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Natural Rocks–Heterogeneous Catalysts for Oil Transesterification in Biodiesel Synthesis

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Abstract: Some of the more recent methods to produce biodiesel are based on heterogeneous catalysis, which has the advantage of easy separation of catalyst from the final product. In this paper, the heterogeneous transesterification of rapeseed oil with methanol is studied. The aim of this work was to investigate the possibilities of using natural catalysts in biodiesel synthesis and to determine the optimal conditions for this process. After the evaluation of catalytic effectiveness of rocks containing calcium and magnesium carbonates, it was determined that dolomite is the most effective catalyst in heterogeneous biodiesel synthesis. The optimal conditions of dolomite preparation are the following: heating at 850 °C for 5 h. The rapeseed oil transesterification was optimized by the application response surface methodology. Optimal conditions for the production of rapeseed methyl esters using dolomite as catalyst are the following: molar ratio of methanol to rapeseed oil of 11.94:1, reaction temperature of 64 °C, dolomite content of 6 wt%, reaction time of 5 h.

Keywords: transesterification; heterogeneous catalysis; dolomite; response surface methodology; optimal conditions

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1. Introduction

Alternative fuels of biological origin, e.g., ethanol, biodiesel, have been intensively explored in recent decades. The high consumption of fossil fuels, the impact on global warming, and concerns about the depletion of energy resources are key aspects that stimulate interest in biofuels. The biodiesel production process can be heterogeneous when the catalyst is in a different phase than the reactant and reaction product, homogeneous when the catalyst is in the same phase, and enzymatic (enzymes can be used both liquid and solid) [1]. Heterogeneous catalysis is considered more environmentally friendly because the solid catalyst is easily separated from the reaction mixture by filtration and can be reused [2]. During heterogeneous catalysis, the reagents are adsorbed on the surface of the catalyst, where a transesterification reaction takes place, and the product is desorbed. Heterogeneous catalysts can be designed to be more active and selective than homogeneous ones, as well as to be used over a longer period of time—reusable. Many different heterogeneous catalysts are developed for the production of biodiesel [3]. Calcined Mg-Al hydrotalcites, zeolite and metal catalysts, and metal oxides, e.g., CaO, MgO, ZrO_2, are used as heterogeneous catalysts [4].

Biocatalysts such as lipases can also be used for biodiesel synthesis. Compared to chemical catalysts, biocatalysts have many advantages in transesterification reactions: They are environmentally friendly, give higher ester yields under standard conditions, decompose little or not at all, require less alcohol during the reaction, and form a purer product [5]. However, biocatalysts are sensitive to high temperatures and expensive, which limits their use in biodiesel production.

CaO and MgO are most commonly used in biodiesel production [4]. Natural calcium carbonate stone is also used, which is a cheap catalyst, but its activity is low, and a high

reaction temperature is required to achieve a conversion of >95%. Na/NaOH/γ-Al_2O_3, as a strong base catalyst used in the transesterification of soybean oil, had similar results to traditional homogeneous NaOH catalysis. Many alkali metal oxides are highly soluble in water, which makes it difficult to separate the product after homogeneous catalysis. Meanwhile, alkaline earth metal oxides are less soluble in water [6].

Albite is a naturally occurring mineral belonging to the silicate class. Using albite as a natural catalyst in biodiesel synthesis, rapeseed oil conversion to methyl esters was 97% [7]. Zeolite is another mineral that can be used in the heterogeneous synthesis of biodiesel. Kusuma et al. [8] investigated the possibilities of using zeolite combined with KOH in the process of palm oil transesterification. Using such a catalyst, the yield of rapeseed oil methyl esters (RME) was found to be 95.09% [8].

The researchers evaluated the possibilities of using various shellfish shells rich in $CaCO_3$ in the synthesis of biodiesel. In the process of transesterification of palm oil using mollusc shells as a heterogeneous catalyst, the yield of RME was 97% [9], and using oil and white bivalve mollusc shells used in the food industry, the yield of biodiesel was 95.84% [10]. Eggshells are another natural catalyst used in the conversion of algal biomass to biodiesel to achieve a 92.03% yield of biodiesel [11]. Dolomite is a natural mineral composed mainly of calcium and magnesium carbonates, and it also contains small amounts of iron, aluminum, silicon, and so on. Given its low cost, low toxicity, and environmental safety, dolomite is used as a building material and a source of ceramic support [12]. Due to its content of Ca^{2+} and Mg^{2+}, dolomite can be used in the synthesis of biodiesel [13]. Dolomite decomposition at high temperature takes place in two stages: The first stage decomposes $MgCO_3$ to form MgO (350–545 °C), and the second stage decomposes $CaCO_3$ to form CaO (825 °C).

CaO is an efficient and promising catalyst in biodiesel production [4]. Therefore, research related to the use of natural rocks containing calcium and magnesium ions in the synthesis of biodiesel is relevant.

Given the rather contradictory results in the scientific literature on the efficiency of using rocks as heterogeneous catalysts for biodiesel synthesis, the very different reported optimal conditions for transesterification, and the need to look for cheaper natural heterogeneous catalysts for biodiesel synthesis, our work focused on rocks found in our country that contain Ca and Mg compounds. Rapeseed oil is commonly used in Europe for the synthesis of biodiesel. Meanwhile, studies on heterogeneous catalysis using rapeseed oil and rocks as a catalyst for transesterification with methanol or other alcohols have been limited. Much attention has been paid to the transesterification of palm oil, but biodiesel derived from palm oil has poor low-temperature properties and is not viable for use in temperate climates. Therefore, we chose rapeseed oil and rocks found in Lithuania for our research. After investigating the catalytic efficiency of these rocks, we found that dolomite has the best properties, so we investigated its preparation process, fractionated the dolomite into several fractions, selected the fraction with better properties, and optimized the process. To optimize the transesterification process, four variables were selected that influence the transesterification reaction. The aim was to determine the conditions under which the yield of methyl esters greater than 96.5% would be obtained in one transesterification step.

2. Results and Discussions

2.1. Use of Various Rocks as Catalysts

In order to evaluate the catalytic efficiency of natural rocks in the transesterification process, studies using selected rocks were performed under uniform conditions. Samples of 0.315–0.1 mm fractions of glauconitic sandstone, opaque, and serpentinite were prepared and calcined at 800 °C.

The 8 wt% catalyst used for the transesterification process, the molar ratio of methanol to rapeseed oil was 8:1, and the reaction was carried out for 5 h at 64 °C. The resulting mixtures were analyzed by thin layer chromatography (Figure 1).

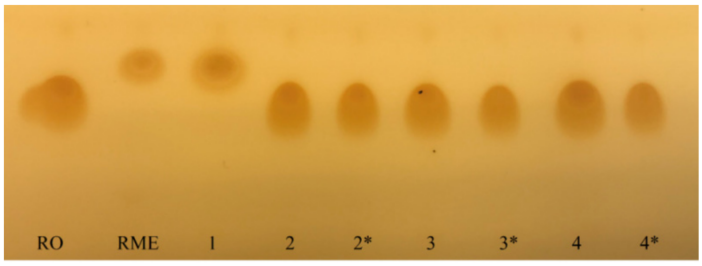

Figure 1. Reaction products of rapeseed oil transesterification with methanol using different natural catalysts: 1—dolomite, 2—glauconitic sandstone, 2 *—glauconitic sandstone, 3—opoka, 3 *—opoka, 4—serpentinite, 4 *—serpentinite, RO—rapeseed oil, RME—rapeseed oil methyl esters.

The data presented in the chromatogram show that dolomite had the highest efficiency; other rocks did not show high efficiency in the transesterification process, so dolomite was chosen for further research and process optimization. Studies by other researchers also suggest that dolomite is an effective catalyst in oil transesterification reactions [4,6].

2.2. Selection of Optimal Conditions for Dolomite Preparation

Examining the amounts of CaO and MgO in dolomite, it was found that dolomite contains 29.29 ± 0.18% of CaO and 19.11 ± 0.12% of, MgO. Similar results were obtained by Korkut and Bairamoglu [14], who found when studying the composition of dolomite that it contained 23.50% Ca and 12.07% Mg. It is important to prepare the catalyst properly before use in transesterification reactions. One of the most important parameters is the size of the catalyst fraction and the temperature at which it is heated.

2.2.1. Fraction Selection

After the fractionation of dolomite into three fractions, 0.63–0.315, 0.315–0.1, and 0.1–0.063 mm and calcination at 800 °C for 2 h, rapeseed oil transesterification tests were performed using 8 wt% dolomite from the oil content and a methanol to rapeseed oil molar ratio of 8:1. The reaction was carried out for 5 h at 64 °C. The obtained reaction products were analyzed by thin layer chromatography (Figure 2).

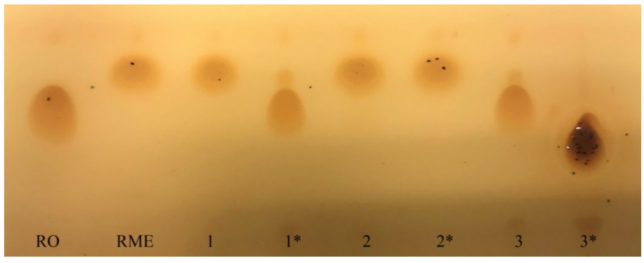

Figure 2. Reaction products of rapeseed oil transesterification with methanol using different fractions of dolomite: 1—0.63–0.315 mm, 1 *—0.63–0.315 mm, 2—0.315–0.1 mm, 2 *—0.315–0.1 mm, 3—0.1–0.063 mm, 3 *—0.1–0.063 mm, RO for rapeseed oil, RME for rapeseed oil methyl esters.

The data show that the fraction of dolomite of 0.315–0.1 mm had the highest efficiency; therefore, the catalysts used in subsequent studies were prepared in the fraction of this size.

2.2.2. Selection of Heating Temperature

The selected dolomite fraction was heated at different temperatures (700, 800, 850, 900 °C) and used for transesterification of the oil, its content was 8 wt% of the oil content, the molar ratio of methanol to rapeseed oil was 8:1, and the process time was 5 h at 64 °C. The results of the thin layer chromatography analysis of the obtained reaction products are shown in Figure 3.

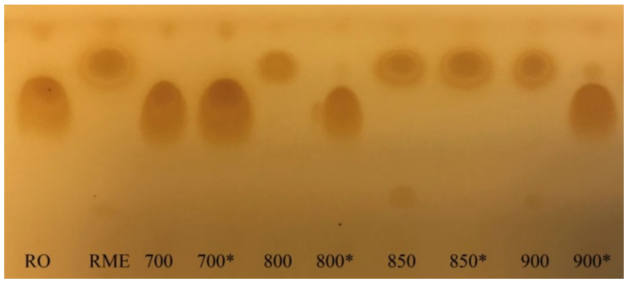

Figure 3. Reaction products of rapeseed oil transesterification with methanol using dolomite heated at different temperatures: the figures correspond to the temperature at which the dolomite was heated, RO—rapeseed oil, RME—methyl esters of rapeseed oil.

Other researchers have also investigated the use of dolomite in the oil transesterification process and found that dolomite is most effective when calcined at 850 °C [4,15]. At lower temperatures (500–600 °C), dolomite was almost ineffective (<3% RME yield), which can be explained by the fact that transesterification reactions are catalyzed by metal oxides, which are formed from metal carbonates in dolomite upon exposure to temperature. The process takes place at a temperature higher than 700 °C.

These results also confirm the results obtained in our study. As we can see in the presented chromatogram, the fraction of dolomite heated at 850 °C had the highest catalytic efficiency; therefore, the dolomite used in subsequent studies was prepared at this temperature.

2.3. Modeling and Determination of Optimal Reaction Conditions Using Response Surface Methodology

The experimental design and responses with the observed values are presented in Table 1. The highest predicted ester yield was 98.05 wt% with a molar ratio of methanol to rapeseed oil of 12:1, reaction temperature of 64 °C, catalyst content of 6 wt%, and reaction time of 5 h. The highest ester yield obtained experimentally under the same conditions was 98.66 ± 0.65 wt%. Estimating the ester content of this sample gave a value of 97.27 ± 0.78 wt%.

ANOVA was used to explore the significant effects of process variables on the response (Table 2). Results show that value of model F is 16.62. This indicates that the model is statistically significant because the p value (P > F) is <0.0001. The components of the model with a p value (P > F) of less than 0.05 are statistically significant. In this case, insignificant components were removed. Equation (1) describes the yield of esters after model modification with only significant components left:

$$EY = 47.08 + 1.95A - 2.87B - 6.80C - 10.36D + 4.69CD + 0.04B^2 \quad (1)$$

where

EY is the ester yield (%);
A is the methanol-to-oil molar ratio;
B is the temperature (°C);
C is the catalyst amount (%); and
D is the process duration (h).

Table 1. Experimental design and influence of independent variables on ester yield.

	Independent Variable				Predicted Ester Yield, wt%	Experimental Ester Yield, wt%
	A: Methanol to Oil Molar Ratio (mol/mol)	B: Temperature, °C	C: Catalyst Account, wt%	D: Duration, h		
1	4.00	20.00	2.00	2.00	1.52	1.60 ± 0.32
2	12.00	20.00	2.00	2.00	11.20	8.78 ± 0.52
3	4.00	64.00	2.00	2.00	12.77	11.10 ± 0.55
4	12.00	64.00	2.00	2.00	28.86	17.76 ± 0.45
5	4.00	20.00	6.00	2.00	2.32	3.50 ± 0.33
6	12.00	20.00	6.00	2.00	9.12	3.09 ± 0.23
7	4.00	64.00	6.00	2.00	28.69	18.20 ± 0.66
8	12.00	64.00	6.00	2.00	44.77	62.29 ± 1.02
9	4.00	20.00	2.00	5.00	3.25	6.26 ± 0.32
10	12.00	20.00	2.00	5.00	15.68	11.17 ± 0.46
11	4.00	64.00	2.00	5.00	5.30	3.33 ± 0.14
12	12.00	64.00	2.00	5.00	21.38	18.10 ± 0.69
13	4.00	20.00	6.00	5.00	58.27	65.05 ± 0.85
14	12.00	20.00	6.00	5.00	74.35	84.53 ± 1.06
15	4.00	64.00	6.00	5.00	81.97	76.48 ± 0.96
16	12.00	64.00	6.00	5.00	98.05	98.66 ± 0.65
17	3.20	42.00	4.00	3.50	1.92	5.20 ± 0.34
18	12.80	42.00	4.00	3.50	21.22	20.20 ± 0.23
19	8.00	20.00	4.00	3.50	36.83	19.21 ± 0.14
20	8.00	64.00	4.00	3.50	57.51	82.39 ± 0.56
21	8.00	42.00	1.60	3.50	2.53	2.34 ± 0.14
22	8.00	42.00	6.40	3.50	33.31	21.80 ± 0.47
23	8.00	42.00	4.00	1.70	2.12	3.55 ± 0.16
24	8.00	42.00	4.00	5.30	28.22	20.51 ± 0.34
25	8.00	42.00	4.00	3.50	19.43	17.10 ± 0.25
26	8.00	42.00	4.00	3.50	19.43	18.20 ± 0.26
27	8.00	42.00	4.00	3.50	19.43	16.20 ± 0.19

Table 2. Analysis of variance of quadratic model.

Source	Sum of Squares	df	Mean Square	F Value	*p*-Value Prob > F	
Model	20,598.31	14	1471.31	16.62	<0.0001	Significant
A-methanol/oil molar ratio	1144.58	1	1144.58	12.93	0.0037	-
B-temperature	2115.53	1	2115.53	23.89	0.0004	-
C-catalyst	6985.52	1	6985.52	78.90	<0.0001	-
D-duration	3001.47	1	3001.47	33.90	<0.0001	-
AB	130.25	1	130.25	1.47	0.2485	-
AC	83.22	1	83.22	0.94	0.3514	-
AD	1.66	1	1.66	0.019	0.8934	-
BC	402.91	1	402.91	4.55	0.0542	-
BD	290.11	1	290.11	3.28	0.0954	-
CD	3168.28	1	3168.28	35.78	<0.0001	-
A^2	361.68	1	361.68	4.08	0.0662	-
B^2	3168.20	1	3168.20	35.78	<0.0001	-
C^2	145.28	1	145.28	1.64	0.2244	-
D^2	224.49	1	224.49	2.54	0.1373	-
Residual	1062.45	12	88.54	-	-	-
Lack of Fit	1060.45	10	46.04	3.69	0.1194	Not significant
Pure Error	2.01	2	1.00	-	-	-
Cor Total	21,660.76	26	-	-	-	-

The coefficient of determination for the adjusted number of the model's parameters, corresponding to the points of a pilot's plan, equals 0.8937; i.e., the model can account for 89.37% of the response's variations. The predicted R2 value predicted is equal to 0.7629 and is close to the adjusted R2 value (Table 3).

Table 3. Statistical parameters determined using ANOVA for the response surface model.

Variable	Value	Variable	Value
Std. Dev.	9.41	R-Squared	0.9510
Mean	27.84	Adj R-Squared	0.8937
C.V.%	33.80	Pred R-Squared	0.7629
PRESS	5135.38	Adeq Precision	15.981

The value of adequate precision equals 15.981 for the model. This value shows the signal/noise ratio. It is desirable for the value to be higher than 4. In the case of this model, the value of adequate precision exceeds the desirable value almost more than four times.

A visual evaluation of reaction parameters that influence the ester yield can be observed in graphical images. Figures 4–7 demonstrate the dependence of the ester yield on the various process parameters. Dependence of the process duration and the temperature on the ester yield when the catalyst amount is 6 wt% is demonstrated in Figure 4. The largest ester yield is obtained when the process duration takes from 4.5 to 5 h and the process temperature is not less than 60 °C. Ilgen [4] studied the transesterification process of canola oil with methanol to biodiesel using dolomite. It was obtained that the ester yield is strongly influenced by the process temperature. The ester yield increased with increasing temperature from room temperature to 60 °C [4].

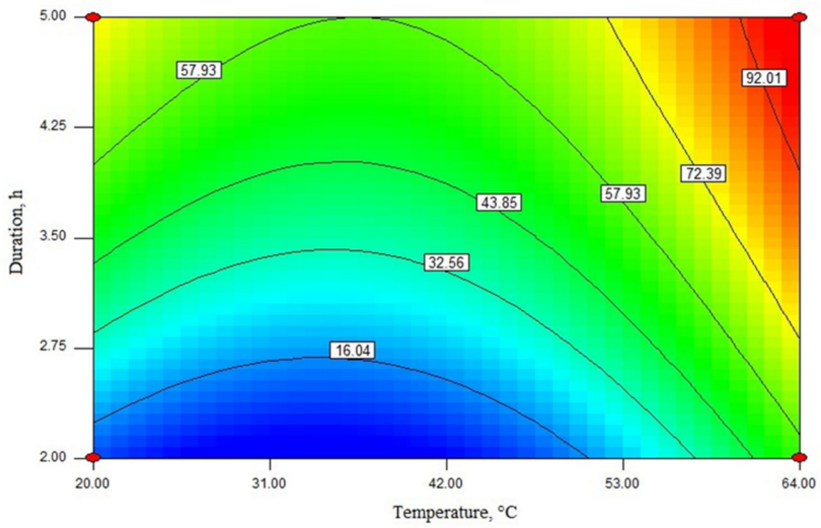

Figure 4. Response surface contour plot for the interaction between the process duration and the temperature for the ester yield when the catalyst amount is 6 wt% and the methanol-to-oil ratio is 12:1.

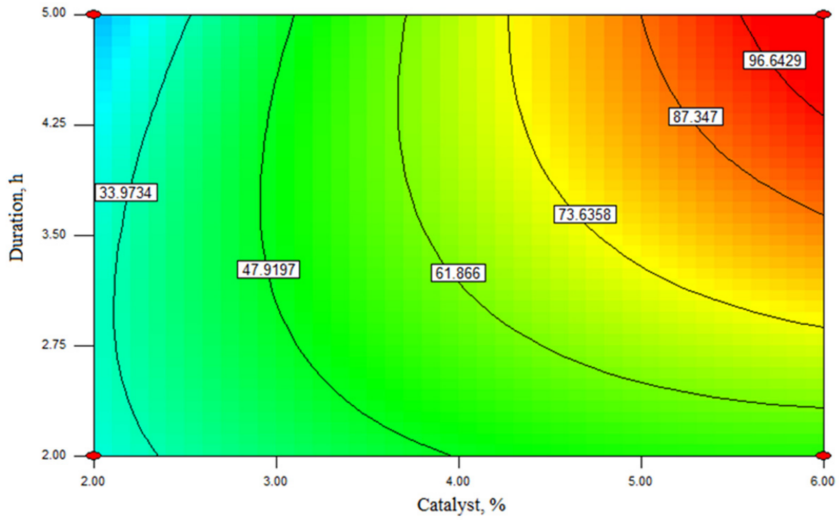

Figure 5. Response surface contour plot for the interaction between the duration and the catalyst amount for the ester yield when the process temperature is 64 °C and methanol-to-oil ratio is 12:1.

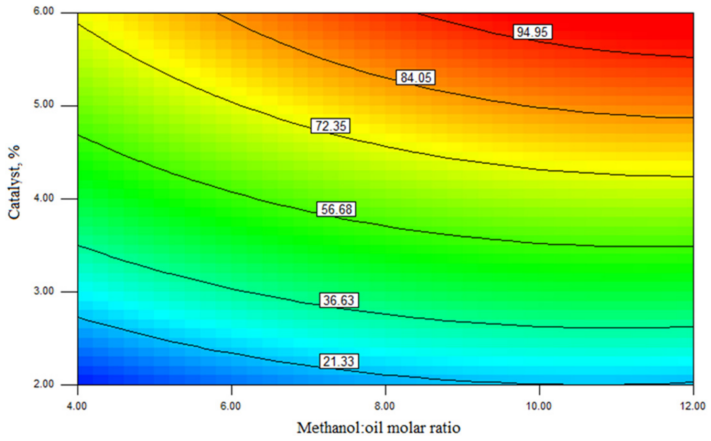

Figure 6. Response surface contour plot for the interaction between the catalyst amount and the methanol-to-oil ratio for the ester yield when the process temperature is 64 °C and the process duration is 5 h.

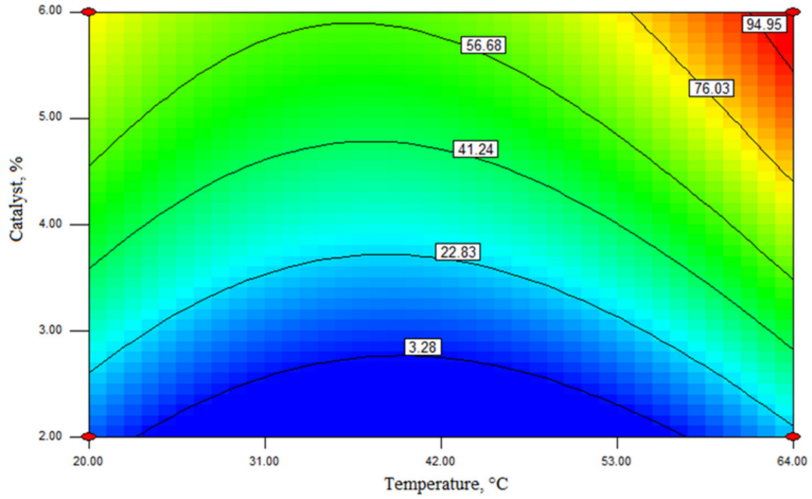

Figure 7. Response surface contour plot for the interaction between the catalyst amount and the temperature for the ester yield when the methanol-to-oil ratio is 12:1 and the process duration is 5 h.

Figure 5 demonstrates the impact of the reaction duration and the catalyst amount, when the process temperature is 64 °C and the methanol-to-oil ratio is 12:1. The process duration had a huge impact on the obtained ester yield. In the case of short duration (2 h), the ester yield is less than 62 wt% when the catalyst amount is 6 wt%. Increasing the duration up to the selected maximum (5 h) increased the ester yield to more than 96 wt%. Catalyst amount is a highly important parameter in biodiesel generation; an increase in catalyst amount leads to an increase in the ester yield. Scientists investigated biodiesel production experiments from palm oil using La-dolomite and methanol and obtained that the biodiesel yield is increased from 52.5% with the catalyst addition of 4 wt% to the 97.9% with the catalyst addition of 7 wt% [16].

Figure 6 demonstrates the impact of the catalyst amount and the methanol-to-oil ratio for the ester yield when the process temperature is 64 °C and the process duration is 5 h. As mentioned earlier, the catalyst amount had a huge impact on the obtained ester yield. The ester yield increased from 36 wt% to more than 94 wt% by increasing the catalyst amount from 3 wt% to 6 wt%. The methanol-to-oil ratio is also an important index for biodiesel production; however, it is possible to reach an ester yield of more than 90 wt% by adding 8:1 methanol to oil while 12:1 methanol to oil gives similar results. Korkut and Bayramoglu investigated the impact of methanol-to-oil ratio on biodiesel production and found that upon increasing the methanol-to-oil ratio, the biodiesel yield increases up to a maximum value at the methanol-to-oil ratio of 9:1 [14]. Choudhury and colleagues obtained the most optimum methanol-to-oil molar ratio of 10:1 for biodiesel production [17].

The impact of catalyst amount and the temperature for the ester yield when the methanol-to-oil ratio is 12:1 and the process duration is 5 h is shown in Figure 7. Temperature plays an important role in biodiesel production. An ester yield of less than 75 wt% was obtained when the temperature was lower than 55 °C. However, the ester yield increased to more than 94 wt% with increasing temperature to 64 °C. Scientists investigated biodiesel production using dolomite incorporated with cerium and determined that the biodiesel yield was only 49.73 wt% at 50 °C and increased to 97.21 wt% with increasing the temperature to 65 °C [18]. The reason for this is that at the higher temperature, the transesterification process is more easily generated, and the higher molecular activity forces the equilibrium to the products [19]. However, a higher temperature than the alcohol boiling point is not desirable due to its evaporation. In this case, methanol's boiling point is 64.7 °C under the atmospheric pressure.

2.4. Optimization of Rapeseed Oil Transesterification

Given that the process of transesterification of rapeseed oil depends on four independent variables, it is important to determine the conditions under which the highest ester yield can be obtained. In the optimization process, all four variables were selected: the methanol-to-oil molar ratio, the temperature, the catalyst amount, and the process duration were selected in range, and the ester yield was maximized. The obtained optimized result for our investigated conditions is presented in Table 4. The data show that the predicted ester yield was 98.66 wt%. The obtained optimal transesterification conditions were verified by a laboratory transesterification test under these conditions. The determined yield of rapeseed oil methyl esters was higher than the predicted yield and reached 98.89 wt%. The high yield of methyl esters obtained indicates that under these conditions, biodiesel meeting the requirements of the biodiesel standard EN14214 can be obtained in one step.

Table 4. Solutions of rapeseed oil transesterification reaction optimization algorithm.

Methanol-to-Oil Molar Ratio, mol/mol	Reaction Temperature, °C	Concentration of Catalyst, % (From Oil Mass)	Duration of Reaction, h	Predicted Ester Yield, wt%	Experimental Ester Yield, wt%
11.94	64.0	6.0	5.0	98.66	98.89 ± 0.42

The results obtained by us correlate with the results obtained by some other researchers (Table 5). A number of studies have been performed using dolomite calcined at 800–900 °C. However, the results of studies on the transesterification of different types of oil with methanol obtained by different authors are quite contradictory. The optimum ratio of methanol to oil for high methyl ester yields ranges from 6:1 for canola oil to 30:1 for palm and olive oil. The optimum amount of catalyst set by various authors' ranges from 1% for canola oil to 15.6% for olive oil. The results of our research showed that the optimal molar ratio of methanol to oil in the transesterification of rapeseed oil is about 12:1, and the optimal amount of dolomite is 6%; these indicators correspond to the average values of previous studies. A molar ratio of methanol to oil greater than 12:1 makes the process uneconomical due to the high energy consumption to separate the methanol from the reaction medium and recover it.

Table 5. Optimal conditions of transesterification using dolomite as catalyst.

Oil	Dolomite	Methanol-to-Oil Molar Ratio	Catalyst Ammount, %	Temperature, °C	Duration, h	Yield, %	References
			Calcined dolomites				
Palm kernel	Calcined at 800 °C	30:1	6	60	3	98	[20]
Canola	Calcined at 850 °C	6:1	1	60	4	98.81	[15]
Canola	Calcined at 850 °C	6:1	3	67.5	3	91.78	[4]
Canola	Calcined at 840 °C, ultrasound assisted	9:1	5	60	1.5	97.4	[14]
Olive	Calcined at 900 °C	30:1	15.6	60	3	>98	[21]
Sunflower	Calcined at 850 °C	9:1	2	60	4	96.52	[15]
Rapeseed	Calcined at 850 °C	11.94	6	64	5	98.66	Our study
			Calcined and modified dolomites				
Canola	Na-CaO/MgO dolomites	12:1	6	65	7	97.6	[22]
Palm	La-dolomite	18:1	7	65	3	98.7	[16]
Palm	Dolomite incorporated with cerium	15:1	0.05	65	2	97.21	[18]
Palm kernel	Modified dolomite	15:1	10	60	3	99.9	[6]
Palm oil	SnO_2 doped dolomite	15:1	1	65	4	99.98	[23]

A high yield of biodiesel from canola oil obtained by Correia et al. [15] seems optimistic under fairly mild conditions using 1% of dolomite and a 6:1 molar ratio of methanol to oil, but we failed to achieve such good results. This can be explained by the fact that the efficiency of the catalyst is greatly influenced by the type of dolomite, the method of catalyst preparation, and the amount and ratio of calcium and magnesium in the dolomite. This also explains the rather different research results of individual researchers.

Although the transesterification temperature affects the reaction rate and yield, it is generally maintained close to the boiling point of methanol. The results of our research showed that the optimal temperature is 64 °C, i.e., slightly higher than the temperature of studies performed by other investigators, which was generally maintained close to 60 °C.

The reaction time also affects the yield of methyl esters, but the data obtained by different investigators are also contradictory. Korkut et al. [14] obtained a yield of 97.4% canola oil methyl esters within 1.5 h, whereas Correia et al. [15] indicate that yields of methyl ethers greater than 96.5% of canola and sunflower seed oil are obtained within 4 h. The results of our research show that the optimal duration of the process is even longer and reaches 5 h. The duration of the process, although insignificant, correlates with the excess methanol in the reaction medium. At a maximum molar ratio of methanol to oil of 30:1, the process time was 3 h [20,21].

The best results were obtained by Correia et al. [15], who using canola oil achieved a yield of 98.81% methyl esters under the mildest conditions. At a molar ratio of methanol to

oil of 6:1, 1% of dolomite was obtained from the oil content by performing the process at 60 °C for 4 h.

Korkut et al. [14] found that the application of ultrasound during the transesterification process significantly shortens its duration. The yield of 97.4% canola oil methyl esters was obtained in 1.5 h, but the molar ratio of methanol to oil was higher and reached 9:1.

Some authors modified calcined dolomite by various additives and methods. The catalytic efficiency of dolomite was expected to increase. The obtained research results are presented in Table 5. They show that modifying dolomite by different methods and with different materials does not always achieve the desired result. The incorporation of cerium, sodium, lanthanum, and SiO_2 into dolomite does not significantly increase its catalytic efficiency. The optimal molar ratio determined using modified dolomite exceeded the optimal molar ratio using calcined dolomite in all cases studied. The optimal catalyst concentration was reduced only in some cases. The optimal process time and methyl ester yield were not significantly higher than with calcined dolomite.

The modification requires the addition of more expensive reagents and the application of new technologies; it makes sense to look for other ways to increase the catalytic efficiency of dolomite or other rocks that could be used as cheap heterogeneous catalysts for biodiesel synthesis.

3. Materials and Methods

3.1. Preparation of Catalysts

Natural rocks containing calcium and magnesium oxides—dolomite, glauconitic sandstone, opoka, and serpentinite—were used in the study. In the initial stage, in order to find out the optimal calcination temperature, the duration, and the size of the heterocatalyst fraction giving better transesterification results, tests were performed using dolomite obtained from a trade lines (manufacturer SC Dolomite). Dolomite contained 29.29 ± 0.18% of CaO and 19.11 ± 0.12% of, MgO. The mineral was ground in a laboratory mill and heated in a muffle furnace (AB UMEGA SNOL 8.2 /1100) for 4 h at 700, 800, 850, and 900 °C. After heating, dolomite was sieved through sieves of different sizes, and three fractions of dolomite (0.63–0.315, 0.315–0.1 and 0.1–0.063 mm) were obtained. Glauconitic sandstone, opoka, and serpantinite (0.315–0.1 mm) were heated in a muffle furnace for 4 h and fractionated. Rapeseed oil (RO) transesterification studies were performed at 800 °C.

3.2. Determination of CaO and MgO in Catalysts

The test sample was decomposed using 2 g of material and 20 mL of royal water (mixture of nitric acid and hydrochloric acid in a molar ratio 1:3). Then, 25 mL of the test solution was mixed with 50 mL of H_2O in the conical flask, 10 mL of ammonia buffer solution, and the dark blue chromogen indicator was added. The solution titrated with trilon B (EDTA). A color change from raspberry to violet was registered. The CaO and MgO content was calculated according to Equations (2) and (3):

$$\mathrm{CaO} = \frac{V_1 \cdot K \cdot 0.0014 \cdot 250}{m \cdot 25} \cdot 100\% \quad (2)$$

$$\mathrm{MgO} = \frac{(V_2 - V_1) \cdot K \cdot 0.001 \cdot 250}{m \cdot 25} \cdot 100\% \quad (3)$$

where

V_1 is the amount of trilon B used for calcium titration, mL;
V_2 is the amount of trilon B used for the titration of calcium and magnesium, mL;
m—mass of the sample, g; and
K—trilon B correction factor.

3.3. Transesterification of Rapeseed Oil

Rapeseed oil (RO) purchased from a local trade network (supplier Lomista foods, Kaisiadorys, Lithuania) met the requirements of the national standard for edible oil. Rapeseed oil contained 4.7% saturated fatty acids, 61.2% monounsaturated fatty acids, and 34.1% polyunsaturated fatty acids. The transesterification of the oil was carried out in a heated chemical reactor with a stirrer and a reflux condenser. The required amount of oil was placed in the reactor and heated to 64 °C. A determined amount of catalyst and methanol (Merck, Darmstadt, Germany 99.5%) was added to the heated oil, and the stirring process was carried out at 64 °C for a set time. After completion, the resulting mixture was filtered, washed with H_3PO_4 (5%), solution (10% by volume of the reaction product), and twice with distilled water (10% by volume of the mixture). After washing, the residual water was evaporated at 110 °C.

3.4. Thin Layer Chromatography

First, 50 µL of the reaction product obtained after washing and evaporation was mixed with 500 µL of diethyl ether (Chempur, Piekary Slaskie, Poland). Then, 2 µL of the resulting mixture was applied to boron-impregnated silica gel G-25 plates (layer thickness 0.25 mm). Rapeseed oil and rapeseed oil methyl esters (RME) were used as controls. The plate with the samples was immersed in a mobile phase consisting of petroleum ether (Sigma-Aldrich, Darmstadt, Germany)/diethyl ether/acetic acid (80:20:1; *v*/*v*), so that the mobile phase covered up to 3 mm of the lower edge of the plate.

After the mobile phase rose to the intended point (≈5 mm to the top), the plate was removed and dried for 3 h at 50 °C; then, it developed in an iodine vapor chamber. When the image was exposed, the plates were analyzed—the spots of the examined samples were compared with the control spots (the position of the spot, its brightness, and its area were taken into account).

3.5. Gas Chromatorgraphy

Ester yield was determined by the amount of glycerides in the samples. Glycerol, monoglycerides, diglycerides, and triglycerides were analyzed with a gas chromatograph Perkin Elmer Clarus 500 (Boston, Massachusetts, Unated States, detector—FID, column—Restek MXT-Biodiesel TG (0.15 m–0.32 mm–0.10 µm) according to the requirements of standard EN 14105).

Ester content was calculated according to Equation (4) [24].

$$C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \quad (4)$$

where

C—ester content, %;
∑A—is the total peak area from methyl ester in C6:0 to that in C24:1;
A_{EI}—is the peak area corresponding to nonadecanoic acid methyl ester;
W_{EI}—is the weight (mg) of the nonadecanoic acid methyl ester being used as internal standard; and
W—is the weight (mg) of the sample.

3.6. Response Surface Methodology

Experiments were planned and results analyzed using response surface methodology (RSM). Design Expert version 8.01 was used determining the conditions for transesterification of rapeseed oil with methanol. Four independent variables were used in the experimental design: alcohol-to-oil molar ratio (mol:mol) (4 to 12), reaction temperature (23 to 64 °C), catalyst (dolomite) content (2 to 6 wt%), and reaction duration (2 to 5 h). The experimental design consisted of 27 experimental trials (Table 1).

After the experiments provided in the experimental plan, the results were analyzed, and the model that best fits the results was applied. After selecting a model corresponding to the experimental values, the values of the independent variables that determine the desired response value—maximum ester yield—were obtained.

4. Conclusions

The biodiesel production process can be performed using heterogeneous and homogeneous catalysts. The advantages of heterogeneous catalysis include the fact that the purification of biodiesel is performed easily; a separated catalyst can be used repeatedly. Among the rocks containing calcium and magnesium carbonates, dolomite was shown to have the highest catalytic in the transesterification of rapeseed oil with methanol. Conditions of dolomite preparation included milling and sieving to 0.315–0.1 mm fraction and calcination at 850 °C for 5 h.

The influence of independent variables and their combined effects on the rapeseed methyl ester yield was investigated. It was found that the biggest influence was an interaction of catalyst amount and duration of process. The optimization of heterogeneous rapeseed oil transesterification with methanol using the surface response methodology resulted in the determining of the following optimal process conditions: molar ratio of methanol to rapeseed oil of 11.94:1, reaction temperature of 64 °C, dolomite content of 6 wt% from the oil content, reaction time of 5 h. Under these conditions, the yield of rapeseed oil methyl esters was 98.66 wt%.

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