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Snail Shells as a Heterogeneous Catalyst for Biodiesel Fuel Production

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Abstract: Homogeneous catalysis is relevant for biodiesel fuel synthesis; however, it has the disadvantage of difficult separation of the catalyst. In the present work, heterogeneous catalysis was applied for rapeseed oil transesterification with methanol, while snail shells were used as a catalyst. CaO content in the catalyst was investigated. Transesterification reactions were carried out in a laboratory reactor, ester yield was analyzed using gas chromatography. Response surface methodology was used for process optimization. It was found that the optimum transesterification conditions when the reaction temperature is 64 °C are the following: a catalyst amount of 6.06 wt%, a methanol-to-oil molar ratio of 7.51:1, and a reaction lasting 8 h. An ester yield of 98.15 wt% was obtained under these conditions.

Keywords: biodiesel; oil; methanol; snail shells; heterogeneous catalysis; optimization

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1. Introduction

Global warming has been a big challenge in recent decades. With the aim of reducing it, the global demand for clean energy is growing, resulting in an increasing search for ways to replace fossil fuels with less polluting and more environmentally friendly fuels. This transformation into cleaner fuels is crucial for achieving the commitments made in the Paris Agreement and the Glasgow Climate Pact [1], where it was decided to reduce emissions 50% by 2030 and to reach net zero by mid-century. In addition to this, the Lithuanian energy independence strategy envisages that the transport sector must reach 15% of consumed energy being from renewable sources by 2030 [2].

One of the main reasons for greenhouse gas emissions is the use of mineral diesel in transport engines, which not only pollutes the environment, but is also produced from a non-renewable resource. One of the alternatives to mineral diesel is the production and use of biofuels made from renewable energy sources. Sustainable biofuel production is crucial in the context of the Green Course in Europe. Biodiesel, which can be used in a mixture with mineral diesel, is one type of biofuel.

Biomass that can be used for biodiesel production absorbs CO_2 from the atmosphere through photosynthesis. Biodiesel is biodegradable, which is a positive property for the environment [3]. Biodiesel or its mixtures with mineral diesel in vehicles reduces CO, SO_2, particulate matter and unburnt hydrocarbon emissions when compared to mineral diesel [4].

Biodiesel can be obtained both in homogeneous and heterogeneous ways. Usually, chemical catalysts are used in homogeneous synthesis, which has good catalytic activity. However, there are some disadvantages, including the inevitable production of wastewater during the washing process, which cannot be reused, and, when using homogeneous catalysts, a one-step process is usually not sufficient to obtain biodiesel of high quality [5–7]. In this context, heterogeneous catalysis has the advantage of using biocatalysts and chemical catalysts [8–10], allowing a one-step process that can be used more than once [11,12].

CaO is the heterogeneous catalyst that has been most widely studied for biodiesel production. It has many advantages, including high activity, low solubility in methanol,

and the possibilities of regeneration and reuse. The reaction of transesterification catalyzed by CaO take place under moderate conditions [13,14]. Natural sources rich in calcium carbonate can be used as cheap raw material for catalyst preparation through the conversion of calcium carbonate to oxide [15]. Various shells rich in $CaCO_3$ are contained in waste derived from the food industry. Oyster shells [16], egg shells, crab shells [17], mussel shells [18], clam shells [19], shrimp shells [20], and crab shells [21] have been used as heterogeneous catalysts for biodiesel production.

Snails belong to the class Gastropoda and the Phylum Mollusca. The edible snail global market is worth EUR 1 billion, corresponding to 300,000 tonnes, per year. Annually, 100,000 tonnes of edible snails are consumed in Europe [22]. After snails are consumed, snail shells remain as waste. They are rich in $CaCO_3$ which can be converted into CaO and used for the heterogeneous transesterification reaction from which biodiesel is obtained.

This study aimed to investigate the catalytic activity of snail shells in the transesterification of rapeseed oil with methanol and to optimize the process conditions.

2. Materials and Methods

2.1. Determination of CaO in Snail Shells

Snail shells were decomposed using royal water. After snail shell decomposition, the water, ammonia buffer solution and the dark blue chromogen indicator were added, and trilon B (EDTA) was used for titration [23]. Equation (1) was used for the calculation of the CaO content:

$$\mathrm{CaO} = \frac{V_1 \times K \times 0.0014 \times 250}{m \times 25} \times 100\% \quad (1)$$

where:

V_1—volume of trilon B used for Ca titration, mL;
m—mass of the snail shell sample, g;
K—trilon B correction factor.

2.2. Snail Shell Preparation

Snail shells from a member of the Helicidae family of Helix Aspersa Maxima were used. Catalyst preparation is a very important step to perform before using it for the transesterification reaction. Snail shells were sieved, and a fraction of 0.315–0.1 mm was obtained [23]. Calcination was performed under the same conditions as described by Gaide et al., who determined 5 h at a temperature of 850 °C to be optimum for dolomite preparation [23]. Laskar et al. investigated snail shell preparation for transesterification reaction and determined that a temperature of at least 800 °C was needed to reach the best catalytic activity (>85%) [24]. Kaewdaeng et al. [25] calcined snail shells at 800 °C, the same as Laskar et al. [24]. Other researchers crushed snail shells calcinated for 3.5 h at 900 °C [26]. Trisupakitti et al. investigated a few methods for snail shell preparation and determined that 1 h at 1050 °C was enough [27].

2.3. Transesterification of Rapeseed Oil

Rapeseed oil was purchased in a local supermarket, and met the national requirements for edible oil. Transesterification reactions were conducted using a laboratory reactor containing a reflux condenser, a thermometer heating device, a temperature controller, and stirrers. Twenty grams of rapeseed oil was placed in a reactor and heated. When the required temperature was reached, the determined amount of catalyst was charged to the reactor, and alcohol was added. The process was carried out at the intended temperature for a set time. At the end of the reaction, the mixture was filtered, and the glycerol phase was removed by using a separation funnel. Rapeseed oil methyl esters were washed with 10% by volume of H_3PO4 (5%) solution, and twice with 10% distilled water, with evaporation of the residual water at 110 °C.

2.4. Ester Yield Evaluation Using Gas Chromatography

The glyceride contents (glycerol, monoglycerides, diglycerides, triglycerides) were investigated and used to determine ester yield in the samples. The contents of glycerides were determined by gas chromatography and a Perkin Elmer Clarus 500 (detector—FID) (Boston, MA, USA) gas chromatographer was used according to the requirements of the EN 14105 standard. First, 100 mg of test sample was dissolved in 200 µL of pyridine. Then 80 µL of 1,2,4-butantriol and 200 µL of standard glyceride stock solution containing monononadecanoate, dinonadecanoate, trinonadecanoate and 200 µL of MSTFA were added to the sample solution. The mixture was shaken for about 30 s, and after 25 min, 8 mL of heptane was added. The received mixture was analyzed using gas chromatography. Analysis was performed under programmed temperature conditions: the initial temperature of 50 °C was maintained for 1 min; then, the temperature was increased at a rate of 15 °C/min to 180 °C, then at a rate of 7 °C/min to 230 °C, and further at a rate of 10 °C/min to 370 °C. After a temperature of 370 °C was reached, it was maintained for 7 min. The injector temperature was greater than oven temperature by 5 °C (detector temperature was constant at 380 °C), the injection volume of the sample was 1 µL, and hydrogen gas was used as carrier gas (at constant pressure—80 kPa).

The ester yield was calculated according to the glyceride levels using Equation (2) [28]:

$$EY = 100 \cdot \left(1 - \frac{0.2411 \cdot MG + 0.1426 \cdot DG + 0.1012 \cdot TG}{10.441}\right) \quad (2)$$

where:

EY—ester yield, %;

MG, DG, and TG—the concentrations of monoglyceride, diglyceride, and triglycerides, respectively, %;

0.2411, 0.1426, and 0.1012—the respective conversion indicators for the glycerides;

10.441—the amount of glycerol obtained from 1 kg of rapeseed oil.

2.5. Analysis of Response Surface

In order to set the experimental plan and analyze results, the response surface methodology (RSM) was used.

Process optimization was performed depending on three variables: the amount of methanol, the snail shell content, and the process duration. The response surface methodology was used to optimize the process based on actual experiments. A laboratory reactor was used to carry out the transesterification reaction under different conditions. The parameters mentioned above were varied as follows: methanol-to-oil molar ratio (mol:mol) (from 4 to 12), catalyst amount (from 2 to 8 wt%), and reaction duration (from 2 to 8 h). The performance of twenty assays concluded the experimental plan.

RSM was used for the creation of a mathematical model. For the determination of the interaction between the transesterification reaction parameters and the biodiesel yield, a quadratic reaction surface model was used.

Three parameters were involved in this study; therefore, Equation (3) can be used to show the mathematical relationship between the factors and the response:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \quad (3)$$

where:

y—predicted response;

β_0—the offset term;

β_i—the linear coefficients;

β_{ii} and β_{ij}—the interaction coefficients;

x_i and x_j—the independent variables [29].

The final model was applied, and the results of the performed experiments were analyzed. The selected model gave the values of variables on which maximum ester yield can be determined.

3. Results

3.1. CaO Content in Snail Shells

CaO is known to be a good heterogeneous catalyst for oil transesterification [13–15]. The process of the transesterification reaction using calcium oxide as a heterogeneous base catalyst consists of two stages. In the first stage, reactants are adsorbed on the surface of the catalyst, and the reaction takes place; in the second stage, the reaction products are desorbed from the surface of the catalyst. During the transesterification process, methanol protons are transformed by the base site of CaO surface with the formation of methoxide anion, which reacts with the carbonyl group of triglycerides to form one molecule of fatty acid alkyl esters and an intermediate compound—diglyceride. In the next stage, the anion reacts with the diglyceride molecule, forming ester and monoglyceride molecules, and in the third stage, the monoglyceride molecule reacts in the same way, forming the third ester molecule and glycerol.

It was determined that the calcinated snail shells used for biodiesel synthesis contained 91.69 ± 0.43% of CaO, meaning that the content of Ca was 65.49%. Other researchers have investigated calcium content in snail shells, and determined results differing from ours: Birla et al. [26] obtained 98.35 wt% of calcium in the form of oxide in calcinated snail shells; Laskar et al. [24], 98.017 wt% of CaO; Kaewdaeng et al. [25], 70.113 wt% of CaO; Roschat et al. [30] 98.5% Ca. Parveen et al. [31] investigated the properties of three freshwater snail shells, namely, Pila globosa, Bellamya bengalensis and Brotia costul, and determined that the amount of $CaCO_3$ ranged between 87 and 96% of the total weight.

3.2. Optimal Reaction Condition Modeling and Determination Using Response Surface Methodology

The experimental design was planned using ANOVA. The predicted ester yield responses and experimental values are shown in Table 1. The highest methyl ester yield obtained was 99.10 wt%, using a methanol-to-oil molar ratio of 12:1, a catalyst content of 8 wt%, and a reaction duration of 8 h. However, a similar methyl ester yield (98.1 wt%) was determined when the alcohol-to-oil molar ratio was 8:1, the catalyst content was 5 wt% and the reaction duration was 9.2 h.

Table 1. Central composite design matrix and observed and modeled results.

No	A: Methanol-to-Oil Molar Ratio, mol/mol	B: Catalyst Amount, wt%	C: Reaction Duration, h	Predicted Methyl Ester Yield, wt%	Experimental Methyl Ester Yield, wt%
1	4.00	2.00	2.00	29.54	25.00± 0.71
2	12.00	2.00	2.00	3.39	8.12 ± 0.25
3	4.00	8.00	2.00	21.40	23.12 ± 0.69
4	12.00	8.00	2.00	14.45	15.50 ± 0.34
5	4.00	2.00	8.00	74.81	79.15 ± 0.69
6	12.00	2.00	8.00	58.86	62.26 ± 0.98
7	4.00	8.00	8.00	86.57	86.70 ± 0.67
8	12.00	8.00	8.00	89.82	99.10 ± 0.64
9	2.40	5.00	5.00	66.65	67.60 ± 0.46
10	13.60	5.00	5.00	50.62	40.36 ± 0.56
11	8.00	0.80	5.00	31.35	28.87 ± 0.36
12	8.00	9.20	5.00	47.33	41.62 ± 0.69
13	8.00	5.00	0.80	23.66	24.34 ± 0.65
14	8.00	5.00	9.20	99.12	98.10 ± 0.84
15	8.00	5.00	5.00	68.32	69.45 ± 0.75
16	8.00	5.00	5.00	68.32	72.47 ± 0.69
17	8.00	5.00	5.00	68.32	71.56 ± 0.67
18	8.00	5.00	5.00	68.32	68.14 ± 0.34
19	8.00	5.00	5.00	68.32	67.47 ± 0.77
20	8.00	5.00	5.00	68.32	70.36 ± 0.63

The F value of the quadratic model is 55.67 and the p value < 0.0001. These values show that the model is statistically significant (Table 2). Values < 0.0500 were considered significant; insignificant (>0.0500) elements were removed. Equation (4) describes the ester yield after it was modified and only significant components were left:

$$EY = 67.74 - 5.48A + 5.60B + 29.82C + 4.29AB + 4.46BC - 4.57A2 - 15.18B2 \quad (4)$$

where:

EY—the ester yield (%);
A—the methanol-to-oil molar ratio;
B—the catalyst (snail shells) amount (wt%);
C—the process duration (h).

Table 2. Analysis of variance of quadratic model.

Source	Sum of Squares	Df	Mean Square	F Value	p-Value Prob > F	
Model	13,981.41	9	1553.49	55.67	<0.0001	Significant
A—Methanol-to-oil molar ratio	358.16	1	358.16	12.84	0.0050	
B—Temperature	373.23	1	373.23	13.38	0.0044	
C—Catalyst	10,598.79	1	10,598.79	379.84	<0.0001	
AB	147.06	1	147.06	5.27	0.0446	
AC	33.21	1	33.21	1.19	0.3009	
BC	159.31	1	159.31	5.71	0.0380	
A2	161.40	1	161.40	5.78	0.0370	
B2	1890.44	1	1890.44	67.75	<0.0001	
C2	32.22	1	32.22	1.15	0.3078	
Residual	279.04	10	27.90			
Lack of Fit	263.04	5	52.61	16.44	0.0040	Not significant
Pure Error	16.00	5	3.20			
Cor Total	14,260.44	19	1553.49			

The "Pred R-Squared" of 0.8555 is in agreement with the "Adj R-Squared" of 0.9628. "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than four is desirable. In our case, the ratio is 27.308 is almost seven times higher than the desirable value, which indicates an adequate signal (Table 3).

Table 3. Statistical parameters determined using ANOVA.

Variable	Value	Variable	Value
Std. Dev.	5.28	R-Squared	0.9804
Mean	55.97	Adj R-Squared	0.9628
C.V. %	9.44	Pred R-Squared	0.8555
PRESS	2061.16	Adeq Precision	27.308

Figure 1 presents a graph comparing the experimental and predicted values of ester yield (wt%). It can be seen that the differences were not significant.

3.3. Effect of the Interaction of Independent Variables on the Effectiveness of Transesterification

3.3.1. The Effect of Methanol-to-Oil Molar Ratio and Amount of Catalyst on FAME Conversion

Figure 2 demonstrates the catalyst content and the impact of the methanol-to-oil molar ratio on the ester yield with a reaction duration of 8 h. A higher catalyst content had a positive effect on ester yield; however, when the catalyst content reached around 6 wt%, the ester yield started decreasing. A higher methanol-to-oil molar ratio also had a positive impact on the ester yield until a certain point. A methanol-to-oil molar ratio greater than

around 8:1 was not found to be desirable for achieving higher ester yield in the present study. Birla et al. [26] obtained similar results when waste frying oil and calcinated snail shells were used as catalysts. When increasing the methanol-to-oil molar ratio, oil conversion increased until a certain point—the highest conversion (95%) was reached at 6.03:1—while when adding a methanol-to-oil molar ratio of 9.65:1, oil conversion was 86.02%. A similar tendency was observed with increasing amount of catalyst: oil conversion increased until 2 wt% catalyst, and after this point, conversion started to decrease [26]. Rochat et al. [30] investigated the process of palm oil transesterification with methanol using heterogeneous catalyst derived from river snail shells and obtained a FAME yield of 98.5% ± 1.5 under an optimal catalyst-to-oil ratio of 5 wt%, an optimal methanol-to-oil molar ratio of 12:1, a reaction temperature of 65 °C, and a reaction time of 90 min. Tendencies were observed whereby when increasing the methanol-to-oil molar ratio from 9:1 to 12:1, the biodiesel yield increased, but when increasing the molar ratio to 15:1, the ester yield did not change. Furthermore, when a methanol-to-oil molar ratio of 18:1 was reached, the ester yield started to decrease. It is believed that this may be due to glycerol being soluble in methanol and inhibiting the mixing of methanol with oil and heterogeneous catalyst [30].

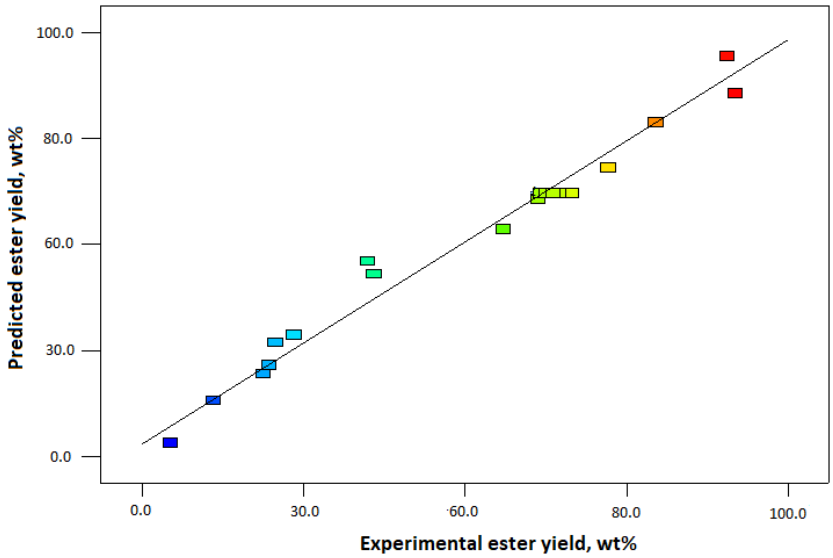


Figure 1. Experimental and predicted values of ester yield (wt%).

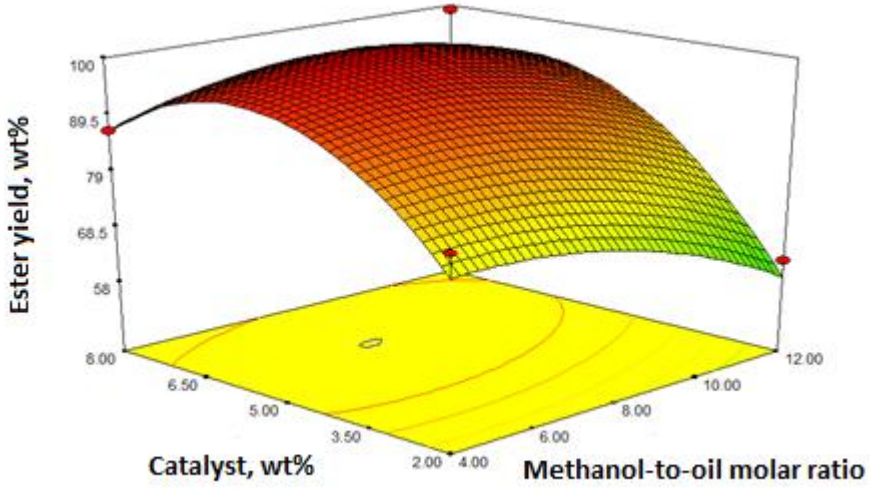


Figure 2. Response surface contour plot for the interaction between the catalyst content and the methanol-to-oil molar ratio with a process duration of 8 h and at a temperature of 64 °C.

When using palm oil for biodiesel synthesis, the optimum amount of catalyst (snail shells) was determined to be 10 wt%, with a methanol-to-oil molar ratio of 12:1 [32]. Under these conditions, a 93.2 wt% ester yield was obtained. These results show that more catalyst and methanol are needed to achieve an ester yield (93.2 wt%) that is even lower that that obtained in our study. However, there is a study in which 3 wt% catalyst and a methanol-to-oil molar ratio of 6:1 was enough to reach an ester yield of 98 wt% [24]. These differences can be explained by the fact that different oils were used, and the reaction durations were different.

Similar tendencies were observed by other researchers, who investigated the oil transesterification process with methanol and heterogeneous catalyst with a high content of CaO. The researchers analyzed the transesterification of different oils (rapeseed, soybean, sunflower) with methanol using eggshells as a catalyst and determined that a high methanol-to-oil molar ratio is not desirable for obtaining high ester yield, as it is believed that a high alcohol-to-oil molar ratio increases reversible reaction [33–35].

3.3.2. Effect of Process Duration and Methanol Content on FAME Conversion

The methanol-to-oil molar ratio and the process duration have a great influence on the methyl ester yield (the snail shells amount is 5 wt%), as shown in Figure 3. As mentioned previously, higher methanol-to-oil molar ratios have a positive effect until around 8:1, whereas longer process times lead to higher methyl ester yields. When the process duration was 6 h, and the methanol-to-oil molar ratio was 6:1, an ester yield of around 80 wt% was achieved, while after 8 h, the yield increased to more than 92 wt%. Birla and colleagues [26] determined the optimal process duration for waste frying oil transesterification to be 8 h, with a methanol-to-oil molar ratio of 6.03:1; under these conditions, a methyl ester yield of 87.28 wt% was obtained.

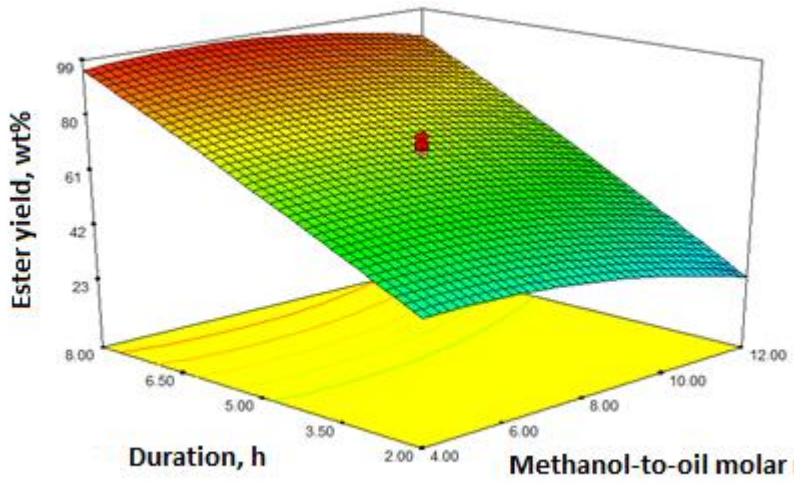


Figure 3. Response surface contour plot for the interaction between the methanol-to-oil molar ratio and the process duration at a temperature of 64 °C with a catalyst content of 5 wt%.

Other researchers have obtained similar results: a soybeen oil methyl ester yield of 98 wt% was achieved with a methanol-to-oil molar ratio of 6:1 and a reaction duration of 7 h [24]. Viriya-empikul et al. [32] and Trisupakitti et al. [27] analyzed palm oil transesterification using methanol and snail shells, whereby the optimal amount of alcohol was determined to be 12:1; however, the reaction durations were very different. Viriya-empikul et al. [32] obtained an ester yield of 93.2 wt% after 2 h, while Trisupakitti et al. [27] obtained similar results (92.5 wt%) after 6 h (catalyst amount 0.8 wt%).

When using different heterogeneous catalysts (dolomite, eggshells, oyster shells) in oil transesterification reactions with methanol, there are tendencies showing that ester yield increases with increasing process duration. It is possible to obtain a similar ester yield

using less alcohol when the reaction takes longer, or with a higher alcohol amount and a shorter duration [23,30,36].

3.3.3. Effect of Process Duration and Heterogeneous Catalyst Amount on FAME Conversion

Figure 4 shows the influence of the catalyst content and the process duration on the yield of rapeseed oil methyl ester when the methanol-to-oil molar ratio is 8:1.

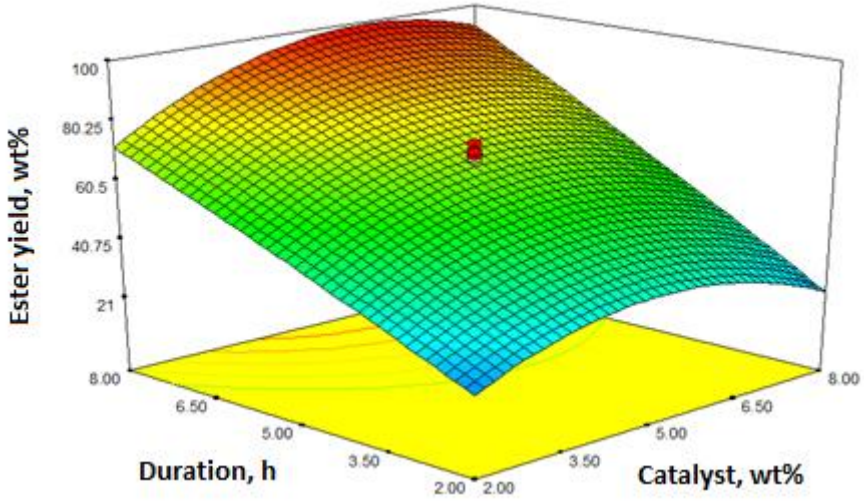


Figure 4. Response surface contour plot for the interaction between the processing time and the catalyst at 64 °C with a methanol-to-oil molar ratio of 8:1.

Longer process times and higher snail shell contents had a positive effect on methyl ester yield; however, when the catalyst amount exceeded around 6 wt%, the ester yield started to decrease. With a process duration of 8 h and a catalyst amount of 3.5 wt%, an ester yield of around 85 wt% was obtained, while when the catalyst amount was increased to 6 wt%, the yield increased to more than 92 wt%. Results obtained by other researchers are very different. Viriya-empikul and colleagues (2012) determined that the optimum catalyst amount was 10 wt%, with a very short optimum duration of 2 h [32]. Other researchers have obtained optimum catalyst amounts of 2–3 wt%, with the process duration varying between 1 and 8 h [24–26]. Trisupakitti and colleagues achieved an ester yield of 92.5 wt% with a reaction duration of 6 h and a snail shell amount of 0.8 wt% [27].

Gaide et al. (2021) investigated oil transesterification using calcinated dolomite and obtained results showing that longer process durations and higher catalyst content lead to a higher methyl ester yield. An ester yield of less than 62 wt% was obtained after 2 h with 6 wt% of catalyst, while after 5 h, ester yield increased to more than 96 wt% [23]. Kumar et al. [36] and Gaide et al. [33] investigated biodiesel production by means of transesterification with methanol, using calcinated eggshells as catalyst, and noticed that increased process duration and catalyst amount had positive effects on ester yield. Nakatani and colleagues [37] investigated soybean oil transesterification using methanol and calcinated oyster shells, and identified a positive effect of reaction duration and catalyst amount on FAME content. The optimal reaction conditions of catalyst concentration and reaction time were determined to be 25 wt% and 5 h, respectively. Under the optimal conditions obtained, the biodiesel yield, relative to the amount of soybean oil, was 73.8%, with high biodiesel purity (98.4 wt%) [37].

3.4. Optimization of the Fatty Acid Methyl Ester Synthesis Process

In this research, three independent variables that influence the synthesis of rapeseed oil methyl esters were investigated. Aiming to determine the optimum conditions for biodiesel production, an optimization step was performed. The predicted and experimental ester yields are presented in Table 4. The optimal conditions at a process temperature of

64 °C are as follows: snail shell concentration, 6.06 wt%; methanol-to-oil molar ratio, 7.51:1; and reaction duration, 8 h.

Table 4. Optimum parameters for rapeseed oil methyl ester production, and predicted and experimental ester yield.

Methanol-to-Oil Molar Ratio, mol/mol	Snail Shells Concentration, wt% (From Oil Mass)	Reaction Duration, h	Predicted Ester Yield, wt%	Experimental Ester Yield, wt%
7.51:1	6.06	8	98.87	98.15 ± 0.35

The results of other studies in which methanol and snail shells have been used as a heterogeneous catalyst are presented in Table 5. The results show ester yields ranging from 87.28 to 98 wt%.

Table 5. Comparison of optimal conditions for fatty acid methyl ester production using snail shells as a heterogeneous catalyst.

Oil	Temperature, °C	Snail Shells Amount	Reaction Duration, h	Methanol-to-Oil Molar Ratio, mol/mol	Ester Yield, wt%	Reference
Waste frying oil	60	2 wt%	8	6.03:1	87.28	[26]
Palm olein oil	60	10 wt%	2	12:1	93.2	[31]
Used cooking oil	65	3 wt%	1	9:1	92.5	[25]
Palm oil	65	0.8 wt%	6	12:1	92.5	[27]
Soybean oil	28	3 wt%	7	6:1	98	[24]

Other researchers have investigated the possibility of using calcinated snail shells for biodiesel synthesis when using methanol. Different results have been obtained, with ester yields varying from 87.28 wt% to 98 wt%. Some studies have been conducted using an optimal temperature of 60 °C [26,31]. In our study, a temperature of 64 °C was used, which is close to methanol's boiling point. Some other transesterification reactions have been investigated at a similar temperature, 65 °C [25,27]. Only Laskar et al. was able to obtain an ester yield of 98 w% using a temperature of 28 °C (7 h, 6:1, 3 wt%) [24]. Birla et al. [26] used waste frying oil for biodiesel production and obtained an ester yield of 87.28 wt% under the following conditions: process temperature, 60 °C; catalyst amount, 2 wt%; process duration, 8 h; methanol-to-oil molar ratio, 6.03:1. Kaewdaeng et al. [25] performed transesterification using cooking oil with a process temperature of 65 °C, a catalyst amount of 3 wt%, a process duration of 1 h, and a methanol-to-oil molar ratio of 9:1, was achieving an ester yield of 92.5 wt%. Using palm oil, Viriya-empikul et al. [31] obtained a 93.2 wt% ester yield (2 h, 12:1, 10 wt%), while a similar ester yield of 93.2 wt% (6 h, 12:1, 0.8 wt%) was obtained by Trisupakitti et al. [27].

3.5. Physical and Chemical Properties of the Obtained Fatty Acid Methyl Esters

In order to use the transesterification product in the transport sector, the physical and chemical properties of the obtained rapeseed oil methyl esters have to meet the requirements of the international standard for biodiesel fuel. The results of the quality analysis are presented in Table 6.

Table 6. The physical and chemical properties of rapeseed oil methyl esters.

Parameter	Units	Requirements of Standard EN 14214	Rapeseed Oil Methyl Esters
Ester content	%	min 96.5	98.15 ± 0.35
Density at 15 °C	kgm^{-3}	min 860 max 900	883 ± 2.50
Viscosity at 40 °C	mm^2s^{-1}	min 3.50 max 5.00	4.78 ± 0.02
Acid value	mg $KOHg^{-1}$	max 0.5	0.25 ± 0.01
Sulfur content	$mgkg^{-1}$	max 10	7.3 ± 0.21
Moisture content	$mgkg^{-1}$	max 500	305 ± 2.10
Iodine value	g $J_2100^{-1}g^{-1}$	max 120	114 ± 0.15
Linolenic acid methyl esters content	%	max 12.0	9.5 ± 0.10
Monoglyceride content	%	max 0.8	0.51 ± 0.09
Diglyceride content	%	max 0.2	0.10 ± 0.02
Triglyceride content	%	max 0.2	0.05 ± 0.01
Free glycerol content	%	max 0.2	0.02 ± 0
Total glycerol content	%	max 0.25	0.21 ± 0.11
Methanol content	%	max 0.2	0.05 ± 0.01
Phosphorus content, ppm		10	7.1 ± 0.09
Metals II (Ca/Mg)	mg kg^{-1}	max 5	4 ± 0.12
Oxidation stability 110 °C	H	min 8	8.3 ± 0.1
Cetane number	-	min 51	53.8 ± 0.15
Cold filter plugging point	°C	−5 °C (in summer) −32 °C (in winter)	−9.5 ± 0.06

An important indicator of biodiesel quality is the ester content, i.e., how many esters were formed from triglycerides. According to the requirements of the standard EN 14214, the fatty acid methyl ester content must be at least 96.5%. It was determined that the ester content of the produced biodiesel was 98.15 ± 0.35 wt%, which is higher than the minimum value indicated in the standard.

The amounts of monoglycerides, diglycerides and triglycerides, and free and total glycerol in biofuels depend on both the production and product purification processes. According to the requirements of the standard, the amounts of monoglycerides, diglycerides and triglycerides, and free and total glycerol in the product cannot exceed 0.8%, 0.2%, 0.2%, 0.2% and 0.25%, respectively. These indicators in the obtained fatty acids methyl esters met the requirements of the standard.

The purity of the biodiesel and the composition of fatty acids in the raw material have an influence on the product density. The density of the triglycerides is reduced with their transesterification; however, the density of the obtained product was higher than that of mineral diesel. This higher fuel density leads to higher fuel consumption and a lower calorific value. The density of the produced biofuel was 883 ± 2.50 kg m^{-3}, which meets the requirements of the standard.

The content of free fatty acids in biodiesel depends on the acidity of the oil used to produce the fatty acid methyl esters and the applied production process, as free fatty acids are formed during production and storage. The standard establishes that the number of acids must not exceed 0.5 mg $KOHg^{-1}$, and the acidity of the obtained and analyzed biofuels was 0.25 ± 0.01 mg $KOHg^{-1}$.

According the EN 14214 standard, the moisture content in biodiesel must not exceed more than 500 mg kg^{-1}. Water can appear during the production process, so it must be removed by drying the biodiesel. In addition, biofuels must be stored in closed containers, as they are hygroscopic and can absorb moisture during storage. The moisture content of the obtained methyl esters reached 305 ± 2.10 mg kg^{-1}.

The amount of sulfur in the fuel has a negative effect on engines, the environment, and living organisms. The sulfur content in biodiesel must not exceed 10 mg kg^{-1}. The sulfur content in the obtained biodiesel was 7.3 ± 0.21 mg kg^{-1}.

In the product, the methanol content must not exceed 0.2% (from mass). The amount of methanol is limited, because excess methanol is used for the transesterification of triglycerides. Therefore, the unreacted alcohol must be removed. The amount of methanol produced in biodiesel is only $0.05 \pm 0.01\%$.

The amount of linolenic acid esters and the iodine number do not depend on the biodiesel production process or its purification. These indicators depend on the fatty acid composition of the oil used. The maximum content of linolenic acid methyl ester must be 12%; in the obtained biofuel it was $9.5 \pm 0.10\%$. The iodine number cannot exceed 120 g $J_2$100-1g^{-1}, and it was 114 ± 0.15 g $J_2100^{-1}g^{-1}$ in the obtained biodiesel.

Since calcium is the main element of the snail shells used for the transesterification reaction, the content of metals II (Ca/Mg) in the biodiesel must be investigated, with these being limited by the standard to 5 mg kg^{-1}; a value of 4 ± 0.12 mg kg^{-1} was obtained in the produced fuel.

Storing biofuels can increase their acidity and reduce their oxidation resistance, i.e., during oxidation processes, fuel stability decreases, which is important in order to store fuels. The esters obtained in this research meet the requirements of the standard (i.e., a minimum resistance of 8 h); their resistance to oxidation was 8.3 ± 0.12 h.

Since fuel is used both in summer and winter, low-temperature properties are very important. Depending on the climatic conditions, there are different requirements for the limits of CFPP value. During the summer in Lithuania, the CFPP of fuel must not be higher than minus 5 °C (class C in the moderate climate zone). The CFPP of the obtained biodiesel was minus 9 ± 0.06 °C.

The fatty acid methyl esters obtained in biodiesel synthesis using rapeseed oil, methanol and snail shells as catalysts were able to meet the requirements of standard EN 14214 for biodiesel.

4. Conclusions

The snail shells selected for heterogeneous biodiesel synthesis contained $91.69 \pm 0.43\%$ CaO. Catalyst preparation is a very important step prior to use for the transesterification reaction. A fraction size of 0.315–0.1 mm was obtained and calcinated for 5 h at a temperature of 850 °C.

Three independent parameters (the methanol-to-oil molar ratio, the snail shell content, and the duration of the reaction) were selected to determine their influence on the efficiency of the transesterification process. It was determined that a larger catalyst amount and a larger methanol-to-oil molar ratio led to a higher ester yield. However, when it reaches a certain point (around 6 wt% of snail shell content and around 8:1 methanol-to-oil molar ratio), the yield of rapeseed oil methyl ester starts to decrease. Longer process duration has a positive effect on the ester yield. Response surface analysis was applied to optimize the rapeseed oil transesterification process with methanol when snail shells are used as a heterogeneous catalyst. The following optimal conditions for rapeseed oil methyl ester synthesis were determined: a methanol-to-oil molar ratio of 7.51:1, a snail shell content of 6.06 wt%, and a reaction time of 8 h at a temperature of 64 °C. Under the determined optimal conditions, rapeseed oil methyl ester yield reached 98.15 wt%. The analysis of the physical and chemical properties of the produced rapeseed oil methyl ester proved that physical and chemical properties of the biodiesel were able to meet the requirements of the EN 14214 standard, and the obtained product was suitable for use in diesel engines during the summer period.

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