





Article

The Regeneration of Dolomite as a Heterogeneous Catalyst for Biodiesel Production

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Abstract: Dolomite as a heterogeneous catalyst can be used in biodiesel synthesis. Process material costs can be reduced by regenerating and reusing the catalyst. Two methods of regeneration of dolomite were studied: (1) washing for 30 min with methanol, filtration, and washing for 30 min with hexane and (2) calcination at high temperature. Catalytic efficiency and catalyst changes after 1–6 cycles were evaluated. X-ray, FTIR, and SEM studies were performed. Calcination has been found to be a more effective method of catalyst regeneration than washing with solvents. The catalytic effectiveness of dolomite only slightly decreased over six application cycles. The results of the instrumental analysis showed that the structure and composition of the dolomite do not change during calcination after three cycles, while obvious changes in the structure of dolomite during catalyst washing were observed.

Keywords: biodiesel; dolomite; regeneration



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1. Introduction

The European Union is one of the main initiators in the United Nations negotiations on climate change mitigation. A set of proposals aimed at reforming the EU's climate, energy, transport, and tax policies in order to reduce greenhouse gas emissions by at least 55% by 2030 compared to 1990 levels were adopted by the European Commission. Since transport pollution has a significant negative impact on climate change, reducing the use of mineral fuels by replacing mineral diesel with biodiesel [1,2] is one of the steps to achieve the set goals.

The biodiesel production process involves the transesterification reaction of oil or fat with alcohols using homogeneous or heterogeneous catalysts [3–5]. Heterogeneous catalysts are preferred over homogeneous catalysts. Heterogeneous catalysts are being increasingly used, which, unlike homogeneous ones, can be reused [6]. Solid acid and solid base catalysts and immobilised enzymes are used as heterogeneous catalysts for biodiesel synthesis. Metal oxides are the promising catalysts in this process. Calcium and magnesium oxides are known as good catalysts for biodiesel synthesis [7,8]. The presence of calcium in the catalyst allows for the use of raw materials with higher moisture content, which have higher content free fatty acids, and the equipment is less exposed to corrosion during such a process [9].

Heterogeneous catalysts, including calcium and magnesium oxides, are low-cost resources for biodiesel synthesis, as they would reduce the cost of biodiesel production while providing cost-effective catalysts. There are several natural sources of calcium, such as dolomite. Dolomite is a carbonate mineral, mostly composed of calcium and magnesium carbonates. Dolomite is a common mineral in both continental and marine sedimentary and metamorphic rocks. It is cheap and non-toxic [10]. As a natural catalyst, dolomite ($\text{CaMg}(\text{CO}_3)_2$) is used. The thermal decomposition of dolomite to CaO and MgO exhibits its

active phases, making it suitable as a catalyst for the production of biodiesel from vegetable oil or animal fat [11–13].

As dolomite contains high amounts of calcium and magnesium, it can be used for the synthesis of biodiesel. However, calcium and magnesium carbonates need to be broken down into oxides [14,15] using thermal treatment.

It is important that the catalysts are effective more than once, as their reuse reduces the amount of raw materials used and the cost of biodiesel. Scientists have found that CaO can be used multiple times in biodiesel synthesis. Reddy et al. conducted studies and found that CaO is inactivated after three cycles for the transesterification of poultry fat and after eight cycles for the transesterification of soybean oil [16]. Yoosuk et al. investigated the use of CaO in the transesterification of palm oil and found that it can be used five times without additional preparation because both fresh and used catalysts have the same morphological structure [17]. There are several studies related to the reuse of dolomite for biodiesel synthesis [18–21]. However, the results obtained are different. Some researchers did not even synthesize biodiesel that met the standard requirements when using dolomite for the first time.

Porous dolomite pellets were prepared and utilized as a catalyst for the breakdown of tar in biomass gasification. The impact of coke formation on the catalytic activity and the ability of the porous dolomite pellets to regenerate were explored, employing acetic acid as a representative tar model. The experimental results revealed a linear decrease in catalytic activity as coke formation increased, ranging from 0 to 4.4% in coke mass fraction. During this progression, the pore volume decreased from $0.74 \text{ cm}^3 \cdot \text{g}^{-1}$ to $0.48 \text{ cm}^3 \cdot \text{g}^{-1}$, and the acetic acid decomposition rate declined from 99.3% to 32.3%. After calcination at 900°C for 2 h, the pore volume of the porous dolomite pellets increased to $0.55 \text{ cm}^3 \cdot \text{g}^{-1}$ while maintaining essentially unchanged mechanical strength. Furthermore, the acetic acid decomposition rate remained at 99.5%, indicating favorable regeneration due to the calcination capability of the porous dolomite pellets [22].

The aim of our work was to determine the possibilities of multiple uses of dolomite in biodiesel synthesis by evaluating its catalytic activity, composition, and properties after regeneration and reuse.

2. Results and Discussion

2.1. Effectiveness of Catalyst Regeneration Methods

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results and their interpretation, as well as the experimental conclusions that can be drawn. After separation from the reaction mixture through filtration, the heterogeneous catalyst could be reused without any treatment or recycled via washing, drying, and/or recalcination. The collection of the catalyst from the reaction mixture is usually carried out via simple filtration. The regeneration method depends on the catalyst and aims to ensure the complete removal of organic substances from the surface of the catalyst. Usually, the solvents used for washing are methanol, ethanol, and hexane. Another way to regenerate the catalyst is through drying at a temperature range from 100°C to 900°C [23].

The results of the ester yield after catalyst regeneration are presented in Table 1. The data show that using a method that includes washing the catalyst, the ester yields strongly decreased with each cycle. After the second cycle, the rapeseed oil methyl ester (RME) yield decreased from 98.66 wt% to 77.85 wt% which does not meet the standard requirement. Less than 50 wt% of the ester yield was obtained after the third cycle when the catalyst was regenerated via the washing method.

Correia et al. (2015) obtained different results from those in our study by investigating canola oil transesterification with methanol using dolomite as a heterogeneous catalyst. By using a calcined dolomite catalyst at 850°C for 3 h for transesterification with three cycles of washing the catalyst twice with methanol and drying at 100°C for 1 h, the (fatty acid methyl ester) FAME yield decreased from 98.81 wt% to 80.97 wt% after three cycles [24].

While in our case, after three cycles, the RME yield only reached 47.11 wt% when using the washing method. The activity of dolomite was significantly reduced when washing with solvents when it was used for the synthesis of esters for the fourth time: the yield of esters reached only 22.45%, i.e., more than 77% of the oil remained unreacted, so further regeneration studies involving the washing of dolomite with solvents were not appropriate.

Table 1. Ester yield after catalyst regeneration.

Cycle Number	Ester Yield, wt%	
	Calcination	Washing
1	98.66 ± 0.21	98.66 ± 0.11
2	98.57 ± 0.18	77.85 ± 0.24
3	98.45 ± 0.15	47.11 ± 0.21
4	98.42 ± 0.19	22.45 ± 0.14
5	97.93 ± 0.22	
6	97.23 ± 0.32	

Korkur and Bayramoglu investigated ultrasound-assisted canola oil transesterification with methanol using dolomite. After the reaction, dolomite was filtrated and mixed with methanol, poured into the reactor, and ultrasonically irradiated for 15 min. It was found that the FAME yield decreased from 96.5 wt% to 89.5 wt% after four cycles [20]. In our case, the ester yield decreased to 22.45 wt% after four cycles.

Meanwhile, using the calcination method, only a slight decrease in the ester yield was noticed. The ester yield decreased from 98.66 wt% to 97.23 wt% after six calcination cycles.

For the discussion of the instrumental analysis data, Figures 1–3 present the data for the prepared but unused catalyst after two cycles of catalyst washing and after three cycles of catalyst calcination. No further data are provided because regeneration through washing is deemed inefficient, and calcification yields identical results.

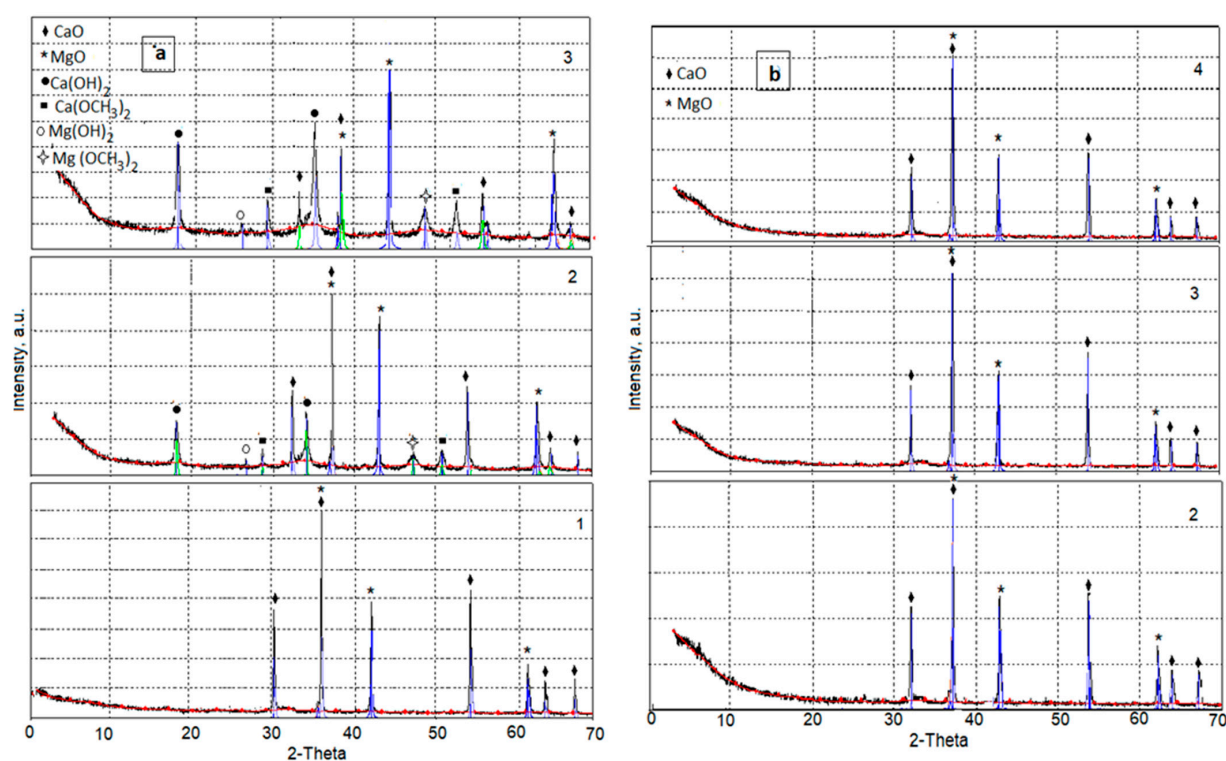


Figure 1. XRD of the catalyst: (a)—washing, (b)—calcination; 1—before use, 2—after the 1st cycle, 3—after the 2nd cycle, and 4—after the 3rd cycle.

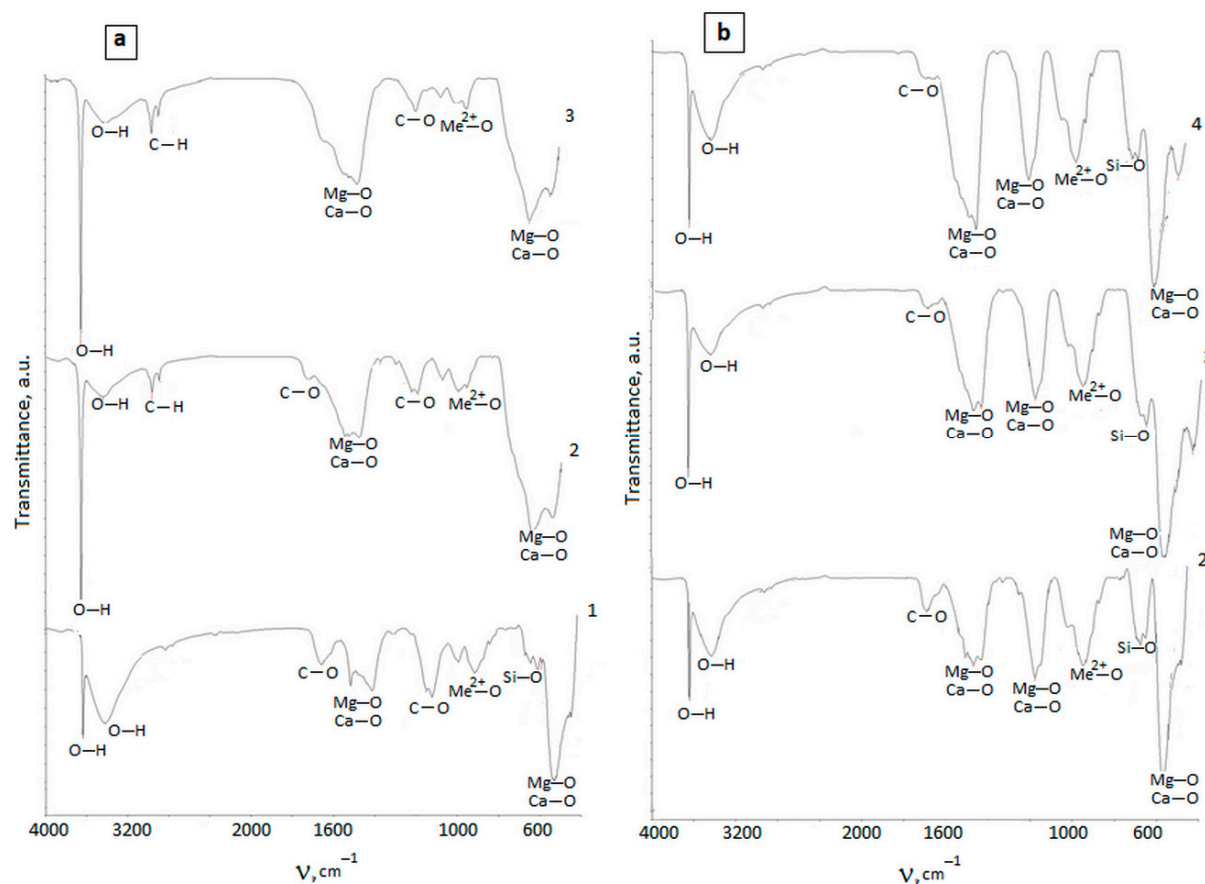


Figure 2. FT-IR of the catalyst: (a)—washing, (b)—calcination; 1—before use, 2—after the 1st cycle, 3—after the 2nd cycle, and 4—after the 3rd cycle.

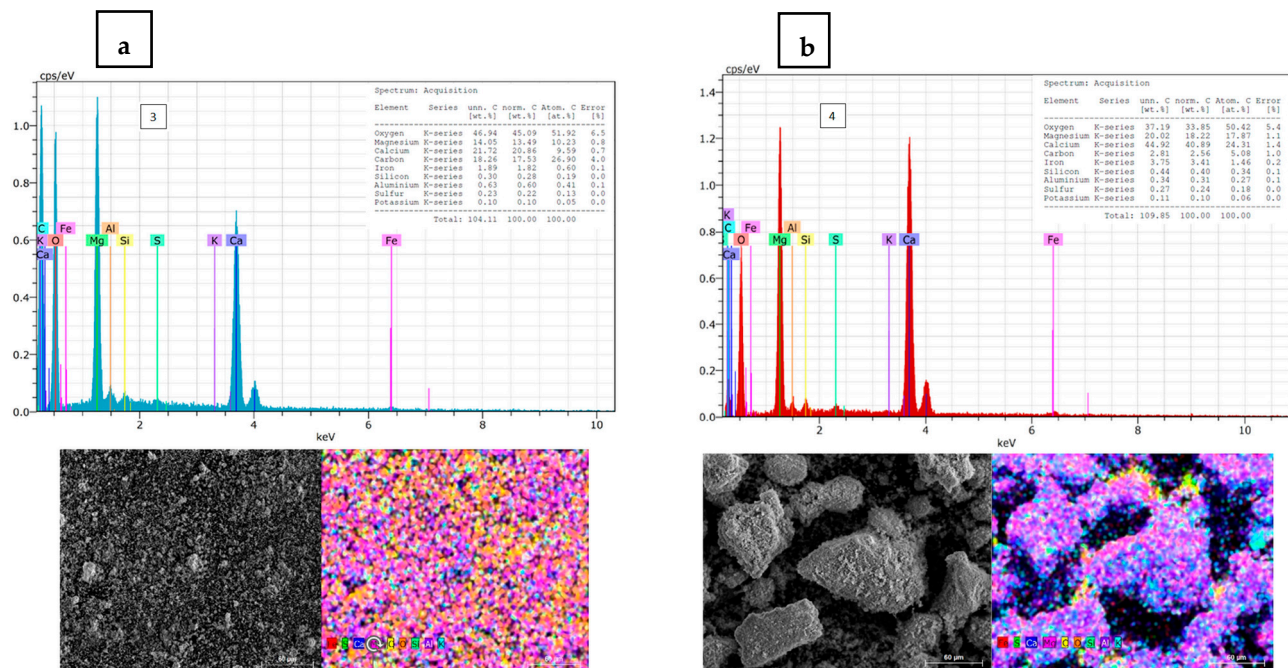


Figure 3. Cont.

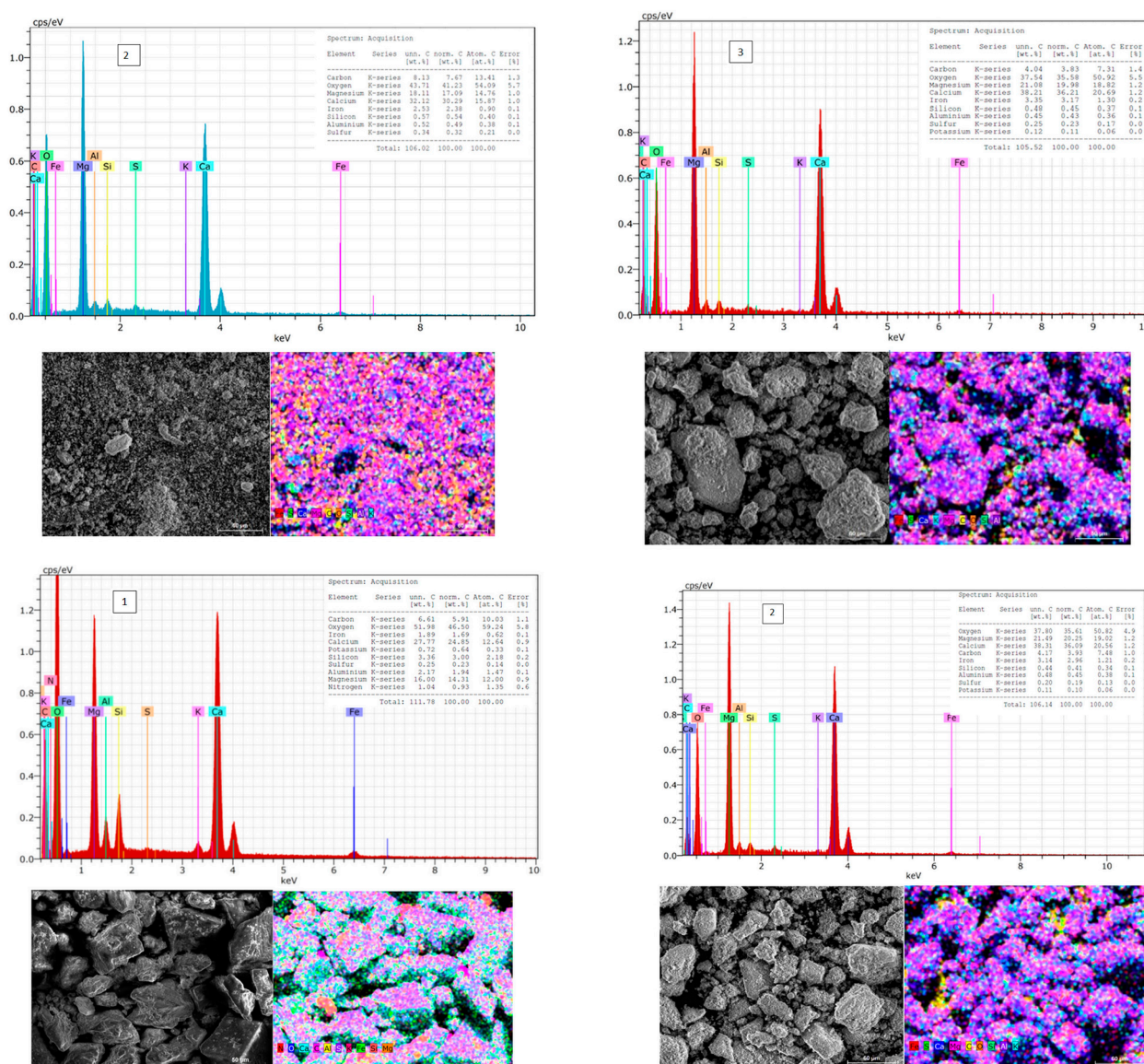


Figure 3. SEM and EDS of the catalyst: (a)—washing, (b)—calcination; 1—before use, 2—after the 1st cycle, 3—after the 2nd cycle, and 4—after the 3rd cycle.

2.2. X-ray Diffraction Analysis (XRDA) Results

The instrumental analysis results showed that washing and drying regeneration processes have different influences on the structure and efficiency of the catalysts.

Because XRDA is the most widely employed technique for general crystalline material characterization and it allows for the identification of diffraction peaks of crystalline phases in bulk materials, it was used for dolomite analysis after several cycles of use–regeneration. Analyzing the XRDA data (Figure 1b, 2–4 curves), it can be seen that if the used dolomite was regenerated through heating at high temperature (5 h at 850 °C), i.e., during calcination, complete regeneration occurs, and the pure catalyst remains. In this case, the XRDA curves (Figure 1b, 2–4 curves) of the regenerated dolomite show only the characteristic peaks of CaO and MgO, which are also visible in Figure 1a curve 1 (dolomite before use). It can be concluded that in this case, the composition and structure of the catalyst do not change even after three use–regeneration cycles. These results correlate well with the results obtained by Widiarti et al. (2023) [25]. Meanwhile, washing the remaining catalyst after the transesterification reaction with a mixture of methanol and hexane (ratio 1:10) does not remove all washing substances, because Figure 1b curves 2

and 3 show many new peaks. The identified peaks can be assigned to such compounds of the interaction of calcium and magnesium with methanol as calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), and magnesium methoxide $\text{Mg}(\text{OCH}_3)_2$, which are formed by the interaction of oxides with methanol. It should be noted that the XRDA 2-Theta axis of other authors' work ends at 40 degrees, thus missing some of the peaks seen in Figure 1, where the 2-Theta cut-off is 70 degrees [25], including the studies of Teo et al. [26], Chumuang and Punsuvon [27], and Saxena et al. [28].

The additional peaks identified in the XRDA curves of the catalyst regenerated via washing suggest that the formed substances exist on the surface of the catalyst and inhibit its catalytic activity. Such a statement correlates well with the results presented in Table 1.

2.3. Fourier-Transformed Infrared Spectroscopy (FTIR) Analysis Results

Infrared molecular absorption spectral analysis (FTIR spectroscopy) was performed on the catalyst prepared from dolomite via thermal treatment [29], as well as the catalyst samples after reactions using washing or the calcination regeneration methods. Through the analysis of the obtained spectra, changes were identified, enabling us to assess alterations in the chemical composition and structure of the samples (Figure 2).

Absorption peaks characteristic of natural dolomite (1438 cm^{-1} , 879 cm^{-1}) associated with a carbonate bond (CO_3^{2-}) disappeared after calcination, indicating that dolomite decomposed to oxides of calcium and magnesium [30,31]. The characteristic peak situated around 3650 cm^{-1} indicates the presence of the OH present in $\text{Ca}(\text{OH})_2$ and also $\text{Mg}(\text{OH})_2$ compounds [32]. In the spectrum, the absorption peaks characteristic of the deformational vibrations of the products formed during the heating of dolomite appears, i.e., Mg–O ($1417\text{--}1520\text{ cm}^{-1}$) and Ca–OH (3642 cm^{-1}) (Figure 2a, curve 1) [30–32]. Some absorption peaks characteristic of the CO_3^{2-} group ($\sim 950\text{--}1000\text{ cm}^{-1}$, $1120\text{--}1150\text{ cm}^{-1}$, 1670 cm^{-1} , and 2926 cm^{-1}) are slightly shifted to the higher energy region. This happens due to a change in the mass of the functional group, as part of the CO_2 is removed from the sample when it is heated. Many peaks of low intensity appear and stand out, which confirm the structural transformation of dolomite into calcite. The band observed at 650 cm^{-1} may be assignable to the Ca–O–Ca stretching vibration characteristic of the CaO phase [30]. A characteristic peak of MgO ($533\text{--}548\text{ cm}^{-1}$) was recorded [31]. Some low-intensity peaks in the region of $600\text{--}900\text{ cm}^{-1}$, characteristic of $\text{Me}^{2+}\text{--O}$ (Me, supposedly Ca, Mg, Al, and Fe) or Si–O bonds, cannot be identified due to the predominance of common absorption bands. These results obtained by us fully correspond with the data presented in the works of other researchers [33].

Catalysts already used in the transesterification process of rapeseed oil, which was regenerated via calcination or washing, were also analyzed using the IR spectroscopy method. Analyzing the FTIR spectra of the calcined dolomite catalyst regenerated via washing with a mixture of methanol and hexane (ratio 1:10), changes in the intensity of the absorption peaks are observed. The characteristic absorption peaks of calcined dolomite remain or are shifted slightly. The intensity of some of these peaks in the spectra recorded after regeneration decreases after one wash and is not even recorded after the second regeneration (Figure 2a, curves 2–3). It was observed that the intensity of the absorption peak ($3642\text{--}3645\text{ cm}^{-1}$) characteristic of the O–H group increases. The intensity of the second O–H characteristic absorption peak (3420 cm^{-1}) decreases, but its width increases. New absorption peaks (2855 cm^{-1}) characteristic of the C–H group appear in the spectra.

The appearance of new low-intensity absorption peaks in the $1300\text{--}1700\text{ cm}^{-1}$ region is attributable to the formation of H–Me bonds [34], and when analyzing the FTIR spectra of the used dolomite, which was regenerated during washing, two absorption bands in the areas of $890\text{--}920\text{ cm}^{-1}$ and $825\text{--}855\text{ cm}^{-1}$ are characteristic of the samples after washing with organic solvents [34–36]. All spectra contain a clear MgO peak (532 cm^{-1}). Some low-intensity peaks in the region $600\text{--}800\text{ cm}^{-1}$, characteristic of $\text{Me}^{2+}\text{--O}$ (Me, supposedly Ca, Mg, Al, and Fe) or Si–O bonds, cannot be identified due to the predominance of common absorption bands, and their intensity weakens.

Analyzing the FTIR spectra of the used dolomite, which was regenerated via calcination (Figure 2b, curves 2–4), an increase in the intensity of the absorption peak characteristic of deformational vibrations of OH groups (3642 cm^{-1}) can be observed. The vibrational band detected at around 1450 cm^{-1} corresponds to the formation of oxide Me (Me = Mg, Ca) [32], and as the number of calcination cycles increases, the intensity and position of this absorption band change. The intensity of the band increases and shifts towards higher wavenumbers. In agreement with Kandiban, a broadband coupling at around $430\text{--}770\text{ cm}^{-1}$ is assigned to the metal–oxygen bending vibration [31]. The increasing intensity of dolomite peaks (1415.88 cm^{-1} , 1156.29 cm^{-1} , 926.04 cm^{-1} , and 544.8 cm^{-1}) is also observed after each catalyst work cycle and regeneration [37]. This is linked to changes in the composition of the catalyst sample and the change in the ratio of the components. Meanwhile, in the region of $600\text{--}1000\text{ cm}^{-1}$ absorption peaks, which are common to $\text{Me}^{2+}\text{--O}$ or Si--O bonds, confirm the calcite structure. The intensity of the absorption peaks of the samples used for catalysis decreases after each cycle, and some of them practically disappear after the third cycle.

2.4. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) Analysis Results

Since the surface of the catalyst is a very important criterion for the efficiency of heterogeneous catalysis, using the results from the SEM and EDS analysis (Figure 3), the surface changes of dolomite particles in several use–regeneration cycles were analyzed. After individual cycles of use–regeneration, changes in the surface were determined by comparing the SEM photos and element maps of the used catalyst and the initial catalyst.

In the case when the catalyst was regenerated after use via washing (Figure 3a) with a mixture of methanol and hexane (ratio 1:10), after the first cycle, it can be seen that the catalyst particles became much smaller, and after the second cycle, they were absolutely small. In parallel with the decreasing particles in the catalyst was the change in chemical composition. As can be seen from the EDS data, the catalyst before use contains not only the main oxides of calcium and magnesium, but also aluminum (2.17%), silicon (3.36%), iron (1.89%), nitrogen (1.04%), and carbon (6.61%). During the experiment and regeneration, no new substances appeared, but the concentrations of all elements changed. Table 2 shows the changes in the concentration of the main elements (Ca, Mg, and C) that influence the activity of the catalyst.

Table 2. The dynamic change in the concentrations of Ca, Mg, and C.

Regeneration Method	Washing			Calcination		
	Concentration, wt%			Ca	Mg	C
Before use	27.77	16.00	6.61	27.77	16.00	6.61
After the first cycle	32.12	18.11	8.13	38.31	21.49	4.17
After the second cycle	21.72	14.05	18.26	38.21	21.08	4.04
After the third cycle	-	-	-	44.92	20.02	2.81

From the data, it is evident that during washing (with a mixture of methanol and hexane) of the catalyst, the concentration of calcium decreases while the concentration of carbon significantly increases. Therefore, carbon poisoning is likely to reduce the activity of the catalyst. Conversely, the completely opposite situation is observed in the dynamics of calcium and carbon concentration changes when the catalyst is regenerated through calcination, explaining its high activity throughout all cycles. Analyzing the variations in other elements, it can be noted that after regeneration, no nitrogen remains, and there is a notable decrease in silicon content, and an increase in iron content, but this does not influence the catalyst activity. These changes in elements are subtly visible on the element map as they alter the color of the images. The colors on the element map differ from the

original dolomite (Figure 3a, 1) but are practically unchanged after the first, second, and third use–regeneration (by calcination) cycles.

Because most heterogeneous catalytic reactions occur on the catalyst's surface, the efficiency of the reaction is strongly influenced by the catalyst's surface area, i.e., the particle size of the catalyst. When the catalyst was regenerated via washing (Figure 3a, 2 and 3), the size of the catalyst particles, compared to the initial particle size (Figure 3a, 1), was greatly reduced. This reduction diminishes the area on which the reaction can take place. When the catalyst was regenerated via calcination (Figure 3b, 2–4), analyzing the SEM data after the first, second, and third cycles, an opposite trend can be observed, i.e., after each cycle, the catalyst consists of progressively larger particles. A higher surface area means more active sites are available for the reactant molecules to adsorb, increasing the likelihood of successful collisions and reactions. Additionally, a larger surface area provides more space for reactant molecules to adsorb, leading to an increased rate of reaction. The presented data correlate with Vedrine's statement that in heterogeneous catalysis, where the reactants and catalyst are in different phases, a larger surface area facilitates the mass transfer of reactants to the catalyst surface and products away from it [38].

The results show that calcined dolomite can be used as a catalyst, but its surface changes after each calcination cycle, so the number of cycles is limited. According to Cong et al.'s data, the SEM images of calcined dolomite had a lot of macropores after 20 calcined cycles, but those pores were almost absent after 50 cycles [39]. The surface of dolomite particles was obviously melted, which caused the deterioration in pore structure.

3. Materials and Methods

3.1. Materials

Dolomite was purchased from a local market (manufacturer SC Dolomite, Petrašiūnai Village, Lithuania). For preparation of the catalyst, the mineral was ground in a laboratory mill and heated in a muffle furnace (AB UMEGA SNOL 8.2/1100, Søborg, Denmark) for 4 h at 850 °C. After heating, the dolomite was sieved through sieves to obtain a 0.315 mm fraction. Food-grade rapeseed oil used for transesterification was purchased from a local market. Methanol (analytical grade) was supplied by Sigma Aldrich (Søborg, Denmark).

3.2. Transesterification of Rapeseed Oil and Studies on the Reusability of Dolomite

The transesterification of rapeseed oil was carried out in laboratory reactors, the reaction mixture was heated using a magnetic stirrer (250 rpm), and a reflux condenser was also used. The reusability of calcinated (5 h 850 °C) dolomite was studied under the following reaction conditions: a methanol-to-oil molar ratio of 11.94:1, catalyst content of 6 wt%, a reaction duration of 5 h, and the reaction temperature of 64 °C [14]. The reaction product was filtered through cellulose paper and the liquid fraction containing rapeseed methyl esters was washed once with H₃PO₄ (5%), (the 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 period, the separated aqueous part was poured off. After washing, the samples were dried in a rotary vacuum evaporator.

3.3. Catalyst Regeneration

The reusability of dolomite was investigated after the synthesis of rapeseed oil methyl ester (RME). Catalyst regeneration was carried out in two ways—calcination and washing. Regeneration procedures and catalytic activity were investigated after each transesterification cycle. In the first case, after the transesterification reaction, dolomite was filtered, and the resulting unfiltered mass was collected and calcined in a muffle furnace (AB UMEGA SNOL 8.2/1100, Utena, Lithuania) for 3 h at a temperature of 850 °C. After calcination, the dolomite was reused for biodiesel synthesis. In the second case, after the transesterification reaction, the filtered dolomite was washed with methanol (ratio 1:10 by volume) at room temperature with stirring (250 rpm) for 30 min; then after filtration, it was washed with

hexane (ratio 1:10 by volume) at room temperature with stirring (250 rpm) for 30 min. After filtering, the resulting dolomite was dried for 24 h at a temperature of 130 °C.

3.4. Determination of Rapeseed Methyl Ester Yield

The ester yield was investigated regarding the glyceride contents (glycerol, monoglycerides, diglycerides, and triglycerides) in the samples. Glyceride contents were determined via gas chromatography using a Perkin Elmer Clarus 500 (detector—FID) (Boston, MA, USA) gas chromatograph according to the requirements of the standard. The RME yield was calculated according to partial glyceride levels [40].

3.5. X-ray Diffraction Analysis

The chemical composition of samples was determined via X-ray diffraction analysis (XRDA) using a Bruker D8 Advance diffractometer (Billerica, MA, USA), equipped with 1-D detector LYNXEYE with a Ni-filter. The step size was 0.05° and the dwell time was 0.5 s; the anodic voltage $U_a = 40$ kV and strength of the current $I = 40$ mA. Data were analyzed using a crystallographic search-match program.

3.6. Fourier-Transform Infrared Spectroscopy Analysis

To identify the functional groups, the dolomite and calcinated powder were characterized using a System SPECTRUM GX 2000 for Fourier-transform infrared spectroscopy (FTIR) analysis (PerkinElmer, Waltham, MA, USA). Transmittance measurement was carried out by preparing the KBr pellet. The final spectrum is shown in a transmittance mode. The transmittance spectrum registration range is 4000–400 cm^{-1} .

3.7. Scanning Electron Microscope and Energy Dispersive Spectroscopy Analysis

The morphological structure of both the natural dolomite and dolomitic catalysts were determined using a scanning electron microscope and energy dispersive spectroscopy (SEM-EDS). Surface morphology and elemental composition were determined via the scanning electron microscopy (SEM) technique by using the Hitachi company's scanning electron microscope model S-3400N. It has a built-in Bruker Quad 5040 EDS detector (Tokyo, Japan). Electron source—a pried-centered cartridge-type tungsten hairpin filament. The electron acceleration voltage was 15 kV. A secondary electron detector is used to produce a topographic SEM image.

4. Conclusions

Calcined dolomite can be used as a heterogeneous catalyst in the synthesis of fatty acid methyl esters due to the presence of calcium and magnesium oxides in it. The cost of biodiesel production could be reduced by regenerating and reusing the catalyst. High-temperature calcination and washing with organic solvents have been studied among the regeneration methods. It was found that after washing with methanol and hexane for 1 h, regenerated dolomite exhibits a significant decrease in catalytic activity compared to dolomite after calcination at 850 °C for 3 h. After the first cycle, the RME yield was 98.66%, and after regenerating the dolomite via washing three times, the obtained RME yield was only 22.45%. Calcination only slightly reduced the catalytic activity of dolomite. When applying it, after six cycles, the RME yield decreased to only 97.23%. The results of the instrumental analysis showed that during calcination, the chemical composition (X-ray and FT-IR) and structure (SEM) of the catalyst do not change even after three use-regeneration cycles. In the case of washing with methanol (ratio 1:10 by volume) and hexane (ratio 1:10 by volume; the catalyst contains compounds from the interaction between calcium and magnesium with methanol or hexane). Analysis of SEM images shows obvious changes in the structure of dolomite during catalyst washing, while changes during calcination are minimal.

Author Contributions: Conceptualization, V.M. and E.S.; methodology, R.Š., R.P. and V.M.; formal analysis, R.Š., R.P., I.G., V.M. and E.S.; investigation, R.Š., R.P., I.G., V.M. and E.S.; resources, R.Š. and E.S.; data curation, R.Š., R.P., I.G., V.M. and E.S.; writing—original draft preparation, R.Š., R.P., I.G., V.M. and E.S.; writing—review and editing, V.M. and E.S.; visualization, R.Š., R.P., I.G., V.M. and E.S.; supervision, V.M.; project administration E.S. All authors have read and agreed to the published version of the manuscript.

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