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Transesterification of Palm Oil Catalyzed by CaO/SiO$_2$ Prepared from Limestone and Rice Husk Silica

Sri Elfina*, Kamisah Delilawati Pandiangan, Novesar Jamarun, Fejri Subriadi, Hafnimardiyanti Hafnimardiyanti, and Roswita Roswita

Abstract

In this study, CaO/SiO$_2$ composites were prepared from rice husk silica (RH-SiO$_2$) and limestone from a local company. The composites with different mass ratios of CaO to SiO$_2$ (1:1, 1:2, 1:3, 1:5, and 1:10) were synthesized using the sol-gel technique and characterized using XRF, XRD, and SEM. The composites were then used as catalysts for the transesterification of palm oil, with the main purpose to investigate the effect of catalyst compositions on the percentage of conversion of the oil. The results of XRD and SEM confirm the existence of RH-SiO$_2$ as an amorphous material, and CaO as crystalline material, while the composites are a mixture of amorphous and crystalline phases. The catalysts were then used in transesterification experiments and the percentage of oil conversion was calculated. To confirm the successful conversion of palm oil into fatty acid methyl esters, the products of the reactions were analyzed using GC-MS. The experimental results demonstrated that the composites prepared exhibit catalytic activity, with the highest conversion (60%) achieved using the catalyst with the CaO to SiO$_2$ ratio of 1:3.

Keywords: Composite; catalyst; limestone; rice husk silica; palm oil; biodiesel

1. INTRODUCTION

In the realm of renewable energy, biodiesel is a non-fossil fuel that has reached a commercial level. Biodiesel has been utilized in several countries in the form of a mixture with petrochemical diesel in a certain ratio, depending on the policy implemented by the government of the countries. As an example, the blend of 20% biodiesel and 80% petrochemical diesel and known as B20, has been used in India [1]. The use of B20 has also been implemented in Indonesia since the year of 2018 and it is projected to use B30 in the year 2030 [2]. Chemically, biodiesel is a mixture of fatty acid methyl esters (FAME) produced from the reaction between vegetable oil and methanol in the presence of a catalyst.

Apart from its increasing role as a fuel, higher price than that of fossil diesel remains a fundamental challenge faced by the biodiesel industry. In this regard, previous workers have suggested that catalyst has a significant role in the reduction of production cost [3][4]. To overcome this problem, the search for low-cost catalyst that works effectively and is environmentally friendly has become a priority of many workers involved in biodiesel studies. In this respect, there has been a shift from homogeneous catalysts to heterogeneous catalysts, leading to the development of various types of solid composites which are mainly composed of metal oxide as active sites supported on porous solids.

One of the metal oxides that has been widely used as site active is CaO. In previous studies, this metal oxide has been used as a pure compound to catalyze transesterification of soybean oil [5][6], and waste cooking oil [7]. This oxide has been supported on various solids and applied for transesterification of various vegetable oils, such as CaO/SiO$_2$ prepared from eggshell and Na$_2$SiO$_3$ for transesterification of palm oil [8] and CaO/SiO$_2$ prepared from eggshell and SiO$_2$ for transesterification of palm oil [9]. In another study, Pandiangan et al. [10] also reported the use of CaO/SiO$_2$ for transesterification of rubber seed oil. The use of CaO/Al$_2$O$_3$ as a catalyst has also been reported for transesterification of *Nannochloropsis oculata* microalga's lipid [11] and biodiesel production from corn oil [12]. The CaO composites with the use of other supports have also been reported, such as NaY zeolites for transesterification of soybean oil [13] and natural zeolite for transesterification of rapeseed oil [14].

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Table 1. Chemical composition of the samples investigated

Sample	Oxide content (%)				
	SiO$_2$	CaO	Al$_2$O$_3$	P$_2$O$_5$	Others
CaO (from limestone)	1.018	**95.943**	1.205	0.969	2.865
SiO$_2$ (from rice husk)	**97.863**	0.246	0.540	0.904	0.447
CaO/SiO$_2$ 1:1	61.152	31.28	1.357	3.047	3.164
CaO/SiO$_2$ 1:2	73.377	22.929	1.714	0.920	1.060
CaO/SiO$_2$ 1:3	81.796	12.041	0.939	2.850	2.374
CaO/SiO$_2$ 1:5	82.507	11.468	0.980	3.456	1.589
CaO/SiO$_2$ 1:10	83.981	9.161	1.149	3.727	1.982

The wide utilization of CaO as an active site of heterogeneous catalyst is based on its strong alkaline strength. This particular oxide is known to have higher alkalinity than MgO and also availability since can be obtained from various sources, limestone, mollusc shells, and eggshells [15][16].

In this study, CaO/SiO$_2$ composites with different compositions were synthesized using a sol-gel technique from rice husk silica and limestone as raw materials, with the main goal to investigate the effect of composition on the catalytic activity of the composites for transesterification of palm oil. For this purpose, the catalysts with the mass ratios of CaO to SiO$_2$ of 1:1, 1:2, 1:3, 1:5, and 1:10 were prepared and then characterized using XRF, XRD, and SEM. The catalysts were then used in transesterification experiments and the percentage of oil conversion was calculated. To confirm the successful conversion of palm oil into FAME, the products of the reactions were analyzed using GC-MS.

2. MATERIALS AND METHODS

2.1. Materials and Equipments

Limestone was obtained from CV. Aikes Tanjung Mandari, a local company in the city of Halaban, West Sumatra. The chemicals of analytical grade sodium hydroxide (NaOH), nitric
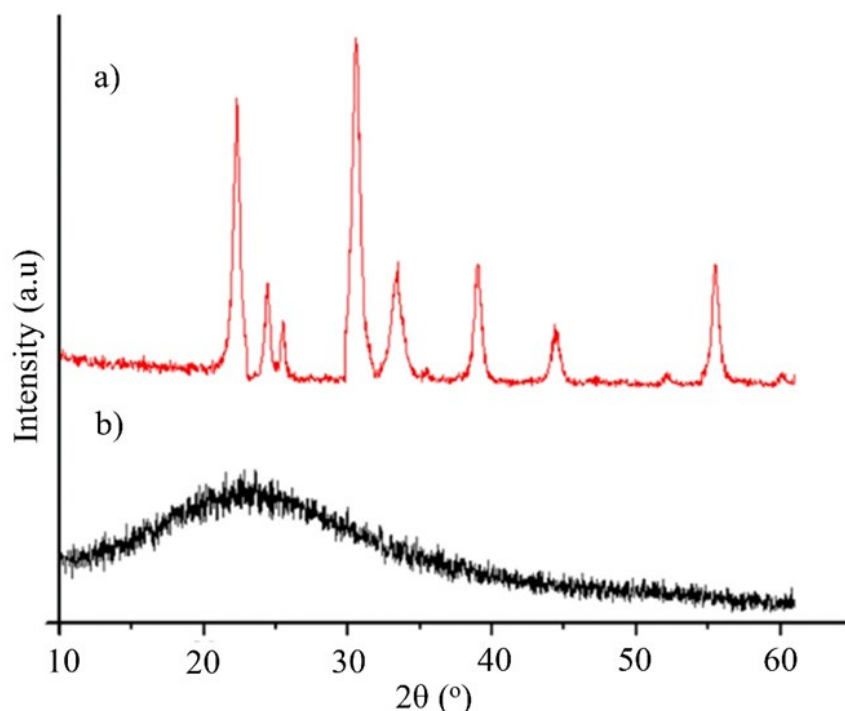
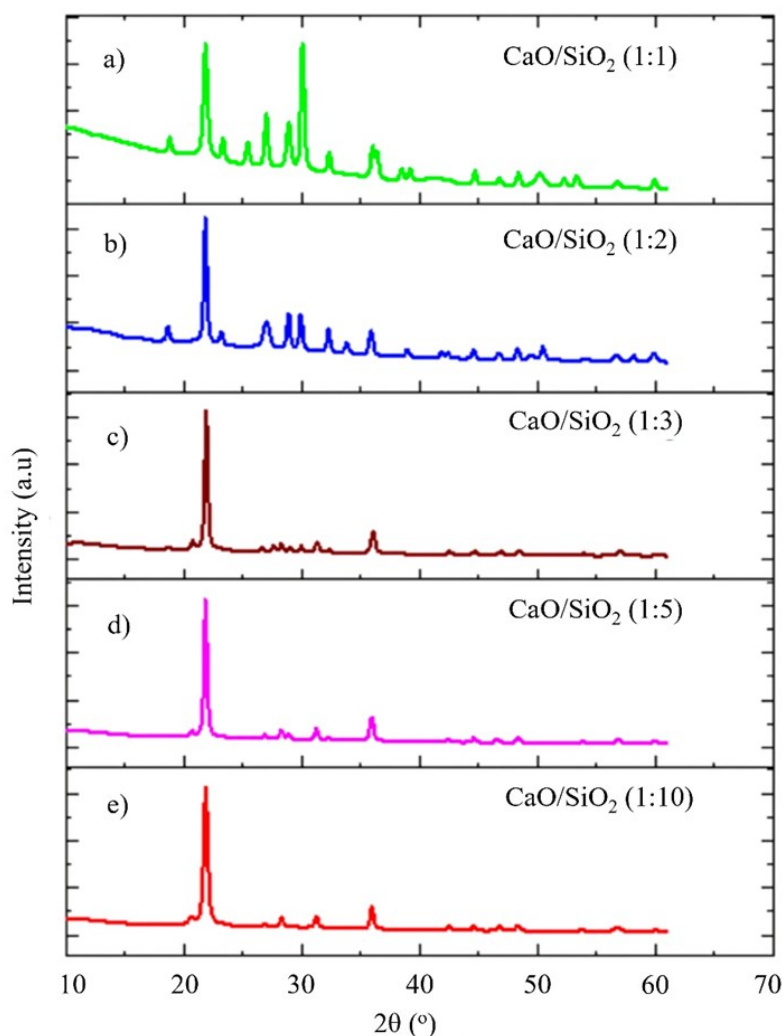**Figure 1.** X-ray diffraction pattern of CaO (a) and rice husk silica (RH-SiO$_2$) (b)

Figure 1. X-ray diffraction pattern of CaO (a) and rice husk silica (RH-SiO$_2$) (b)

acid (HNO$_3$), and methanol (CH$_3$OH) were purchased from Merck. Rice husk silica was collected from a local source in Bandar Lampung. Palm oil was collected from a local company in Pesisir Selatan, West Sumatra. Equipments used were analytical balance (AES 104 120-4), pH meter (Metrohm model), oven (Memmert UN universal 321 model), electrical heater (Stuart AM 500C), furnace (Thermolyne Muffle thermolyne 1100), hotplate stirrer, thermometer, and reflux apparatus. Instruments used were XRF (PANalytical Epsilon 3), XRD (Bruker D8 Advance), SEM/EDS (S50 type EDAX AMETEK), and GC-MS (GCMS-QP2010 SE SHIMADZU).

2.2. Methods

2.2.1. Extraction of RH-SiO$_2$

Extraction of RH-SiO$_2$ was carried out following the previously reported procedure [10]. Rice husks

were cleaned of impurities by soaking in hot water and then allowed at room temperature overnight to separate the floating and sinking husks. The sinking husks, presumably containing high silica content, were collected while the floating husks were discharged. To extract the silica, a sample of 500 g of rice husk was soaked in 500 mL of 1.5% NaOH solution. The mixture was boiled and allowed to stand for 30 min. The sample was then filtered and the filtrate containing dissolved silica was collected. To precipitate silica, a 10% HNO$_3$ solution was added gradually to the filtrate. The gel was then separated and washed with hot distilled water to remove excess acid. The silica obtained from this treatment was then dried in an oven at 100 °C for 24 h to remove the water content.

2.2.2. Preparation of CaO

To obtain CaO, limestone (CaCO$_3$) was subjected to calcination treatment at 600 °C for 5 h.

The obtained CaO solid was ground into powder and then sieved with a 200 mesh sieve.

2.2.3. Preparation of CaO/SiO$_2$ Composites

In this study, the CaO/SiO$_2$ composites with different mass ratios of 1:1, 1:2, 1:3, 1:5, and 1:10 were prepared using the sol-gel procedure. A specified mass of RH-SiO$_2$ was dissolved in NaOH 1.5% solution and a specified mass of CaO was dissolved in concentrated HNO$_3$. After both raw materials were completely dissolved, the solutions were mixed by slow addition of CaO solution into RH-SiO$_2$ solution and allowed to stand for the gel formation. The gel was oven dried at 100 °C for 8 h, and then ground into powder and sieved using a 200 mesh sieve. The composites were then characterized using XRF, XRD, and SEM.

2.2.4. Catalytic Activity Test

The activity of the catalyst samples as heterogeneous catalysts was then evaluated through the transesterification of palm oil using methanol, to convert the oil into methyl esters. Each CaO/SiO$_2$ catalyst was tested for the transesterification reaction. All experiments were run at fixed oil-to-methanol ratio of 1:8 and a catalyst load of 10% relative to the mass of the oil. The experiments were run for 6 h at 70 °C in a 500 mL round-bottom flask connected to a water condenser. After the completion of reaction time, the reaction mixture was allowed to cool and then filtered into a separatory funnel and allowed at room temperature for 24 h to allow the separation between the biodiesel and excess methanol (upper layer) and the remaining oil (bottom layer). The excess methanol was removed from the upper layer by evaporation, and the volume of biodiesel was measured to calculate the percentage of conversion of the oil, according to the equation (1) reported by Pandiangan et al. [17].

$$\% \ conversion = \frac{V_i - V_f}{V_i} \ x \ 100 \ \% \qquad (1)$$

where V_i is the initial volume of oil (mL) and V_f is the volume of unreacted oil (mL).

3. RESULTS AND DISCUSSIONS

3.1. XRF Analysis

The chemical composition of SiO$_2$, CaO, and CaO/SiO$_2$ composites was determined using the XRF technique. The main components, in the form of oxide, are shown in Table 1.

The data presented in Table 1 display that the CaO and SiO$_2$ from rice husk (RH-SiO$_2$) used in this study have a purity of 95.943 and 97.863 %,
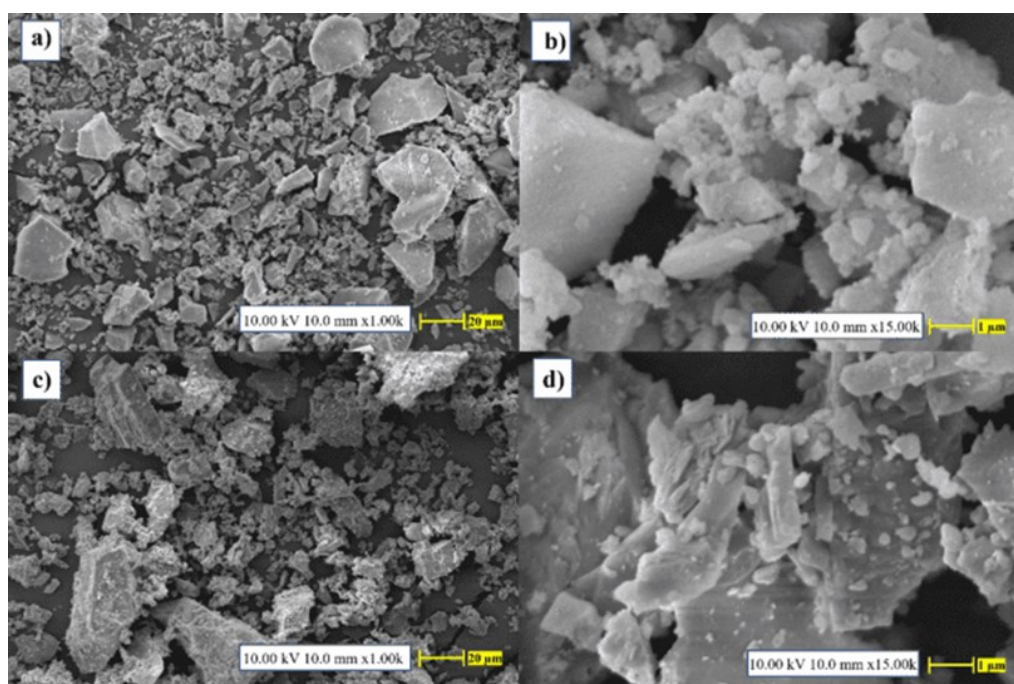

Figure 3. SEM micrographs of RH-SiO$_2$ with 1000x magnification (a), 15000x magnification (b), and micrographs of CaO with 1000x magnification (c), and 15000x magnification (d)
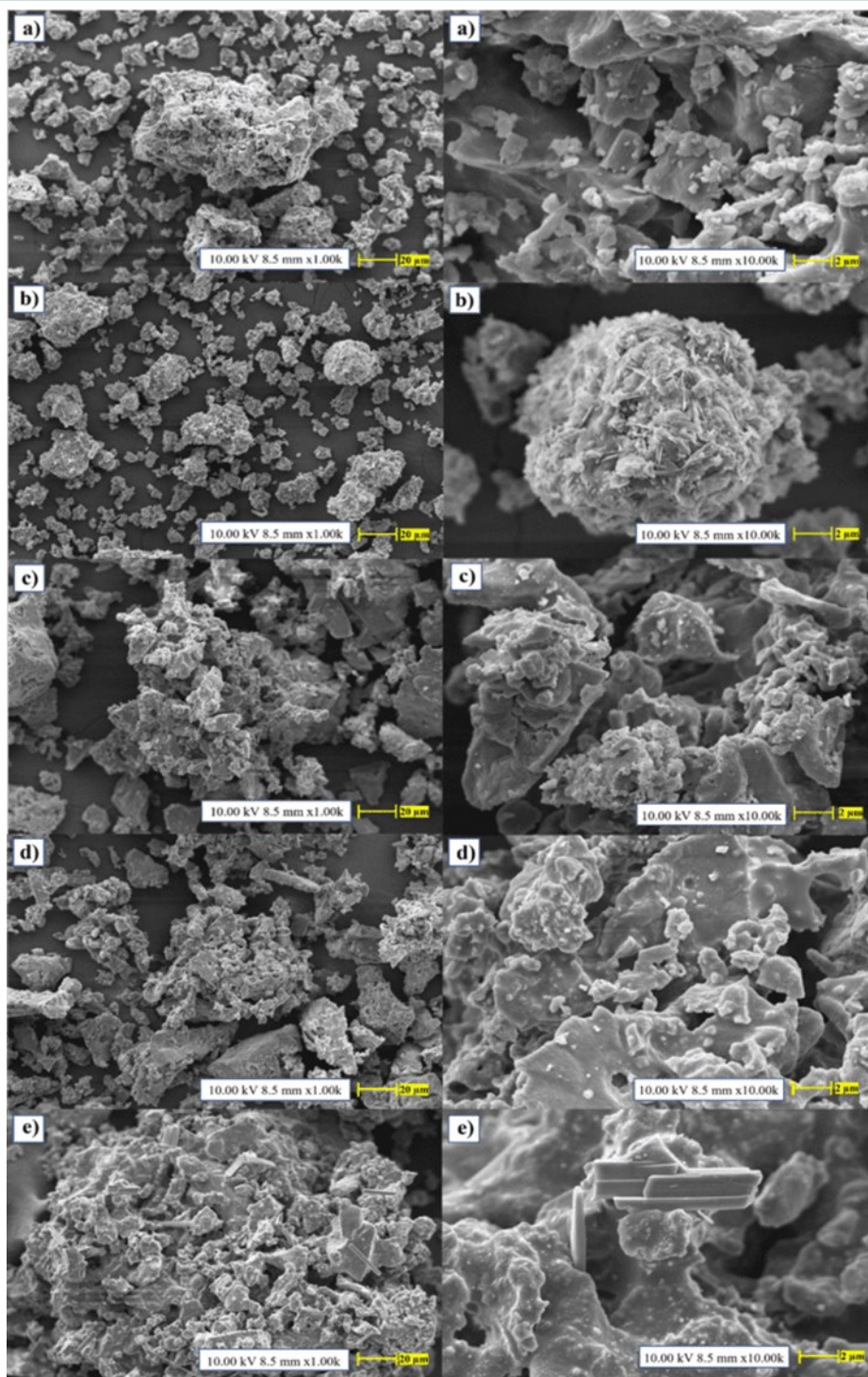
Figure 4. SEM micrographs of the composites with different compositions: (a) CaO/SiO$_2$ 1:1, (b) CaO/SiO$_2$ 1:2. (c) CaO/SiO$_2$ 1:3, (d) CaO/SiO$_2$ 1:5, and (e) CaO/SiO$_2$ 1:10

respectively, suggesting that the characteristics and the catalytic activity of the CaO/SiO$_2$ composites synthesized are practically determined by these two main chemical components, although some minor components were also detected.

3.2. XRD Characterization

To investigate the phase composing the samples, the CaO, RH-SiO$_2$, and the composites prepared were characterized using XRD technique. The XRD diffractograms of the samples are presented in Figure 1.

The XRD diffractogram of the CaO sample is characterized by the existence of sharp peaks and agrees with the pattern for CaO standard recorded in PCPDF-WIN database (ICDD 04-0777 and 82-
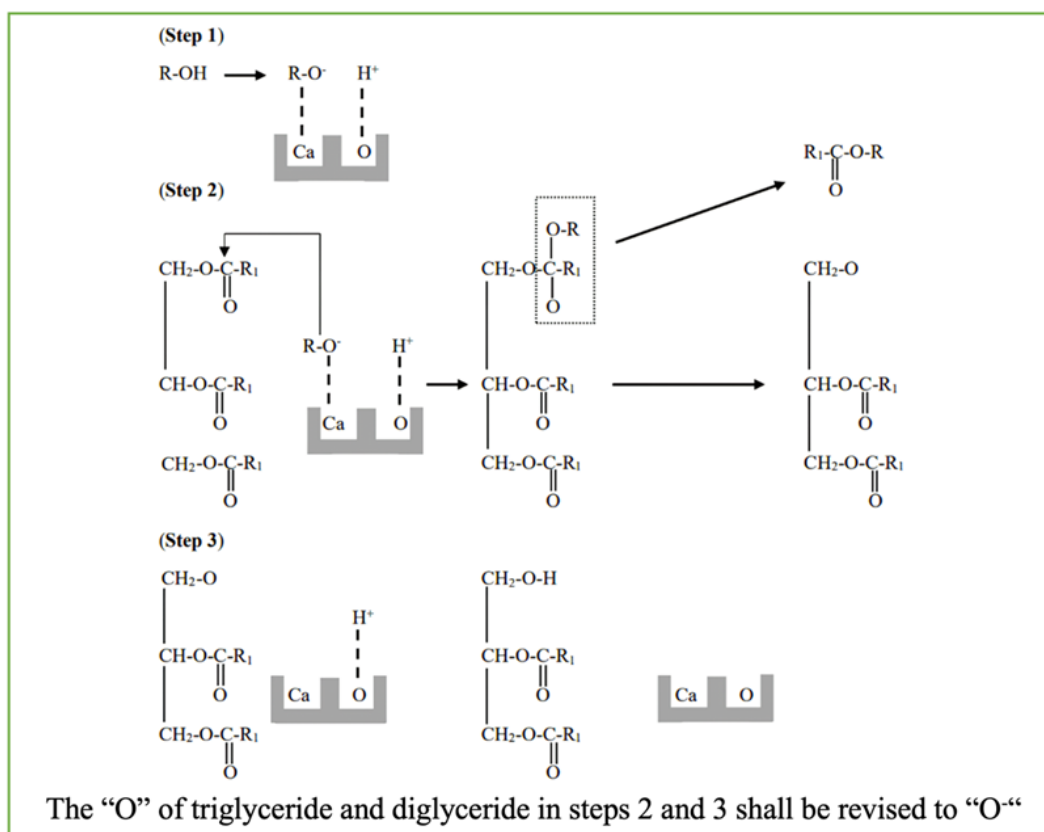
The "O" of triglyceride and diglyceride in steps 2 and 3 shall be revised to "O⁻"

Figure 5. Transesterification mechanism of vegetable oil using CaO as an active site of catalyst

1690). The XRD diffractogram of RH-SiO$_2$, which is characterized by a broad peak at $2\theta = 22.6°$, is also in agreement with the pattern for SiO$_2$ standard provided in PCPDF-WIN database (ICDD 01-0424) with diffraction peaks around $2\theta = 22–24°$.

To investigate the effect of composition on the structure of the composites, the samples were characterized using XRD, and the diffractograms of the composites are shown in Figure 2. As can be seen in Figure 2, the diffractograms of the samples are very similar and resemble the pattern observed for CaO. The only quite significant difference between the diffractograms is the relative intensity of the peaks which tends to decrease with increasing amount of silica in the composite material.

3.3. SEM Characterization

To investigate the surface morphology, which is another important characteristic of solid materials, the samples of RH-SiO$_2$, CaO, and the composites were characterized using SEM. The micrographs of the RH-SiO$_2$ and CaO obtained are shown in Figure 3. As displayed in Figure 3, the RH-SiO$_2$ is characterized by heterogeneous surface features, in terms of particle sizes and distribution of the particles on the surface. In addition, the sample is marked by the irregular shapes of the particles, justifying the existence of the sample as amorphous material, as has been demonstrated by the XRD diffractogram in Figure 1(b). The heterogeneous surface morphology is also displayed by the micrograph of CaO, however, the existence of rectangular particles can be observed, although the particles are not well separated but tend to agglomerate to form large particles.

The composites were also characterized using SEM and the micrographs obtained are compiled in Figure 4. As can be seen in Figure 4, the surface morphologies observed suggest the existence of all samples as a mixture of amorphous and crystalline materials, forming agglomerates as has also been observed by others [18]. In addition, the heterogeneity of the samples in terms of particle sizes and distribution of the particles on the surface of the samples is very evident, as displayed by the micrographs. Related to the application of the composites as catalyst, the amorphous phase, presumably the RH-SiO$_2$ is the component to play the role as the host for the reaction while the CaO
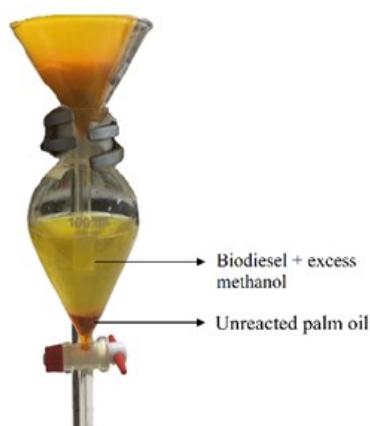
Figure 6. Typical example of transesterification product obtained in this study

as the crystalline component acted as an active site of the catalyst, as depicted in reaction mechanism in Figure 5 [19].

3.4. Catalytic Activity Test

A typical example of a transesterification reaction is shown in Figure 6. The upper layer is the biodiesel layer mixed with excess methanol and the bottom layer is unreacted oil. The volume of unreacted oil was measured to determine the percentage of conversion using the equation presented in the experimental section. The results obtained are presented in Table 2.

As can be seen in Table 2 there is no evident trend that shows the effect of composite compositions on the oil conversion achieved. However, it can be noted that the highest oil conversion (60%) was achieved with the use of the CaO/SiO_2 composite with aratio of CaO to SiO_2 of 1:1. Based on these results, it should be noted that the oil conversion achieved in this study relatively lower compared to those reported by others for the same oil [20][21]. In this respect, it should be acknowledged that more study is required to

optimize the performance of the CaO/SiO_2 composites, in recognition of the higher performance of this catalyst reported by other works [3][19], together with the existence of the limestone and rice husk as low-cost raw materials.

4. CONCLUSIONS

The experimental results obtained in this study demonstrated that the CaO/SiO_2 composites with different CaO to SiO_2 ratios prepared from limestone and rice husk silica exist as a mixture of amorphous and crystalline phases according to XRD characterization. According to SEM results, the surface morphology of the samples is characterized by heterogeneous features in terms of particle size and shape, as well as particle distribution on the surface of the samples. The transesterification experiments revealed that the highest oil conversion achieved is 60% with the use of composite with the CaO to SiO_2 ratio of 1: 3. This conversion is relatively higher than the results for the same oil with the use of different catalysts, but relatively lower compared to the results reported by others. In this respect, it should be acknowledged that more study is required to optimize the performance of the CaO/SiO_2 composites. Despite this relatively low performance, this type of composite is still a promising catalyst system since the better performance was reported by other researchers. In addition, both limestone and rice husk are abundantly available and categorized as low-cost raw materials.

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Table 2. Conversion of oil using catalyst with different compositions

No.	Catalyst composition (CaO/SiO₂ ratio)	Oil conversion (%)
1	1:1	48
2	1:2	52
3	1:3	60
4	1:5	43
5	1:10	36

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Author Contributions

For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, S. E.; K. D. P. and N. J.; Methodology, S. E. and K. D. P.; Formal Analysis, S. E.; K. D. P.; Investigation, F. S.; Resources, N. J.; F. S. and H.; Data Curation, N. J.; Writing – Original Draft Preparation, K. D. P. and S. E.; Writing – Review & Editing, K. D. P..; Visualization, F. S.; Project Administration, R.".

Conflicts of Interest

The author(s) declare no conflict of interest.

REFERENCES

[1] S. Kour and W. K. Balwan. (2021). "A Systematic Review of Biofuels: The Cleaner Energy for Cleaner Environment". *Indian Journal of Scientific Research.* **12** (1): 1– 9. 10.32606/ijsr.V12.I1.00025.

[2] I. Chandra Setiawan, Indarto, and Deendarlianto. (2021). "Quantitative analysis of automobile sector in Indonesian automotive roadmap for achieving national oil and CO2 emission reduction targets by 2030". *Energy Policy.* **150** : 1–14. 10.1016/j.enpol.2021.112135.

[3] B. Thangaraj, P. R. Solomon, B. Muniyandi, S. Ranganathan, and L. Lin. (2019). "Catalysis in biodiesel production—a review". *Clean Energy.* **3** (1): 2-23. 10.1093/ce/zky020.

[4] A. K. Endalew, Y. Kiros, and R. Zanzi. (2011). "Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO)". *Energy.* **36** (5): 2693-2700. 10.1016/j.energy.2011.02.010.

[5] C. A. Colombo, L. H. Chorfi Berton, B. G. Diaz, and R. A. Ferrari. (2017). "Macauba: a promising tropical palm for the production of vegetable oil". *Ocl.* **25** (1): 1–9. 10.1051/ocl/2017038.

[6] A. A. Ayoola, O. S. I. Fayomi, O. A. Adeeyo, J. O. Omodara, O. Adegbite, and M. Kunelbayev. (2019). "Impact assessment of biodiesel production using CaO catalyst obtained from two different sources". *Cogent Engineering.* **6** (1): 1–12. 10.1080/23311916.2019.1615198.

[7] R. Djayasinga, A. Setiawan, A. Purnomo, A. Z. Amien, and H. Hartanti. (2022). "Utilization of Breed Chicken Eggshells for Biodiesel Preparation from Waste Cooking Oil". *Journal of Multidisciplinary Applied Natural Science.* **2** (1): 41-46. 10.47352/jmans.2774-3047.90.

[8] G. Chen, R. Shan, S. Li, and J. Shi. (2015). "A biomimetic silicification approach to synthesize CaO–SiO 2 catalyst for the transesterification of palm oil into biodiesel". *Fuel.* **153** : 48-55. 10.1016/j.fuel.2015.02.109.

[9] S. N. M. Khazaai, S. Yiting, M. H. A. Rahim, M. L. Ibrahim, and G. P. Maniam. (2021). "Application of Waste Catalyst, CaO-SiO2 in the Transesterification of Palm Oil". *Malaysian Journal of Analytical Sciences.* **25** (3): 490–493.

[10] K. D. Pandiangan, W. Simanjuntak, M. Rilyanti, N. Jamarun, and S. Arief. (2017). "Influence of Kinetic Variables on Rubber Seed Oil Transesterification Using Bifunctional Catalyst CaO-MgO/SiO2". *Oriental Journal of Chemistry.* **33** (6): 2891-2898. 10.13005/ojc/330623.

[11] E. S. Umdu, M. Tuncer, and E. Seker. (2009). "Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts". *Bioresource Technology.* **100** (11): 2828-31. 10.1016/j.biortech.2008.12.027.

[12] G. Moradi, M. Mohadesi, R. Rezaei, and R. Moradi. (2015). "Biodiesel Production using CaO/γ-Al_2O_3Catalyst Synthesized by Sol-Gel Method". *The Canadian Journal of Chemical Engineering.* **93** (9): 1531-1538. 10.1002/cjce.22258.

[13] H. Wu, J. Zhang, Q. Wei, J. Zheng, and J. Zhang. (2013). "Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts". *Fuel Processing Technology.* **109** (13–18): 13-18. 10.1016/j.fuproc.2012.09.032.

[14] P. Mierczynski, L. Szkudlarek, K. Chalupka, W. Maniukiewicz, S. K. Wahono, K. Vasilev, and M. I. Szynkowska-Jozwik. (2021). "The Effect of the Activation Process and Metal Oxide Addition (CaO, MgO, SrO) on the Catalytic and Physicochemical Properties of Natural Zeolite in Transesterification Reaction". *Materials (Basel).* **14** (9). 10.3390/ma14092415.

[15] X. Liu, S. Xing, L. Yang, J. Fu, P. Lv, X. Zhang, M. Li, and Z. Wang. (2021). "Highly active and durable Ca-based solid base catalyst for biodiesel production". *Fuel.* **302** (121094): 1–11. 10.1016/j.fuel.2021.121094.

[16] N. Viriya-Empikul, P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop, and K. Faungnawakij. (2010). "Waste shells of mollusk and egg as biodiesel production catalysts". *Bioresource Technology.* **101** (10): 3765-7. 10.1016/j.biortech.2009.12.079.

[17] K. D. Pandiangan, W. Simanjuntak, S. Hadi, I. Ilim, and H. Amrulloh. (2021). "Physical characteristics and utilization of ZSM-5 prepared from rice husk silica and aluminum hydroxide as catalyst for transesterification of Ricinus communis oil". *Materials Research Express.* **8** (6): 1–12. 10.1088/2053-1591/ac0365.

[18] N. S. Zainal, Z. Mohamad, M. S. Mustapa, N. A. Badarulzaman, M. I. Masirin, and Z. A. S. A. Salim. (2018). "Study of Characteristics of Rice Husk and Silica Obtained from Rice Husk". *International Journal of Chemical Engineering and Applications.* **9** (5): 158-162. 10.18178/ijcea.2018.9.5.718.

[19] M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, and J. Hidaka. (2008). "Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production". *Fuel.* **87** (12): 2798-2806. 10.1016/j.fuel.2007.10.019.

[20] A. E. Ramírez Sanabria, L. L. López, and M. I. Orozco. (2020). "Optimización del proceso de transesterificación del aceite de palma usando la técnica basada en Ultrasonido". *Ciencia en Desarrollo.* **11** (2): 151-157. 10.19053/01217488.v11.n2.2020.11142.

[21] F. Ishola, D. Adelekan, A. Mamudu, T. Abodunrin, A. Aworinde, O. Olatunji, and S. Akinlabi. (2020). "Biodiesel production from palm olein: A sustainable bioresource for Nigeria". *Heliyon.* **6** (4): e03725. 10.1016/j.heliyon.2020.e03725.

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