separation do not require neutralizing and washing, the glycerol formed in the reaction can be used as a target product.

The E-factor is an indicator of the process environmental acceptability. A high value of the E-factor indicates a large amount of generated waste and significant environmental harm caused by the manufacturer [16]. We calculated the E-factor value in two ways. One is without considering the possible regeneration of unreacted alcohol, and the second is taking into account the regeneration of alcohol (for example, using distillation).

The E-factor was calculated using the following equation:

$$E_f = \frac{m_w}{m_p}, \tag{1}$$

where m_w is the mass of waste produced during the sunflower oil transesterification (kg); and m_p is the mass of the reaction products (higher fatty acids esters and glycerol) (kg).

The atom economy indicator characterizes environmental sustainability by minimizing the theoretical amount of waste [16]. The effectiveness of its application is significantly limited since atom economy does not consider the yield of the target product. Therefore, it is more appropriate to use the atom efficiency indicator, which is the product of the atom economy and the yield of the target product.

Atom efficiency (AE) was calculated using the following equation:

$$AE = \frac{\nu_e M_e}{\nu_{tg} M_{tg} + \nu_a M_a} \cdot \eta, \tag{2}$$

where M_i is the average molar mass of higher fatty acid esters and triglyceride, respectively, (g/mol); ν_i is stoichiometric coefficients of ester, triglyceride and alcohol, respectively; and η is the yield of higher fatty acid esters (%).

Mass intensity (MI) and mass productivity (MP) were calculated according to the following equations:

$$MI = \frac{\sum m_i}{m_p}, \tag{3}$$

$$MP = \frac{1}{MI} \cdot 100, \tag{4}$$

where Σm_i is the sum of the masses of all substances used in the process (kg).

A mass intensity of 1 kg/kg is an ideal value. The higher value of MI means less perfection in the process considering the environment.

Reaction mass efficiency (RME) was determined by the following equation:

$$RME = \frac{1}{1 + E_f}, \tag{5}.$$

Since the use of studied catalysts allows regenerating unreacted alcohol, its excess amount we considered as a solvent, and the solvent's mass should not be considered when calculating atom utilization (AU) [16]. Therefore, AU was calculated according to the following equation:

$$AU = \frac{m_p}{\sum m_{p,i} - m_a}, \tag{6}$$

where $\Sigma m_{p,i}$ is the sum of the all products masses (kg); and m_a is the mass of unreacted alcohol (kg).

Solvent and catalyst environmental impact parameter (f) was determined by the following equation:

$$f = \frac{\sum m_i}{m_e}, \tag{7}$$

where m_e is the mass of obtained higher fatty acid esters.

Stoichiometric factor (SF) was calculated according to the equation

$$SF = 1 + \frac{AE \cdot \sum m_{a,exc}}{m_{e,t}}, \qquad (8)$$

where $m_{a,exc}$ is the alcohol mass excess over its stoichiometric quantity (kg); and $m_{e,t}$ is the mass of higher fatty acid esters provided their yield of 100% (kg).

Results and discussion

We used the experimental results concerning the sunflower oil transesterification with C_2–C_4 alcohols catalyzed by ion exchange resins to calculate sustainability indicators (Table 1).

As can be seen from Table 1, the waste mass significantly depends on the yield of higher fatty acid esters. Obviously, the influence of a catalyst on sustainability indicators is primarily determined by the yield of esters of higher fatty acids achieved in the presence of the studied catalyst (Table 2). In the case of incomplete oil conversion, the above-mentioned intermediate reaction products remain in the esters of higher fatty acids after the separation of glycerol and unreacted alcohol. However, they should be classified as waste since their properties do not correspond to the properties of the esters of higher fatty acids. It is evident that the increase in the amount of waste results in the deterioration of the values of sustainability indicators (Table 2).

We used the experimental results [13,15] to determine the dependences of sustainability indicators on the reagents molar ratio and catalyst content.

The dependence E-factor vs. the ethyl alcohol:triglyceride molar ratio catalyzed by 2 wt.% H-cation exchange resin KU-2-8 without the alcohol regeneration after ethanolysis shows a minimum (Fig. 1,a). The minimum E-factor is 0.121 at the ethyl alcohol:triglyceride molar ratio of 5:1. This corresponds to the reagents optimal molar ratio of (4–5):1 [13]. However, considering the low boiling point of ethyl alcohol, it is advisable to regenerate the alcohol from the reaction products. On this, the minimum of the E-factor (0.022) is by the regeneration of unreacted alcohol at the ethyl alcohol: triglyceride molar ratio of 5:1. In this case, the E-factor is approximately six times lower than without alcohol regeneration. When the molar excess of ethyl alcohol increases, the E-factor remains practically unchanged (Fig. 1,a). Such results are because a significant amount of unreacted ethyl alcohol remains in the reaction products by high molar alcohol excess

Table 1

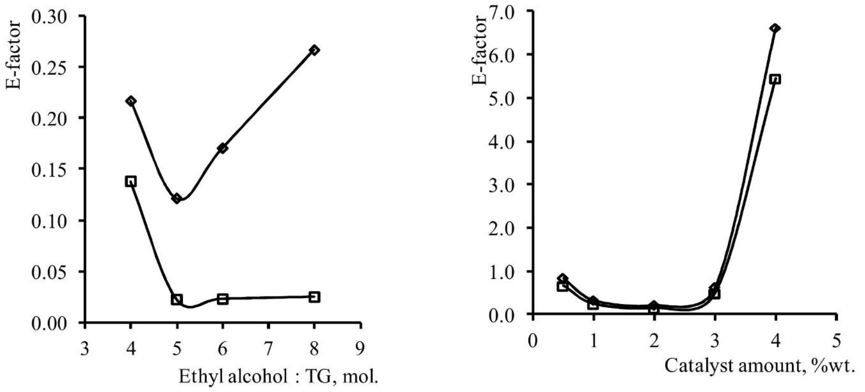
The input data for the sustainability indicators calculation. The catalyst content is 2 wt.%

Catalyst	η, %	Reagents, g			Products, g		Waste, g	
		$m_{tg,0}$	$m_{a,0}$	m_{cat}	m_g	m_e	without alcohol regeneration, m_w	with alcohol regeneration, m_w'
The ethyl alcohol:triglyceride molar ratio is 4:1, the reaction temperature is 353 K								
KU-2-8/H$^+$	88.3	55.665	12.200	1.357	5.152	51.747	12.323	7.851
KU-2-8/Zn^{2+}	66.9	54.037	11.800	1.317	3.785	38.018	25.351	19.229
KU-2-8/Sn^{2+}	82.5	54.016	11.800	1.318	4.667	46.876	15.590	10.791
KU-2-8/Ni^{2+}	51.9	53.857	11.800	1.313	2.928	29.409	34.633	27.225
KU-2-8/Co^{2+}	51.4	54.225	11.800	1.321	2.921	29.339	35.085	27.667
KU-2-8/Cu^{2+}	45.1	53.894	11.800	1.314	2.546	25.569	38.893	30.912
The 1-propyl alcohol:triglyceride molar ratio is 4:1, the reaction temperature is 353 K								
KU-2-8/H$^+$	64.7	36.099	10.200	0.926	2.446	25.684	19.095	13.681
KU-2-8/Zn^{2+}	85.7	36.950	10.450	0.948	3.320	34.858	10.171	6.216
KU-2-8/Sn^{2+}	92.7	35.835	10.200	0.927	3.481	36.550	6.931	3.541
KU-2-8/Ni^{2+}	97.0	35.988	10.200	0.924	3.659	38.416	5.037	1.996
KU-2-8/Co^{2+}	92.4	36.677	10.450	0.943	3.551	37.280	7.239	3.735
KU-2-8/Cu^{2+}	82.0	71.302	20.664	1.839	6.130	64.367	23.309	14.638
AV-17-8	53.5	36.692	10.450	0.943	2.057	21.595	24.433	18.007
The 1-butyl alcohol:triglyceride molar ratio is 10:1, the reaction temperature is 383 K								
KU-2-8/H$^+$	54.2	108.062	94.770	2.878	6.139	67.266	132.305	52.349
KU-2-8/Zn^{2+}	51.7	53.402	45.855	2.015	2.894	31.713	66.665	27.794
KU-2-8/Sn^{2+}	49.2	108.227	95.580	4.076	5.574	61.076	141.232	59.104
KU-2-8/Ni^{2+}	54.6	110.652	97.200	4.157	6.334	69.395	136.280	54.363
KU-2-8/Co^{2+}	42.0	110.050	96.390	4.129	4.846	53.098	152.624	67.929
KU-2-8/Cu^{2+}	24.4	108.755	95.580	4.087	2.780	30.460	175.182	86.310

Table 2

Sustainability indicators of sunflower oil transesterification with C_2–C_4 alcohols catalyzed by ion exchange resins. The catalyst content is 2 wt.%

Catalyst	E_f	AE, %	MI	MP, %	RME, %	AU, %	f	SF
The ethyl alcohol:triglyceride molar ratio is 4:1, the reaction temperature is 353 K								
KU-2-8/H^+	0.138	80.3	1.217	82.2	87.9	87.9	1.338	1.054
KU-2-8/Zn^{2+}	0.460	60.8	1.606	62.2	68.5	68.5	1.766	1.053
KU-2-8/Sn^{2+}	0.209	75.0	1.302	76.8	82.7	82.7	1.432	1.053
KU-2-8/Ni^{2+}	0.842	47.2	2.071	48.3	54.3	54.3	2.277	1.054
KU-2-8/Co^{2+}	0.858	46.8	2.088	47.9	53.8	53.8	2.295	1.052
KU-2-8/Cu^{2+}	1.099	41.0	2.383	42.0	47.6	47.6	2.621	1.053
The 1-propyl alcohol:triglyceride molar ratio is 4:1, the reaction temperature is 353 K								
KU-2-8/H^+	0.486	59.0	1.679	59.6	67.3	67.3	1.839	1.064
KU-2-8/Zn^{2+}	0.163	78.3	1.266	79.0	86.0	86.0	1.387	1.065
KU-2-8/Sn^{2+}	0.088	84.6	1.173	85.2	91.9	91.9	1.285	1.066
KU-2-8/Ni^{2+}	0.047	88.6	1.120	89.3	95.5	95.5	1.226	1.065
KU-2-8/Co^{2+}	0.091	84.4	1.177	84.9	91.6	91.6	1.289	1.066
KU-2-8/Cu^{2+}	0.208	74.9	1.331	75.2	82.8	82.8	1.457	1.070
AV-17-8	0.761	48.8	2.033	49.2	56.8	56.8	2.227	1.066
The 1-butyl alcohol:triglyceride molar ratio is 10:1, the reaction temperature is 383 K								
KU-2-8/H^+	0.713	49.7	2.802	35.7	58.4	58.4	3.058	1.527
KU-2-8/Zn^{2+}	0.803	47.4	2.926	34.2	55.5	55.5	3.193	1.512
KU-2-8/Sn^{2+}	0.887	45.0	3.119	32.1	53.0	53.0	3.404	1.533
KU-2-8/Ni^{2+}	0.718	46.8	2.800	35.7	58.2	58.2	3.055	1.499
KU-2-8/Co^{2+}	1.172	38.5	3.634	27.5	46.0	46.0	3.966	1.527
KU-2-8/Cu^{2+}	2.597	22.4	6.270	15.9	27.8	27.8	6.842	1.529



a **b**

Fig. 1. The E-factor vs. the ethyl alcohol: triglyceride molar ratio (a) and the catalyst content in the reaction mixture (b): ◇ – without alcohol regeneration, and □ – with alcohol regeneration

without its regeneration.

The dependence E-factor vs. the catalyst amount at the ethyl alcohol:triglyceride molar ratio 4:1 has an identical character both with regeneration and without ethyl alcohol regeneration (Fig. 1,b). The minimum of the E-factor in both cases is when the catalyst content is 2 wt.%. The E-factor is 0.138 and 0.217, respectively. An increase in the content of the cation exchange resin KU-2-8 with H^+ ions of more than 3 wt.% leads to a sharp increase in E-factor (by 30–40 times). This result is primarily associated with a sharp decrease in triglyceride conversion and a low yield of higher fatty acid esters. Ethyl alcohol is an «environmentally friendly» substance manufactured by using renewable raw materials. This fact should be considered together with the low E-factor of the sunflower oil ethanolysis.

The E-factor dependences on the alcohol:triglyceride molar ratio by the sunflower oil butanolysis and ethanolysis catalyzed by 2 wt.%

cation exchange resin KU-2-8 with immobilized Ni^{2+} ions are different (Fig. 2,a). In particular, the butanolysis E-factor is almost an order of magnitude higher than the ethanolysis E-factor. Suppose that the E-factor is calculated without considering the alcohol regeneration. In that case, a slight decrease to 1.717 is observed when the alcohol: triglyceride molar ratio increases from 6:1 to 8:1. When the butyl alcohol:triglyceride molar ratio increases to 10:1, the E-factor increases by less than 5% (Fig. 2). The high E-factor (1.7–2.0) is due to the low triglyceride conversion, which does not exceed 55%, even with the butyl alcohol:triglyceride molar ratio of 10:1. Since the unreacted butyl alcohol from the reaction mixture is regenerated by distillation, it is more appropriate to focus on the E-factor calculated considering the alcohol regeneration. In this case, the E-factor decreases linearly from 1.196 to 0.718 in the range of the butyl alcohol:triglyceride molar ratio of (6–10):1.

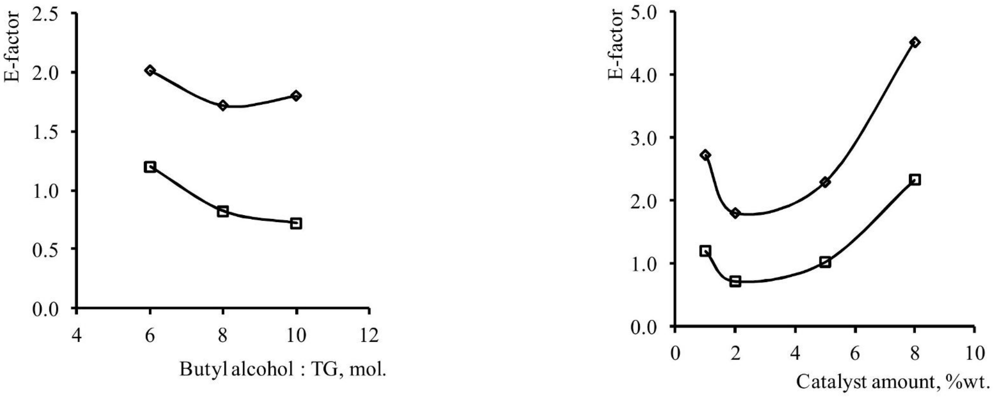
The E-factor dependence on the amount of cation exchange resin KU-2-8 with immobilized Ni^{2+} ions as a catalyst by the sunflower oil butanolysis at the butyl alcohol:triglyceride molar ratio 10: 1 has a pronounced minimum (Fig. 2,b). A high value of E-factor by catalyst content of 1–8 wt.% is due to a low triglyceride conversion and therefore a low yield of butyl esters of higher fatty acids. The minimum E-factor (0.718) of the sunflower oil butanolysis is observed at the optimal catalyst content of 2 wt.% (Fig. 2,b).

The transesterification atom efficiency calculated from the molecular masses of triglyceride, alcohol, and the corresponding ester, is 0.909, 0.913, and 0.916 for ethyl alcohol, 1-propyl alcohol, and 1-butyl alcohol, respectively. The atom efficiency, which also relates to the yield of the higher fatty acid esters, is lower and primarily determined by the yield of higher fatty acid esters (Table 2).

The mass intensity of the sunflower oil ethanolysis catalyzed by 2 wt.% H-cation exchange resin KU-2-8 has a minimum reached when the ethyl alcohol: triglyceride molar ratio is 5:1 (Fig. 3,a). A further slight increase of this indicator, despite the 100% yield of ethyl esters of higher fatty acids, is obviously associated with the use of an ethyl alcohol significant excess. The qualitative dependence of the mass intensity on the butyl alcohol:triglyceride molar ratio is similar. However, the mass intensity of the sunflower oil butanolysis catalyzed by 2 wt.% cation exchange resin KU-2-8 with immobilized Ni^{2+} ions is significantly higher than the ideal value of this indicator. The mass intensity of the triglyceride transesterification with butyl alcohol ranges from 2.717 to 3.013. Such high mass intensity is caused by a significant molar excess of alcohol over the theoretical and incomplete triglyceride conversion, which does not exceed 55%. The dependence of mass intensity on the catalyst content for ethanolysis at a molar ratio of ethyl alcohol:triglyceride=4:1 and butanolysis at a molar ratio of butyl alcohol:triglyceride=10:1 is shown in Fig. 3,b.

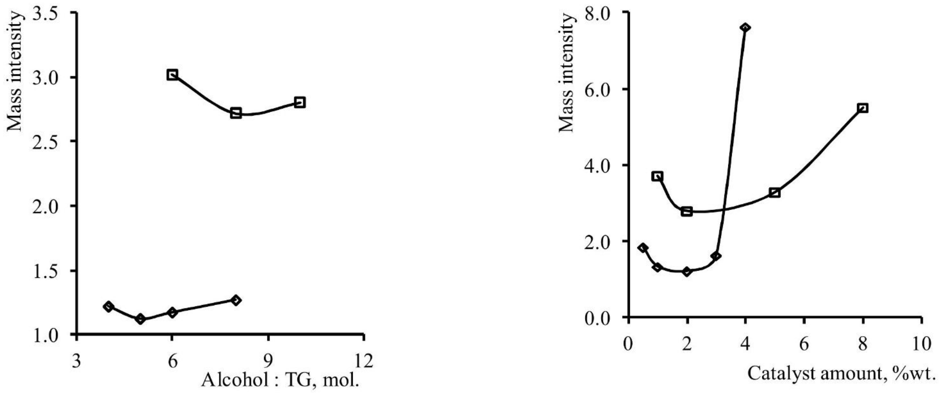
Comparison of the calculated E-factor values with those reported in the literature [16] demonstrates the high environmental friendliness of the process, especially when using a molar ratio of ethyl alcohol:TG=(5–6):1 with ethyl alcohol regeneration (Table 3).

The mass productivity dependences for reactions involving ethyl and butyl alcohol are opposite to their mass intensity. These dependences are naturally based on the calculation formula for



a **b**

Fig. 2. The E-factor vs. the butyl alcohol: triglyceride molar ratio (a) and the catalyst content in the reaction mixture (b): ◇ – without alcohol regeneration, and □ – with alcohol regeneration



a b

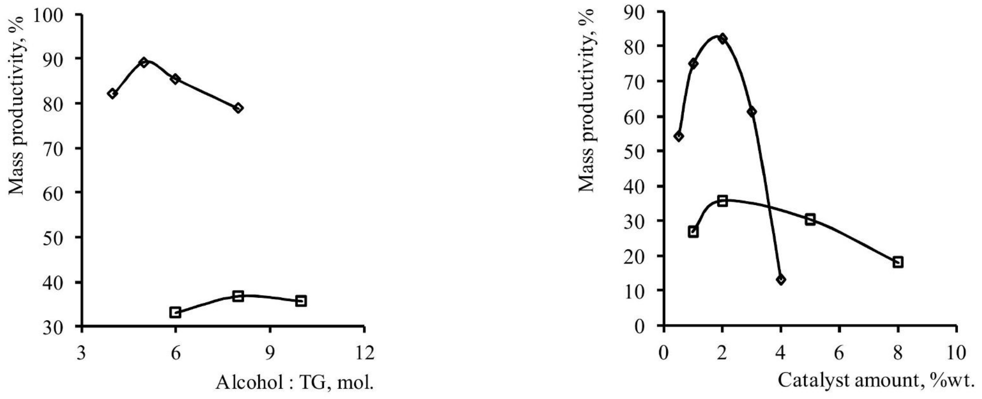
Fig. 3. The mass intensity vs. the alcohol; triglyceride molar ratio (a) and the catalyst content in the reaction mixture (b): ◇ – ethyl alcohol, and □ – butyl alcohol

Table 3

The E-factor of vegetables oil triglycerides transesterification with ethyl alcohol

Catalyst	Catalyst content	Ethyl alcohol: triglyceride molar ratio	Temperature, K	E_f
KU-2-8/Sn^{2+}	2 wt.%	4:1	353	0.209
KU-2-8/H^{+}	2 wt.%	4:1	353	0.138
KU-2-8/H^{+}	2 wt.%	5:1	353	0.022
KU-2-8/H^{+}	2 wt.%	6:1	353	0.023
NaOH [16]	1 wt.%	6 : 1	353	0.131

mass intensity (Fig. 4). The mass productivity indicator of the sunflower oil ethanolysis catalyzed by 2 wt.% H-cation exchange resin KU-2-8 reaches almost 90% under optimal conditions (Fig. 4,a). It was found that changing the catalyst content for the sunflower oil ethanolysis at the ethyl alcohol:triglyceride molar ratio of 4:1 significantly affects mass productivity (Fig. 4,b). When increasing the catalyst amount in the reaction mixture to 4 wt.%, there is a sharp (up to 13.1%) decrease in mass productivity. This value is even 1.38–2.72 times lower than the mass productivity indicator for triglyceride transesterification with butyl alcohol. Obviously, the sharp decrease in the mass productivity of the sunflower oil ethanolysis due to a significant decrease in the triglyceride conversion and consequently the ethyl esters yield of higher fatty acids are associated with an increase in the catalyst



a b

Fig. 4. The mass productivity vs. the alcohol:triglyceride molar ratio (a) and the catalyst content in the reaction mixture (b): ◇ – ethyl alcohol, and □ – butyl alcohol

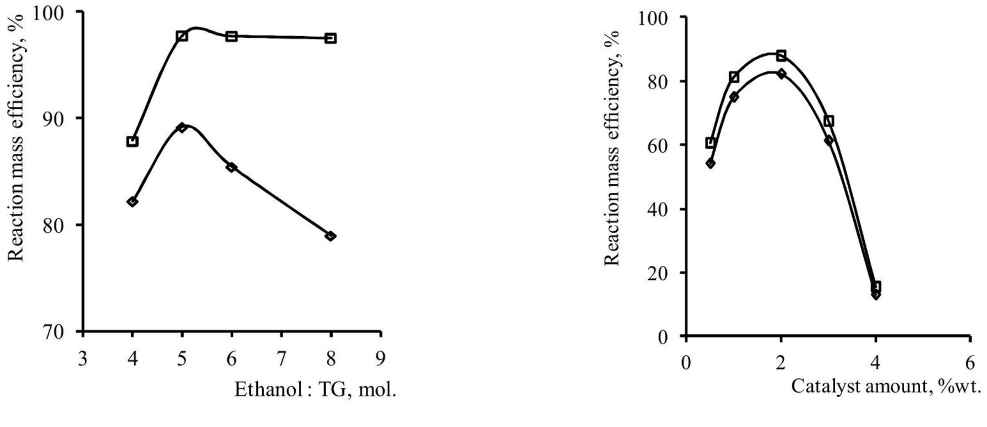
content in the reaction mixture.

The reaction mass efficiency is important for assessing the process environmental impact. This indicator allows us to simultaneously consider the reaction stoichiometry, the yield, and the atom economy indicator. Given that the reaction mass efficiency is related to the E-factor (Eq. (5)), its dependence on the ethyl alcohol: triglyceride molar ratio (catalyst is H-cation exchange resin KU-2-8, 2 wt.%) and the content of the catalyst at the ethyl alcohol:triglyceride molar ratio of 4:1 will be inverse to the dependence on the E-factor (Fig. 5). If the regeneration of unreacted ethyl alcohol is not taken into account when calculating the reaction mass efficiency, then the dependence of the reaction mass efficiency on the alcohol:triglyceride molar ratio will have an extremum with a maximum of 89.2%. This extremum is reached at the alcohol:triglyceride molar ratio of 5:1. A further increase in excess alcohol, despite the ethyl esters yield of 100%, decreases the reaction mass efficiency to 79.0% when the alcohol:triglyceride molar ratio increases to 8:1. It is evident that the reaction mass efficiency is one of the criteria for determining the expediency of regenerating unreacted alcohol. When regenerating unreacted ethyl alcohol, the reaction mass efficiency also reaches its maximum value at the ethyl alcohol:triglyceride molar ratio of 5:1. However, with a further increase in the molar alcohol excess, the reaction mass efficiency remains practically unchanged (Fig. 5,a).

The dependence of the reaction mass efficiency on the catalyst amount shows a maximum when the cation exchange resin content in the reaction mixture is 2 wt.%. In this case, the reaction mass efficiency weakly depends on whether the regeneration of unreacted ethyl alcohol is taken into account (Fig. 5,b). The regeneration of unreacted alcohol increases the reaction mass efficiency by only 6% in the reaction mixture's investigated range of catalyst amount.

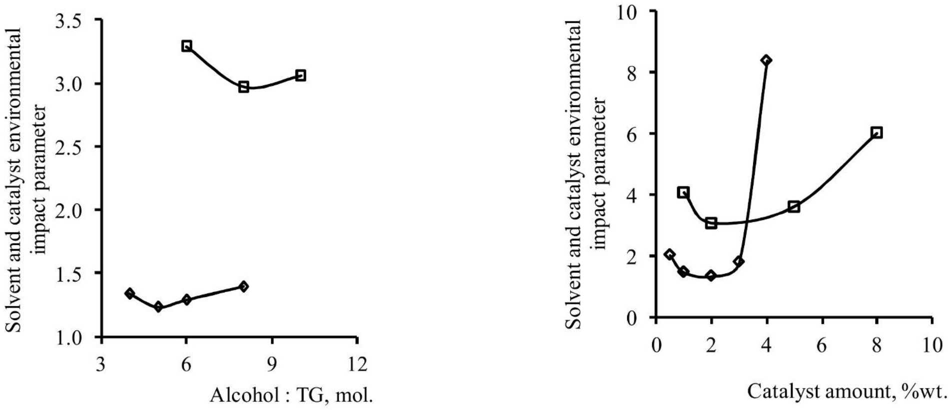
We do not consider catalyst consumption when calculating sustainability indicators. Consequently, the dependence of the solvent and catalyst environmental impact parameter practically does not differ from the dependence observed for mass intensity (Fig. 6). The catalysts are H-cation exchange resin KU-2-8 (ethyl alcohol) and cation exchange resin KU-2-8 with immobilized Ni^{2+} ions (butyl alcohol). The catalyst content is 2 wt.%, the ethyl alcohol:triglyceride molar ratio is 4:1 and the butyl alcohol:triglyceride molar ratio is 10:1; the reaction temperature is 353 K (ethyl alcohol) or 383 K (butyl alcohol). When calculating the solvent and catalyst environmental impact parameter, we attribute only higher fatty acid esters as target products [16]. Therefore, the solvent and catalyst environmental impact parameter is slightly higher than the value of mass intensity.

The stoichiometric factor by a molar excess of alcohol should be greater than 1. Therefore, it is a significant indicator of the sunflower oil transesterification [16]. Figure 7 shows that the stoichiometric factor during the ethanolysis and butanolysis of triglycerides naturally increases with increased alcohol molar excess. The catalysts are H-cation exchange resin KU-2-8 (ethyl alcohol) and cation exchange resin KU-2-8 with immobilized Ni^{2+} ions (butyl alcohol). The catalyst content is 2 wt.%, the reaction temperature is 353 K (ethyl alcohol) or 383 K (butyl alcohol). With the same molar ratio of alcohol:triglyceride (from 6:1 to 8:1) of reagents,



a b

Fig. 5. The reaction mass efficiency vs. the ethyl alcohol: triglyceride molar ratio (a) and the catalyst content in the reaction mixture (b): ◇ – without alcohol regeneration, and □ – with alcohol regeneration



a **b**

Fig. 6. The solvent and catalyst environmental impact parameter vs. the alcohol:triglyceride molar ratio (a) and the content of the catalyst in the reaction mixture (b): ◇ – ethyl alcohol, and □ – butyl alcohol

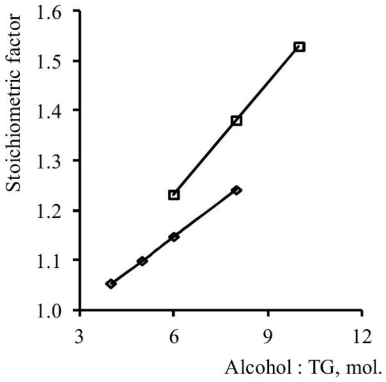


Fig. 7. The stoichiometric factor vs. the alcohol: triglyceride molar ratio: ◇ – ethyl alcohol, and □ – butyl alcohol

the stoichiometric factor of sunflower oil butanolysis is 7.3 to 11.2% higher than its ethanolysis. This result is due to the higher molecular weight of butyl alcohol.

Martinez-Guerra and Gude [16] claimed that the sustainability indicators of triglyceride transesterification with ethyl alcohol catalyzed by sodium hydroxide indicated low process environmental safety. Our results suggest that cation exchange resin KU-2-8 with H^+ or immobilized metal ions as a catalyst provides good sustainability indicators and high triglyceride conversion.

Conclusions

It was shown that the yield of higher fatty acid esters achieved by the transesterification of sunflower oil with ethyl, 1-propyl, and 1-butyl alcohol catalyzed by anion exchange resin AV-17-8 with OH^- ions, cation exchange resin KU-2-8 with H^+ or immobilized metal ions significantly affects the sustainability indicators.

It was established that the dependence of the E-factor, mass intensity, mass productivity, and reaction mass efficiency on the reaction mixture's catalyst amount is extreme by the sunflower oil butanolysis and ethanolysis. The optimal conditions of these processes can be determined using these sustainability indicators considering their environmental friendliness.

It was determined that by etanolysis of sunflower oil catalyzed by cation exchange resin KU-2-8 with H^+ ions and by regeneration of unreacted alcohol, the E-factor is 0.022–0.025, indicating the high environmental efficiency of the process. The E-factor reaches a minimum at the ethyl alcohol:triglyceride molar ratio, corresponding to the maximum of the yield of higher fatty acid esters.

REFERENCES

1. *The catalysed* transformation of vegetable oils or animal fats to biofuels and bio-lubricants: a review / Hajek M., Vavra A., de Paz Carmona H., Kocik J. // Catalysts. – 2021. – Vol.11. – No.9. – Art. No. 1118.

2. *Keneni Y.G. (Trine) Hvoslef-Eide A.K., Marchetti J.M.* Optimization of the production of biofuel form Jatropha oil using a recyclable anion-exchange resin // Fuel. – 2020. – Vol.278. – Art. No. 118253.

3. *Alkaline* transesterification of sunflower oil triglycerides by butanol-1 over potassium hydroxide and alkoxides catalysts / Patrylak L.K., Zubenko S.O., Konovalov S.V., Povazhnyi V.A. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2019. – No. 5. – P.93-103.

4. *A review* for key challenges of the development of biodiesel industry / Manaf I.S.A., Embong N.H., Khazaai S.N.M., et al. // Energy Convers. Manage. – 2019. – Vol.185. – P.508-517.

5. *Encinar J.M., Nogales S., Gonzalez J.F.* Biodiesel and biolubricant production from different vegetable oils through transesterification // Eng. Rep. – 2020. – Vol.2. – No. 12. – Art. No. e12190.

6. *Suppalakpanya K., Ratanawilai S., Tongurai C.* Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth // Appl. Energy. – 2010. – Vol.87. – P.2356-2359.

7. *Esterificacao* e transesterificacao homogenea de oleos vegetais contendo alto teor de acidos graxos livres / Vieira J.S.C., Sousa T.L., Rosas L.S., et al. // Quim. Nova. – 2018. – Vol.41. – No. 1. – P.10-16.

8. *The reaction* of oleic acid with a mixture of ethanolamines / Melnyk S., Danyliuk R., Melnyk Yu., Reutskyy V. // Chem. Chem. Technol. – 2018. – Vol.12. – No. 1. – P.13-17.

9. *Solid* acid resin Amberlyst 45 as a catalyst for the transesterification of vegetable oil / Cabral N.M., Lorenti J.P., Plass W., Gallo J.M.R. // Front. Chem. – 2020. – Vol.8. – Art. No. 305.

10. *Melnyk Yu., Starchevskyi R., Melnyk S.* Transesterification of sunflower oil triglycerides by 1-butanol in the presence of d-metal oxides // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2019. – No. 4. – P.95-100.

11. *Melnyk Yu., Starchevskyi R., Melnyk S.* Technological aspects of vegetable oils transesterification with ethanol in the presence of metal oxides // Kem. Ind. – 2020. – Vol.69. – No. 7-8. – P.365-370.

12. *Melnyk Yu.R., Tierin A.A., Melnyk S.R.* Porivniannia aktyvnosti oksydiv metaliv u reaktsii transesteryfikatsii tryhlitserydiv spyrtamy C_1–C_4 // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2020. – No. 6. – P.99-105.

13. *Research* into transesterification of triglycerides by aliphatic alcohols C_2–C_4 in the presence of ionites / Melnyk Yu., Melnyk S., Palyukh Z., Dzinyak B. // East. Eur. J. Enterprise Technol. – 2018. – Vol.1/6. – No. 94. – P.10-16.

14. *Vorobyova V., Vasyliev G., Skiba M.* Eco-friendly «green» synthesis of silver nanoparticles with the black currant pomace extract and its antibacterial, electrochemical, and antioxidant activity // Appl. Nanosci. – 2020. – Vol.10. – No. 12. – P.4523-4534.

15. *Green* synthesis of silver nanoparticles in the presence of polysaccharide: optimization and characterization / Skiba M.I., Vorobyova V.I., Pivovarov A., Makarshenko N.P. // J. Nanomater. – 2020. – Vol.2020. – Art. No. 3051308.

16. *Martinez-Guerra E., Gude V.G.* Assessment of sustainability indicators for biodiesel production // Appl. Sci. – 2017. – Vol.7. – No. 9. – Art. No. 869.

17. *Melnyk Yu.R. Paliukh Z.Yu., Melnyk S.R.* Alkoholiz tryhlitserydiv etanolom u prysutnosti kationitu KU-2-8, modyfikovanoho ionamy metaliv // Visnyk Skhidnoukrainskoho NU im. Volodymyra Dalia. – 2015. – No. 3(220). – P.78-82.

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ОЦІНЮВАННЯ ІНДИКАТОРІВ СТАЛОСТІ ТРАНСЕСТЕРИФІКАЦІЇ ТРИГЛІЦЕРИДІВ АЛІФАТИЧНИМИ СПИРТАМИ В ПРИСУТНОСТІ ІОНООБМІННИХ СМОЛ

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Метою досліджень було встановлення впливу показників процесу трансестерифікації тригліцеридів соняшникової олії етанолом, пропанолом і бутанолом на індикатори сталості. Як каталізатор використовували аніоніт АВ-17-8 або катіоніт КУ-2-8 у Н-формі чи з іммобілізованими іонами Zn^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}. З-поміж індикаторів сталості визначено такі показники як Е-фактор, атомна ефективність, масова інтенсивність та масова продуктивність, ефективність реакційної маси, стехіометричний фактор тощо. Встановлено, що вплив іммобілізованого іона металу на показники сталості значною мірою визначається виходом естерів вищих жирних кислот, який може бути досягнутий при каталізі трансестерифікації дослідженими іонообмінними смолами. Показано, що регенерування непрореагованого спирту дає змогу істотно знизити значення Е-фактору та підвищити ефективність реакційної маси. Встановлено, що при етанолізі соняшникової олії мінімальне значення Е-фактору досягається при оптимальному з технологічної точки зору співвідношенні тригліцерид:етанол. Показано, що значення ефективності реакційної маси, розраховане без врахування регенерування непрореагованого спирту, є одним з критеріїв доцільності його регенерування. Показано, що індикатори сталості можуть бути додатково застосовані для вибору оптимальних умов реакції трансестерифікації соняшникової олії аліфатичними спиртами, каталізованої іонообмінними смолами. Розраховані показники сталості свідчать про те, що досліджені іонообмінні смоли як гетерогенні каталізатори трансестерифікації забезпечують високий вихід естерів вищих жирних кислот. Використання досліджених каталізаторів забезпечує низьке значення Е-фактора, що робить процес екологічно чистим.

Ключові слова: трансестерифікація, соняшникова олія, спирт, іонообмінна смола; індикатор сталості.

THE ASSESSMENT OF SUSTAINABILITY INDICATORS FOR TRIGLYCERIDES TRANSESTERIFICATION WITH ALCOHOLS CATALYZED BY ION EXCHANGE RESINS

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The research was aimed at determining the dependences of sustainability indicators on the parameters of the sunflower oil transesterification with ethyl, propyl, and butyl alcohol catalyzed by anion exchange resin AV-17-8 with OH^- ions or cation exchange resin KU-2-8 with H^+ or immobilized Zn^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} ions. Such sustainability indicators as the E-factor, atomic efficiency, mass intensity and mass productivity, reaction mass efficiency, stoichiometric factor, etc., have been determined. We established that sustainability indicators of transesterification catalyzed by ion exchange resins depend on the yield of higher fatty acid esters that can be achieved by immobilized metal ions. The unreacted alcohol regeneration significantly reduces the E-factor value and increases the reaction mass efficiency. During the sunflower oil ethanolysis, the minimum E-factor value is achieved at the ethyl alcohol:triglyceride molar ratio corresponding to the maximum yield of higher fatty acid esters. The reaction mass efficiency calculated without considering the unreacted alcohol regeneration is one of the criteria for determining its regeneration expediency. The sustainability indicators are the additional criteria for selecting optimal conditions of the sunflower oil transesterification with aliphatic alcohols catalyzed by ion exchange resins. The calculated sustainability indicators indicate that the investigated ion exchange resins as heterogeneous transesterification catalysts provide a high yield of higher fatty acid esters. Using the researched catalysts ensures a low E-factor, making the process environmentally friendly.

Keywords: transesterification; sunflower oil; alcohol; ion exchange resin; sustainability indicator.

REFERENCES

1. Hajek M, Vavra A, de Paz Carmona H, Kocik J. The catalysed transformation of vegetable oils or animal fats to biofuels and bio-lubricants: a review. *Catalysts*. 2021; 11(9): 1118. doi: 10.3390/catal11091118.

2. Keneni YG, (Trine) Hvoslef-Eide AK, Marchetti JM. Optimization of the production of biofuel form Jatropha oil using a recyclable anion-exchange resin. *Fuel*. 2020; 278: 118253. doi: 10.1016/j.fuel.2020.118253.

3. Patrylak LK, Zubenko SO, Konovalov SV, Povazhnyi VA. Alkaline transesterification of sunflower oil triglycerides by butanol-1 over potassium hydroxide and alkoxides catalysts. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2019; (5): 93-102. doi: 10.32434/0321-4095-2019-126-5-93-103.

4. Manaf ISA, Embong NH, Khazaai SNM, Rahim MHA, Yusoff MM, Lee KT, et al. A review for key challenges of the development of biodiesel industry. *Energy Convers Manage*. 2019; 185: 508-517. doi: 10.1016/j.enconman.2019.02.019.

5. Encinar JM, Nogales S, Gonzalez JF. Biodiesel and biolubricant production from different vegetable oils through transesterification. *Eng Rep*. 2020; 2(12): e12190. doi: 10.1002/eng2.12190.

6. Suppalakpanya K, Ratanawilai SB, Tongurai C. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. *Appl Energy*. 2010; 87: 2356-2359. doi: 10.1016/j.apenergy.2009.12.006.

7. Vieira JSC, Sousa TL, Rosas LS, Lima AL, Ronconi CM, Mota CJA. Esterificacao e transesterificacao homogenea de oleos vegetais contendo alto teor d acidos graxos livres [Homogeneous esterification and transesterification of vegetable oils with high free fatty acids content]. *Quim Nova*. 2018; 41(1): 10-16. (*in Portuguese*). doi: 10.21577/0100-4042.20170148.

8. Melnyk S, Danyliuk R, Melnyk Yu, Reutskyy V. The reaction of oleic acid with a mixture of ethanolamines. *Chem Chem Technol*. 2018; 12(1): 13-17. doi: 10.23939/chcht12.01.013.

9. Cabral NM, Lorenti JP, Plass W, Gallo JMR. Solid acid resin Amberlyst 45 as a catalyst for the transesterification of vegetable oil. *Front Chem*. 2020; 8: 305. doi: 10.3389/fchem.2020.00305.

10. Melnyk Yu, Starchevskyi R, Melnyk S. Transesterification of sunflower oil triglycerides by 1-butanol in the presence of d-metal oxides. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2019; (4): 95-100. doi: 10.32434/0321-4095-2019-125-4-95-100.

11. Melnyk Y, Starchevskyi R, Melnyk S. Technological aspects of vegetable oils transesterification with ethanol in the presence of metal oxides. *Kem Ind*. 2020; 69(7-8): 365-370. doi: 10.15255/KUI.2019.059.

12. Melnyk Yu, Tierin A, Melnyk S. Comparisons of metal oxides activity in the transesterification of triglycerides by C1–C4 alcohols. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2020; (6): 99-105. doi: 10.32434/0321-4095-2020-133-6-99-105.

13. Melnyk Yu, Melnyk S, Palyukh Z, Dzinyak B. Research into transesterification of triglycerides by aliphatic alcohols C2–C4 in the presence of ionites. *East Eur J Enterprise Technol*. 2018; 1.1/6(94): 10-16. doi: 10.15587/1729-4061.2018.122938.

14. Vorobyova V, Vasyliev G, Skiba M. Eco-friendly «green» synthesis of silver nanoparticles with the black currant pomace extract and its antibacterial, electrochemical, and antioxidant activity. *Appl Nanosci*. 2020; 10: 4523-4534. doi: 10.1007/s13204-020-01369-z.

15. Skiba MI, Vorobyova VI, Pivovarov A, Makarshenko NP. Green synthesis of silver nanoparticles in the presence of polysaccharide: optimization and characterization. *J Nanomater*. 2020; 2020: 3051308. doi: 10.1155/2020/3051308.

16. Martinez-Guerra E, GudeVG. Assessment of sustainability indicators for biodiesel production. *Appl Sci*. 2017; 7(9): 869. doi: 10.3390/app7090869.

17. Melnyk YuR, Paliukh ZYu, Melnyk SR. Alkoholiz tryhlitserydiv etanolom u prysutnosti kationitu KU-2-8, modyfikovanoho ionamy metaliv [Alcoholysis of triglycerides with ethanol in the presence of KU-2-8 cationite modified with metal ions]. *Visnyk Skhidnoukrainskogo NU im Volodymyra Dalia*. 2015; 3(220): 78-82. (*in Ukrainian*).