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**Research Article**

# SYNTHESIS OF A HETEROGENEOUS CaO-SiO2 CATALYST FROM CRAB SHELLS AND RICE HUSKS FOR OLEIC ACID CONVERSION

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## ABSTRACT

*Biodiesel is considered a renewable, sustainable, and environmentally friendly energy source that can replace fossil fuels. Biodiesel can be produced either by esterification of fatty acids or transesterification of triglycerides. In this study, crab shells were recycled as a source of CaO. CaO was combined with $SiO_2$ from rice husks to form a new heterogeneous catalyst for esterification. The catalyst was characterized using XRD, FT-IR, and SEM-EDX. Synthesized CaO and CaO-$SiO_2$ were used for esterification of oleic acid. The effects of catalyst type, temperature, reaction time, and MeOH:oleic acid molar ratio were investigated. The results revealed that the addition of $SiO_2$ could improve the reaction rate, while increasing the calcination temperature enhanced the activity of the CaO-$SiO_2$ catalyst. The reaction temperature and time affected oleic acid conversion more significantly than the MeOH:oleic acid molar ratio. The highest conversion (78.49%) was achieved at 68 °C for 7 h, with a catalyst loading of 10 wt% CaO-$SiO_2$ (900 °C) and a MeOH:oleic acid molar ratio of 10:1.*

***Keywords:*** Biodiesel; CaO-$SiO_2$; crab shell; esterification; oleic acid; rice husk

## 1. Introduction

Biodiesel has attracted considerable attention due to its sustainability, renewability, and environmental friendliness. Biodiesel can be produced from renewable sources, including animal fats (e.g., fish, chicken, and pork), edible oils (e.g., soybean, corn, canola, and palm oils), inedible oils (e.g., jatropha, neem, and rubber seed oils), and waste cooking oil (Amenaghawon et al., 2022; Kosuru et al., 2024). Biodiesel production can help reduce greenhouse gas emissions, making it more sustainable than fossil oil. Biodiesel, which mainly contains fatty acid methyl esters (FAMEs), is the product of the transesterification of triglycerides with methanol (MeOH) in the presence of catalysts. While traditional homogeneous catalysts (KOH, NaOH, $H_2SO_4$) are widely used in biodiesel production, heterogeneous catalysts have attracted much attention in recent decades (Kosuru et al., 2024;

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Melo et al., 2024). Solid catalysts in the transesterification process may include base catalysts (CaO, MgO), acid catalysts (Zeolite X, Al-MCM-41, $WO_3$-$ZrO_2$), or composite catalysts ($Fe_3O_4$/CaO, Na-$SiO_2$, CaO/$A1_2O_3$, Ni-Co/CaO, etc.) (Ajala et al., 2022; Kosuru et al., 2024). These heterogeneous catalysts become more attractive since they can overcome the disadvantages of homogeneous catalysts, including difficulties with catalyst separation, corrosiveness, saponification, and disposal (Chen et al., 2015; Park et al., 2008). CaO from seafood shells, such as clam, crab, and snail shells, is a potential source of transesterification catalysts since it is a strong base catalyst (Correia et al., 2014). Both CaO and $Ca(OH)_2$ compounds could provide catalytic sites for transesterification, with CaO exhibiting higher activity (Maafa et al., 2024).

The predominant method of biodiesel production is transesterification, where triglycerides are reacted with methanol or ethanol in the presence of a catalyst to yield FAMEs and glycerol (Palitsakun et al., 2021). However, free fatty acids (FFAs) can inhibit the reaction between triglycerides and methanol due to their ability to react with basic catalysts (i.e., NaOH or CaO), leading to saponification (Kosuru et al., 2024). To address this issue, FFAs can be removed by either neutralization or esterification, with acid-catalyzed esterification preferred because it produces valuable FAMEs. In general, the FFA content of feedstocks should be maintained below 1% (Lucena et al., 2008; Mathew et al., 2021). The esterification pretreatment must be considered mandatory for materials with high FFA contents, such as waste cooking oil and jatropha oil (Lucena et al., 2008; Palitsakun et al., 2021). FFAs were removed through esterification with methanol in the presence of a homogeneous catalyst (sulfuric acid) (Hanh et al., 2009; Lucena et al., 2008; Palitsakun et al., 2021). Recently, Moradi et al. (2021) applied an electrolysis technique for the esterification of oleic acid using both NaOH and $H_2SO_4$ catalysts. Besides homogeneous catalysts, heterogeneous catalysts were also investigated for the esterification process. Park et al. (2008) carried out the esterification of oleic acid in a batch reactor with various solid catalysts ($Al_2O_3$, $SiO_2$, H zeolite, $ZrO_2$, $WO_3/ZrO_2$, etc.), in which $WO_3/ZrO_2$ was chosen as the best catalyst for a continuous production test. Moreover, Son et al. (2011) used a cation exchange resin (Amberlyst-15) as the catalyst for oleic acid esterification in a fixed-bed reactor. This setup allowed the process to work continuously at higher temperatures (100–120 °C), thereby keeping the water produced in the vapor phase and preventing catalyst deactivation. In summary, improving the esterification step using a heterogeneous catalyst compatible with the transesterification process appears promising.

In this study, a simple impregnation method was used to combine CaO from crab shells and $SiO_2$ from rice husks to form a heterogeneous catalyst for the esterification reaction. The esterification between oleic acid and methanol was carried out in a reflux reactor. The effects of calcination temperature and the reaction conditions on oleic acid conversion were also clarified.

## 2. Experimental methods

### *2.1. Catalyst preparation*

Crab shells (CS) from Ca Mau, Vietnam, were collected from seafood restaurants in Ho Chi Minh City. Rice husks were supplied by local rice mills in Dong Nai, Vietnam. Oleic

acid and ethanol (Xilong Scientific, China), methanol (HPLC grade, Fisher), and double-distilled water were used without further pretreatment.

The CS was carefully washed with tap water and boiled water to remove organic matter and other contaminants. The clean CS was dried in sunlight and then in an oven at 105 °C for 6 h. After that, the CS was ground with a mortar and pestle into pieces approximately 1 mm in size. CaO was synthesized by calcining CS at 900 °C for 4 h in air. The CaO powder was finely ground and sieved to 0.125 mm particles. Meanwhile, the rice husk (RH) was dried at 105 °C and then treated in air at 500 °C for 4 h to obtain $SiO_2$. The rice husk ash (RHA) was powdered to 0.125 mm particles. All fine calcined powders were stored in a desiccator for further synthesis. Calcination temperatures of CS and RH were chosen based on thermogravimetric analysis (TGA) results (data not shown).

CaO-$SiO_2$ was prepared by a simple wet impregnation method reported by Amenaghawon et al. (2022). A 24 g mixture of CaO and $SiO_2$ (mass ratio of 5:1) was added to 100 mL of double-distilled water and stirred thoroughly for 6 h at 80 °C using a magnetic stirrer hotplate. The mixture was cooled to room temperature; then the solid phase was separated using a Büchner funnel. The resulting solid mixture was dried at 105 °C for 14 h and then calcined at 500, 750, and 900 °C for 4 h in air to obtain catalysts designated CS-RH-500, CS-RH-750, and CS-RH-900, respectively. The obtained CaO-$SiO_2$ catalyst was ground and sieved to obtain particles in the 45–120 mesh size range.

### *2.2. Catalyst characterization*

To investigate the physical and chemical properties of the synthesized catalysts, the solid samples were characterized by several techniques. The surface morphology and elemental composition were analyzed using scanning electron microscopy and energy-dispersive X-ray analysis (SEM-EDX) with a JSM-IT200 IntouchScope™ SEM-EDX (JEOL – Japan). Powder X-ray diffraction (XRD) was performed on an Empyrean (Malvern Panalytical) X-ray diffractometer using Cu $K_\alpha$ radiation. Fourier-transform infrared spectroscopy (FT-IR) was performed on a Nicolet 6700 FT-IR Spectrometer from Thermo Fisher Scientific.

### *2.3. Oleic acid esterification*

The esterification experiment was conducted in a reflux reactor. The reactants and catalyst were added to a round-bottom flask fitted with a condenser and placed on a magnetic stirrer hotplate. The mass of oleic acid was fixed while the amounts of MeOH and catalyst were varied according to the experimental conditions.

After each experiment, the mixture in the reactor was cooled and allowed to settle. Then, the sample was collected and titrated with a 0.1 M NaOH standard solution using a few drops of phenolphthalein in ethanol as the indicator. The titration was repeated three to four times to obtain the average oleic acid concentration. The conversion of oleic acid was calculated using Equation (1):

$$H\% = \frac{m_o - m_i}{\mathrm{m_o}} \times 100\ \% \quad (1)$$

where $m_o$ is the initial mass of oleic acid, and $m_i$ is the mass of oleic acid in the product.

## 3. Results and discussion

### *3.1. Catalyst characterization*

SEM-EDX results of $SiO_2$ (RHA), CaO (CS), and CaO-$SiO_2$ (CS-RH) are summarized in Figure 1 and Table 1. The CaO particles formed agglomerates with uneven shapes. Comparison of ***Figure 1***A and 1B shows that the CS-RH catalyst had a more interconnected structure than CaO (CS). In addition, some fibers from RHA were also observed.

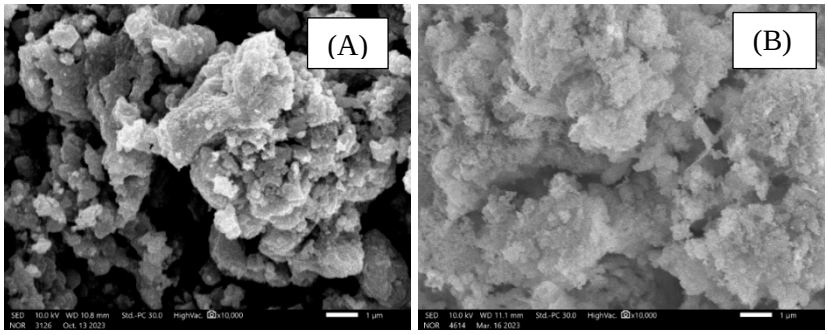



***Figure 1.*** *SEM Images of (A) CaO From Crab Shells and (B) CS-RH CaO-$SiO_2$*

Table 1 shows that the CaO from crab shells contained three main elements: Ca, O, and Mg. Moreover, Si and O were found as the major elements (>97 atomic %) in the RHA sample, whereas Mg, Ca, K, and Al were detected as minor elements. Hence, combining RHA and CS resulted in the presence of Ca, Si, and Mg atoms in the CS-RH sample. Interestingly, the appearance of P was only observed in CS-RH samples, which might reflect signal enhancement. Previous research (Amenaghawon et al., 2022) also revealed the absence of P in CS-derived CaO, whereas others observed the presence of P (34%) (Cardoso et al., 2020; Ismail et al., 2022) in SEM-EDX results. This difference might reflect the low P content of crab shell samples, which was difficult to detect using SEM-EDX. The mass ratio of CS/RHA was set at 5:1, leading to the Ca/Si atom ratio being around 5.36 (ideally excluding moisture and impurities). However, Table 1 gave a Ca/Si atom ratio of 7.74, which is higher than expected.

***Table 1.*** *Elemental composition of catalysts from SEM-EDX results*

| **$SiO_2$ (RHA)** | | | **CaO (CS)** | | | **CaO-$SiO_2$ CS-RH** | | |
|---|---|---|---|---|---|---|---|---|
| Atom | Mass (%) | Atomic (%) | Atom | Mass (%) | Atomic (%) | Atom | Mass (%) | Atomic (%) |
| O | 43.60 | 58.08 | O | 45.68 | 66.83 | O | 41.46 | 62.06 |
| Mg | 0.40 | 0.35 | Mg | 3.79 | 3.65 | Mg | 3.38 | 3.33 |
| Si | 51.81 | 39.32 | Si | - | - | Si | 4.32 | 3.68 |
| P | - | - | P | - | - | P | 3.12 | 2.41 |
| Ca | 1.59 | 0.84 | Ca | 50.53 | 29.52 | Ca | 47.72 | 28.51 |

The XRD results are shown in Figure 2A. $SiO_2$-RH showed a broad peak at around 23, which was attributed to amorphous silica (Tran et al., 2016). The presence of CaO and $Ca(OH)_2$ in calcined CaO (CS) was observed in the XRD pattern based on JCPDS 01-082-1690 and JCPDS 01-078-0315, respectively. $Ca(OH)_2$ peaks had higher intensity than CaO peaks, suggesting that CaO interacted strongly with moisture to form $Ca(OH)_2$. Moreover, calcium hydroxyapatite (HAp) - $Ca_5(PO_4)_3(OH)_2$ was also observed in all XRD samples, which indicated the existence of phosphorus atoms in the crab shell. Raya et al. (2015) found that the

calcination of crab shells at temperatures above 700 °C resulted in the formation of HAp. The HAp signal of CS-based CaO had a lower intensity than that of the CS-RH samples. Since hydroxyapatite was also observed in CS-based CaO, it implied that phosphorus existed in crab shell samples. Meanwhile, MgO was also observed in all CS-RH samples as a contaminant originating from CS (see Table 1). In addition, $Ca_2SiO_4$ appeared as a new component in the CS-RH-900 catalyst, as can be seen clearly in Figure 2B. The solid-state reaction between CaO and $SiO_2$ started at 800 °C and occurred significantly at 1000 °C (Maafa et al., 2024; Phuttawong et al., 2015). In summary, adding $SiO_2$ to CaO reduced the intensity of CaO and $Ca(OH)_2$ peaks and produced calcium silicate as a new component.

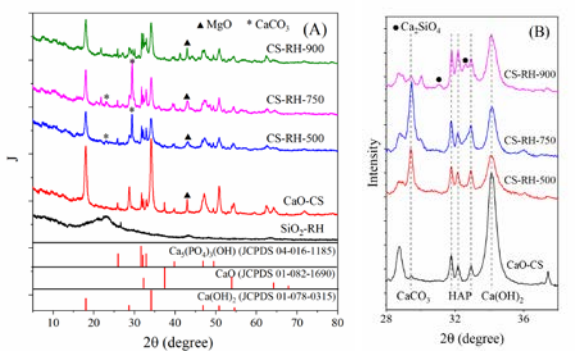



***Figure 2.*** *XRD patterns of CS-RH catalyst at different calcination temperatures: (A) full 2θ range, (B) narrow 2θ range*

The catalysts were further analyzed with FR-IR to identify surface functional groups, and the results are shown in ***Figure 3***. The FR-IR spectra of all CS-RH samples showed OH (3600 $cm^{-1}$), CO (1460 cm-1), OCO (870 $cm^{-1}$), and PO (1040 $cm^{-1}$) vibrational bands associated with adsorbed water, carbonate, and phosphate, respectively (Maafa et al., 2024; Suwannasingha et al., 2022). Moreover, CS-RH-900 showed a new signal in the 970–850 $cm^{-1}$ range, associated with the CaOSi bond (Phuttawong et al., 2015), which is in agreement with the preceding discussion of the XRD results.

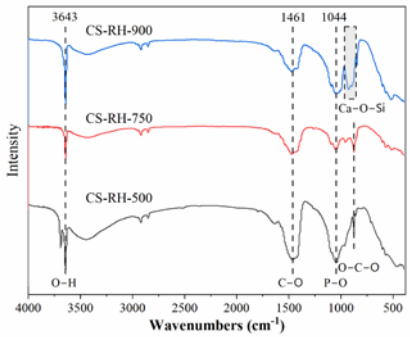



***Figure 3.*** *FT-IR spectra of CS-RH catalysts at different calcination temperatures*

### *3.2. Esterification experiments*

*3.2.1. Effect of catalyst type*

CaO and CaO-$SiO_2$ can be used as catalysts for esterification and transesterification in biodiesel production. ***Figure 4***A demonstrates the effects of different catalysts on oleic acid

conversion, clarifying the roles of $SiO_2$ and calcination temperature. In general, adding $SiO_2$ helped improve the conversion of oleic acid. Only CS-RH-500 showed a lower conversion than CS-based CaO, suggesting that a calcination temperature of 500 °C was insufficient to activate the catalyst. Moreover, CS-RH-500 and CS-RH-700 produced lower conversion than CS-RH-900, which can be explained by the presence of $CaCO_3$ in these catalysts. Based on these results, CS-RH-900 was identified as the best catalyst for esterification and chosen for further experiments. A higher calcination temperature produced more active sites ($Ca(OH)_2$ and $Ca_2SiO_4$), resulting in higher catalyst activity. Temperature-programmed desorption ($CO_2$-TPD) from previous studies (B. Zhao et al., 2019; Y. Zhao et al., 2017) indicated that $SiO_2$ had weak basic sites, while combining CaO and $SiO_2$ generated both weak and strong basic sites. The strength and number of basic sites depended mostly on the CaO percentage in the catalyst. Furthermore, the addition of $SiO_2$ helped increase the specific surface area of CaO (Costa et al., 2020). In summary, CS-RH-900 showed the highest oleic acid conversion due to its greater number of active sites and better surface properties.

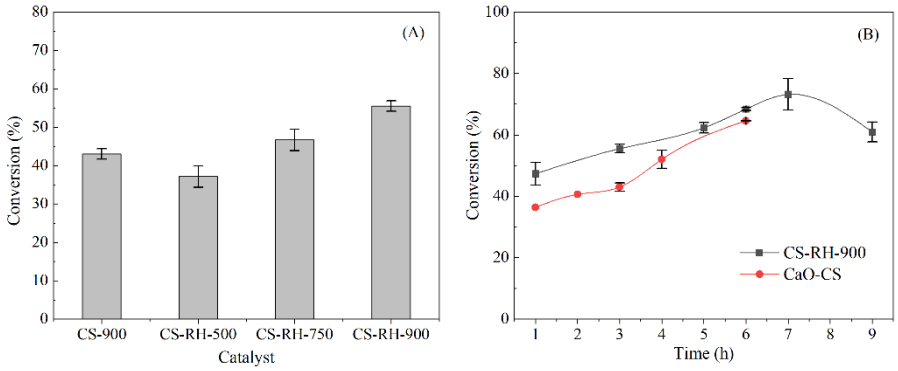



***Figure 4.*** *Effect of catalyst type (A) and reaction time (B) (Temperature: 68 °C, time: 3 h, catalyst loading: 10 wt%, molar ratio of MeOH/oleic acid: 10:1)*

*3.2.2. Effect of reaction time*

***Figure 4***B demonstrates the effect of reaction time on oleic acid esterification over CaO (CS) and CaO-$SiO_2$ (CS-RH-900) catalysts. ***Figure 4***B reveals that CaO-$SiO_2$ had greater efficiency in oleic acid conversion than CaO, suggesting that the addition of $SiO_2$ to CaO could enhance the reaction rate significantly. The oleic acid conversion changed only slightly with a further increase in reaction time from 7 to 9 h because the reaction had reached equilibrium. Conversion might be limited by the water produced in Reaction (2).

$$RCOOH + MeOH \overset{Catalyst}{\longleftrightarrow} RCOOMe + H_2O \quad (2)$$

Water in the products inhibited Reaction (2) since it could react rapidly with the base catalyst, leading to the formation of soaps (Kosuru et al., 2024; Lucena et al., 2008). In batch reactors without water removal, fatty acid conversion reached only approximately 80% (Kong et al., 2019; Park et al., 2008). Lucena et al. (2008) showed that water elimination in the product was necessary to improve the conversion of oleic acid, as they used a zeolite column at the top of the reactor to adsorb water vapor. The oleic acid conversion increased from 88.2% to 99.7% when the water adsorption column was used. Meanwhile, Singh et al. (2013) also found that

simultaneous water removal increased the esterification of oleic acid significantly. In the present study, the simple experimental setup limited the esterification reaction.

*3.2.3. Effect of temperature*

Reaction temperature significantly affected oleic acid conversion, as shown in ***Figure 5***A. Because a reflux batch reactor was used, the reaction temperature was limited by the boiling point of methanol (65 °C). Hence, the reaction temperature varied from room temperature to 68 °C (the maximum temperature that the reactant mixture could achieve). Consistent with previous research, increasing the reaction temperature improved the reaction rate significantly (Hanh et al., 2009; Park et al., 2008). Increasing the reaction temperature above the boiling point of water (100 °C) could lead to a higher conversion of FFA (Lucena et al., 2008; Son et al., 2011) because it facilitates removal of the water produced.

*3.2.4. Effect of MeOH/oleic acid molar ratio*

In the esterification reaction between oleic acid and methanol, the stoichiometric molar ratio is 1:1. In this study, we varied the MeOH/oleic acid molar ratio from 3 to 13 to examine the effect of excess methanol on this reaction (see ***Figure 5***B). The molar ratio of MeOH-to-oleic acid did not affect the conversion significantly. However, excess methanol led to a decrease in oleic acid conversion. This can be explained by using excess methanol, which might reduce the contact surface between the catalyst and oleic acid. However, the molar ratio of MeOH-to-oleic acid of 3:1 was not recommended due to limitations in agitation and temperature control. Based on this result, the molar ratio of MeOH-to-oleic acid of 10 was chosen. Lucena et al. (2008) also observed the highest conversion at an alcohol-to-oleic acid molar ratio of 9:1.

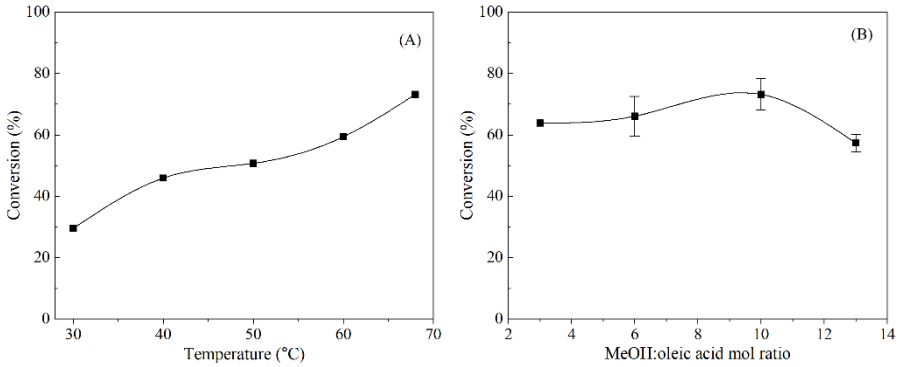



***Figure 5.*** *Effect of reaction temperature (A) and MeOH/oleic acid molar ratio (B) (CS-RH-900, time: 7 h, catalyst loading: 10 wt%)*

## 4. Conclusions

Oleic acid esterification was conducted in the reflux system with CaO and CaO-$SiO_2$ catalysts. In summary, the highest conversion of oleic acid was achieved at approximately 78% using the CaO-$SiO_2$ (CS-RH-900) catalyst at 68 °C for 7 h and a MeOH-to-oleic acid molar ratio of 10. The combination of CaO and $SiO_2$ increased catalyst activity since it could generate strong basic sites and a higher specific surface area. The impregnated CaO-$SiO_2$ calcined at 900 °C (CS-RH-900) showed more promise for esterification than the others. The

CS-RH-900 catalyst, with the presence of $Ca_2SiO_4$ and the absence of $CaCO_3$, provided more active sites for the esterification reaction. In addition, changes in the reaction time and temperature affected the conversion more significantly than changes in the molar ratio of MeOH-to-oleic acid. Although the conversion of oleic acid was not as high as expected, the heterogeneous catalyst CS-RH-900 appears to be a promising catalyst for esterification and transesterification in biodiesel production.


- ***Conflicts of Interest:*** *Authors have no conflict of interest to declare.*
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## REFERENCES


Ajala, E. O., Ehinmowo, A. B., Ajala, M. A., Ohiro, O. A., Aderibigbe, F. A., & Ajao, A. O. (2022). Optimisation of $CaO$-$Al_2O_3$-$SiO_2$-$CaSO_4$-based catalysts performance for methanolysis of waste lard for biodiesel production using response surface methodology and meta-heuristic algorithms. *Fuel Processing Technology*, *226*, 107066. https://doi.org/10.1016/j.fuproc.2021.107066

Amenaghawon, A. N., Obahiagbon, K., Isesele, V., & Usman, F. (2022). Optimized biodiesel production from waste cooking oil using a functionalized bio-based heterogeneous catalyst. *Cleaner Engineering and Technology*, *8*, 100501. https://doi.org/10.1016/j.clet.2022.100501

Cardoso, C. C., Cavalcanti, A. S., Silva, R. O., Alves Junior, S., Sousa, F. P. de, Pasa, V. M. D., Arias, S., & Pacheco, J. G. A. (2020). Residue-Based CaO Heterogeneous Catalysts from Crab and Mollusk Shells for FAME Production Via Transesterification. *Journal of the Brazilian Chemical Society*, *31*, 756–767. https://doi.org/10.21577/0103-5053.20190240

Chen, G., Shan, R., Li, S., & Shi, J. (2015). A biomimetic silicification approach to synthesize CaO–$SiO_2$ catalyst for the transesterification of palm oil into biodiesel. *Fuel*, *153*, 48–55. https://doi.org/10.1016/j.fuel.2015.02.109

Correia, L. M., Saboya, R. M. A., de Sousa Campelo, N., Cecilia, J. A., Rodríguez-Castellón, E., Cavalcante, C. L., & Vieira, R. S. (2014). Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sunflower oil. *Bioresource Technology*, *151*, 207–213. https://doi.org/10.1016/j.biortech.2013.10.046

Costa, J. de R. M., Santos, R. C. R., Coutinho, L. P., Silva, O. R., Barros, H. O., Freire, V. N., & Valentini, A. (2020). $CO_2$ role on the glycerol conversion over catalyst containing $CaO$-$SiO_2$ doped with Ag and Pt. *Catalysis Today*, *344*, 199–211. https://doi.org/10.1016/j.cattod.2019.02.009

Hanh, H. D., Dong, N. T., Okitsu, K., Nishimura, R., & Maeda, Y. (2009). Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition. *Renewable Energy*, *34*(3), 780–783. https://doi.org/10.1016/j.renene.2008.04.001

Ismail, R., Cionita, T., Shing, W. L., Fitriyana, D. F., Siregar, J. P., Bayuseno, A. P., Nugraha, F. W., Muhamadin, R. C., Junid, R., & Endot, N. A. (2022). Synthesis and Characterization of Calcium Carbonate Obtained from Green Mussel and Crab Shells as a Biomaterials Candidate. *Materials*, *15*(16), Article 16. https://doi.org/10.3390/ma15165712

Kong, P. S., Pérès, Y., Wan Daud, W. M. A., Cognet, P., & Aroua, M. K. (2019). Esterification of Glycerol With Oleic Acid Over Hydrophobic Zirconia-Silica Acid Catalyst and Commercial Acid Catalyst: Optimization and Influence of Catalyst Acidity. *Frontiers in Chemistry*, *7*, 205. https://doi.org/10.3389/fchem.2019.00205

Kosuru, S. M. Y., Delhiwala, Y., Koorla, P. B., & Mekala, M. (2024). A review on the biodiesel production: Selection of catalyst, Pre-treatment, Post treatment methods. *Green Technologies and Sustainability*, *2*(1), 100061. https://doi.org/10.1016/j.grets.2023.100061

Lucena, I. L., Silva, G. F., & Fernandes, F. A. N. (2008). Biodiesel Production by Esterification of Oleic Acid with Methanol Using a Water Adsorption Apparatus. *Industrial & Engineering Chemistry Research*, *47*(18), 6885–6889. https://doi.org/10.1021/ie800547h

Maafa, I. M., A Sayed Alahl, Amr., Abd El-Magied, M. O., Cui, X., & Dhmees, A. S. (2024). Eco-friendly self-terminated process for preparation of CaO catalyst based on chitosan production wastes for biodiesel production. *Journal of Materials Research and Technology*, *30*, 1217–1227. https://doi.org/10.1016/j.jmrt.2024.03.091

Mathew, G. M., Raina, D., Narisetty, V., Kumar, V., Saran, S., Pugazhendi, A., Sindhu, R., Pandey, A., & Binod, P. (2021). Recent advances in biodiesel production: Challenges and solutions. *Science of The Total Environment*, *794*, 148751. https://doi.org/10.1016/j.scitotenv.2021.148751

Melo, V. M. e, Ferreira, G. F., & Fregolente, L. V. (2024). Sustainable catalysts for biodiesel production: The potential of CaO supported on sugarcane bagasse biochar. *Renewable and Sustainable Energy Reviews*, *189*, 114042. https://doi.org/10.1016/j.rser.2023.114042

Moradi, P., Saidi, M., & Najafabadi, A. T. (2021). Biodiesel production via esterification of oleic acid as a representative of free fatty acid using electrolysis technique as a novel approach: Non-catalytic and catalytic conversion. *Process Safety and Environmental Protection*, *147*, 684–692. https://doi.org/10.1016/j.psep.2020.12.032

Palitsakun, S., Koonkuer, K., Topool, B., Seubsai, A., & Sudsakorn, K. (2021). Transesterification of Jatropha oil to biodiesel using SrO catalysts modified with CaO from waste eggshell. *Catalysis Communications*, *149*, 106233. https://doi.org/10.1016/j.catcom.2020.106233

Park, Y.-M., Lee, D.-W., Kim, D.-K., Lee, J.-S., & Lee, K.-Y. (2008). The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catalysis Today*, *131*(1), 238–243. https://doi.org/10.1016/j.cattod.2007.10.052

Phuttawong, R., Chantaramee, N., Pookmanee, P., & Puntharod, R. (2015). Synthesis and Characterization of Calcium Silicate from Rice Husk Ash and Shell of Snail *Pomacea canaliculata* by Solid State Reaction. *Advanced Materials Research*, *1103*, 1–7. https://doi.org/10.4028/www.scientific.net/AMR.1103.1

Raya, I., Mayasari, E., Yahya, A., Syahrul, M., & Latunra, A. I. (2015). Shynthesis and Characterizations of Calcium Hydroxyapatite Derived from Crabs Shells (Portunus pelagicus) and Its Potency in Safeguard against to Dental Demineralizations. *International Journal of Biomaterials*, *2015*, 469176. https://doi.org/10.1155/2015/469176

Singh, D., Patidar, P., Ganesh, A., & Mahajani, S. (2013). Esterification of Oleic Acid with Glycerol in the Presence of Supported Zinc Oxide as Catalyst. *Industrial & Engineering Chemistry Research*, *52*(42), 14776–14786. https://doi.org/10.1021/ie401636v

Son, S. M., Kimura, H., & Kusakabe, K. (2011). Esterification of oleic acid in a three-phase, fixed-bed reactor packed with a cation exchange resin catalyst. *Bioresource Technology*, *102*(2), 2130–2132. https://doi.org/10.1016/j.biortech.2010.08.089

Suwannasingha, N., Kantavong, A., Tunkijjanukij, S., Aenglong, C., Liu, H.-B., & Klaypradit, W. (2022). Effect of calcination temperature on structure and characteristics of calcium oxide powder derived from marine shell waste. *Journal of Saudi Chemical Society*, *26*(2), 101441. https://doi.org/10.1016/j.jscs.2022.101441

Tran, N. T. T., Uemura, Y., Chowdhury, S., & Ramli, A. (2016). Vapor-phase hydrodeoxygenation of guaiacol on Al-MCM-41 supported Ni and Co catalysts. *Applied Catalysis A: General*, *512*, 93–100. https://doi.org/10.1016/j.apcata.2015.12.021

Zhao, B., Wang, J., Zhu, D., Song, G., Yang, H., Chen, L., Sun, L., Yang, S., Guan, H., & Xie, X. (2019). Adsorption Characteristics of Gas Molecules ($H_2O$, $CO_2$, CO, $CH_4$, and $H_2$) on CaO-Based Catalysts during Biomass Thermal Conversion with in Situ $CO_2$ Capture. *Catalysts*, *9*(9), Article 9. https://doi.org/10.3390/catal9090757

Zhao, Y., Zhang, X., Song, X., & Liu, F. (2017). Highly Active and Recyclable Mesoporous Molecular Sieves CaO(SrO,BaO)/SBA-15 with Base Sites as Heterogeneous Catalysts for Methanolysis of Polycarbonate. *Catalysis Letters*, *147*(12), 2940-2949. https://doi.org/10.1007/s10562-017-2193-3

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# TỔNG HỢP XÚC TÁC DỊ THỂ CaO-$SiO_2$ TỪ VỎ CUA VÀ TRẤU ĐỂ ỨNG DỤNG CHO CHUYỂN HÓA OLEIC ACID

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## TÓM TẮT

*Biodiesel được xem là một nguồn năng lượng tái tạo, bền vững và thân thiện với môi trường để có thể thay thế các nguồn nhiên liệu hóa thạch. Biodiesel có thể được sản xuất bằng cách ester hóa các acid béo tự do hoặc chuyển hóa ester các triglyceride. Trong nghiên cứu này, vỏ cua được tận dụng như là một nguồn cung cấp CaO. CaO này được kết hợp với $SiO_2$ từ trấu để tạo nên một xúc tác mới cho phản ứng ester hóa. Các đặc tính của xúc tác được nghiên cứu bằng các phương pháp XRD, FT-IR và SEM-EDX. Các xúc tác CaO và CaO-$SiO_2$ đã được tổng hợp và ứng dụng cho phản ứng ester hóa oleic acid. Sự ảnh hưởng của xúc tác, nhiệt độ, thời gian phản ứng và tỉ lệ mol MeOH:oleic acid đã được khảo sát. Kết quả cho thấy việc thêm $SiO_2$ đã làm tăng tốc độ phản ứng, trong khi tăng nhiệt độ nung đã làm tăng hiệu quả của xúc tác CaO-$SiO_2$. Nhiệt độ và thời gian phản ứng ảnh hưởng đến hiệu suất chuyển hóa oleic acid nhiều hơn là tỉ lệ mol MeOH:oleic acid. Hiệu suất chuyển hóa cao nhất là 78.49% đạt được tại các điều kiện phản ứng 68°C, 7h, 10% xúc tác CaO-$SiO_2$ (900℃) và tỉ lệ MeOH:oleic acid là 10:1.*

***Từ khóa*:** biodiesel; CaO-$SiO_2$; ester hóa; oleic acid; trấu; vỏ cua