# Application of snail shells as a heterogeneous catalyst for rapeseed oil butyl esters production

## Ieva Gaide, Violeta Makareviciene, Egle Sendzikiene, Rasa Slinksiene & Rasa Paleckiene

Published online: 29 Nov 2023.

Submit your article to this journal ⎘

View related articles ⎘

View Crossmark data ⎘

Taylor & Francis
Taylor & Francis Group

# Application of snail shells as a heterogeneous catalyst for rapeseed oil butyl esters production

Ieva Gaide [a], Violeta Makareviciene [a], Egle Sendzikiene [b], Rasa Slinksiene [c] and Rasa Paleckiene [c]

aDepartment of Environment and Ecology, Faculty of Forest Sciences and Ecology, Agriculture Academy, Vytautas Magnus University, Kaunas, Lithuania; bInstitute of Bioeconomy Research, Agriculture Academy, Vytautas Magnus University, Kaunas, Lithuania; cDepartment of Physical and Inorganic Chemistry, Kaunas University of Technology, Kaunas, Lithuania

**ABSTRACT**

Synthesis of fatty acid butyl esters using snail shells is attractive and increases the share of renewable resources because the snail shells are a waste of the food industry and 1-butanol can be obtained from renewable resources. Chemical and instrumental analysis methods (XRDA, FT-IR, EDS) were used for the evaluation of the chemical composition of snail shells. It was found that composition slightly depends on the kind and growing conditions, but in all the cases the main component in raw shells is $CaCO_3$. After calcination for 5 h at a temperature of 850 °C, almost pure CaO (93.69 ± 0.43% %) is formed, which is used as a catalyst in the triglyceride transesterification process. SEM studies showed that the structure of the shells becomes porous after calcination, which increases the efficiency of the process. The Response surface methodology was used for the optimization of rapeseed oil transesterification with 1-butanol. It was found that the optimum transesterification conditions when the reaction temperature is 110°C are the following: 1-butanol-to-oil molar ratio of 10.6:1, a snail shell content of 7.53 wt%, and a reaction time of 10.77 h. Under these conditions, the 99.25 wt% yield of rapeseed butyl esters was obtained.
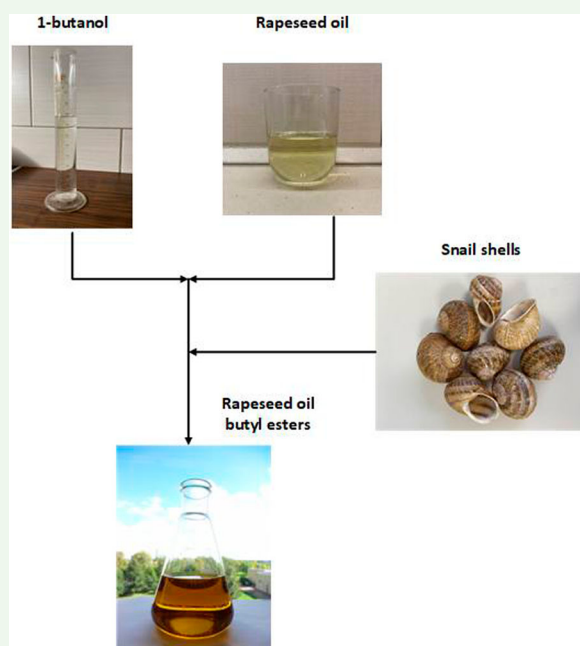
## 1. Introduction

The transport sector is one of the sectors polluting the environment with greenhouse gases (1). Environmental concerns and energy security are driving the expansion of electric vehicle use (2). However, this process is not fast, in the transport sector there are many vehicles

**CONTACT** Ieva Gaide ✉ ieva.gaide@vdu.lt 🔗 Department of Environment and Ecology, Faculty of Forest Sciences and Ecology, Agriculture Academy, Vytautas Magnus University, Donelaicio str. 58, Kaunas LT-44248, Lithuania

using diesel engines. Biodiesel can be used in a mixture with mineral diesel in any ratio. Therefore, replacing at least part of mineral diesel with biodiesel produced from renewable resources would reduce environmental pollution and increase energy independence. Reducing the negative impact of transport is an important goal of the European Green Deal.

Lithuania has set ambitious goals and plans to significantly contribute to the implementation of the EU's energy and climate policy goals. It is expected to reach 45% renewable energy resources in the final energy consumption, among them the share of renewable energy resources in transport should increase to 15% by 2030 and Lithuania would become the leader in energy innovation in the region. The largest part of the Lithuanian transport fleet consists of almost 1.5 million passenger cars, of which 69% are using diesel. The average age of these cars is 15 years and average $CO_2$ emissions are 160–170 g/km ([3]). Therefore, research related to the production of renewable fuels for diesel engines is relevant.

Industrially biodiesel is usually produced from oil and methanol and the process is accelerated by chemical homogeneous catalysts ([4–6]). However, there are questions regarding the classification of such biodiesel as a fully renewable fuel since chemical reagents are used in its production process. Therefore, more and more biodiesel production research are being conducted using more environmentally friendly alcohols: ethanol ([7–9]) or butanol ([10,11]). Butanol has attracted great interest due to the good properties of the final product (high energy value, good mixing, low volatility, and corrosion). The most popular method of butanol production is via acetone–butanol–ethanol (ABE) fermentation from sugars or starch as substrates. Recently, research on the production of butanol from lignocellulose has been developed. Lignocellulosic biomass is the most abundant, sustainable form of biomass, so its use provides all sorts of benefits: carbon fixation from the atmosphere, energy independence from oil-importing countries, and reduction of environmental pollution with agricultural and forestry waste ([12]).

In the synthesis of biodiesel, the aim is to replace homogeneous catalysts with heterogeneous ones because homogeneous chemical catalysts, although they have good catalytic activity, cannot be reused, the biodiesel purification process is more complicated and a two-stage transesterification process is applied ([13]). The application of heterogeneous catalysis in biodiesel synthesis is becoming more popular, biocatalysts or metal oxides and their mixtures are usually used ([14,15]). Calcium oxide is known as an efficient catalyst for biodiesel synthesis ([16]). Therefore, there is an interest in environmentally friendly calcium oxide-containing raw

materials that can catalyze the oil transesterification process. The food industry generates large amounts of waste, which consists of calcium carbonate, which can be converted to calcium oxide. Molluscs containing shells are used in the food industry, and the shells are a high-calcium waste that could be used as heterogeneous catalysts. One of the types of molluscs is snails. The total consumption of snails in 2014 was about 450,000 tons. About 15% (67,500 tons) of this amount is snails collected from snail farms. The remaining 382,500 tons (of all goods sold) are snails collected from nature ([17]). More than 80% of consumed snails belong to the *Helix aspersa* subspecies. One hundred thousand tons of edible snails are consumed in Europe per year and their demand is met only by 60–70% ([18]). In most cases, a shell consists one-third of the snails' body weight ([19]). From 1200–1600 t of grape snails, 343–457 t of shells are collected and processed in Lithuania per year, furthermore about 12 t of *Helix aspersa* are grown on farms, from which 3.6 t of shells are produced.

The aim of the study is the use of snail shells as heterogeneous catalysts for biodiesel production using butanol.

## 2. Materials and methods

### 2.1. Catalyst preparation and characterization

The catalyst must be treated before being used in the transesterification reaction. The main step is calcination, which converts $CaCO_3$ to $CaO$. $CaO$ is known to be a good catalyst for the biodiesel synthesis reaction. In this study, snail shells were processed according to Gaide et al. ([20]). Snail shells were crushed and calcined for 5 h at a temperature of 850°C and sieved, obtaining a size fraction of 0.315–0.1 mm. After treatment, the catalyst was kept in a weighing bottle in a desiccator in order to avoid contact with any moisture which can lead to a reverse reaction: $CaO \rightarrow CaCO_3$.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)\ \Delta H^0 = 183.49\ kJ/mol \quad (1)$$
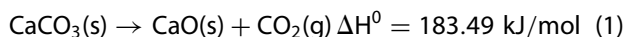
The amount of $CaO$ in a snail shell was determined after it was calcinated. Determination was done according to Gaide et al. ([21]).

Since the effectiveness of the catalyst is highly dependent on the amount of moisture it contains, a study of the hygroscopicity of raw snail shell and calcined (5 h at 850°C temperature) snail shell powders was performed. The study was performed by placing the samples in the desiccator of two different environments: saturated sodium nitrite solution and water vapor. During the experiment, the temperature in the desiccator filled with saturated sodium nitrite ($NaNO_2$) solution

was 20.8 ± 0.4°C and the relative humidity was 62.4 ± 1.0%. In the desiccator filled with water: temperature was 20.5 ± 0.2°C and the relative humidity 99.5 ± 0.6%, respectively. To determine the amount of water vapor absorbed, the samples were weighed periodically for 16 days. Every test sample was performed in duplicate.

X-ray diffraction analysis (XRDA) was carried out using Bruker X-ray AXS D8 Advance diffractometer with monochromatic CuK α radiation at an anodic voltage Ua = 40 kV and strength of the current was I = 40 mA. The diffraction data for the materials were collected for the step size of 0.05° and a dwell time of 0.5 s. The accuracy of XRDA measurements is 2θ = 0.01°. The data analysis was carried out using a crystallographic SearchMatch5 Crystallographica Search-Match Version 2, 1, 1, 1 program.

Fourier transform infrared spectroscopy (FT-IR) spectrum of the analyzed materials was recorded in the range of 400–4000 cm$^{-1}$ with a SPECTRUM GX 2000 (PerkinElmer, Great Britain) operating in the transmission mode. A pellet for analysis was prepared by an extruded mixture of optically pure dry KBr and the test sample (raw snail shell and calcined snail shell powders).

For scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), scanning electron microscope S-3400N with a Bruker Quad 5040 EDS detector (Hitachi, Japan) was used. SEM electron acceleration voltage is 5 kV and EDS electron acceleration voltage is 15 kV. The secondary electron detector is used to produce a topographic SEM image. Electron source – prie-centered cartridge type tungsten hairpin filament. EDS Basic technical data: Silicon drift detector, LN2-free; energy resolution <133 eV, detection from B (Z = 5), scan generator capable of up to 4096 × 4096 pixel images and hybrid pulse processor combining both analogue and digital electronics.

## 2.2. Biodiesel synthesis and purification of the product

Rapeseed oil was used for transesterification reactions and was purchased in a local store. The reactions with 1-butanol (99.5%, Chempur) were carried out in laboratory reactors, which were connected to reflux condensers in order to avoid the evaporation of alcohol. A magnetic stirrer was used to keep the reaction mixture constantly mixing at 250 rpm, thermocouple was allowed to maintain a temperature of 110°C.

The final mixture was filtered through cellulose paper, washed once with $H_3PO_4$ (5%), (solution used 10% by volume of the mixture), and twice with distilled water (10% by volume of the mixture). The washings were performed in a separatory funnel, after each washing, the separated aqueous part was poured off. After washing, the residual water was evaporated using a rotary evaporator (80°C, 40 mbar).

## 2.3. Surface response methodology

The biodiesel synthesis reactions were planned and the results were analyzed by the Design Expert 8.01 (Stat-Ease, 91 Minneapolis) program with the response surface methodology (RSM) tool. This design was used for the transesterification reactions of rapeseed oil using 1-butanol and snail shells. Three variables were used in the experimental plan – 1-butanol-to-oil molar ratio (mol:mol) (from 8 to 16), snail shells amount (from 4 to 8 wt%), and reaction time (from 6 to 12 h). The experimental design consisted of 20 experimental trials. After performing the experiments provided in the experimental plan, the results were analyzed, and the model that best matches the results was applied. After selecting a model that fits the experimental values, the values of the independent variables that determine the desired response value, i.e. maximum ester yield, were determined.

## 2.4. Determination of ester yield and its physical and chemical properties

Glyceride contents (glycerol, monoglycerides, diglycerides, triglycerides) in the samples were determined, and results were used to investigate the ester yield. Gas chromatography using a Perkin Elmer Clarus 500 (detector – FID) (Boston, Massachusetts, United States) gas chromatograph was used to determine glycerides contents according to the requirements of the EN 14105 standard. The ester yield was calculated according to Gaide et al. (2023).

About 100 mg of the test sample was dissolved in 200 μL of pyridine. About 80 μL of 1,2,4-butantriol and 200 μL of standard glycerides stock solution, containing monononadecanoate, dinon-adecanoate, trinonadecanoate, and 200 μL of MSTFA were added to the sample solution. The mixture was shaken for 30 s and after 25 min, 8 mL of the heptane was added. The received mixture was analyzed using a gas chromatograph. Analysis was done under programmed temperature conditions: the initial temperature of 50°C was maintained for 1 min, then the temperature was raised at a rate of 15°C/min to 180°C, then – at a rate of 7°C/min to 230°C, further – at a rate of 10°C/min to 370°C. After reaching a temperature of 370°C, it was maintained for 7 min. The injector temperature was 5°C greater than oven temperature (detector temperature was constant – 380°C), injection volume of the sample was 1 μL, and

hydrogen gas was used as carrier gas (at constant pressure – 80 kPa).

Standard EN ISO 14214 was used to analyze the physical and chemical properties of the final product.

## 3. Results and discussions

### 3.1. Snail shells characterization

Snail shells are a natural source rich in calcium compounds. Snail shells were collected after using snails grown on a local farm. Snails belong to the *Aspersa Helix Maxima* subspecies. In the present work, snail shells were calcined in order to obtain CaO. It was determined that calcinated snail shells contain 93.69 ± 0.43% of CaO.

The XRDA data of raw (uncalcined) snail shell powders and calcined (5 h at 850°C temperature) snail shells are shown in Figure 1. It can be observed that $CaCO_3$ as an aragonite crystalline phase is the main component of the raw snail shells. Our chemical analysis studies have shown that the concentration of CaO in raw snail shells is 52.99% (or 94.63% $CaCO_3$) and that of calcined snail shells is 93.69%, but there are other elements such as Al, Si, and Mg (22). Practically all peaks that are visible in Fig. X a coincides with aragonite

peaks from database on the RRUFF project website (23,24) and from the database Crystallographica Search-Match Version 2. Two small peaks corresponding to diffraction angles 29.310 and 33.043 can be assigned to $Fe_2O_3$ and $Al_2O_3$, respectively. It should also be mentioned that according to the Search-Match database, peaks with diffraction angles of 26.122 and 41.095 are characteristic not only of calcite but also of manganite (MnO(OH)). Manganite impurities can be matched with data on the chemical composition of the snail shell published by Laskar et al. On the other hand, in the snail shells that we studied, not a single peak was identified that could be attributed to another $CaCO_3$ crystalline phase – calcite (25).

In Figure 1(b) can be seen the intense and sharp peak of the calcined snail shells revealed the crystalline nature of the catalyst. Calcined snail shells peak appeared at 2θ of 32.23°, 37.41°, 53.93°, 64.26°, 67.48°, 79.1°, and 88.56°, which is characteristic peaks of CaO, these data correspond to the results presented in the work of other researchers (26,27). The results match well with papers reported by Laskar et al. (25), Hu et al. (28) and Muhammad et al. (29).

This allows us to conclude that although the chemical composition of the raw snail shells depends somewhat
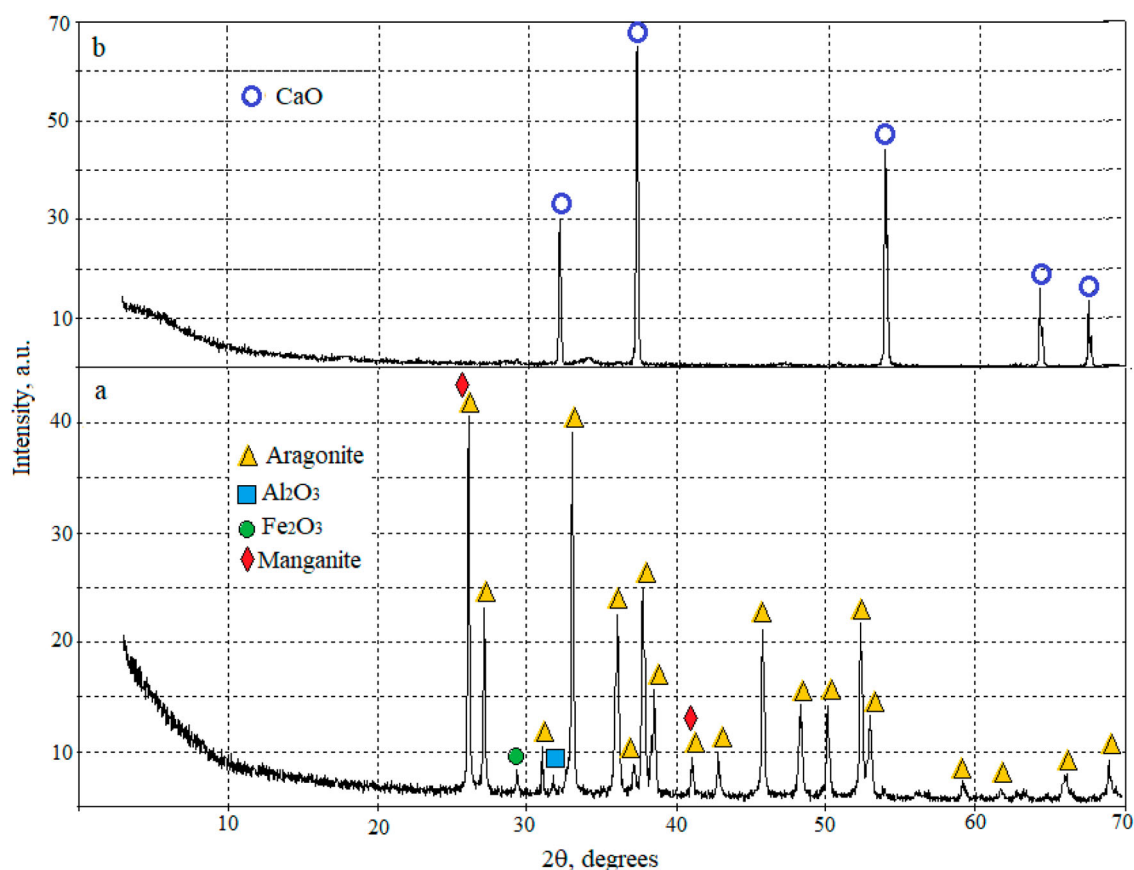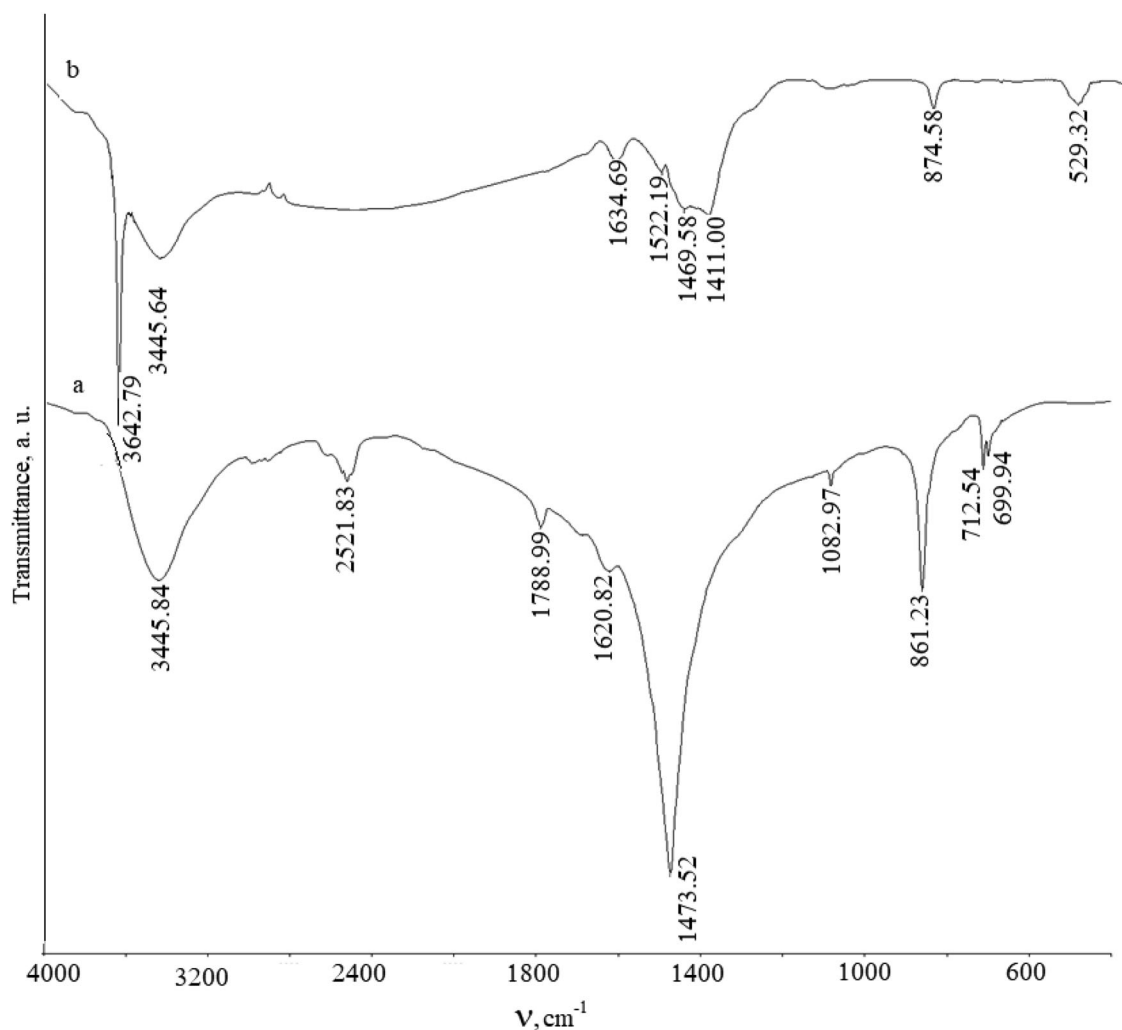


**Figure 1.** XRDA data of: a – raw snail shell powders, b – calcined (5 h at 850°C temperature) snail shell powders.

on the conditions or species of snails, after calcined, pure CaO is obtained.

Molecular absorption spectral analysis (FT-IR spectroscopy) of the infrared spectrum of snail shells and their calcined samples was performed (Figure 2). Absorption band characteristics in the spectrum of unheated snail shells (Figure 2(a)) are registered and identified as the carbonate group at 712, 861, 1082, 1473, and 1789 cm$^{-1}$.

The maximum intensity peak is at 1473 cm$^{-1}$. This is typical of the $CO_3^{2-}$ group. The weak peak registered in the region of 1620 cm$^{-1}$ is characteristic of the $C=O$ bond. The low-intensity absorption band at 2521 cm$^{-1}$ is due to valence and asymmetric vibrations involving hydrogen atoms, and is characteristic of both C–H and O–H groups. The absorption band of medium intensity (3445.84 cm$^{-1}$) is characteristic of O–H bond vibrations and is due to the moisture present in the composition. In the spectrum of the calcined shells (Figure 2(b)), the intensity of the absorption peaks characteristic of the

$CO_3^{2-}$ group decreases significantly and shifts or disappears altogether. Several peaks of low intensity are registered in the region 1411––1634 cm$^{-1}$. The disappearance of some of the peaks and the changed position of the peaks allow us to confirm the structural transformations occurring during heating. This happens due to a change in the mass of the functional group, as part of the $CO_3^{2-}$ is removed from the sample when it is heated. At 3642 cm$^{-1}$, a new, strong peak attributed to the O–H bond is registered, which is characteristic of the presence of calcium hydroxide (Ca(OH)$_2$). It is likely that the formation of the O–H bond is due to the high hygroscopicity (Table 1) of calcined snail shells. These results correspond to the results presented in the works of other researchers (22,25). After performing infrared molecular absorption spectral analysis (FT-IR spectroscopy) of snail shells and heated samples and analyzing the obtained spectra, it was found that the chemical composition and structure of the sample changes.



**Figure 2.** FT-IR analysis data of: a – raw snail shell powders, b – calcined (5 h at 850°C temperature) snail shell powders.
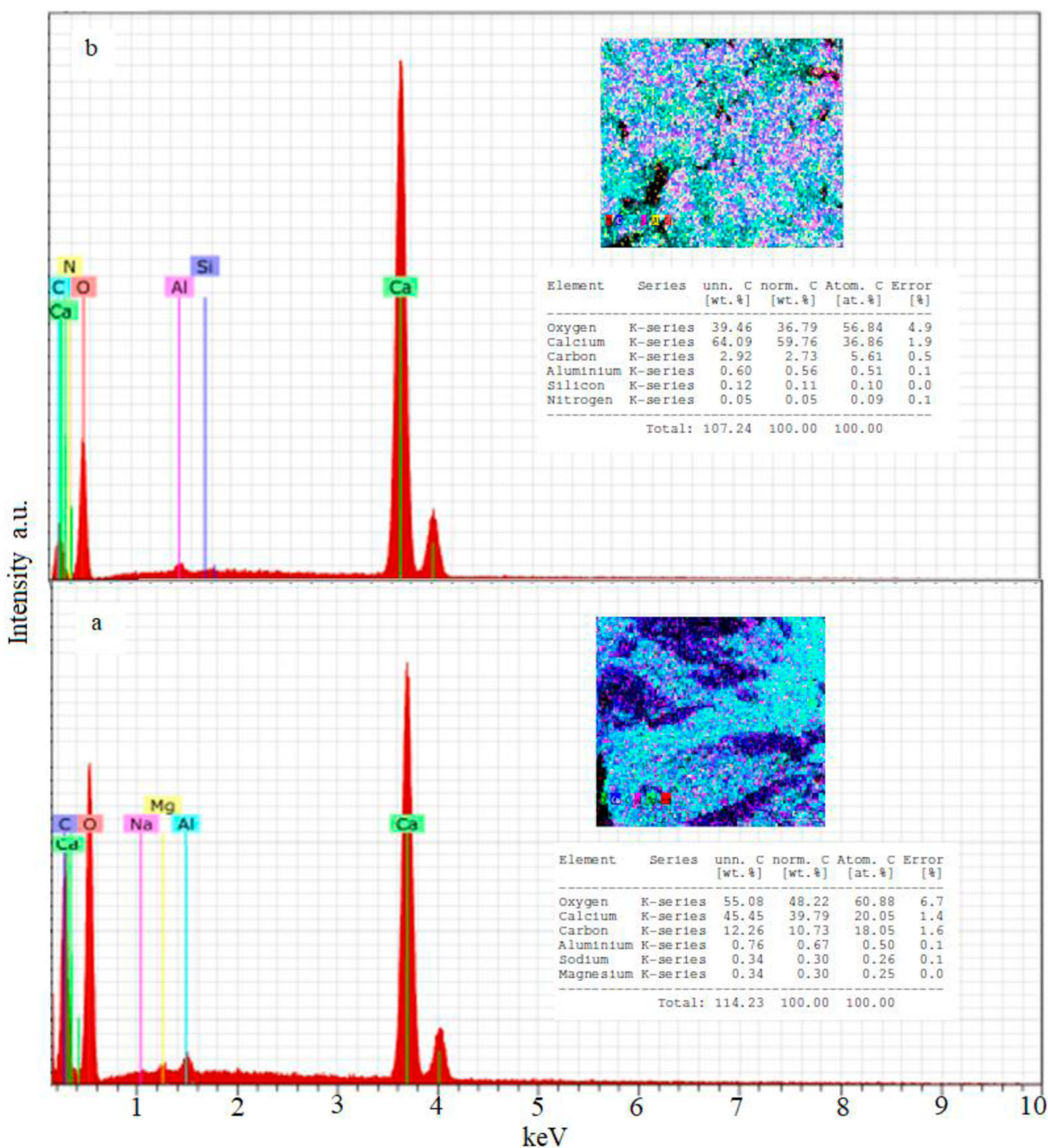
**Table 1.** Hygroscopicity data of raw and calcined snail shell powders.

| Snail shell powders | Water vapor absorption after a certain time, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 d | 2 days | 3 days | 4 days | 7 days | 8 days | 9 days | 10 days | 11 days | 16 days |
| In saturated NaNO₂ solution environment | | | | | | | | | | |
| Raw | 0.00 | 0.19 | 0.20 | 0.24 | 0.36 | 0.39 | 0.39 | 0.43 | 0.45 | 0.58 |
| Calcined | 12.45 | 19.25 | 32.64 | 33.77 | 34.34 | 34.53 | 34.53 | 34.91 | 34.91 | 35.09 |
| In H₂O vapor environment | | | | | | | | | | |
| Raw | 0.18 | 0.53 | 1.23 | 1.29 | 1.49 | 1.52 | 1.58 | 1.65 | 1.71 | 1.76 |
| Calcined | 18.84 | 35.07 | 44.09 | 50.90 | 52.51 | 52.91 | 53.91 | 54.31 | 55.51 | 62.12 |

SEM was carried out to analyze the morphology of the raw snail shells and the snail shells calcined 5 h at 850°C temperature. Raw snail shells after grinding up to 0.315–0.1 mm particles have an irregular shape but are similar in size (Figure 3(a)) and feature an uneven rough surface (Figure 3(c)). After calcination of the snail shells the surface becomes morphologically quite uniform and porous (Figure 3(b,d)). The surface area is very important for the activity of the catalyst, so due to the release of $CO_2$ during the decomposition of $CaCO_3$ formed pores have a positive effect on the efficiency of the process. The obtained data correlate well with the published Laskar et al.'s results (25).

EDS analysis was carried out to determine the mapping of elements in the raw and calcined snail shell samples. The main elements Ca and O were found in all the samples. Other chemical elements such as C, Na, Mg, Cd, and Al in the raw snail shells (Figure 4(a)) or C, N, Al, and Si in the calcined snail shells (Figure 4(b)) were detected. The carbon percentage decreases and the calcium percentage increases after calcination, but in summary the distribution of elements is more uniform after calcination. All mentioned components were also observed in the XRD analysis and the analysis of results published by other scientists (25,28,29).
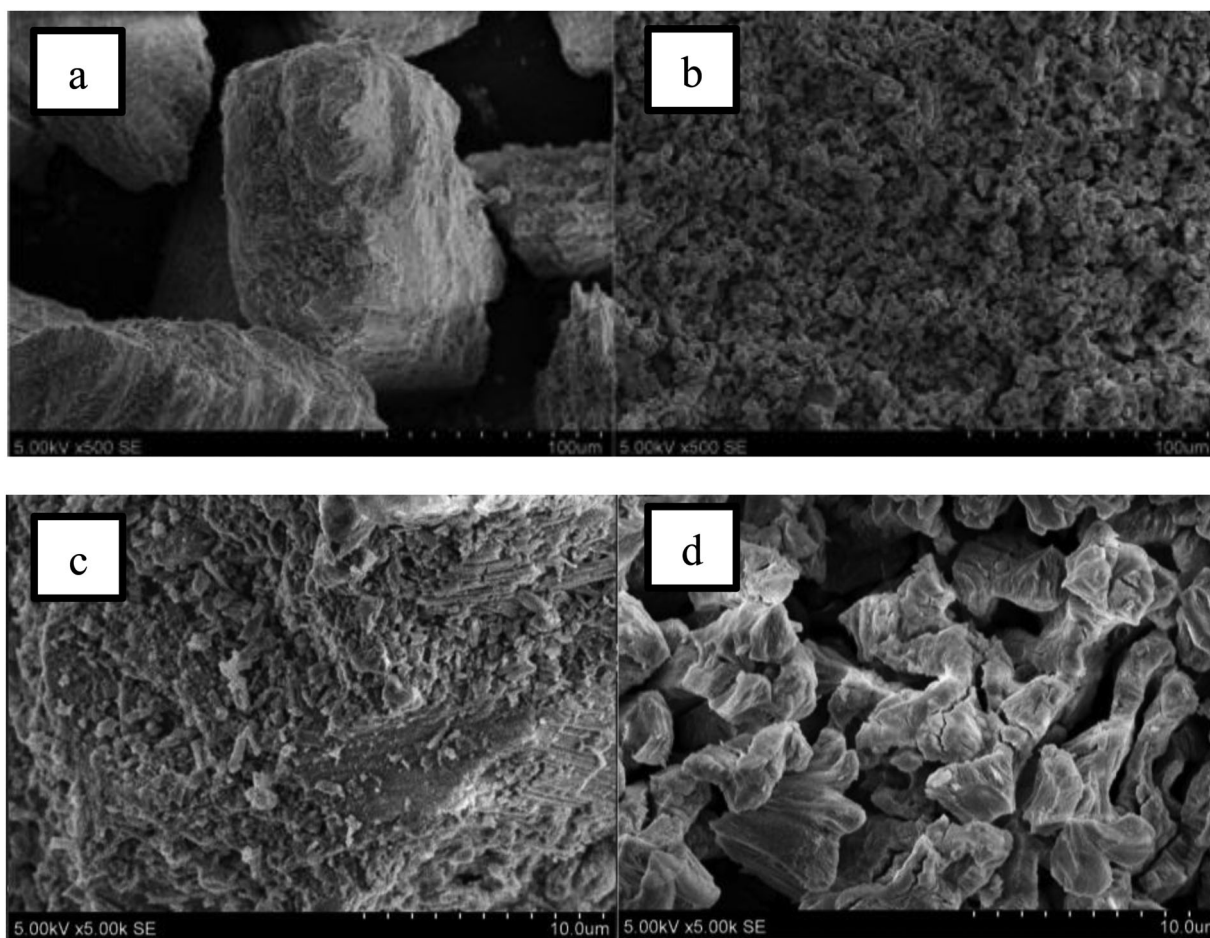


**Figure 3.** SEM photos of: a, c – raw snail shells, b, d – calcined (5 h at 850°C temperature) snail shells.

b

```
Element      Series  unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Oxygen     K-series  39.46   36.79   56.84    4.9
Calcium    K-series  64.09   59.76   36.86    1.9
Carbon     K-series   2.92    2.73    5.61    0.5
Aluminium  K-series   0.60    0.56    0.51    0.1
Silicon    K-series   0.12    0.11    0.10    0.0
Nitrogen   K-series   0.05    0.05    0.09    0.1
-------------------------------------------------
           Total: 107.24   100.00  100.00
```

a

```
Element      Series  unn. C norm. C Atom. C Error
                     [wt.%]  [wt.%]  [at.%]   [%]
-------------------------------------------------
Oxygen     K-series  55.08   48.22   60.88    6.7
Calcium    K-series  45.45   39.79   20.05    1.4
Carbon     K-series  12.26   10.73   18.05    1.6
Aluminium  K-series   0.76    0.67    0.50    0.1
Sodium     K-series   0.34    0.30    0.26    0.1
Magnesium  K-series   0.34    0.30    0.25    0.0
-------------------------------------------------
           Total: 114.23   100.00  100.00
```

**Figure 4.** EDS spectra of: a – raw snail shells, b – calcined (5 h at 850°C temperature) snail shells.

### 3.2. Selection of optimal conditions using response surface methodology

One of the most important parameters of the synthesis reaction is temperature. During the heterogeneous synthesis of biodiesel, when natural catalysts are used, it is useful to keep the process temperature as high as possible because this leads to a greater activity of molecules and more frequent collisions between them (30). Also, when using natural heterogeneous catalysts, high temperature does not have a negative effect on the catalyst, as in biocatalysts case. However, it is important to take into account that a higher temperature than alcohol's boiling point can lead to the evaporation of the alcohol. Therefore, the results of other scientists show that the appropriate temperature depends on the type of alcohol and is close to its boiling point. At higher temperatures, chemical processes take place more easily, as the energy of the molecules increases by increasing the temperature. In this case, butanol with a boiling point of 117.7°C was used, so all transesterification reactions were carried out at 110°C. Many researchers who studied the process of oil transesterification with butanol carried out the

reaction at higher temperatures compared with the process where methanol or ethanol is used. Keneni and Marchetti (*31*) transesterified Jatropha oil with butanol using heterogeneous catalysts at 90.48°C and obtained a 95.64% yield of esters. Jha et al. carried out the butanol transesterification process of Jatropha curcas oil at 105°C (*32*). Gaide et al. conducted studies on oil transesterification with butanol using dolomite as a catalyst and found the optimum process temperature to be 110°C (*33*). When studying the production process of vegetable oil butyl esters using sodium methoxide as a catalyst, the reaction temperature was 114°C (*34*). Ursaki et al. used calcium oxide as a catalyst at a temperature of 120°C in the butanolysis process of triolein (*35*).

Transesterification reactions were plotted using ANOVA. Table 2 presents data showing predicted and experimentally determined ester yields under different reaction conditions.

The highest predicted ester yield was 99.88 wt% when the 1-butanol-to-oil molar ratio is 8:1, snail shells amount to 4 wt%, reaction duration 12 h. Under these conditions experiment was conducted, 99.21 wt% of ester yield was obtained.

Analysis of the variance of the quadratic model is presented in Table 3.

Values that are less than 0.05 are significant, in this case insignificant values are not determined. The butyl ester yield is represented in Equation (1):

$$EY = -331.37 + 5.64A + 7.15B + 71.31C$$
$$+ 0.39AB - 0.39AC - 0.60BC - 0.16A^2 - 0.45B^2 - 2.93C^2$$

$$(1)$$

**Table 2.** Experimental plan, predicted and experimental ester yield depending on independent variables.

| | 1-butanol-to-Oil Molar Ratio, mol/mol | Catalyst amount, wt% | Duration, h | Predicted Butyl Ester Yield, wt% | Experimental Butyl Ester Yield, wt% |
|---|---|---|---|---|---|
| 1 | 8.00 | 4.00 | 6.00 | 27.55 | 27.03 ± 0.86 |
| 2 | 16.00 | 4.00 | 6.00 | 35.88 | 35.00 ± 0.46 |
| 3 | 8.00 | 8.00 | 6.00 | 31.68 | 31.00 ± 0.47 |
| 4 | 16.00 | 8.00 | 6.00 | 54.49 | 55.00 ± 0.63 |
| 5 | 8.00 | 4.00 | 12.00 | 99.88 | 99.21 ± 0.25 |
| 6 | 16.00 | 4.00 | 12.00 | 94.99 | 95.00 ± 0.33 |
| 7 | 8.00 | 8.00 | 12.00 | 96.96 | 97.17 ± 0.24 |
| 8 | 16.00 | 8.00 | 12.00 | 99.25 | 99.10 ± 0.15 |
| 9 | 7.20 | 6.00 | 9.00 | 92.37 | 94.00 ± 0.42 |
| 10 | 16.80 | 6.00 | 9.00 | 98.74 | 98.98 ± 0.36 |
| 11 | 16.80 | 3.60 | 9.00 | 94.05 | 96.00 ± 0.62 |
| 12 | 12.00 | 8.40 | 9.00 | 99.09 | 99.01 ± 0.54 |
| 13 | 12.00 | 6.00 | 5.40 | 23.88 | 25.00 ± 0.39 |
| 14 | 12.00 | 6.00 | 12.60 | 98.52 | 99.06 ± 0.38 |
| 15 | 12.00 | 6.00 | 9.00 | 99.16 | 97.98 ± 0.51 |
| 16 | 12.00 | 6.00 | 9.00 | 99.16 | 98.98 ± 0.42 |
| 17 | 12.00 | 6.00 | 9.00 | 99.16 | 98.60 ± 0.44 |
| 18 | 12.00 | 6.00 | 9.00 | 99.16 | 98.80 ± 0.63 |
| 19 | 12.00 | 6.00 | 9.00 | 99.16 | 98.82 ± 0.59 |
| 20 | 12.00 | 6.00 | 9.00 | 99.16 | 98.90 ± 0.24 |

where EY – the butyl ester yield (wt%); A – the 1-butanol-to-oil molar ratio; B – the catalyst content (wt%); C – the reaction duration (h).

In order to determine the relationship between independent variables and response values, a second-order polynomial equation was used. Positive coefficient symbols show greater interaction with the ester yield, while negative coefficient symbols indicate less interaction. According to the given Equation (1), it can be seen that all three variables have a positive influence on the butyl ester yield, however, the biggest influence has the duration of the reaction.

The predicted $R^2$ and adjusted $R^2$ values are 0.9941 and 0.9984, respectively, which shows that experimental values are in reasonable agreement with software-predicted values and that the model can account for 99.84% of the response's variations. The ratio of signal to noise is indicated by the value of adequate precision. This ratio is desirable to exceed 4. In this case, the value of adequate precision is 42.061 (Table 4).

Figure 5 represents the graph between experimental and predicted values of butyl ester yield (wt%). It can be seen that there are no significant differences between experimental and predicted values.

The two-dimensional surface plot of the butyl ester yield with varying catalyst loading (from 4 to 8 wt%) and 1-butanol concentration (from 8:1 to 16:1), when the reaction duration is 9 h is presented in Figure 6. At a 1-butanol-to-oil molar ratio 10:1 and above and catalyst content of 6 wt% and above, ester yields greater than 97 wt% are obtained. Furthermore, it is possible to reach 97 wt% with lower than 6 wt% of catalyst using higher than 10:1 1-butanol-to-oil molar ratio. At the same time, we cannot reach same ester yield by increasing alcohol amount and decreasing the catalyst. As we can see, by increasing both the amount of catalyst and the amount of alcohol, the ester yield increases.

The same trends (as the alcohol and catalyst amounts increase, the ester yield increases) were observed by other scientists who studied the process of transesterification of jojoba oil with n-butanol using calcined mussel shells. The researchers performed the dependence of jojoba oil conversion on the butanol-to-oil molar ratio and the amount of catalyst (temperature 85°C, duration 600 min) (*36*). When studying the conversion of triolein with 1-butanol, the amount of CaO varied from 1 to 4 wt% and the duration from 0 to 120 min at a constant temperature of 120°C. The conversion of triolein with 1-butanol and 4 wt% catalyst after 120 min of synthesis was 100%. In the investigated experimental range, jojoba oil conversion increased with increasing n-butanol concentration and catalyst content, indicating a possible interaction between n-butanol and CaO

**Table 3.** Analysis of variance of quadratic model.

| Source | Sum of squares | df | Mean square | F value | p-value prob > F | |
|---|---|---|---|---|---|---|
| Model | 15,944.59 | 9 | 1771.62 | 1303.87 | <0.0001 | Significant |
| A: 1-butanol-to-oil molar ratio | 76.64 | 1 | 76.64 | 56.40 | <0.0001 | |
| B: catalyst amount | 48.00 | 1 | 48.00 | 35.33 | 0.0001 | |
| C: duration | 10,522.25 | 1 | 10,522.25 | 7744.15 | <0.0001 | |
| AB | 104.84 | 1 | 104.84 | 77.16 | <0.0001 | |
| AC | 210.54 | 1 | 210.54 | 154.95 | <0.0001 | |
| BC | 102.96 | 1 | 102.96 | 75.78 | <0.0001 | |
| $A^2$ | 32.50 | 1 | 32.50 | 23.92 | 0.0006 | |
| $B^2$ | 16.78 | 1 | 16.78 | 12.35 | 0.0056 | |
| $C^2$ | 3604.66 | 1 | 3604.66 | 2652.95 | <0.0001 | |
| Residual | 13.59 | 10 | 1.36 | | | |
| Lack of Fit | 12.92 | 5 | 2.58 | 19.32 | 0.28 | Not significant |
| Pure Error | 0.67 | 5 | 0.13 | | | |
| Cor Total | 15,958.17 | 19 | | | | |

**Table 4.** Statistical data determined by ANOVA.

| Variable | C.V. % | R-Squared | Adj R-Squared | Pred R-Squared | Adeq Precision |
|---|---|---|---|---|---|
| Value | 1.41 | 0.9991 | 0.9984 | 0.9941 | 42.061 |

catalyst. The regression model used by the researchers showed a good correlation between the experimental results and the predicted value (35). Gaide et al. (33) optimized the transesterification process of rapeseed oil with 1-butanol (catalyst-calcined chicken eggshells) using the surface response methodology. Results showed that a higher catalyst amount leads to a higher ester yield, as using a small amount (<6 wt%)

the maximum ester yield was not reached. Ester yield increases until the 1-butanol-to-oil molar ratio reaches 11:1, however, a further increase in alcohol amount leads to the butyl ester yield decrease.

The influence of process duration and alcohol content on ester yield when the catalyst amount is 6 wt% is shown in Figure 7.

The duration varied from 6 to 12 h, the 1-butanol-to-oil molar ratio varied from 8:1 to 16:1. As it was mentioned earlier, the increase in the alcohol content has a positive effect on the ester yield, however, more than 99 wt% of ester yield can be achieved at a lower (8:1) 1-butanol-to-oil molar ratio when the catalyst is 6 wt% and the process duration is 9 h. Process duration also
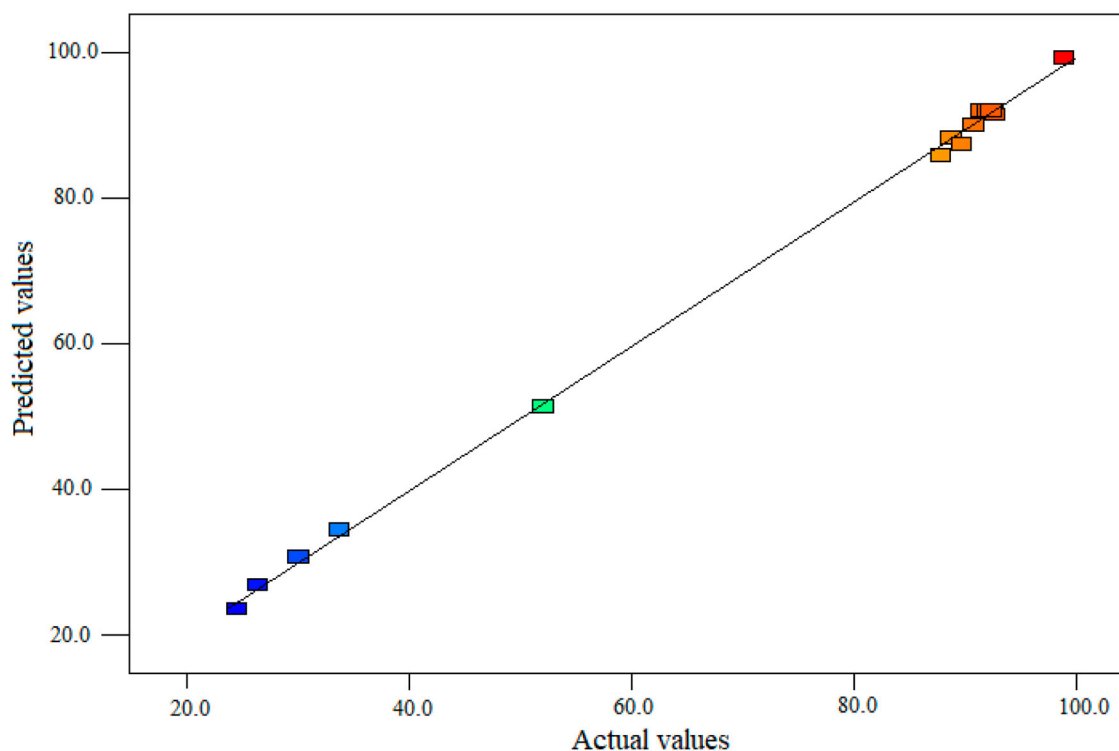


**Figure 5.** Actual and predicted values of ester yield (wt%).
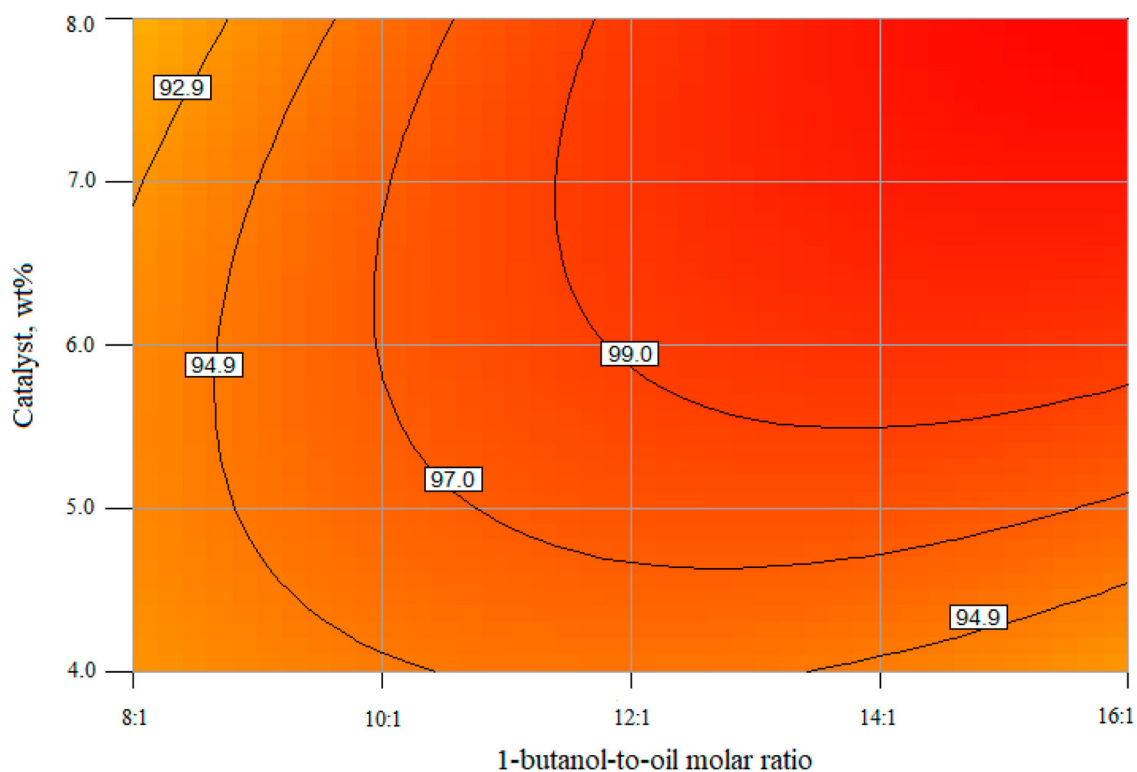
**Figure 6.** Response surface for the interaction between the catalyst and alcohol content for the butyl ester yield when the process duration is 9 h and the process temperature is 110°C.
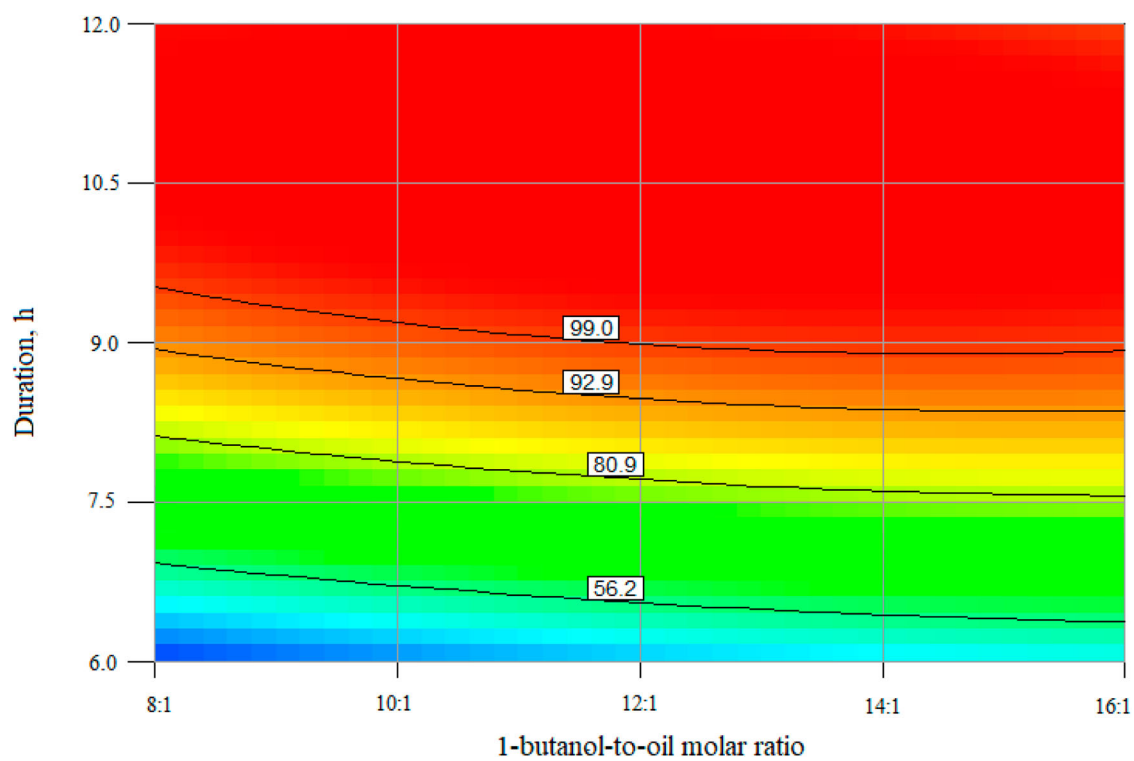


**Figure 7.** Response surface for the interaction between the process duration and the alcohol amount for the butyl ester yield when the catalyst amount is 6 wt% and the process temperature is 110°C.

has a positive effect on the ester yield, yet >99 wt% of ester yield can be achieved after 9 h of reaction when the 1-butanol-to-oil molar ratio is >11:1 and the catalyst amount is 6 wt%.

Avhad and colleagues investigated the influence of duration on the butanolysis process of jojoba oil at a constant alcohol-to-oil molar ratio of 10:1 and 12 wt% of mussel shell. After 10 h at a reaction temperature of 85°C, jojoba conversion was greater than 52%. By extending the reaction time to 30 h, a maximum jojoba oil conversion of 96.11% was achieved (*36*).

When studying the triolein conversion process with 1-butanol, an alcohol-oil molar ratio of 6:1 was used, with a duration of up to 120 min. A maximum conversion of 100% triolein was obtained after 2 h of the reaction (4 wt% catalyst CaO, temperature 120°C) (*35*).

Investigation of the butanolysis process of rapeseed oil using calcined eggshells as a catalyst was done. The influence of process duration on biodiesel production was tested, it was obtained that ester yield increased with time. Ester yield increased (reached >98 wt%) after 12 h by increasing the 1-butanol-to-oil molar ratio to 11:1 (*33*).

Figure 8 shows the interaction between reaction duration (varied from 6 to 12 h) and catalyst amount (varied from 4 to 8 wt%) when the 1-butanol-to-oil molar ratio is 12:1.

In the case of a short (<9 h) transesterification reaction duration, maximum ester yield cannot be obtained. While using even small amounts (4 wt%) of snail shells, when the reaction lasts more than 9 h, more than 99 wt% of ester yield can be obtained. Therefore, it is clear, that transesterification of rapeseed oil using 1-butanol and snail shells as a heterogeneous catalyst mostly depends on process duration.

Avhad et al. investigated the influence of duration and catalyst (mussel shell) on the butanolysis process of jojoba oil at a constant alcohol-to-oil molar ratio of 10:1 and 85°C temperature. The researchers varied the amount of catalysts from 6.3 wt% to 17.7 wt% and found that when the catalyst was loaded up to 17.7 wt%, the conversion of jojoba oil decreased (duration 10 h). The reason for that can be an increase in the viscosity of the reaction mixture (*36*). In the case we analyzed, no such trends were observed since the maximum catalyst content of 8 wt% was investigated.

Gaide et al. studied the process of transesterification of rapeseed oil with 1-butanol and using eggshells as a catalyst, found that the ester yield increases with the increase of the process time and the amount of catalyst. About 98.78 wt% of butyl ester yield was achieved with a duration of 11.81 h and the catalyst content was 7.41 wt% (*33*).
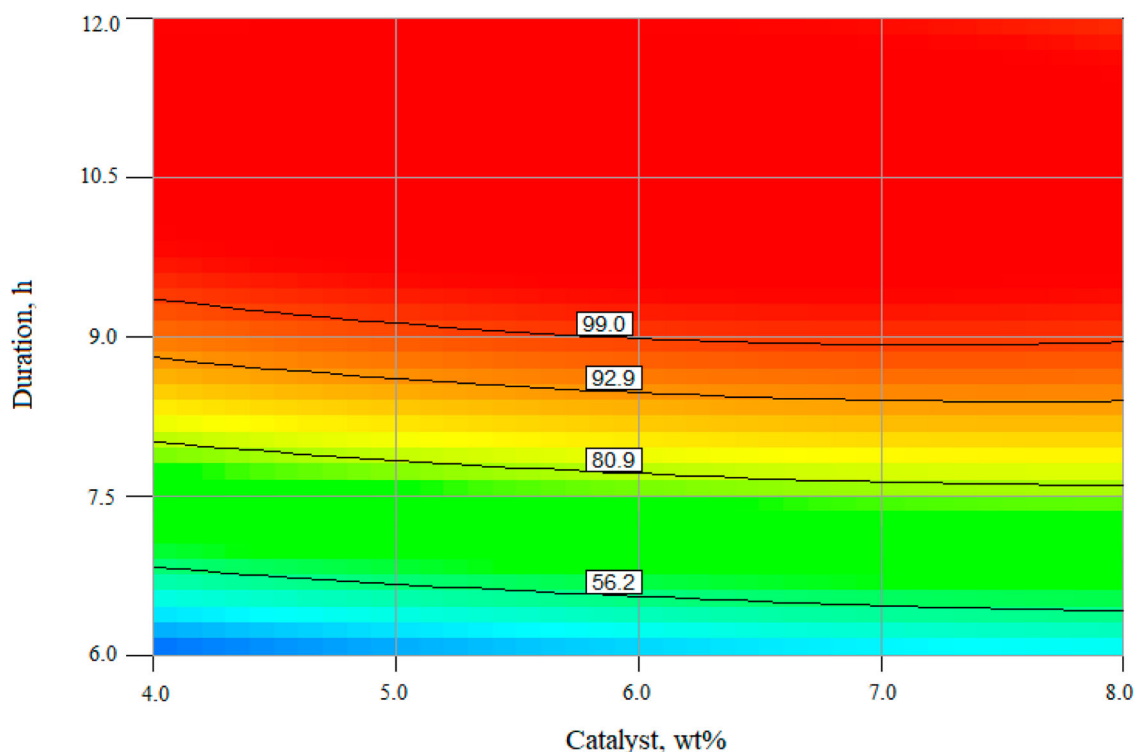


**Figure 8.** Response surface for the interaction between the processing time and the catalyst content for the butyl ester yield when the 1-butanol-to-oil molar ratio is 12:1 and the process temperature is 110°C.

Lascar and his colleagues used waste snail shell (*Pila* spp.) as a catalyst in the production of soybean oil methyl esters, a high biodiesel yield of 98% was achieved after 7 h (*37*). The same optimal duration of 7 h was chosen in the production of waste frying oil methyl esters using calcined snail shell as a catalyst, biodiesel conversion of 99.58% was obtained with a yield of 87.28% (*38*).

## 3.3. Process optimization

In this research, the influence of transesterification reaction duration, catalyst, and alcohol on the butyl ester yield was investigated. In order to obtain optimum process conditions, optimization was applied. Optimum conditions, modeled, and experimental results of ester yield are shown in Table 5. Optimum rapeseed oil transesterification process conditions when the reaction temperature is 110°C are the following: the 1-butanol-to-oil molar ratio 10.61:1, the snail shells content 7.53 wt%, and the reaction duration 10.77 h, modeled ester yield 99.52 wt%. Transesterification reaction was conducted under the determined optimum conditions, 99.25 ± 0.41 wt% of butyl ester yield was obtained.

Avhad et al. obtained 96.11 wt% yield of jojoba oil butyl esters using 12 wt% mussel shells as a heterogeneous catalyst, process time 30 h, temperature 85°C, and alcohol-to-oil molar ratio 10:1. For the transesterification process, Avhad et al. obtained the same optimal alcohol amount as in our study, a lower temperature was used, however, 3 times longer duration and more than 1.5 times of catalyst were required to obtain high yields of esters (*36*).

Gaide et al. studied rapeseed oil transesterification using 1-butanol and eggshells as a heterogeneous catalyst. After process optimization (ester yield 98.78 wt%), optimum process conditions were the following: 1-butanol-to-oil molar ratio 11.3:1, eggshells content 7.41 wt%, and reaction duration 11.81 h (*39*). These results are similar compared with ours, as same oil and alcohol were used, and both catalysts contain around 90% of CaO.

There are not many studies on oil butanolysis with molluscs, snails, and oyster shells. The discussion also reviews the studies of butanolysis performed by other authors using CaO or other natural raw materials as catalysts since the content of calcium oxide in the snail shells used by us is 91.69 ± 0.43%.

Keneni and Marchetti achieved a 95.64% yield of jatropha oil butyl esters when at the optimum temperature of 90.48°C and 1-butanol-to-oil molar ratios 13.24:1, the amount of CaO used was constant at 15 wt% and the glycerol used was 15 wt% (from the catalyst) (*31*).

Hvidsten and Marchetti studied the process of transesterification of waste salmon oil with butanol, using glycerol-doped CaO as a catalyst. It was determined that the optimum process temperature was 80°C, the butanol-to-oil molar ratio 6:1, the amount of catalyst was 20 wt%, and the yield of esters was 95.95, 97.48, and 97.9 wt%, respectively, after 60, 75, and 90 min. (*40*).

Scientists studied the reaction of triolein transesterification with various alcohols like methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol using CaO as a catalyst. Using the 1-butanol-to-oil molar ratio of 6:1 and 4 wt% of the catalyst, 100% triolein conversion was achieved at 120°C after 2 h (*35*). Urasaki et al. achieved good results with a shorter process time and lower catalyst and alcohol contents, however they used a chemically pure CaO catalyst and higher temperature.

Investigating the process of transesterification of rapeseed oil with 1-butanol using calcined eggshells as a catalyst, an ester yield of 98.78 wt% was obtained after 11.81 h, with a catalyst content of 7.41 wt%, alcohol-to-oil molar ratio of 11.3:1, a process temperature of 110°C (*33*).

More research has been done using different oils, different mollusc shells and methanol. CaO derived from *Chicoreus brunneus* shell was used as a catalyst in the biodiesel production process from rice bran oil using methanol. About 93.5 wt% of ester yield was achieved when the methanol-to-oil molar ratio was 30:1, catalyst amount was 0.4 wt%, and reaction time was 2 h (*41*). Researchers also investigated the use of different heterogeneous catalysts (waste egg shells, golden apple snail, and M*eretrix venus*) in the methanolysis process of palm oil. In all catalysts, a higher than 95 wt% ester yield was achieved in 2 h, with a molar ratio of methanol-to-oil of 18:1, a catalyst content of 10 wt%, and a temperature of 60°C (*42*). In the production of methyl esters of palm oil using Waste capiz (*Amusium cristatum*) shell as a catalyst, 93 wt% of ester yield was achieved, after 6 h of reaction time, alcohol-to-molar ratio 8:1, temperature 60°C, and 3 wt% of catalyst (*43*).

Calcined scallop shell was used in the production of methyl esters from waste cooking oil, in 2 h an 86 wt% of ester yield was achieved at 65°C, with a alcohol-to-

**Table 5.** Optimal conditions for biodiesel production, modeled and experimental ester yield.

| 1-butanol-to Oil Molar Ratio, mol/mol | Snail shells amount, wt % (from oil mass) | Reaction Duration, h | Modeled Butyl Ester Yield, wt% | Experimental Butyl Ester Yield, wt% |
|---|---|---|---|---|
| 10.61:1 | 7.53 | 10.77 | 99.52 | 99.25 ± 0.41 |

molar ratio of 12:1, a catalyst loading amount of 5 wt% (44). Other scientists conducted research on the production of soybean oil methyl esters with CaO (obtained from calcined scallop shell) and calcium diglyceroxide. Catalysts with a loading of 5 wt% (oil basis) and a methanol to oil molar ratio of 12:1, reaction time 1.5 h, the yield in both cases is greater than 90 wt% (45). The lime catalyst of Dias et al. study shows good catalytic properties in the methanolysis of rapeseed oil, resulting in a 97% FAME yield after 3 h of reaction at atmospheric pressure and 60°C. Lime catalyst presents good catalytic effectiveness during the rapeseed oil methanolysis and allows to obtain a FAME yield of 97% after 3 h of reaction at atmospheric pressure and 60°C (46).

Many researchers conduct research at process temperatures close to the boiling point of alcohol, however Laskar et al obtained 98 wt% soyabean oil methyl ester yield in 7 h, at the methanol-to-oil molar ratio 6:1 and calcined waste snail shell 3 wt% using a temperature of 28°C (25).

## 3.4. Quality parameters of rapeseed oil butyl esters

Table 6 shows the physical and chemical properties of rapeseed oil butyl esters obtained under optimal conditions.

One of the most important indicators of the quality of biodiesel is the ester content, which determines the amount of fatty acid esters formed from the oil. The amount of esters required by the standard EN 14214 must be at least 96.5%, ours is 99.25 ± 0.41 wt%.

The density and viscosity of fuels are important to the proper work of the engine. The density of the produced biofuel at a temperature of 15°C – 885 ± 0.24 kg m$^{-3}$ meets the requirements of the standard. According to the requirements of the standard, at a temperature of 15°C, it must be 860–900 kg m$^{-3}$. Viscosity at 40°C must be min 3.50 and max 5.00 mm$^2$ s$^{-1}$, obtained fatty acid butyl esters – 4.78 ± 0.05 mm$^2$ s$^{-1}$.

EN 14214 standard specifies the maximum limiting value of acid number – 0.5 mg KOHg$^{-1}$. The number of acids depends on the quality of the raw material used for the production of biodiesel and the production process. The acid number of the obtained fuel is 0.35 ± 0.003 mg KOHg$^{-1}$.

The amount of sulfur in esters is limited, which must not exceed 10 mgkg$^{-1}$. Sulfur compounds in biodiesel can come from rapeseed oil. The sulfur content in the obtained butyl esters of rapeseed oil is 8.8 ± 0.04 mg kg$^{-1}$.

Water may remain in biodiesel if the product is not fully dried after cleaning. Moisture content in the obtained biodiesel reaches 228 ± 1.50 mg kg$^{-1}$, when the standard requires it to be no more than 500 mg kg$^{-1}$.

Since a catalyst is used in the biodiesel production process, the main component of which is calcium, therefore, the amount of Group II metals (Ca + Mg) in the product is a very important indicator. The amount of Group II metals (Ca + Mg) in rapeseed oil butyl esters did not exceed the maximum 5 mg kg$^{-1}$ which is required by the standard.

Iodine number and linolenic acid methyl ester content determine the degree of unsaturation of fatty acids. These indicators depend on the fatty acid composition of the oil. The rapeseed oil used in this study is free of high levels of mono- and polyunsaturated fatty acids, so the final product meets the standard requirements.

The efficiency of transesterification of triglycerides and the purity of the obtained esters are defined by the amounts of mono-, di- and triglycerides, free glycerol, and total glycerol in biodiesel. In the obtained biodiesel, the following were present monoglycerides – 0.72 ± 0.21%, diglycerides – 0.15 ± 0.01%, triglycerides – 0.16 ± 0.01%, free glycerol – 0.17 ± 0.38%, and total glycerol 0.21 ± 0.09%. According to these indicators, biodiesel meets the requirements of the standard.

Oxidation resistance is an important indicator, as the fuel must maintain the required properties during storage. In contact with oxygen, oxidation processes occur, which deteriorate the properties of the fuel during which free fatty acids, peroxides, aldehydes,

**Table 6.** Physical and chemical parameters of biodiesel.

| Parameter | Units | EN 14214 requirements | Rapeseed oil butyl esters |
|---|---|---|---|
| Ester content | % | min 96.5 | 99.25 ± 0.41 |
| Density at 15°C | kg m$^{-3}$ | min 860 max 900 | 867 ± 0.85 |
| Viscosity at 40°C | mm$^2$ s$^{-1}$ | min 3.50 max 5.00 | 4.78 ± 0.05 |
| Acid value | mg KOH g$^{-1}$ | max 0.5 | 0.35 ± 0.003 |
| Sulfur content | mg kg$^{-1}$ | max 10 | 8.8 ± 0.04 |
| Moisture content | mg kg$^{-1}$ | max 500 | 228 ± 1.50 |
| Group II metals (Ca + Mg) | mg kg$^{-1}$ | max 5 | 4 ± 0.78 |
| Iodine value | g J$_2$ 100$^{-1}$ g$^{-1}$ | max 120 | 118 ± 0.75 |
| Linolenic acid esters content | % | max 12.0 | 10.2 ± 0.08 |
| Monoglyceride content | % | max 0.8 | 0.72 ± 0.21 |
| Diglyceride content | % | max 0.2 | 0.15 ± 0.01 |
| Triglyceride content | % | max 0.2 | 0.16 ± 0.01 |
| Free glycerol content | % | max 0.2 | 0.17 ± 0.38 |
| Total glycerol content | % | max 0.25 | 0.21 ± 0.09 |
| Oxidation stability 110°C | h | min 8 | 8.4 ± 0.15 |
| Cold filter plugging point | °C | −5°C (in summer) −32°C (in winter) | −12 ± 0.10 |

and polymers are formed. The oxidation resistance of the obtained butyl esters is $8.4 \pm 0.15$ h, while at least 8 h are specified in the requirements of the standard.

Depending on the CFPP of the fuel, the possibility of using the fuel in the cold period also depends. The CFPP of the obtained biodiesel is minus $12 \pm 0.10°C$, so it can be used in Lithuania in the summer period (the standard requires the CFPP in the summer period to be no higher than minus 5°C (class C of the moderate climate zone)).

Biodiesel –rapeseed butyl esters obtained under the specified conditions meet the requirements of the EN 14214 standard for biodiesel.

## 4. Conclusions

Snail shells calcinated for 5 h at 850°C temperature and sieved to fraction size of 0.315–0.1 mm could be used as heterogeneous catalysts for biodiesel production by the application of rapeseed transesterification with 1-butanol. It was determined that $CaCO_3$ existing in raw shells after calcination at 850°C for 5 h is decomposed into CaO (concentration $93.69 \pm 0.43\%$). In this way, a porous, highly efficient, but very hygroscopic (35.09–62.12% depending on the relative humidity of the environment) catalyst for the transesterification of triglycerides was obtained. Three independent parameters (the 1-butanol-to-oil molar ratio, the snail shells amount, and the reaction duration) were selected to investigate optimum conditions for rapeseed oil transesterification reaction, also the influence of these parameters was investigated. It was found that longer process duration has a positive effect on the ester yield, while after less than 9 h, maximum ester yield cannot be achieved. High alcohol and catalyst amount have good influence on the yield of esters; however more than 99 wt% of yield can be obtained using smaller amount of 1-butanol and snail shells, but performing reaction longer than 9 h. Using response surface analysis, the rapeseed oil transesterification process using snail shells and 1-butanol was optimized. Optimum butyl ester synthesis conditions were obtained: a 1-butanol-to-oil molar ratio of 10.6:1, a snail shell content of 7.53 wt%, and a reaction time of 10.77 h at 110°C. Under these conditions the butyl ester yield of 99.25 wt% was obtained. The produced biodiesel is suitable for using it for diesel engines during the summer period, as their physical and chemical properties meet the requirements of the EN 14214 standard.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

## ORCID

Ieva Gaide http://orcid.org/0009-0006-3990-0163
Violeta Makareviciene http://orcid.org/0000-0002-6296-4812
Egle Sendzikiene http://orcid.org/0000-0002-4341-1489
Rasa Slinksiene http://orcid.org/0000-0003-0614-5027
Rasa Paleckiene http://orcid.org/0000-0001-9600-9744

## References

[1] Huang, S.Z.; Sadiq, M.; Chien, F. *Environ. Sci. Pollut. Res.* **2023,** *30*, 42813–42828.
[2] Wang, N.; Tang, L.; Pan, H. *Sustain. Cities Soc.* **2019,** *44*, 597–603.
[3] Lithuanian Energy Agency. https://www.ena.lt/aei-transporte/. (accessed July 2, 2023).
[4] Makareviciene, V.; Gumbyte, M.; Yunik, A.; Kalenska, S.; Kalenskii, V.; Rachmetov, D.; Sendzikiene, E. *Ind. Crops Prod.* **2013,** *50*, 633–637. doi:10.1016/j.indcrop.2013.08.036.
[5] Karciauskiene, D.; Sendzikiene, E.; Makareviciene, V.; Zaleckas, E.; Repšienė, R.; Ambrazaitienė, D. *Agriculture* **2014,** *101*, 161–168.
[6] Aslan, V.; Eryilmaz, T. *Energy* **2020,** *209*, 118386.
[7] da Costa, J.M.; de Andrade Lima, L.R.P. *Fuel* **2021,** *293*, 120446.
[8] Santaraite, M.; Sendzikiene, E.; Makareviciene, V.; Kazancev, K. *Energies* **2020,** *13* (10), 2588.
[9] Makareviciene, V.; Gumbyte, M.; Skorupskaite, V.; Sendzikiene, E. *J. Renew. Sustain. Energy* **2017,** *9* (2), 023101.
[10] Acherki, H.; Bouaid, A.; Marchetti, J. *Biofuels Bioprod. Bioref.* **2022,** *16*, 219–227. doi:10.1002/bbb.2309.
[11] Kumar, R.S.; Prasad, A.K.V. *SN Appl. Sci.* **2019,** *1*, 872.
[12] Guo, Y.; Liu, Y.; Guan, M.; Tang, H.; Wang, Z.; Lin, L.; Pang, H. *RSC Adv.* **2022,** *12*, 18848–18863.
[13] Hariprasath, P.; Selvamani, S.T.; Vigneshwar, M.; Palanikumar, K.; Jayaperumal, D. *Mater. Today: Proc.* **2019,** *16* (2), 1357–1362.
[14] Sendzikiene, E.; Santaraite, M.; Makareviciene, V. *Processes* **2020,** *8* (9), 1118.
[15] Pratika, R.A.; Wijaya, K.; Trisunaryanti, W. *J. Environ. Chem. Eng.* **2021,** *9* (6), 106547.
[16] Ling, J.S.J.; Tan, Y.H.; Mubarak, N.M.; Kasedo, J.; Saptoro, A.; Nolasco-Hipolito, C. *SN Appl. Sci.* **2019,** *1*, 810.
[17] Touchstone snails https://touchstonesnailfranchise.com/snail-market/ (accessed 2 July 2023).
[18] Rygało-Galewska, A.; Zglińska, K.; Niemiec, T. *Animals. (Basel).* **2022,** 12, 2732.
[19] Nkansah, M.A.; Agyei, E.A.; Opoku, F. *Heliyon* **2021,** *10* (7), e08149.
[20] Gaide, I.; Makareviciene, V.; Sendzikiene, E.; Kazancev, K. *Catalysts* **2021,** *11* (3), 384.
[21] Gaide, I.; Makareviciene, V.; Sendzikiene, E. *Catalysts* **2022,** *12* (3), 246.
[22] Anjaneyulu, U.; Pattanayak, D.; Vijayalakshmi, U. *Mater. Manuf. Process* **2016,** *31* (2), 206–216.
[23] RRUFF, 2023, https://rruff.info/Aragonite/R040078 (accessed 13 March 2023).
[24] Parveen, S.; Chakraborty, A.; Chanda, D.K.; Pramanik, S.; Barik, A.; Aditya, G. *ACS Omega* **2020,** *5* (40), 25757–25771.

[25] Laskar, I.B.; Rajkumari, K.; Gupta, R.; Chatterjee, S.; Paul, B.; Rokhum, S.L. *RSC Adv.* **2018,** *8*, 20131. doi:10.1039/C8RA02397B.

[26] Kaewdaeng, S.; Sintuya, P.; Nironsin, R. *Energy Procedia* **2017,** *138*, 937–942.

[27] Viriya-empikul, N.; Krasae, P.; Nualpaeng, W.; Yoosuk, B.; Faungnawakij, K. *Fuel* **2012,** *92*, 239–244.

[28] Hu, S.; Wang, Y.; Han, H. *Biomass Bioenerg.* **2011,** *35* (8), 3627–3635.

[29] Muhammad, C.; Almustapha, M.N.; Tambuwal, A.D.; Idris, B.; Abdullahi, B.H. *J. Fundam Renew. Energy Appl.* **2021,** *11*, 1–9.

[30] Goli, J.; Sahu, O. *Renew. Energ.* **2018,** *128*, 142–154.

[31] Keneni, Y.G.; Marchetti, J.M. *Fuel* **2021,** *289* (1), 119908.

[32] Jha, M.K.; Gupta, A.K.; Kumar, V. Kinetics of Transesterification on Jatropha Curcas Oil to Biodiesel Fuel. In *Proceedings of the World Congress on Engineering and Computer Science*; Ao, S.I., Douglas, C, Grundfest, W.S., Schruben, L, Wu, X, Eds.; San Francisco, USA; 2007.

[33] Gaide, I.; Makareviciene, V.; Sendzikiene, E.; Gumbyte, M. *Sustain. Energy Technol. Assess* **2022,** *52*, 102278.

[34] Freedman, B.; Pryde, E.H.; Mounts, T.L. *J. Am. Oil Chem. Soc.* **1984,** *61* (10), 1638–1643.

[35] Urasaki, K.; Takagi, S.; Mukoyama, T.; Christopher, J.; Urasaki, K.; Kato, S.; Yamasaki, A.; Kojima, T.; Satokawa, S. *Appl. Catal. A. Gen.* **2012,** *411–412*, 44–50. doi:10.1016/j.apcata.2011.10.019.

[36] Avhad, M.R.; Sanchez, M.; Pena, E.; Bouaid, A.; Martínez, M.; Aracil, J.; Marchetti, J.M. *Fuel* **2016,** *179*, 332–338.

[37] Laskar, I.B.; Rajkumari, K.; Gupta, R.; Chatterjee, S.; Paul, B.; Rokhum, L. *RSC Adv.* **2018,** *8*, 20131–20142.

[38] Birla, A.; Singh, B.; Upadhyay, S.N.; Sharma, Y.C. *Bioresour. Technol.* **2012,** *106*, 95–100.

[39] Gaide, I.; Makareviciene, V.; Sendzikiene, E.; Gumbytė, M. *Catalysts* **2023,** *13*, 302.

[40] Hvidsten, I.B.; Marchetti, J.M. *Fuel* **2023,** *333* (1), 126272.

[41] Mazaheri, H.; Ong, H.C.; Masjuki, H.H.; Amini, Z.; Harrison, M.D.; Wang, C.T.; Kusumo, F.; Alwi, A. *Energy* **2018,** *144*, 10–19.

[42] Viriya-empikul, N.; Krasae, P.; Puttasawat, B.; Yoosuk, B.; Chollacoop, N.; Faungnawakij, K. *Bioresour. Technol.* **2010,** *101*, 3765–3767.

[43] Suryaputra, W.; Winata, I.; Indraswati, N.; Ismadji, S. *Renew. Energ.* **2013,** *50*, 795–799.

[44] Sirisomboonchai, S.; Abuduwayiti, M.; Guan, G.; Samart, C.; Abliz, S.; Hao, X.; Kusakabe, K.; Abudula, A. *Energy Convers. Manag.* **2015,** *95*, 242–247.

[45] Catarino, M.; Martins, S.; Dias, A.P.S.; Pereira, M.F.C.; Gomes, J. *J. Environ. Chem. Eng.* **2019,** *7*, 3.

[46] Dias, A.P.S.; Puna, J.; Gomes, J.; Correia, M.J.N.; Bordado, J. *Renew. Energ.* **2016,** *99*, 622–630.