

Reusability and regeneration of solid catalysts used in ultrasound assisted biodiesel production

Mahmut BAYRAMOĞLU¹, İbrahim KORKUT², Başak TEMUR ERGAN^{1*}

¹Chemical Engineering Department, Gebze Technical University, Gebze, Turkey

²Chemical Engineering Department, Sivas University of Science and Technology, Sivas, Turkey

Received: 20.08.2020 • Accepted/Published Online: 08.12.2020 • Final Version: 28.04.2021

Abstract: Reusability of two heterogeneous catalysts in ultrasound (US) assisted biodiesel production was investigated in comparison to each other. An ultrasound (US) generator (200 W, 20 kHz) equipped with a horn type probe (19 mm) was used. Regeneration experiments were planned according to second order central composite design (CCD) method. After the eighth use of the catalysts, biodiesel yield decreased from 99.1% to 90.4% for calcined calcite (CaO) and from 98.8% to 89.8% for calcined dolomite (CaO.MgO). Furthermore, regeneration of spent catalysts by calcination was investigated; optimum temperature and time were found as 750 °C and 90 min, lower than fresh catalyst preparation conditions. The regenerated catalysts were reused in a second process cycle; biodiesel yield was calculated as 97.2% for CaO and 96.5% for CaO.MgO. Finally, the process showed that calcination is an energetically favorable regeneration process of spent catalysts.

Key words: Biodiesel, ultrasound assisted transesterification, calcium oxide, calcined dolomite, heterogeneous catalyst regeneration

1. Introduction

Transesterification reaction transforms oil or fats with methanol (CH₃OH) into biodiesel in presence of a catalyst, with glycerol as a by-product [1,2]. Usually, homogeneous basic catalysts such as potassium hydroxide (KOH) or homogeneous acidic catalysts such as sulfuric acid (H₂SO₄) are used [3]. However, the homogeneously catalyzed transesterification process has some drawbacks such as the formation of soap and water, which consume more catalyst and reduce the biodiesel yield and the biodiesel quality. Furthermore, additional water is spent for purification of biodiesel and glycerol and more wastewater is formed, disposal of which increases the process cost [4]. The heterogeneously catalyzed transesterification process exhibits various advantages; the catalyst can be easily removed by filtration from the reaction medium, the process includes fewer number of unit operations, more pure products (biodiesel and glycerol) are obtained, wastewater formation during product purification steps is greatly reduced, heterogeneous catalyst is reused until a catalyst regeneration step, which reduces biodiesel production cost [5]. Meanwhile, the major drawback of heterogeneous catalysis is the slow reaction rate compared to homogeneous counterpart. Fortunately, the process can be accelerated by applying ultrasound in the reaction medium [1,6].

In virtue of these advantages, studies on biodiesel production in the presence of heterogeneous catalysts have been increasing over the last 10 years [6]. The commercialization of heterogeneously catalyzed biodiesel production requires profitability, raw material availability, and cost-effective production [7]. In this respect, the reusability of catalyst is a very important issue that should be examined, which has not been investigated in detail except a few studies without any mention about the catalyst regeneration; Piker et al. reused the CaO catalyst ten times with fresh oil and four times with waste cooking oil at the same reaction conditions; biodiesel yield decreased from 95% to 75% in the case of fresh oil and decreased from 93% to 62% in case of using waste cooking oil [8]. Viola et al. investigated the catalytic activity of CaO in the reuse experiments and found that the loss of efficiency was due to the attached glycerin on the catalyst surface [9]. Kurayama et al. used Ca-loaded microcapsules as catalyst for the transesterification of rapeseed oil, and they found that the biodiesel yield declined from 95.5% to 80.9% at the end of fourth reuse [10]. Castro et al. prepared CaO/MgAl oxide catalysts, and they found that the catalyst could be reused for at least 5 reuse cycles without effective decline of the catalyst activity [11]. Wen et al. prepared KF/CaO nano catalyst by impregnation method for transesterification of Chinese tallow seed oil and reused the catalyst 16 times with a slight loss of biodiesel yield [12]. Hu et al. prepared a nanomagnetic

* Correspondence: btemur@gtu.edu.tr

catalyst, $\text{KF}/\text{CaO}-\text{Fe}_3\text{O}_4$, using an impregnation method for biodiesel production and reused the catalyst 16 times [13]. Yu et al. synthesized different compositions of $\text{CaO}-\text{CeO}_2$ mixed metal oxides for using solid base catalysts and found that the biodiesel yield decreased slowly until the fifth reuse when a significant loss in the catalytic activity was observed [14].

On the other hand, catalyst regeneration methods can be classified into two groups. In the first group, after catalyst filtration, regeneration is accomplished by washing and drying the catalyst at a temperature usually lower than 200 °C. In the second one, calcination alone or combined with other methods is applied [6]. Madhu et al. found that reused catalysts must be calcinated in order to activate the catalyst active sites [15]. Boey et al. reused the waste cockle shell derived CaO catalyst at least for three times, with a purity above 96.5%. Before it was reused, the spent catalyst was washed with methane and n-hexane to remove the adsorbed materials and calcined at 900 °C for 2 h. The washed uncalcined spent catalyst consisted of $\text{Ca}(\text{OH})_2$ and traces of $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$ (calcium diglyceride, CaDG). After calcination at 900 °C for 2 h, the structure of the calcined dolomite catalyst was changed to CaO [16].

The literature survey shows that calcination is a more appropriate method to regenerate the activity of CaO and Ca based catalysts; it is a simple process with no waste solvent or solid waste product formation, also the heat of combustion of some organic compounds formed during the esterification such as CaDG or adsorbed impurities on the spent catalyst may diminish the heat duty of the calcination process.

By considering these points, calcination was selected in this study for catalyst regeneration, which it is expected to be more energetically favorable process compared to fresh catalyst preparation.

2. Experimental section

2.1. Chemicals

Commercial canola oil with the following relevant properties was used without purification: free acid content: 0.5%; density: 0.93 g/cm³. Kinematic viscosity: 77 mm²/s; unsaponifiables: 0.7%; triglycerides: 97.2% of total lipids. Dolomite ($\text{CaCO}_3, \text{MgCO}_3$) and calcite (CaCO_3) were obtained from chemical supplier located in Kocaeli, Turkey. They were calcined at 840 °C for 3 h [17].

2.2. Catalyst reuse experiments

The schematic representation and details of the experimental setup were given in a previous study [1]; an ultrasonic generator (Bandelin 2200 sonopuls, 200 W, 20 kHz, Sigma–Aldrich, city, country?) equipped with a horn type probe was used to deliver pulsed ultrasound (US) with controllable power in a 300 mL three-necked cylindrical glass reactor equipped with a reflux condenser and a magnetic stirrer.

The experiments were carried out at the optimum conditions determined in this study. At the end of the run, the reaction slurry was poured into specially designed bottom screwed centrifuge tubes, which allowed the catalyst recovery almost completely. Until the next run, the catalyst was kept in refrigerator in CH_3OH to avoid contact with atmospheric CO_2 and H_2O . The next run required CH_3OH for the desired feed $\text{CH}_3\text{OH}/\text{oil}$ molar ratio, and oil was added to the sonoreactor with some fresh catalyst to compensate for the catalyst loss (approximately 5%).

2.3. Catalyst regeneration experiments

The purpose of these experiments was to find calcination conditions energetically (and economically) favorable than the fresh catalyst production by calcination from raw materials. Catalysts (obtained after the eighth use) were divided into samples of 1-g after washing with methanol. Catalyst regeneration experiments were carried out using 1-g catalyst samples. The statistical second order central composite (CCD) design was used in planning of regeneration experiments using Design-Expert software (demo version, Stat-Ease Inc, MN, USA?). In addition, temperature and time were selected as process factors in the experimental plan; as seen in Table 1, positive levels of factors were determined from fresh catalyst preparation conditions, and the negative levels were determined from similar catalyst regeneration studies cited in the literature [18,19].

The second order central composite (CCD) experimental plan is given in Table 2. Eleven regeneration experiments were made for this purpose. The response of the experimental plan was the mass loss (%) of the spent catalyst at the end

Table 1. Factor levels for central composite experimental design.

Factor	-1	+1	- α	+ α
Temperature (°C)	550	750	450	850
Time (min)	90	150	60	180

Table 2. Experimental plan and mass loss of the spent catalysts.

Temperature (°C)	Time (min)	Mass loss (%)
450	120	54.56
550	90	56.99
550	150	57.24
650	60	59.48
650	120	64.64
650	120	64.30
650	120	64.84
650	180	66.67
750	90	74.00
750	150	74.60
850	120	74.60

of the calcination, high mass loss indicating the success of the calcination. The standard deviation of mass loss calculated from the center point experiments results was found as 0.27%.

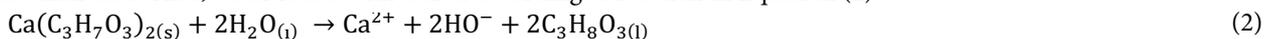
3. Results and discussion

3.1. Catalyst reuse experiments

The serial experiments were carried out until the yield decreased to approximately 90%. Experimental results are depicted in Figure 1. Different heterogeneous catalyst deactivation mechanisms are proposed in literature; Oueda, et al. pointed out especially to the leaching of active sites on the catalyst surface, the surface poisoning and/or pore filling, and the structural collapse of catalysts [6]. To detect phase transformation during the process, X-ray diffraction (XRD) patterns of fresh and spent catalysts with crystal phases are shown in Figure 2; as also noted by Granados et al. the oxide form disappears in both catalysts and new peaks arise which show that CaO is transformed to CaDG (the characteristic XRD peaks of CaDG at 2θ are 8.1° , 10.1° , 21.1° , 24.2° , 26.6° , 34.3° and 36.4°) according to the reaction in Equation (1) [20].



CaDG is less active transesterification catalyst than CaO catalyst. Furthermore, CaDG is more soluble in the glycerol phase than CaO. Also, water reacts with CaDG according to reaction in Equation (2).



Furthermore, Ca^{2+} reacts with the free fatty acid (FFA) in the oil and forms calcium soaps $\text{Ca}(\text{FFA})_2$ according to the reaction in Equation (3), which results in the reduction of the reaction yield and biodiesel purity.



3.2. Catalyst regeneration experiments

The XRD data was used to check the success of calcination procedures and synthesis of CaDG. As seen in Figure 2, sharp and highly intense XRD peaks define the well crystallized structure of the regenerated spent catalysts. Because, the crystallinity or crystallite size of the catalyst is an important feature determining the catalytic activity. Therefore, the crystallite size for all phases was obtained from the XRD patterns using the Scherrer equation (Equation 4) [21–23].

$$L = \frac{\alpha\lambda}{\beta\cos\theta} \quad (4)$$

where, L is the mean average crystallite size (Å), α is a constant equal to 0.94, β is the full width at the half maximum in radians (obtained for the high intensity peak), and λ (Å) is the wavelength of the X-rays (1.54059 Å). For eighth reuse calcined dolomite (CaO.MgO), eighth reuse calcined calcite (CaO), fresh calcined dolomite (CaO.MgO) and fresh calcined calcite (CaO), the average crystallite size values were 64.4 Å, 99.0 Å, 70.6 Å, and 105.8 Å, respectively. In this study, the maximum average crystallite size was observed at fresh calcined calcite (CaO). Crystallite size values in optimum calcination conditions of the fresh and used catalyst are shown in Table 3.

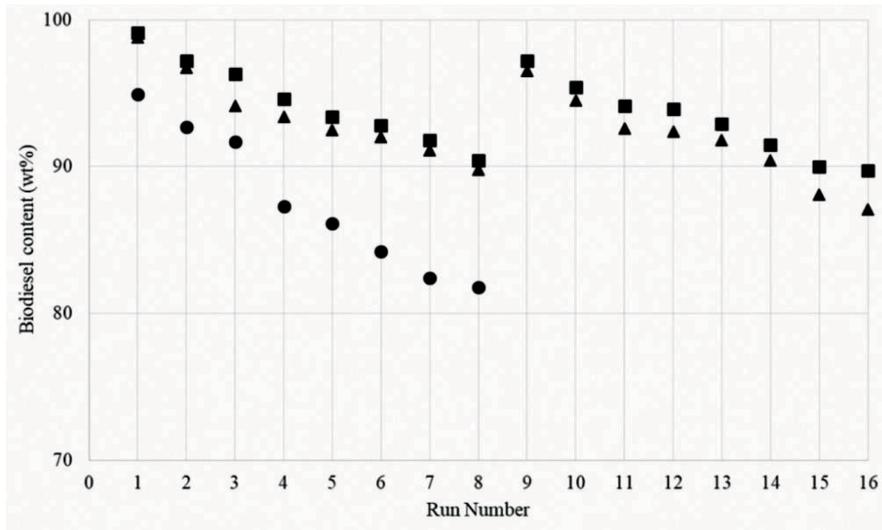


Figure 1. Reusability of catalysts in the transesterification of canola oil. (■ CaO catalyst ultrasound assisted transesterification experiments, ▲ calcined dolomite ultrasound assisted transesterification and ● CaO silent transesterification experiments).

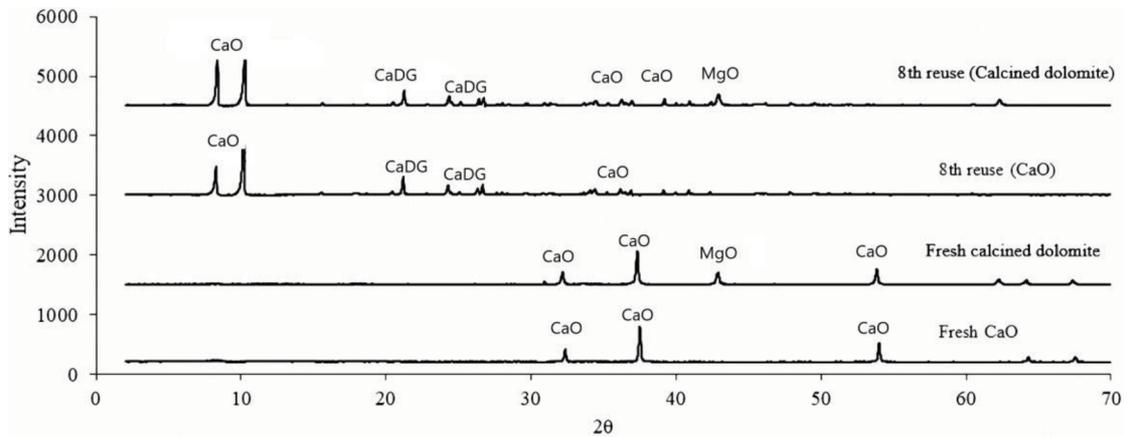


Figure 2. The XRD patterns of fresh and used catalysts.

Table 3. The crystallite size of the fresh and used catalysts.

Catalysis	Temperature (°C)	Time (min)	Crystallite size (Å)
8th CaO.MgO	750	90	64.4
8th CaO	750	90	99.0
Fresh CaO.MgO	840	180	70.6
Fresh CaO	840	180	105.8

When CaDG is completely oxidized to CaO, a mass loss of 74.7% occurs according to the reaction in Equation (5).



Thus, the highest mass loss in Table 2 (74.6%) refers to optimum regeneration conditions; 750 °C and 90 min. which are sufficient to convert CaDG completely to CaO.

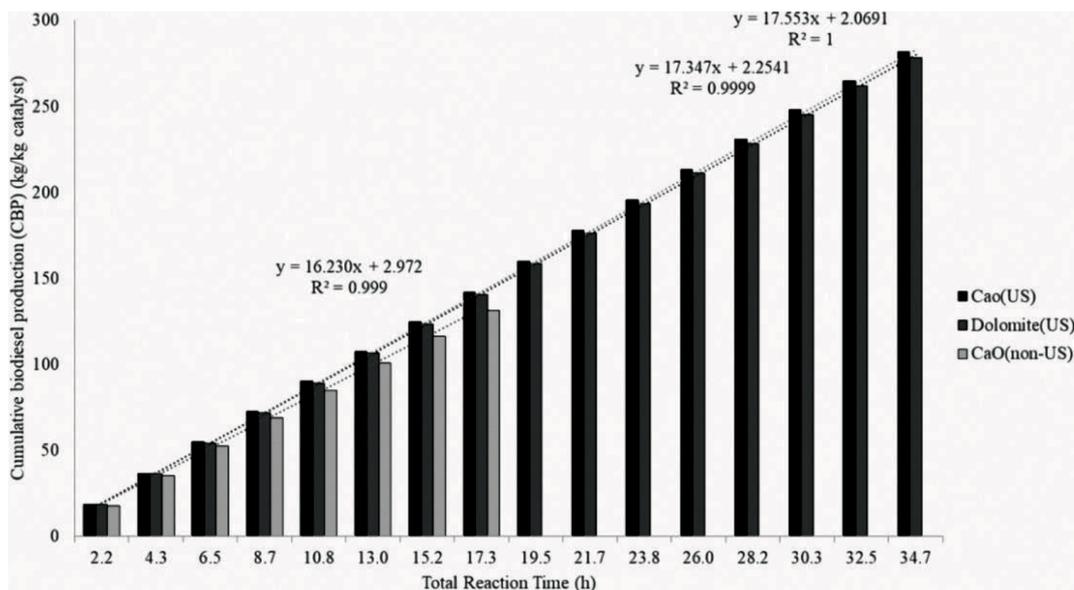


Figure 3. Cumulative biodiesel production as a function of total reaction time.

In the second cycle of the biodiesel production with regenerated catalyst, yield was realized as 97.2% for CaO. For dolomite catalyst the same calcination conditions was used for regeneration step and 96.5% yield was obtained.

Finally, for an overall assessment of the process, biodiesel production per kg of catalyst (BP) was calculated by Equation (6), where m_{oil} is amount of canola oil (kg), α is the stoichiometric correction factor, x is the biodiesel content of product and $m_{catalyst}$ is the amount of used catalyst (kg). The cumulative biodiesel production per kg of catalyst value (CBP) is obtained by accumulating the BP values. The CBP results are given in Figure 3. As seen, the CBP values of both catalysts are very close to each other.

$$BP = \frac{m_{oil} \cdot \alpha \cdot x}{m_{catalyst}} \quad (6)$$

On the other hand, cumulative biodiesel production rate (BPR) is obtained by dividing CBP values by reaction time. BPR values (kg biodiesel/kg catalyst h) were calculated as 17.55, 17.35, and 16.23 for CaO (US), calcined dolomite (US), and CaO (silent) respectively. The cumulative productivity rate of US assisted biodiesel production is 8% higher than the silent biodiesel production, but for a more detailed energy analysis of the biodiesel production process, the comparison may be more accurate by taking into account ultrasound energy used during the reaction.

4. Conclusion

The reusability performances of calcined calcite (CaO) and calcined dolomite (CaO.MgO) in the ultrasound assisted transesterification reactions were tested in successive transesterification runs. The yields decreased from 99.1% and 98.8% for CaO and calcined dolomite to 90.4% and to 89.8% after eighth reuse, respectively. These results are consistent with the average crystallite size results and also with XRD patterns.

The regenerated catalysts were reused in a second process cycle with negligible activity losses compared to fresh catalysts. Furthermore, an overall assessment of the process by means of various criteria shows that the performance of ultrasound assisted biodiesel production using CaO catalyst is 8% higher than the silent biodiesel production.

While the use of ultrasound in biodiesel production decreases the process cost and process time, the eighth reuse of calcined calcite and calcined dolomite catalysts reduces the energy requirement in catalyst preparation.

In conclusion, the experimental results confirmed that spent catalyst calcination at 750 °C for 90 min. is more energetically favorable when compared to fresh catalyst preparation at 840 °C for 3 h. Finally, reusability of heterogeneous catalyst is an important issue affecting technical, environmental and economic aspects of the biodiesel production process.

Acknowledgment

We thank the Gebze Technical University research fund for partial support.

References

1. Korkut I, Bayramoglu M. Selection of catalyst and reaction conditions for ultrasound assisted biodiesel production from canola oil. *Renewable Energy* 2018; 116: 543-551. doi: 10.1016/j.renene.2017.10.010
2. Ramachandran K, Suganya T, Nagendra Gandhi N, Renganathan S. Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst-a review. *Renewable and Sustainable Energy Reviews* 2013; 22: 410-418. doi: 10.1016/j.rser.2013.01.057
3. Choudhury HA, Chakma S, Moholkar VS. Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst. *Ultrasonics Sonochemistry* 2014; 21: 169-181. doi: 10.1016/j.ultsonch.2013.04.010
4. Reyer I, Arzamendi G, Gandía LM. Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. *Chemical Engineering Research and Design* 2014; 92: 1519-1530. doi: 10.1016/j.cherd.2013.11.017
5. Korkut I, M. Bayramoglu M. Ultrasound assisted biodiesel production in presence of dolomite catalyst. *Fuel* 2016; 180: 624-629. doi: 10.1016/j.fuel.2016.04.101
6. Oueda N, Bonzi-Coulibaly YL, Ouédraogo IWK. Deactivation processes, regeneration conditions and reusability performance of CaO or MgO based catalysts used for biodiesel production-a review. *Materials Science and Applications* 2017; 08: 94-122. doi: 10.4236/msa.2017.81007
7. Teo SH, Islam A, Yusaf T, Taufiq-Yap YH. Transesterification of nannochloropsis oculata microalga's oil to biodiesel using calcium methoxide catalyst. *Energy* 2014; 78: 63-71. doi: 10.1016/j.energy.2014.07.045
8. Piker A, Tabah B, Perkas N, Gedanken A. A green and low-cost room temperature biodiesel production method from waste oil using egg shells as catalyst. *Fuel* 2016; 182: 34-41. doi: 10.1016/j.fuel.2016.05.078
9. Viola E, Blasi A, Valerio V, Guidi I, Zimbardi F et al. Biodiesel from fried vegetable oils via transesterification by heterogeneous catalysis. *Catalysis Today* 2012; 179: 185-190. doi: 10.1016/j.cattod.2011.08.050
10. Kurayama F, Yoshikawa T, Furusawa T, Bahadur NM, Handa H et al. Microcapsule with a heterogeneous catalyst for the methanolysis of rapeseed oil. *Bioresource Technology* 2013; 135: 652-658. doi: 10.1016/j.biortech.2012.11.014
11. Castro CS, Garcia LCF, Assaf JM. The enhanced activity of Ca/MgAl mixed oxide for transesterification. *Fuel Processing Technology* 2014; 125: 73-78. doi: 10.1016/j.fuproc.2014.03.024
12. Wen L, Wang Y, Lu D, Hu S, Han H. Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. *Fuel* 2010; 89: 2267-2271. doi: 10.1016/j.fuel.2010.01.028
13. Hu S, Guan Y, Wang Y, Han H. Nano-magnetic catalyst KF/CaO-Fe₃O₄ for biodiesel production. *Applied Energy* 2011; 88: 2685-2690. doi: 10.1016/j.apenergy.2011.02.012
14. Yu X, Wen Z, Li H, Tu ST, Yan J. Transesterification of Pistacia chinensis oil for biodiesel catalyzed by CaO-CeO₂ mixed oxide. *Fuel* 2011; 90: 1868-1874. doi: 10.1016/j.fuel.2010.11.009
15. Madhu D, Chavan SB, Singh V, Singh B, Sharma YC. An economically viable synthesis of biodiesel from a crude *Milletia pinnata* oil of Jharkhand, India as feedstock and crab shell derived catalyst. *Bioresource Technology* 2016; 214: 210-217. doi: 10.1016/j.biortech.2016.04.055
16. Boey PL, Maniam GP, Hamid SA, Ali DMH. Utilization of waste cockle shell (*Anadara granosa*) in biodiesel production from palm olein: optimization using response surface methodology. *Fuel* 2011; 90: 2353-2358. doi: 10.1016/j.fuel.2011.03.002
17. Ilgen O. Dolomite as a heterogeneous catalyst for transesterification of canola oil. *Fuel Processing Technology* 2011; 92: 452-455. doi: 10.1016/j.fuproc.2010.10.009
18. Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. *Fuel* 2010; 89: 1818-1825. doi: 10.1016/j.fuel.2009.12.023
19. Satya Lakshmi SBAV, Niju S, Khadhar Mohamed MSB, Narayanan A. Catalyst reusability and kinetic modeling of biodiesel produced from rubber seed oil. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 2020; 1-16. doi: 10.1080/15567036.2020.1785056
20. Granados ML, Alonso DM, Sádaba I, Mariscal R, Ocón P. Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: the case of triglycerides methanolysis using CaO. *Applied Catalysis B: Environmental* 2009; 89: 265-272. doi: 10.1016/j.apcatb.2009.02.014
21. Kashif I, Soliman AA, Sakr EM, Ratep A. XRD and FTIR studies the effect of heat treatment and doping the transition metal oxide on LiNbO₃ and LiNb₃O₈ nano-crystallite phases in lithium borate glass system. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2013; 113: 15-21. doi: 10.1016/j.saa.2013.04.084
22. Ergan BT, Gengec E. Dye degradation and kinetics of online electro-fenton system with thermally activated carbon fiber cathodes. *Journal of Environmental Chemical Engineering* 2020; 8: 104217. doi: 10.1016/j.jece.2020.104217
23. Wang R, Li H, Chang F, Luo J, Hanna MA et al. A facile, low-cost route for the preparation of calcined porous calcite and dolomite and their application as heterogeneous catalysts in biodiesel production. *Catalysis Science and Technology* 2013; 3: 2244-2251. doi: 10.1039/c3cy00129f