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Transesterification of Palm Oil Catalyzed by CaO/SiO_2 Prepared from Limestone and Rice Husk Silica

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AUTHOR CONTIBUTIONS

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.".

CONFLICT OF INTEREST

The authors declare no conflict of interest.

Transesterification of Palm Oil Catalyzed by CaO/SiO_2 Prepared from Limestone and Rice Husk Silica

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_2SiO_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_2O_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]. 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 acid (HNO_3), and methanol (CH_3OH) 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].

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

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.

Table 1. Chemical composition of the samples investigated

Sample	Oxide content (%)				
	SiO_2	CaO	Al_2O_3	P_2O_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 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 %, 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.

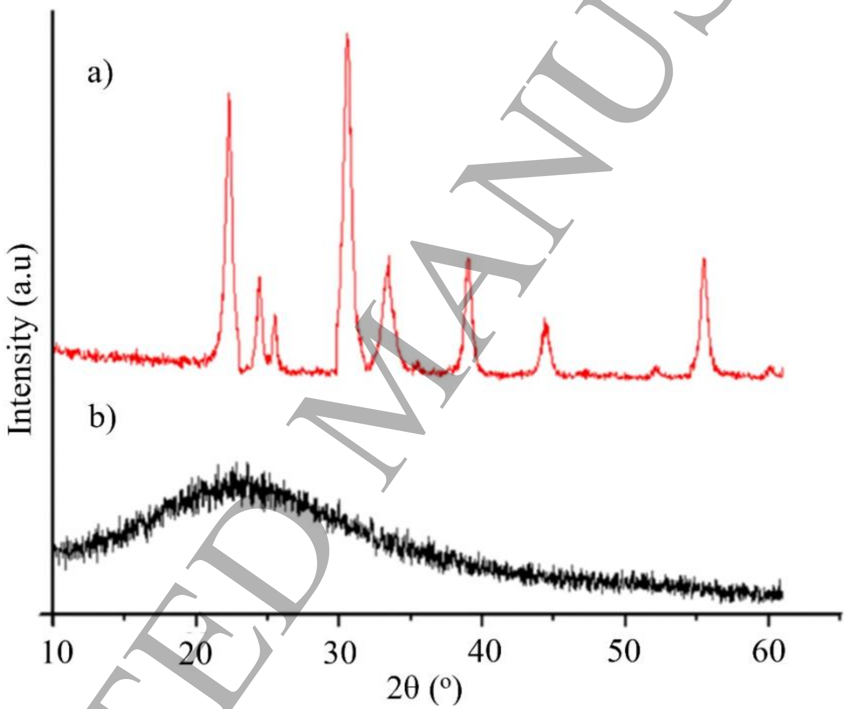

Figure 1. X-ray diffraction pattern of CaO (a) and rice husk silica (RH-SiO_2) (b).

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 82-1690). 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.

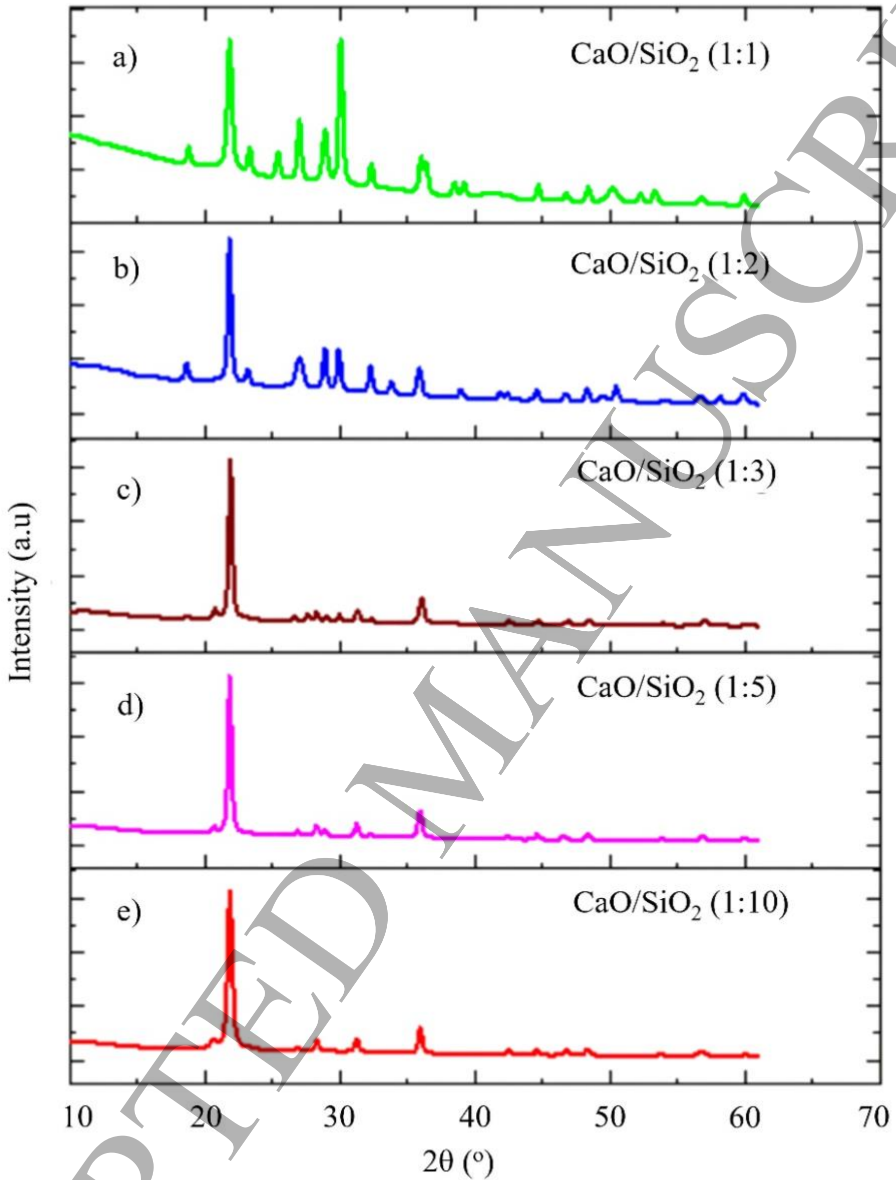

Figure 2. The X-ray diffraction patterns of composites at different compositions.

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.

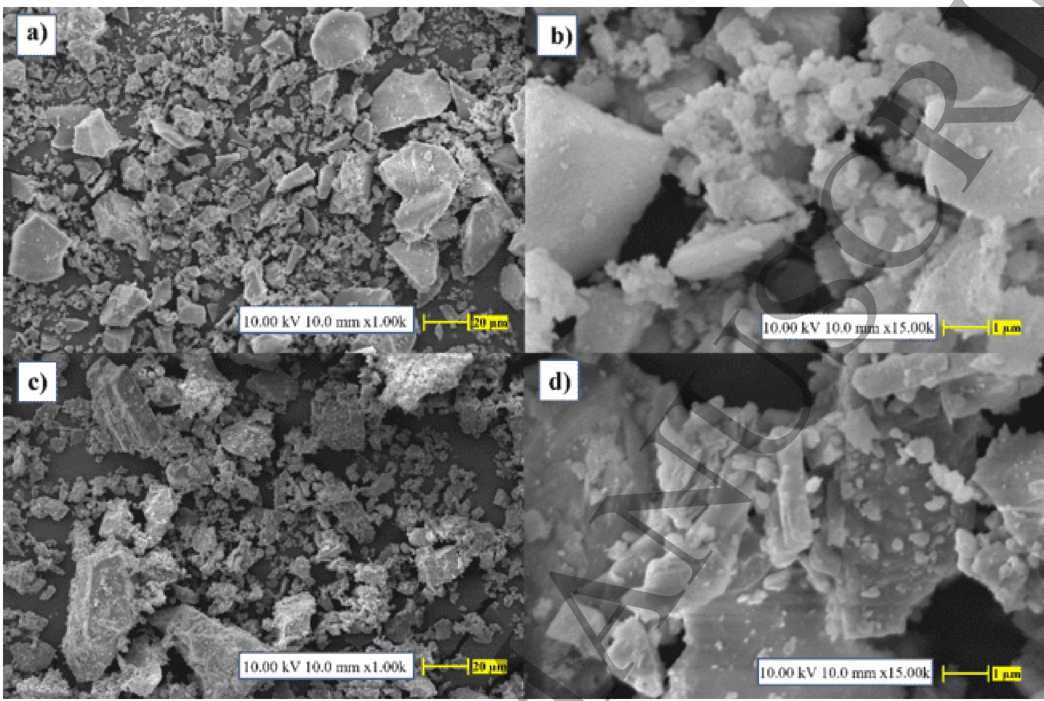

Figure 3. SEM micrographs of RH-SiO_2 with 1000x magnification (a), 15000x magnification (b), and micrographs of CaO with 1000x magnification (c), and 15000x magnification (d).

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

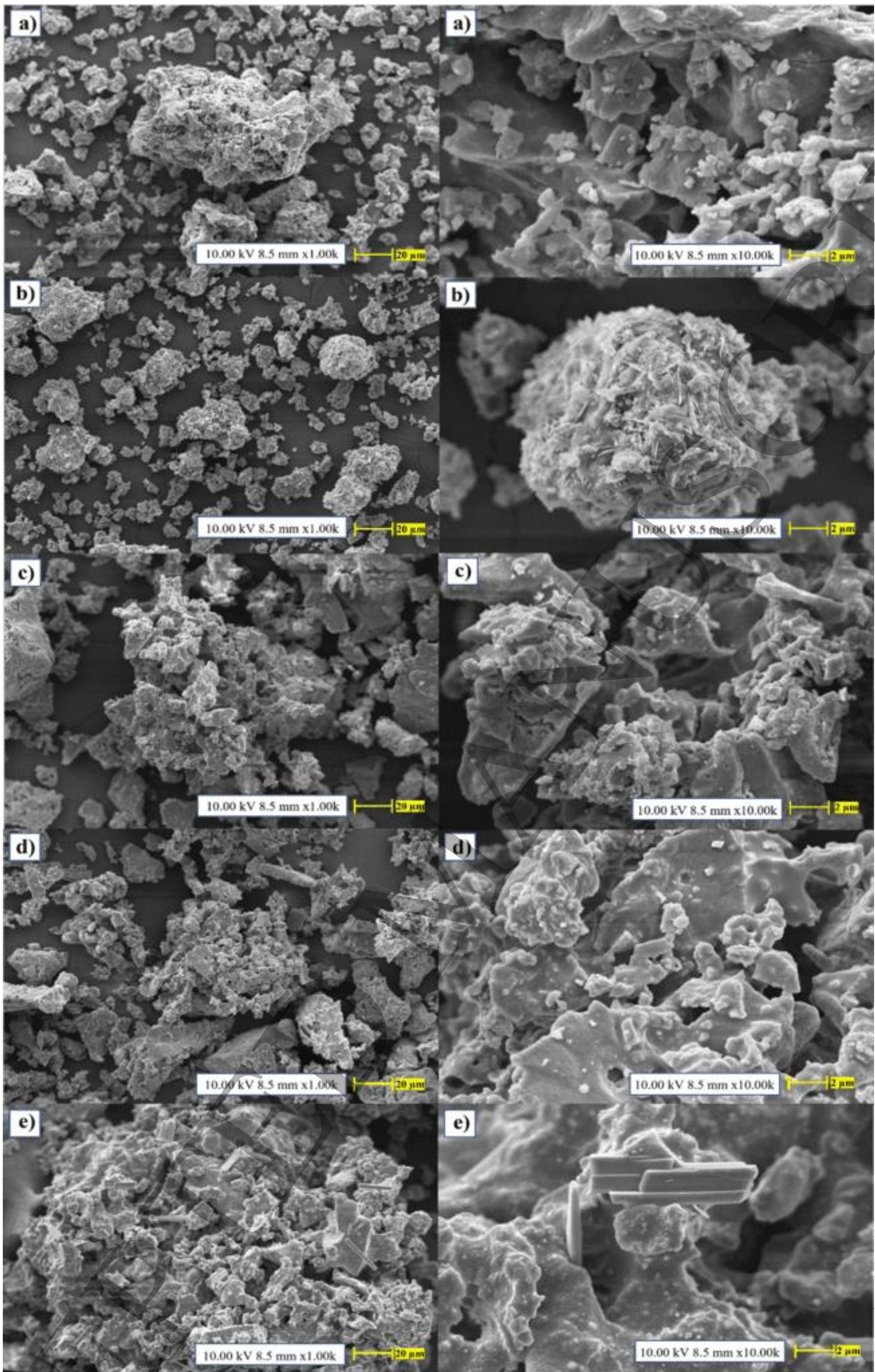

Figure 4. SEM micrographs of the composites with different compositions: (a) CaO/SiO_2 1:1, (b) CaO/SiO_2 1:2. (c) CaO/SiO_2 1:3, (d) CaO/SiO_2 1:5, and (e) CaO/SiO_2 1:10.

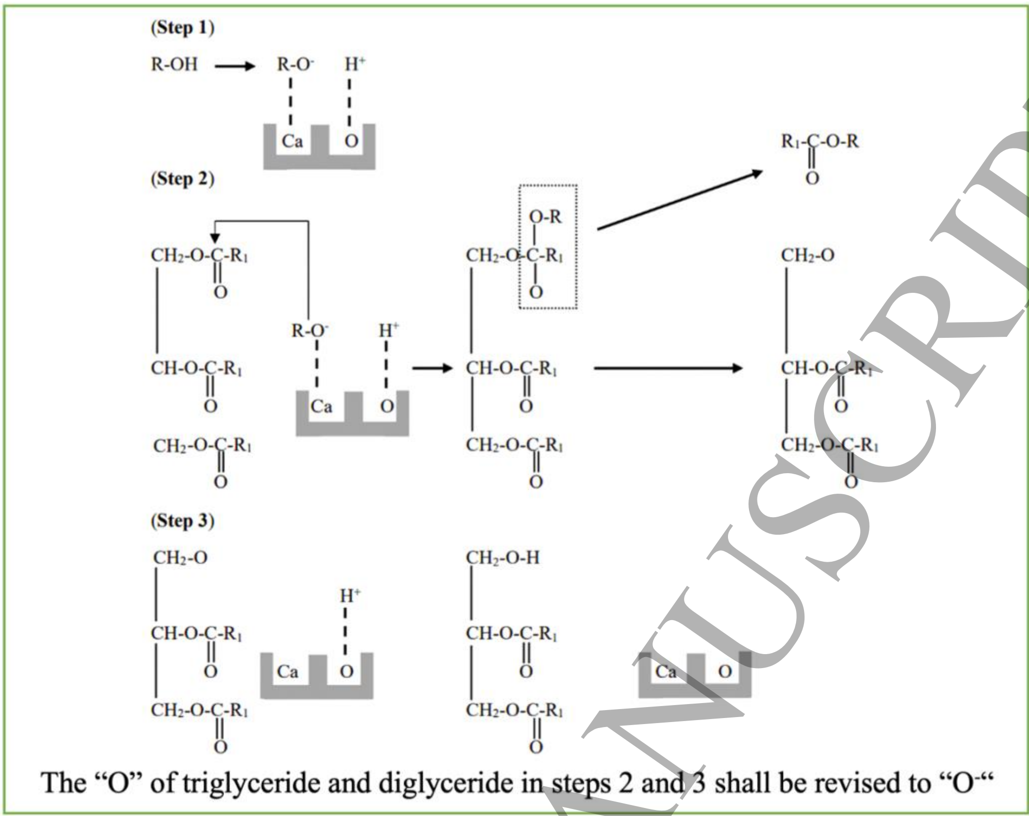

Figure 5. Transesterification mechanism of vegetable oil using CaO as an active site of catalyst.

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.

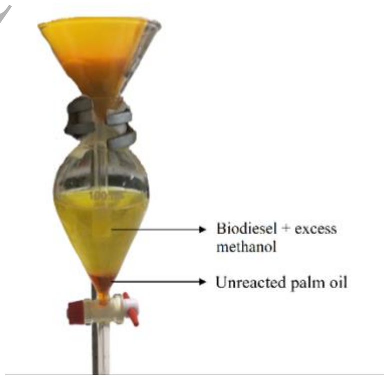

Figure 6. Typical example of transesterification product obtained in this study.

Table 2. Conversion of oil using catalyst with different compositions

No.	Catalyst composition (CaO/SiO_2 ratio)	Oil conversion (%)
1	1:1	48
2	1:2	52
3	1:3	60
4	1:5	43
5	1:10	36

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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