

## THE EFFECT OF TRIGLYCERIDE TRANSESTERIFICATION CATALYST ON THE SUSTAINABILITY INDICATORS

*Yurii Melnyk<sup>1</sup>, Stepan Melnyk<sup>1</sup>, Halyna Mahorivska<sup>1</sup>*

<sup>1</sup> Lviv Polytechnic National University, 12, S. Bandery str., Lviv, 79013, Ukraine

✉ [yurii.r.melnyk@lpnu.ua](mailto:yurii.r.melnyk@lpnu.ua)

© Melnyk Yu., Melnyk S., Mahorivska H., 2025

<https://doi.org/10.23939/chcht19.04.705>

**Abstract.** The effect of a triglyceride transesterification catalyst on sustainability indicators has been examined. Among the catalysts studied, zinc and nickel (II) oxides proved to be the most effective for triglyceride ethanolysis and butanolysis. The optimal catalyst content of 0.25 wt. % minimizes the E-factor. Increasing the molar ratio of alcohol to triglyceride decreases the E-factor by 3.6 to 8.0 times in triglyceride butanolysis catalyzed by zinc and nickel (II) oxides. It was found that the regeneration of unreacted n-butyl alcohol from the reaction mixture increases atom efficiency by 2.1 to 2.2 times.

**Keywords:** green chemistry, sustainability indicators, E-factor, metal oxide, triglyceride, ethanol, butanol, transesterification.

### 1. Introduction

Sustainability is being considered in the research and development of organic synthesis processes.<sup>1,2</sup> Triglyceride transesterification is recognized as a green chemistry process.<sup>1,3</sup> One of the products obtained by oil transesterification is methyl esters of higher fatty acids, commonly known as biodiesel. Biodiesel is recognized as a renewable, environmentally friendly, and less toxic alternative to fossil fuels.<sup>4</sup> One of its advantages is biodegradability. However, despite the renewable nature of oils, the high yields of methyl esters of higher fatty acids, and the manufacture of glycerol as a valuable by-product, the transesterification reaction generates waste. In particular, homogeneous basic catalysts, such as potassium or sodium hydroxides and methoxides, cannot be recovered from the reaction mixture and require wastewater treatment. This is an essential drawback of homogeneous catalysts that adversely affects sustainability indicators.

Anhydrous potassium methylate dissolved in alcohol has been studied as a catalyst for triglyceride transesterification with ethyl and butyl alcohol.<sup>5</sup> To achieve high ester yields, ethyl and butyl alcohols with water contents of 0.14 % and less than 0.5 %, respectively, were used as reagents. The reaction was carried out at room temperature, yielding 66 % butyl esters after 2 minutes and 82 % after 40 minutes.

Transesterification catalyzed by homogeneous catalysts has also been performed in two stages. Sodium hydroxide was used as a catalyst for transesterification of sunflower, rapeseed, olive oils, and waste cooking oil with ethyl alcohol.<sup>6</sup> The catalyst content ranged from 0.25 to 1.5 wt. %, with a molar ratio of ethyl alcohol to triglyceride from 6: 1 to 12: 1, and a reaction temperature from 5 to 90 °C. The maximum yield of fatty acid ethyl esters was achieved at the first transesterification stage with 1 wt. % sodium hydroxide, a molar ratio of ethyl alcohol to triglyceride of 12: 1 and a reaction temperature of 80 °C. In the second stage, the yield of ethyl esters was 16 % of that in the first stage at a molar ratio of ethyl alcohol to triglycerides of 6: 1 and a catalyst content of 0.75 wt. %. Ethyl esters exhibit similar properties to methyl esters and can be used as biodiesel.

Basic and acidic heterogeneous catalysts enhance technical and sustainability indicators of the transesterification process. These catalysts are less sensitive to impurities in the raw materials, particularly water and free fatty acids content. Heterogeneous catalysts sufficiently active and selective can be easily separated from the reaction mixture, and are reusable.<sup>7,8</sup> The use of heterogeneous catalysts (*e.g.*, CaO, SO<sub>4</sub>/Fe-Al-TiO<sub>2</sub>, MgO, Fe-Mn-SO<sub>4</sub>/ZrO<sub>2</sub>, CaO/CuFe<sub>2</sub>O) allows the industrial transesterification process to be implemented as a continuous one.<sup>9,10</sup>

However, heterogeneous transesterification catalysts require a significant number of auxiliary

operations and more stringent reaction conditions, such as higher temperatures and a higher molar ratio of alcohol to triglycerides, which negatively affect the environmental performance of the process.

Ash and limestone have been used as raw materials for the manufacture of transesterification catalysts.<sup>11</sup> Both wet and dry methods were employed to synthesize heterogeneous catalysts at an equal ratio of ash to limestone. The obtained mixture was calcined at a temperature of 1073–1273 K. The catalyst prepared via the wet method and calcined at 1073 K achieved a methyl ester yield of approximately 88.6 % in the transesterification of palm oil with methanol. A key ecological and economic advantage of the heterogeneous catalyst developed by the authors is its reusability. Specifically, its activity remained at 91.87 % of the initial value after four cycles.

A polyaniline-based composite decorated with magnetic iron oxide and cobalt oxide nanoparticles has been investigated as a catalyst for triglyceride transesterification with methanol.<sup>12</sup> The catalyst parameters were determined using field-emission scanning electron microscopy, Fourier transform infrared spectroscopy, vibrating-sample magnetometry, and energy-dispersive X-ray spectroscopy. The catalyst exhibited acid-base properties. It was found that, at a molar ratio of methanol to waste cooking oil of 10: 1 and a reaction temperature of 363 K for 240 minutes, the yield of higher fatty acid methyl esters exceeded 93 %.

The applicability of heterogeneous catalysts for waste cooking oil transesterification represents a key advantage. The transesterification of waste cooking oil with methanol, catalyzed by CaO derived from animal bone waste, has been studied.<sup>13</sup> The oil was pre-filtered to remove solid impurities and treated with activated carbon to reduce its free fatty acid content. The treated oil was transesterified at a temperature of 338 K, a stirring speed of 400 min<sup>-1</sup>, a molar ratio of methanol to triglycerides from 6: 1 to 18: 1, and a catalyst content of 1 to 9 wt. %. Under optimal conditions (a molar ratio of methanol to triglycerides of 12: 1 and a catalyst content of 5 wt. %), the yield of higher fatty acid methyl esters was approximately 97.5 %.

Heterogeneous d-metal oxides catalyze the transesterification of sunflower oil triglycerides with butyl alcohol.<sup>14</sup> Among them, zinc and nickel (II) oxides have proven to be the most active catalysts. The triglyceride conversion exceeded 97 % after 150 minutes of reaction at a catalyst content of 0.25–0.30 wt. % and a molar ratio of butyl alcohol to triglycerides of 15: 1. Increasing the molar ratio to 20: 1 provides almost 100 % triglyceride conversion within 120 minutes.

Eugenol and cajuput oil have been explored as biocatalysts for the transesterification of palm oil and methyl acetate at 333 K, a molar ratio of methyl acetate to

triglycerides of 6: 1, a catalyst content of 0.75 wt. %, and a stirring rate of 300 min<sup>-1</sup>.<sup>15</sup> Eugenol was found to be more effective catalyst than cajuput oil, yielding 83.16 % higher fatty acid methyl esters within 15 minutes reaction. The density of the obtained methyl esters was 0.892 g/cm<sup>3</sup>, and their acid number was 0.3 mg KOH/g. The methyl esters met the biodiesel standard requirements.

Sustainability indicators are used to assess the environmental friendliness of a process. A low E-factor value indicates a small amount of waste generated during production. The atom efficiency value, which considers the yield of the target product in an ecological process, should be as close to 100 % as possible, while the mass intensity value should not exceed 1 kg/kg. In addition to these sustainability indicators, reaction mass efficiency is employed to characterize the process, which relates to the E-factor value, atom utilization, the environmental impact of solvents and catalysts, and the stoichiometric factor.

Sustainability indicators are used to evaluate the environmental impact of a process.<sup>1</sup> A low E-factor value signifies minimal waste generation during production. Atom efficiency, which considers the target product yield in an ecological process, should be as close to 100 % as possible, while the mass intensity should not exceed 1 kg/kg. In addition to these sustainability indicators, reaction mass efficiency is also used to evaluate the process, as it relates to the E-factor, atom utilization, the environmental impact of solvents and catalysts, as well as the stoichiometric factor.

The research aimed to determine the effect of metal oxide catalysts and the parameters of triglyceride transesterification with lower aliphatic alcohols on sustainability indicators.

## 2. Experimental

### 2.1. Materials

Sunflower oil (DSTU 4492:2017), rapeseed oil (DSTU 8175:2015), linseed oil (DSTU ISO 150-2002), ethyl alcohol (DSTU 4221:2003), and butyl alcohol (reagent grade) were used as reagents. Ethyl alcohol was dried over pre-calcined magnesium sulfate before use. The residual water content of ethyl alcohol after drying did not exceed 0.5 wt. %. Zinc, nickel (II), copper (II), iron (II), tin (IV), cobalt (II), manganese (II), chromium (III), magnesium, and lead (II) oxides (all reagent grade) were used as catalysts.

### 2.2. Methods

The reaction temperature was 348 K for the transesterification of triglycerides with ethyl alcohol and 383 K for the transesterification with butyl alcohol. A

decrease in temperature significantly reduces the conversion of the reactants. As a result, the reaction temperature was maintained near the boiling point of the alcohol, thereby ensuring a high reaction rate and maximal triglyceride conversion. The molar ratio of ethyl alcohol to triglycerides varied from 10: 1 to 20: 1. The catalyst content in the reaction mixture ranged from 0.125 to 0.5 wt. %.

The transesterification of triglycerides with ethyl or butyl alcohol was carried out in a three-necked round-bottom flask equipped with a reflux condenser and a magnetic stirrer. Once the reaction temperature was reached, the catalyst was added to the reaction mixture, marking the beginning of the reaction. At specified intervals, samples of the reaction mixture were taken, and the alcohol content was determined chromatographically. The conversion of alcohol and triglycerides was calculated based on the determined alcohol concentration.<sup>16</sup> Unreacted alcohols were regenerated by distillation. Ethyl or butyl esters were distilled from tri-, di-, and monoglycerides by vacuum distillation in an argon environment.

Sustainability indicators, particularly the E-factor, were calculated without considering the regeneration of unreacted alcohol from the reaction mixture, and with its regeneration.<sup>17, 1</sup>

The following equations were used to calculate the sustainability indicators:

- E-factor

$$E_f = \frac{m_w}{m_p}, \quad (1)$$

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

- Atom efficiency

$$AE = \frac{v_e M_e}{v_{tg} M_{tg} + v_a M_a} \cdot \eta \quad (2)$$

where  $M_i$  is the average molar mass of higher fatty acid esters and triglyceride, respectively, g/mol;  $v_i$  is the stoichiometric coefficients of ester, triglyceride, and alcohol, respectively;  $\eta$  is the yield of higher fatty acid esters, %.

- Mass intensity

$$MI = \frac{\sum m_i}{m_p}, \quad (3)$$

where  $\sum m_i$  is the sum of the masses of all substances used in the process, g.

- Reaction mass efficiency

$$RME = \frac{1}{1+E_f}. \quad (4)$$

### 3. Results and Discussion

The results of our previous studies (Table 1, 2) were used to assess the impact of metal oxides on the sustainability indicators of the triglyceride transesterification process.<sup>14, 18</sup> The effect of metal oxide on the E-factor in the ethanolysis process was investigated at two molar ratios of ethyl alcohol to triglycerides of 4: 1 and 5.7: 1 (Fig. 1). The lowest E-factor values in both cases are observed in triglyceride transesterification catalyzed by zinc, nickel (II), tin (II), and magnesium oxides. It was found that at a higher excess of ethyl alcohol, the E-factor was significantly affected by the process conditions. When ethyl alcohol was regenerated from the reaction mixture and reused, the E-factor values decreased by 2.4 to 6.2 times compared to the process without ethyl alcohol regeneration (Fig. 1, b).

The experimental data for sustainability indicators evaluation are given in Table 1 and 2.

**Table 1.** Experimental data for evaluating the effect of metal oxide on sustainability indicators of the transesterification of sunflower, rapeseed, and linseed oil triglycerides with ethyl or butyl alcohol. Temperatures are 348 K (ethanolysis) and 383 K (butanolysis), and the catalyst content is 0.25 wt. %

Catalyst	Yield, %	Loaded, g			Received, g				
		triglyceride	alcohol	catalyst	with alcohol regeneration			without alcohol regeneration	
					glycerin	esters	waste	alcohol	waste
1	2	3	4	5	6	7	8	9	10
Sunflower oil & ethyl alcohol									
ZnO	96.7	44.375	9.850	0.136	4.497	45.170	4.693	3.104	1.589
NiO	89.8	56.870	11.838	0.172	5.353	53.764	9.763	3.809	5.954
FeO	77.8	56.870	11.838	0.172	4.636	46.565	17.679	4.884	12.795
CuO	70.1	56.870	11.838	0.172	4.180	41.984	22.716	5.568	17.148
Co <sub>2</sub> O <sub>3</sub>	59.0	56.870	11.838	0.172	3.519	35.338	30.024	6.561	23.463
Co <sub>3</sub> O <sub>4</sub>	63.6	56.870	11.838	0.172	3.789	38.057	27.034	6.155	20.879

Continuation of Table 1

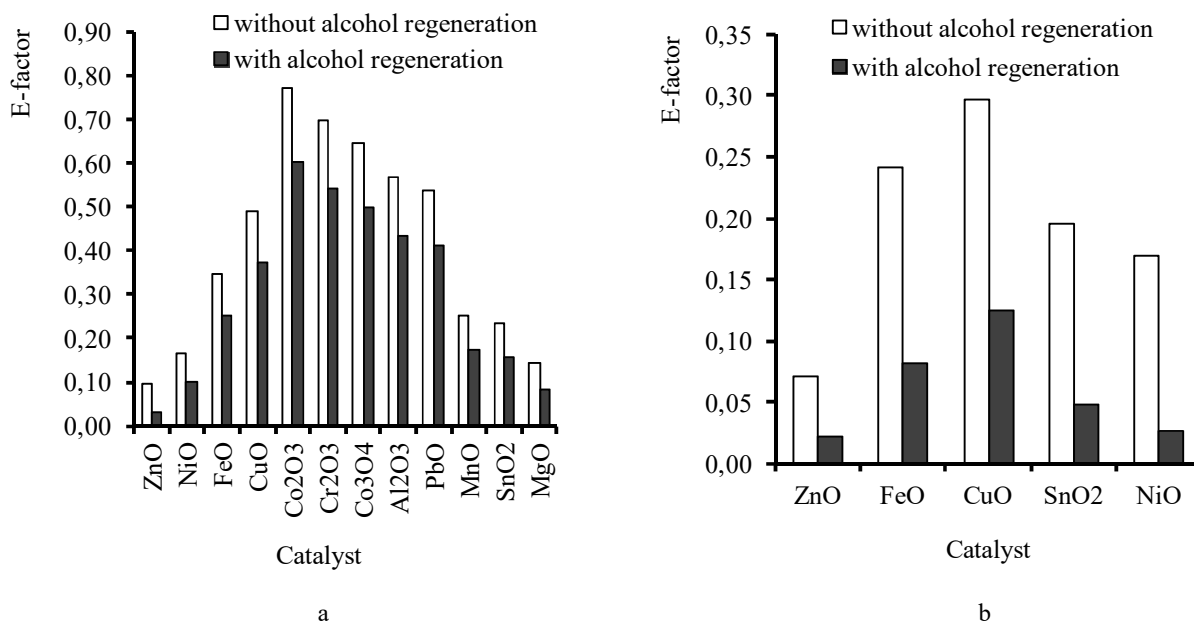
1	2	3	4	5	6	7	8	9	10
MnO	83.6	56.870	11.838	0.172	4.984	50.054	13.843	4.363	9.480
Cr <sub>2</sub> O <sub>3</sub>	61.6	56.870	11.838	0.172	3.672	36.879	28.329	6.331	21.999
Al <sub>2</sub> O <sub>3</sub>	66.8	56.870	11.838	0.172	3.981	39.979	24.921	5.868	19.053
SnO <sub>2</sub>	84.9	56.870	11.838	0.172	5.061	50.829	12.991	4.247	8.743
MgO	91.4	56.870	11.838	0.172	5.447	54.704	8.730	3.668	5.061
PbO	68.0	56.870	11.838	0.172	4.051	40.691	24.138	5.761	18.377
FeO	91.6	30.330	9.471	0.100	2.911	29.234	7.756	5.105	2.651
CuO	87.7	30.330	9.471	0.100	2.786	27.983	9.131	5.291	3.840
NiO	97.3	30.330	9.471	0.100	3.091	31.048	5.761	4.834	0.927
SnO <sub>2</sub>	95.1	30.330	9.471	0.100	3.021	30.342	6.537	4.939	1.598
ZnO	97.7	56.870	11.838	0.124	5.822	58.477	4.533	3.105	1.429
Linseed oil & ethyl alcohol									
ZnO	90.2	30.330	9.471	0.100	2.866	28.784	8.250	5.172	3.078
NiO	84.6	30.330	9.471	0.100	2.689	27.005	10.207	5.438	4.769
Rapeseed oil & ethyl alcohol									
ZnO	94.8	30.330	9.471	0.100	3.014	30.267	6.620	4.950	1.669
NiO	89.2	30.330	9.471	0.100	2.836	28.487	8.576	5.216	3.360
Sunflower oil & butyl alcohol									
FeO	56.8	110.190	96.390	0.500	6.561	71.889	128.630	80.557	48.072
Co <sub>2</sub> O <sub>3</sub>	57.9	43.597	38.880	0.206	2.645	28.982	51.056	32.497	18.559
Co <sub>3</sub> O <sub>4</sub>	58.6	36.800	32.400	0.173	2.258	24.739	42.376	26.952	15.425
CuO	71.7	36.800	32.400	0.173	2.764	30.279	36.331	25.731	10.599
ZnO	77.9	35.587	31.386	0.164	2.904	31.821	32.411	24.378	8.034
NiO	78.2	36.800	32.400	0.173	3.016	33.049	33.308	25.121	8.186

**Table 2.** Experimental data for evaluating the sustainability indicators of the transesterification of sunflower oil triglycerides with ethyl or butyl alcohol. Temperatures are 348 K (ethanolysis) and 383 K (butanolysis)

Catalyst	Yield, %	Loaded, g			Received, g				
		triglyceride	alcohol	catalyst	with alcohol regeneration			without alcohol regeneration	
					glycerin	triglyceride	alcohol	alcohol	waste
1	2	3	4	5	6	7	8	9	10
Sunflower oil & ethyl alcohol									
ZnO	97.3	45.490	11.838	0.143	4.639	46.594	6.238	4.880	1.359
ZnO	91.1	37.910	11.838	0.156	3.617	36.328	9.959	6.413	3.546
ZnO	83.6	37.910	11.838	0.187	3.319	33.334	13.282	6.860	6.422
ZnO	67.6	37.910	11.838	0.249	2.685	26.964	20.349	7.811	12.538
ZnO	72.7	37.910	11.838	0.062	2.887	28.998	17.926	7.508	10.418
Sunflower oil & butyl alcohol									
FeO	25.7	36.800	32.400	0.087	0.991	10.856	57.439	30.009	27.430
FeO	54.7	36.800	32.400	0.260	2.110	23.114	44.236	27.309	16.926
FeO	35.7	36.800	32.400	0.346	1.378	15.093	53.075	29.076	23.999
FeO	63.7	40.320	40.500	0.202	2.689	29.464	48.869	34.011	14.858
ZnO	85.0	40.320	40.500	0.202	3.592	39.350	38.080	31.834	6.247
NiO	85.0	40.320	40.500	0.202	3.592	39.350	38.080	31.834	6.247
FeO	85.2	30.670	40.500	0.178	2.738	29.998	38.612	33.893	4.719
ZnO	97.1	30.670	40.500	0.178	3.119	34.174	34.055	32.974	1.081

Continuation of Table 2

1	2	3	4	5	6	7	8	9	10
NiO	93.2	43.427	57.510	0.252	4.243	46.484	50.463	47.272	3.190
FeO	90.2	24.200	40.500	0.162	2.288	25.067	37.506	34.979	2.527
ZnO	100.0	24.200	40.500	0.162	2.536	27.783	34.543	34.381	0.162
NiO	94.7	34.133	59.902	0.235	3.387	37.109	53.774	51.729	2.045

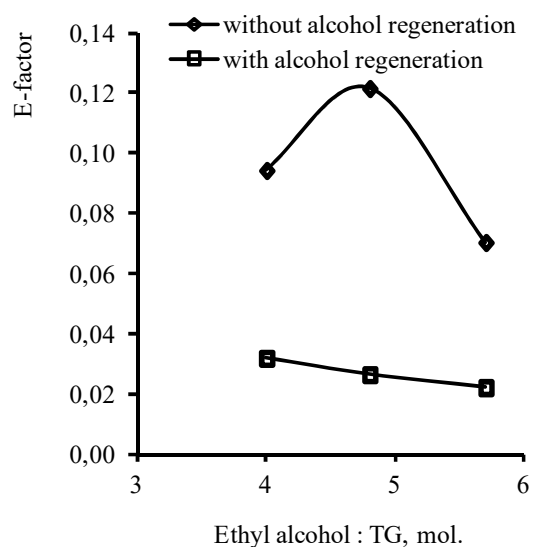


**Fig. 1.** The E-factor dependence on metal oxide in triglyceride ethanolsis. The molar ratio of ethyl alcohol to triglyceride is 4: 1 (a) and 5.7: 1 (b), the temperature is 348 K, and the catalyst content is 0.25 wt. %

The lowest E-factor values, both with and without ethyl alcohol regeneration, were observed in triglyceride ethanolsis catalyzed by zinc, nickel (II), and magnesium oxides. It was found that increasing the molar ratio of ethyl alcohol to triglyceride from 4: 1 to 5.7: 1 resulted in a decrease in the E-factor value. Specifically, for zinc oxide, the E-factor value decreased by 1.34 times without ethyl alcohol regeneration. However, when nickel (II) oxide was used, the E-factor value remained unchanged. With ethyl alcohol regeneration, the E-factor values for zinc and nickel (II) oxides decreased by 1.44 and 3.71 times, respectively, as the molar excess of alcohol increased.

The transesterification process conditions significantly affected the E-factor value. In particular, increasing the molar ratio of ethyl alcohol to triglyceride from 4: 1 to 5.7: 1 resulted in an E-factor of 0.07–0.12 without alcohol regeneration, which sharply decreased to 0.02–0.03 with alcohol regeneration (Fig. 2).

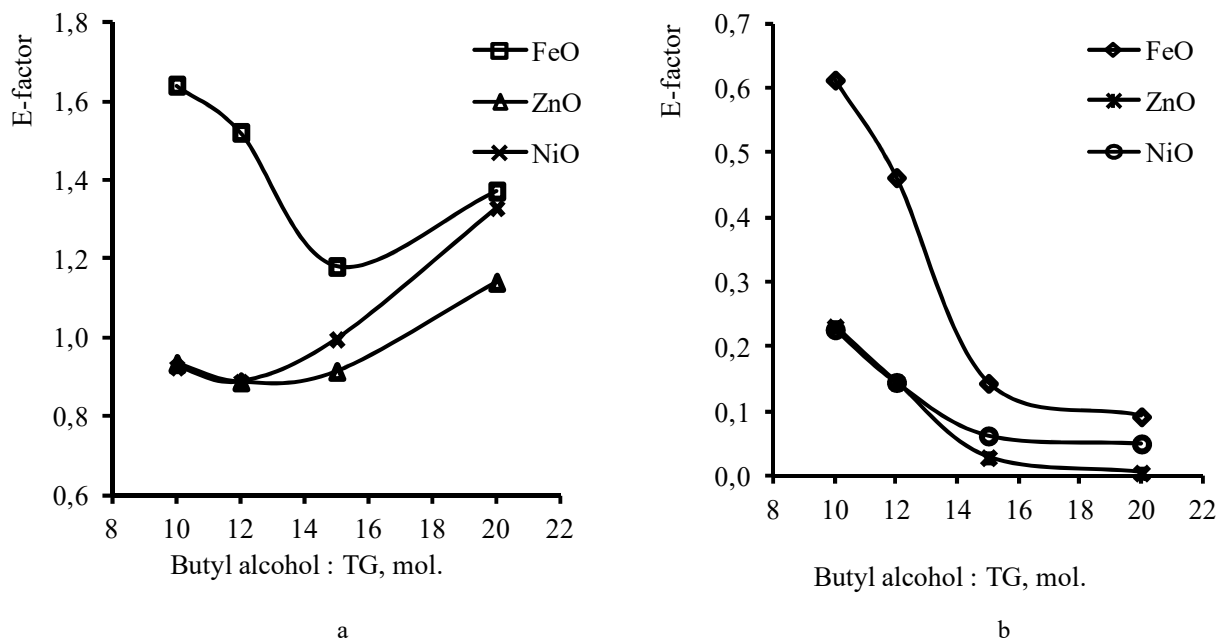
A low E-factor value of 0.92–0.93 without butyl alcohol regeneration and 0.23 with alcohol regeneration was achieved in triglyceride transesterification catalyzed by nickel (II) oxide (Fig. 3).



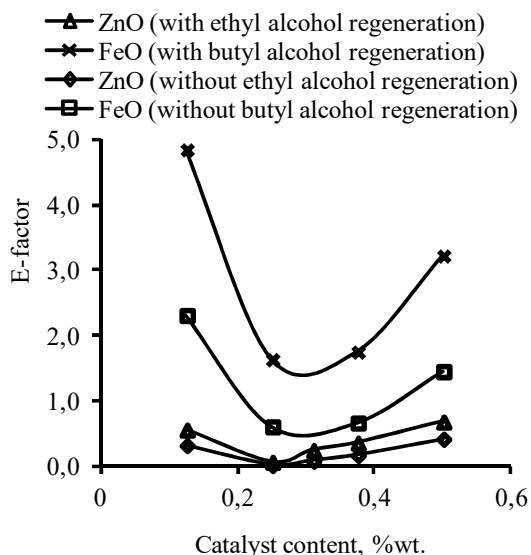
**Fig. 2.** The E-factor dependence on the molar excess of ethyl alcohol to triglyceride in transesterification catalyzed by ZnO. The temperature is 348 K and the catalyst content is 0.25 wt. %

The E-factor value decreased slightly (by 1.04–1.05 times) in butanolysis catalyzed by nickel (II) and zinc oxides and significantly (by 1.39 times) when catalyzed by iron (II) oxide as the molar excess of alcohol increased to 12–15 times without alcohol regeneration. Increasing the molar excess of butyl alcohol from 15: 1 to 20: 1

enhanced the triglyceride conversion by 1.5 % (NiO catalyst) and 5.0 % (FeO catalyst), consequently reducing the E-factor. However, if the starting amount of butyl alcohol was increased by 33.3 %, the E-factor rose significantly, which could not be offset by the increase in triglyceride conversion.



**Fig. 3.** The E-factor dependence on the molar excess of butyl alcohol to triglyceride: a – without alcohol regeneration, b – with alcohol regeneration. The temperature is 388 K and the catalyst content is 0.25 wt. %



**Fig. 4.** The E-factor dependence on the catalyst content in triglyceride transesterification with alcohols. The molar ratio of ethyl alcohol to triglyceride is 4: 1 and butyl alcohol to triglyceride is 10: 1, the temperature is 388 K, and the catalyst content is 0,25 wt. %

The E-factor value significantly decreased with butyl alcohol regeneration in the transesterification process. Moreover, increasing the alcohol molar excess by 15 times reduced the E-factor value by 3.6 to 8.0 times. Further increase in alcohol amount had a negligible effect on the E-factor value.

The E-factor exhibited an extreme dependence on catalyst content in the transesterification of triglycerides with both ethyl and butyl alcohol (Fig. 4). For ethyl alcohol, regardless of whether alcohol was regenerated from the reaction mixture or not, the minimum E-factor value in catalysis by zinc and iron (II) oxides was observed at a catalyst content of 0.25 wt. %. In triglyceride butanolysis, the optimal catalyst content for minimizing the E-factor ranged from 0.25 to 0.375 wt. %.

The general trends in mass intensity values for triglyceride ethanolysis and butanolysis align with those observed for the E-factor. In contrast, the changes in atom efficiency and reaction mass efficiency (with and without alcohol regeneration) follow opposing trends. The maximum atom efficiency in triglyceride ethanolysis ranges from 81.1 % to 88.0 % at a molar ratio of alcohol to triglycerides of 4: 1, reaching 88.5 % to 88.9 % when

the molar ratio increases to 5.7: 1. These atom efficiency values were achieved using zinc and nickel (II) oxides (at molar ratios of 4: 1 and 5.7: 1) and magnesium oxide (at a molar ratio of 5.7: 1), demonstrating the high efficiency of these catalysts in terms of sustainability indicators.

In comparison, atom efficiency in triglyceride butanolysis is significantly lower than in ethanolysis, which correlates well with the results presented in previous studies. When catalyzed by zinc and nickel (II) oxides at a molar ratio of butyl alcohol to triglycerides of 10: 1, the atom efficiency is 71.4 % and 71.7 %, respectively. At a molar ratio of 20: 1, the atom efficiency rises to 91.6 % and 86.8 %, respectively (Table 3).

Increasing the molar ratio of alcohol to triglycerides has a negligible effect on atom efficiency in triglyceride ethanolysis, which remains between 88.0 % and 88.9 % across the studied range (Table 3). However, in triglyceride butanolysis, increasing the molar ratio of butyl alcohol to triglycerides from 10: 1 to 20: 1 by zinc

oxide catalysis raises atom efficiency from 71.4 % to 91.6 %. This indicates that an excess of alcohol has a greater effect on the sustainability indicators of triglyceride butanolysis than their ethanolysis.

The reaction mass efficiency in triglyceride ethanolysis is only slightly affected by alcohol regeneration (Table 3). Regeneration slightly increases atom efficiency, particularly at a molar ratio of ethyl alcohol to triglycerides of 5.7: 1, where alcohol regeneration raises the value by 4.7 %. In triglyceride butanolysis, alcohol regeneration from the reaction mixture significantly enhances reaction mass efficiency. Specifically, when unreacted alcohol is regenerated at a molar ratio of butyl alcohol to triglycerides of 20: 1 by zinc and nickel (II) oxide catalysis, reaction mass efficiency increases by 2.1 and 2.2 times, respectively. At a high molar ratio of alcohol to triglycerides, regenerating unreacted alcohol provides substantial advantages, both technologically (by reducing alcohol consumption) and in terms of sustainability indicators.

**Table 3.** Dependence of sustainability indicators on the molar ratio of alcohol to triglycerides.

The ethanolysis and butanolysis temperature is 348 K and 383 K, and the catalyst content is 0.25 wt. %

Alcohol : TG molar ratio	Sustainability indicators					
	E-factor		Atom efficiency	Mass intensity	Reaction mass efficiency	
	without alcohol regeneration	with alcohol regeneration			without alcohol regeneration	with alcohol regeneration
Ethyl alcohol, catalyst is ZnO						
5.7	0.07	0.02	88.0	1.07	93.4	97.8
4.0	0.09	0.03	88.5	1.09	91.4	96.9
4.8	0.12	0.03	88.9	1.12	89.1	97.4
Butyl alcohol, catalyst is ZnO						
10	0.93	0.23	71.4	1.93	51.7	81.2
12	0.89	0.15	77.9	1.89	53.0	87.3
15	0.91	0.03	88.9	1.91	52.3	97.2
20	1.14	0.01	91.6	2.14	46.7	99.5
Butyl alcohol, catalyst is NiO						
10	0.92	0.23	71.7	1.92	52.0	81.5
12	0.89	0.15	77.9	1.89	53.0	87.3
15	0.99	0.06	85.4	1.99	50.1	94.1
20	1.33	0.05	86.8	2.33	43.0	95.2

As the E-factor, atomic efficiency, mass intensity, and reaction mass efficiency depend extremely on catalyst content (Table 4). The maximum atomic efficiency in triglyceride ethanolysis (88.9 %) was achieved at a zinc oxide content of 0.25 wt. %. In triglyceride transesterification with butyl alcohol catalyzed by iron (II) oxide, the highest atomic efficiency was 52.1 % at a molar ratio of butyl alcohol to triglycerides of 10: 1 and a catalyst content of 0.25 wt. %.

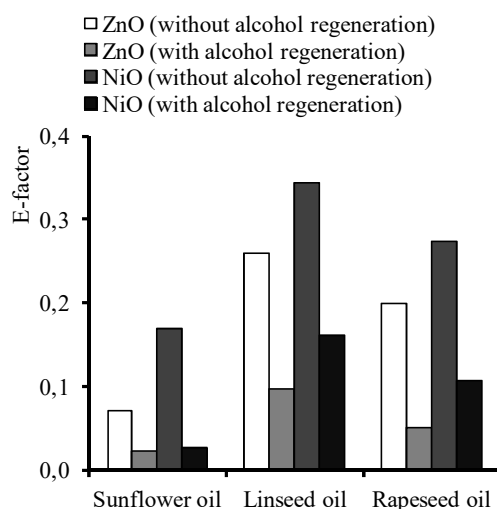
Changes in catalyst content significantly affect reaction mass efficiency, both with and without alcohol regeneration. When the catalyst content deviates from

the optimal value, regenerating unreacted butyl alcohol after the reaction increases the reaction mass efficiency by 1.15–1.19 times (Table 4).

The origin and purification degree of the oil also have a considerable impact on the E-factor (Fig. 5). The highest E-factor was observed in the triglyceride ethanolysis of linseed oil. However, when unreacted ethyl alcohol was regenerated, the E-factor decreased slightly, approaching values observed in sunflower oil transesterification without alcohol regeneration. Since only sunflower oil among the studied oils was refined, it can be concluded that the origin and purification degree of the oil influence sustainability indicators (Table 5).

**Table 4.** Dependence of sustainability indicators on the catalyst content. The ethanolysis and butanolysis temperature is 348 K and 383 K, and the catalyst content is 0.25 wt. %

Catalyst content, % wt.	Sustainability indicators					
	E-factor		Atom efficiency	Mass intensity	Reaction mass efficiency	
	without alcohol regeneration	with alcohol regeneration			without alcohol regeneration	with alcohol regeneration
ethyl alcohol : TG molar ratio – 5.7 :1, catalyst – ZnO						
0.125	0.56	0.33	66.1	1.56	64.0	75.4
0.25	0.07	0.02	88.9	1.07	93.4	97.8
0.31	0.25	0.09	82.8	1.25	80.0	91.8
0.375	0.36	0.18	76.0	1.36	73.4	85.1
0.5	0.69	0.42	61.5	1.69	59.3	70.3
ethyl alcohol : TG molar ratio – 10.0 :1, catalyst – FeO						
0.125	4.85	2.32	23.5	5.85	17.1	30.2
0.25	1.64	0.61	52.1	2.64	37.9	62.0
0.375	1.75	0.67	50.1	2.75	36.3	59.8
0.5	3.22	1.46	32.7	4.22	23.7	40.7

**Fig. 5.** The E-factor dependence on oil origin. The ethanolysis and butanolysis temperature is 348 K and 383 K, and the catalyst content is 0.25 wt. %**Table 5.** Dependence of sustainability indicators on oil origin. The molar ratio of ethyl alcohol to triglyceride is 5.7: 1, the temperature is 348 K, and the catalyst content is 0.25 wt. %.

Catalyst	Sustainability indicators					
	E-factor		Atom efficiency	Mass intensity	Reaction mass efficiency	
	without alcohol regeneration	with alcohol regeneration			without alcohol regeneration	with alcohol regeneration
sunflower oil						
ZnO	0.07	0.02	88.9	1.07	93.4	97.8
NiO	0.17	0.03	88.5	1.17	85.6	97.4
linseed oil						
ZnO	0.26	0.10	82.0	1.26	79.3	91.1
NiO	0.34	0.16	76.9	1.34	74.4	86.2
rapeseed oil						
ZnO	0.20	0.05	86.2	1.20	83.4	95.2
NiO	0.27	0.11	81.2	1.27	78.5	90.3

In linseed and rapeseed oil ethanolysis, even by optimal conditions, the atom efficiency does not exceed 82.0 %, except under zinc oxide catalysis, where it reaches 86.0 %. Regenerating unreacted ethyl alcohol significantly enhances reaction mass efficiency, especially when crude oil is used. For instance, in the ethanolysis of linseed oil catalyzed by zinc and nickel (II) oxides, the reaction mass efficiency increased by 1.14–1.16 times when unreacted alcohol was regenerated. These findings highlight the effectiveness of alcohol regeneration in improving sustainability indicators in linseed and rapeseed oil ethanolysis.

## 4. Conclusions

It has been established that metal oxides affect technological indicators of triglyceride transesterification (notably triglyceride conversion) and sustainability indicators. In triglyceride ethanolysis and butanolysis, the optimum sustainability indicator values are achieved using zinc and nickel (II) oxide catalysis.

Sustainability indicators are strongly affected by the transesterification method, particularly unreacted alcohol regeneration. Notably, in the ethanolysis of sunflower oil triglycerides, regenerating unreacted alcohol reduces the E-factor from 0.07–0.12 to 0.02–0.03.

Sustainability indicators exhibit an extreme dependence on metal oxide content. The minimum E-factor and mass intensity and the maximum atom efficiency and reaction mass efficiency are achieved at a catalyst content of 0.25 wt. % in ethanolysis and 0.25–0.375 wt. % in butyl alcohol transesterification.

It was found that increasing the molar ratio of butyl alcohol to triglycerides from 10: 1 to 15: 1 reduces the E-factor by 3.6–8.0 times, provided that unreacted alcohol is regenerated. However, the effect of the molar ratio of ethyl alcohol to triglycerides on sustainability indicators is less significant.

The oil origin and purification degree significantly affect sustainability indicators. When unrefined oils are used, regenerating unreacted alcohol substantially improves sustainability indicators, increasing reaction mass efficiency by 1.14–1.16 times in the ethanolysis of linseed oil triglycerides.

The optimal conditions for triglyceride transesterification, based on sustainability and technical indicators, are similar.

## References

- [1] Martínez-Guerra, E.; Gude, V. Assessment of Sustainability Indicators for Biodiesel Production. *Appl. Sci.* **2017**, *7*, 869. <https://doi.org/10.3390/app7090869>
- [2] Muratov, M.; Kurniawan, T. A.; Eshmetov, R.; Salikhanova, D.; Eshmetov, I. Adizov, B.; Khandamov, D.; Madaminov, B.; Onn, C. W. Promoting Sustainability: Micellization and Surface Dynamics of Recycled Monoethanolamine Surfactants. *J. Mol. Liq.* **2024**, *414*, 126010. <https://doi.org/10.1016/j.molliq.2024.126010>
- [3] Hájek, M.; Vávra, A.; de Paz Carmona, H.; Kocík, J. The Catalysed Transformation of Vegetable Oils or Animal Fats to Biofuels and Bio-Lubricants. *Rev. Catal.* **2021**, *11*, 1118. <https://doi.org/10.3390/catal11091118>
- [4] Živković, S.; Veljković, M. Environmental Impacts of the Production and Use of Biodiesel. *Environ. Sci. Pollut. Res.* **2017**, *25*, 191–199. <https://doi.org/10.1007/s11356-017-0649-z>
- [5] Kononov, S.; Patrylak, L.; Zubenko, S.; Okhrimenko, M.; Yakovenko, A.; Levterov, A.; Avramenko, A. Alkali Synthesis of Fatty Acid Butyl and Ethyl Esters and Comparative Bench Motor Testing of Blended Fuels on their Basis. *Chem. Chem. Technol.* **2021**, *15*, 105–117. <https://doi.org/10.23939/chcht15.01.105>
- [6] Anastopoulos, G.; Zannikou, Y.; Stamoulis, S.; Kalligeros, S. Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies.* **2009**, *2*, 362–376. <https://doi.org/10.3390/en20200362>
- [7] Wang, B.; Wang, B.; Shukla, S. K.; Wang, R. Enabling Catalysts for Biodiesel Production via Transesterification. *Catalysts* **2023**, *13*, 740. <https://doi.org/10.3390/catal13040740>
- [8] Bothon, F. T. D.; Montcho, P. S.; Nonviho, G.; Dossa, C. P. A.; Tchiakpe, L.; Adomou, A. A.; Avlessi, F. L. Physicochemical Variability and Biodiesel Potential of Seed Oils of Two Hibiscus sabdariffa L. Phenotypes. *ACS Omega.* **2020**, *5*, 25561–25567. <https://doi.org/10.1021/acsomega.0c01838>
- [9] Purwanto, P.; Buchori, L.; Istadi, I. Reaction Rate Law Model and Reaction Mechanism Covering Effect of Plasma Role on the Transesterification of Triglyceride and Methanol to Biodiesel over a Continuous Flow Hybrid Catalytic Plasma Reactor. *Heliyon* **2020**, *6*, e05164. <https://doi.org/10.1016/j.heliyon.2020.e05164>
- [10] Buchori, L.; Istadi, I.; Purwanto, P. Advanced Chemical Reactor Technologies for Biodiesel Production from Vegetable Oils – A Review. *Bull. Chem. React. Eng. Catal.* **2016**, *11*, 406–430. <https://doi.org/10.9767/bcrec.11.3.490.406-430>
- [11] Widayat, W.; Christwardana, M.; Syaiful, S.; Satriadi, H.; Khaibar, A.; Almaki, M. M. Development of Heterogeneous Alkali Methoxide Catalyst from Fly Ash and Limestone. *Chem. Chem. Technol.* **2020**, *14*, 521–530. <https://doi.org/10.23939/chcht14.04.521>
- [12] Bahadoran, A.; Ramakrishna, S.; Oryani, B.; Al-Keridis, L. A.; Nodeh, H. R.; Rezaia, S. Biodiesel Production from Waste Cooking Oil Using Heterogeneous Nanocatalyst-Based Magnetic Polyaniline Decorated with Cobalt Oxide. *Fuel.* **2022**, *319*, 123858. <https://doi.org/10.1016/j.fuel.2022.123858>

- [13] Buchori, L.; Anggoro, D. D.; Ma'ruf, A. Biodiesel Synthesis from the Used Cooking Oil Using CaO Catalyst Derived from Waste Animal Bones. *Chem. Chem. Technol.* **2021**, *15*, 583–590. <https://doi.org/10.23939/chcht15.04.583>
- [14] Melnyk, Yu.; Starchevskiy, R.; Melnyk, S. Transesterification of Sunflower Oil Triglycerides by 1-Butanol in the Presence of d-Metal Oxides. *Vopr. khimii khimicheskoi tekhnologii.* **2019**, *4*, 95–100. <https://doi.org/10.32434/0321-4095-2019-125-4-95-100>
- [15] Daryono, E. D.; Jimmy; H. Setyawati, H. Production of Biodiesel Without Catalyst Separation with Palm Oil Interesterification Process Using Essential Oil Biocatalyst. *Chem. Chem. Technol.* **2024**, *18*, 356–362. <https://doi.org/10.23939/chcht18.03.356>
- [16] Melnyk, Yu. R.; Melnyk, S. R.; Mahorivska, H. Ya. Transesterifikatsiia tryhlitserydiv roslynnykh olii holovnoiu fraktsiieiu etylovooho spirtu. *Visnyk Natsionalnoho tekhnichnoho universytetu „KhPI”. Seriya: Novi rishennia v suchasnykh tekhnolohiiakh* **2021**, *1*, 72–79. <https://doi.org/10.20998/2413-4295.2021.01.11>
- [17] Melnyk, Yu.; Melnyk, S.; Mahorivska, H. The Assessment of Sustainability Indicators for Triglycerides Transesterification with Alcohols Catalyzed by Ion Exchange Resins. *Pytannia khimii ta khimichnoi tekhnolohii.* **2023**, *4*, 58–68. <https://doi.org/10.32434/0321-4095-2023-149-4-58-68>
- [18] Melnyk, Y.; Starchevskiy, R.; Melnyk, S. Technological Aspects of Vegetable Oils Transesterification with Ethanol in the Presence of Metal Oxides. *Kem. Ind.* **2020**, *69*, 365–370. <https://doi.org/10.15255/KUI.2019.059>

Received: February 26, 2025 / Revised: April 28, 2025 / Accepted: June 05, 2025

## ОЦІНКА ВПЛИВУ КАТАЛІЗАТОРІВ ТРАНСЕСТЕРИФІКАЦІЇ ТРИГЛІЦЕРИДІВ НА ПОКАЗНИКИ СТІЙКОСТІ

**Анотація.** Досліджено вплив каталізаторів та умов трансестерифікації на показники сталості. Визначено, що найкращими серед досліджених каталізаторів етанолізу та бутанолізу тригліцеридів є оксиди цинку та нікелю. Встановлено оптимальний вміст вказаних каталізаторів, який становить 0,25 мас. % і забезпечує мінімальне значення E-фактора. Показано, що підвищення мольного надлишку спирту ефективніше за бутанолізу, оскільки дає змогу під час каталізу оксидами цинку та нікелю знизити E-фактор у 3,61–7,98 разів. Встановлено, що регенерація непрореагованого спирту із реакційної суміші дає змогу під час бутанолізу в присутності оксидів цинку та нікелю підвищити атомну ефективність у 2,13–2,22 разів.

**Ключові слова:** зелена хімія, показники сталості, E-фактор, оксиди металів, тригліцериди, етанол, бутан-1-ол, трансестерифікація.