



Contents list available at IJRED website

International Journal of Renewable Energy Development

Journal homepage: <https://ijred.undip.ac.id>



Research Article

Synthesis and Characterization of Physically Mixed V_2O_5 .CaO as Bifunctional Catalyst for Methyl Ester Production from Waste Cooking Oil

M. Mulyatun^{a,b}, I. Istadi^{a*}, W. Widayat^a

^aDepartment of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang, Central Java, 50275, Indonesia

^bDepartment of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Walisongo Semarang, Central Java, 50185, Indonesia

Abstract. Synthesis of the solid bifunctional vanadium-calcium mixed oxides catalyst was accomplished by application of a simple physical mixing approach. In this work, we compared the catalytic activity of CaO and 2% V_2O_5 .CaO catalyst. Various characterization methods, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), BET surface area, and temperature-programmed desorption (TPD) of CO_2 and NH_3 , were involved in studying the newly synthesized catalysts. The presence of CaO, $CaCO_3$, and $Ca(OH)_2$ compounds in the synthesized catalyst were detected by XRD and FTIR analysis. The existence of 2% V_2O_5 on the CaO catalyst surface was demonstrated by XRF analysis. From TPD- NH_3 , TPD- CO_2 , and BET surface area analysis, it was known that the 2% V_2O_5 -CaO catalyst had a higher total number of acid-base sites and surface area than the CaO catalyst. In the fatty acid methyl esters (FAME) production from waste cooking oil (WCO) with higher free fatty acid (FFA), CaO could only catalyze the transesterification reaction. In contrast, 2% V_2O_5 -CaO could successfully catalyze both the esterification of FFA and the transesterification of triglyceride (TG) simultaneously in a one-step reaction process. Thus, these results prove that 2% V_2O_5 .CaO can act as a bifunctional catalyst in the production of biodiesel from WCO. Moreover, the synthesized 2% V_2O_5 .CaO catalyst could achieve a maximum FAME yield of 51.30% under mild reaction conditions, including a 20:1 methanol to oil molar ratio, 60°C reaction temperature, 1 wt% of catalyst loading, and 3 hours of reaction time.

Keywords: physically mixed; CaO; V_2O_5 ; bifunctional catalyst; waste cooking oil; biodiesel



@ The author(s). Published by CBIORE. This is an open access article under the CC BY-SA license (<http://creativecommons.org/licenses/by-sa/4.0/>).

Received: 20th Dec 2022; Revised: 28th Jan 2023; Accepted: 5th Feb 2023; Available online: 14th Feb 2023

1. Introduction

Waste cooking oil or WCO could serve as one of the potential feedstocks for biodiesel production due to its low price, abundant availability, and reducing pollutants in soil and water. Both the public sector and the business sector have recently shown interest in manufacturing biodiesel using oil extracted from WCO. Due to its limited solubility in water, WCO poses a significant disposal challenge because it pollutes land and water (Shatesh Kumar *et al.*, 2020). It has been suggested that using WCO as a feedstock for biodiesel production could be a sustainable solution to the waste management issue (Rezania *et al.*, 2019). When the WCO is utilized as a feedstock, biodiesel production costs can be reduced by 70 to 95%. Although WCO has some advantages in producing biodiesel, WCO also has some disadvantages, including significant levels of water and free fatty acids (FFA) (Roy *et al.*, 2020). The high FFA content of WCO in conventional biodiesel production using a solid base catalyst causes saponification, resulting in a very viscous, emulsified, and foamy soap by product, decreasing biodiesel yield, catalyst deactivation, and purification difficulties. Meanwhile, using solid acid catalysts in biodiesel production requires excess alcohol and the reaction rate was slow (Faruque *et al.*, 2020).

Therefore, it is a challenge to find a new heterogeneous solid catalytic system that is simple to operate and can conduct moderate esterification and transesterification with low soap formation. This new system allows optimal utilization of the high FFA content WCO as a raw material for biodiesel production. The system is a bifunctional catalyst. The fact that bifunctional solid catalysts can convert FFA and triglycerides into FAME in one reaction step is a great way to cut down on the cost of biodiesel production (Asikin-Mijan *et al.*, 2015). This integrated solid catalyst system provides a bifunctional acid-base system supporting WCO-based biodiesel production. In this catalyst, the acid sites are involved in the esterification reaction of FFA with methanol and the conjugated base sites are responsible for activating the transesterification of triglyceride simultaneously (Shobhana-Gnanaserkhar *et al.*, 2020).

CaO base catalyst was one of the catalysts that is widely used in the development of bifunctional catalysts. Some of the advantages of the CaO catalyst include having high catalytic activity, strong base characteristics, low cost, being non-corrosive, ecologically friendly, and being affordable (Buasri *et al.*, 2012; Li *et al.*, 2012; Piker *et al.*, 2016). Despite its many advantages, CaO can only enable the transesterification of low FFA (<2%) raw materials, resulting in low catalytic activity and reaction rate or even inactivity (Krishnamurthy *et al.*, 2020). An

* Corresponding author
Email: istadi@che.undip.ac.id (I. Istadi)

alternative to increasing the catalytic activity of CaO in the production of WCO-based biodiesel is to add promoter metal oxides containing both Lewis and/or Brønsted acid sites.

Several studies on CaO-based bifunctional catalysts, such as $\text{Fe}_2\text{O}_5/\text{CaO}$, $\text{CaO-La}_2\text{O}_3$, $\text{W}_{0.6}\text{-Mo}_{0.4}/\text{CaO}$, and CaO/SnO_2 , have been found to actively convert FFA and triglycerides into FAME in one reaction step (Rahman *et al.*, 2019). The high tolerance of FFAs and water in vegetable oil that bifunctional catalysts have is the reason behind their ability, as stated by Ezzah-Mahmudah *et al.* (2016). Furthermore, the $\text{Fe}_2\text{O}_5/\text{CaO}$ catalyst successfully supported in producing biodiesel with high FFA feedstock in one reaction step without inducing saponification or emulsification. The incorporation of the CaO base catalyst on metal oxide La_2O_3 caused the appearance of an acid side on the CaO base catalyst. It causes an increase in the catalytic activity of the $\text{CaO-La}_2\text{O}_3$ catalyst in biodiesel production from low-quality oil (Lee *et al.*, 2015).

One of the potential metal oxides to develop CaO-based bifunctional catalysts is V_2O_5 . Metal oxides, such as V_2O_5 have Lewis acid sites as well as Brønsted acid sites (Kung, 1989). The addition of an acid metal oxide, like V_2O_5 , which contains both Brønsted and Lewis acid sites, is very advantageous because it increases the strength of the acidity compared to only adding an acid metal oxide containing a Lewis acid site (Yadav & Nair, 1999). A bifunctional catalyst with high acid-base strength improves catalytic activity in the production of WCO-based biodiesel. One principal factor in the catalytic activity and selectivity of bifunctional acid-base catalysts in the production of biodiesel from feedstocks containing high FFA is the strength of the acid and base sites of the catalyst (Jeon *et al.*, 2019). In addition, the V_2O_5 metal oxide has also been used in the synthesis of a silica-supported vanadium pentoxide-based catalyst ($\text{V}_2\text{O}_5/\text{RHA}$) showing Brønsted and Lewis acid sites for producing biodiesel from low quality raw materials like used cooking oil and chicken fat (Almeida *et al.*, 2016).

This research aimed to improve the efficiency of producing biodiesel from WCO by synthesizing the bifunctional catalyst $2\%\text{V}_2\text{O}_5.\text{CaO}$ via the physical mixing method. There has been no substantial research done in the biodiesel industry that explores the synthesis and characterization of a physically mixed $2\%\text{V}_2\text{O}_5.\text{CaO}$ catalyst yet. The designed $2\%\text{V}_2\text{O}_5.\text{CaO}$ catalyst is an acid-base bifunctional catalyst that is expected to support simultaneously esterifying FFA and transesterifying Triglycerides in the high-FFA waste cooking oil as a bifunctional catalyst, and this hypothesis has been proven. Therefore, the synthesized $\text{V}_2\text{O}_5.\text{CaO}$ catalyst's physico-chemical properties and catalytic activity were studied.

2. Material and Methods

2.1 Materials

The $2\%\text{V}_2\text{O}_5.\text{CaO}$ catalyst was prepared from precursors of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$) Merck, 99%), sodium carbonate (Na_2CO_3 , Merck, 99%), ammonium metavanadate (NH_4VO_3 , Fluka, >99%), n-Hexane (98%), sodium hydroxide (NaOH , 99%), while the analytical grade methanol (CH_3OH , 99.9%) were purchased from Merck. Methyl heptadecanoate as internal standard for GC-MS were obtained from Fluka (Switzerland).

WCO was collected from restaurants in Semarang city area of Indonesia. Additional physico-chemical analyses of the WCO were then carried out, i.e. acid value, FFA concentration, and molecular weight based on ASTM (American Society for Testing and Materials) standard as summarized in Table 1.

Table 1

Waste Cooking Oil (WCO) physico-chemical properties

Properties	Analysis	Standard method
Acid value (mg KOH.g ⁻¹)	25.907	ASTM (D464)
FFA content (%)	12.953	ASTM (D974(00))
Molecular weight (g.mol ⁻¹)	898.9	ASTM (D974(00))

2.2 Catalyst Preparation

The CaO metal oxide was prepared by co-precipitation method using $\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$ precursor. An amount of $\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$ was dissolved in deionized water. The resulted solution was adjusted to be alkaline (pH = 10) by using the dropwise addition of Na_2CO_3 and NaOH to $\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$ at room temperature until reached constant pH of 10. After that, the solid-gel mixture was stirred constantly for 24 hours at a temperature of 60°C. After centrifugation, washing with deionized water, and drying at 100°C, the white solid was obtained (Lee *et al.*, 2015). The CaO metal oxide was produced after calcining the resulted white solid in air at 900 °C for 6 hours. The purpose of the calcination stage was to produce metal oxides from insoluble precursors including metal carbonates, nitrates, oxalates, and hydroxide. High-temperature calcination decomposed loaded $\text{Ca}(\text{NO}_3)_2$ to CaO (Xie & Zhao, 2013). In order to synthesis a $2\%\text{V}_2\text{O}_5.\text{CaO}$ by physically mixing process, the powdered NH_4VO_3 (which is a precursor of V_2O_5) and CaO catalyst (prepared by co-precipitation) were mixed physically and ground at a mortar (Ngaosuwan *et al.*, 2021). The resulted mixed solid was then dried at 600°C for 4 hours.

2.3 Catalyst Characterizations

X-ray fluorescence (XRF) (Philips Xpert MPD) was utilized in order to determine elements composition. The structure of the synthesized heterogeneous solid catalyst was examined using X-ray diffraction (XRD). Powder X-ray diffractometer (Shimadzu model XRD 6000) with specifications: Cu-K α radiation (27.7 kW and 30 mA), 1.54 Å wavelength (λ), 2° min⁻¹ screening speed with a 0.04° step spanning the 2 range of 10–80° was used to analyze the samples. FT-IR spectra with attenuated total reflectance at room temperature between 400–4000 cm⁻¹ were utilized to investigate surface functional groups of catalysts. Moreover, by multi-point nitrogen adsorption-desorption isotherms (at 77 K) over Quantachrome Nova Instruments was used to determine the surface area, pore volume, and pore size distribution based on the Brunauer-Emmet-Teller (BET) theory. Temperature Programmed Desorption (TPD) CO_2 and NH_3 were then utilized to analyze the basicity and acidity strength, respectively, by utilizing a Thermo Finnigan TPD/R/O 1100 series apparatus equipped with a thermal conductivity detector (TCD). Pretreatment of sample consisted of heating at 350 °C for 1 hour under N_2 gas flow. After 30 minutes of NH_3 absorption, elimination of excess NH_3 gas was carried out with He gas pretreatment. Meanwhile, TPD- CO_2 was used to determine the basicity of the sample by employing CO_2 as the probe gas. Both NH_3 and CO_2 chemisorption were performed at 30 mL.min⁻¹ for 30 minutes. He gas of 30 mL.min⁻¹ for 30 minutes flowed in the system to flush the excess CO_2 and NH_3 in the system. The desorption of NH_3 and CO_2 happened at 50 to 900°C with a 10°C.min⁻¹ flowrate using He as a carrier gas. Thermal Conductivity Detector (TCD) was utilized to measure the amount of desorbed NH_3 and CO_2 .

2.4 The catalytic activity of V_2O_5 .CaO in esterification and transesterification simultaneously

Performance of the designed physically mixed 2% V_2O_5 .CaO catalyst was measured by its ability to produce biodiesel. The 2% V_2O_5 .CaO catalyst was used to support a simultaneous one-step esterification and transesterification reaction in a batch reactor according to Widayat *et al.* (2020). The biodiesel was produced in a batch catalytic reactor of round bottom flask with a capacity of 250 mL and a water-cooled reflux condenser. The reaction mixture contained 20 grams of waste cooking oil with methanol (a ratio of molar methanol to oil of 20:1) and 1 wt% of a catalyst (wt% catalyst based on the total weight of oil). The batch reactor was carried out completed with a close reflux condenser system that was heated to 60°C using a steady magnetic stirring at a speed of 750 rpm for 3 hours. After the reaction, the catalyst was recovered by centrifuging the reaction product at 4500 rpm for 15 minutes and it was washed with n-hexane. The catalyst was calcined at 550°C for 5 hours before it was loaded into the reactor.

The obtained mixture after the reaction was rich in FAME and still contained by products; hence separation process was carried out to separate glycerol, soap, excess methanol, and other undesirable products before vacuum evaporation to yield the final FAME product and biodiesel (Widiarti *et al.*, 2021). The resulting biodiesel was heated for 15–30 minutes at a temperature of 100 °C with a stirring speed of 150 rpm. It is required to dry biodiesel in order to get rid of any remaining water, which encourages the growth of biological organisms and raises the acidity index of the biodiesel that is produced as a result of this process (Ali *et al.*, 2020).

2.5 FAME Yield Analysis

To identify the composition of the Biodiesel product, the Gas Chromatography-Mass Spectrometry (GCMS) of QP 2010S SHIMADZU equipped with DB-1 column was used to analyze the FAME composition. Finally, the Eq. (1) was used to calculate the yield of the biodiesel according to standard method (EN 14103) (Li *et al.*, 2013):

$$\text{FAME Yield (\%)} = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{M} \times 100\% \quad (1)$$

where, $\sum A$ represents the total peak area of the methyl ester (C_{14} – C_{18}), A_{IS} represents the peak area of the internal standard, C_{IS} represents the internal standard concentration ($\text{mg} \cdot \text{mL}^{-1}$), V_{IS} standards represent the internal standard volume (mL), and, the mass of the sample (mg) are represented by M .

AOCS was used to quantify free fatty acids in the reaction mixture (Das *et al.*, 2017). FFA titrimetric measurement in samples and end product determined reaction conversion. The FFA conversion is the ratio of feedstock acid value change before and after reaction to initial acid value. The Eq. (2) was used to calculate the FFA conversion with AV_f and AV_p representing the WCO acid value and the biodiesel product, respectively.

$$\text{FFA conversion (\%)} = \frac{AV_f - AV_p}{AV_f} \times 100\% \quad (2)$$

3. Results and Discussion

3.1 Catalyst Characterization

The XRF analysis was used to determine the composition of the metal oxide present in the produced catalyst, as presented in Table 2. The existence of 2% V_2O_5 on the CaO catalyst surface was demonstrated by the detection of V_2O_5 in a 2% V_2O_5 .CaO catalyst, which was synthesized by a simple physical mixing method at a weight percentage of around 1.99% by weight.

Table 2

Compound composition of CaO and 2% V_2O_5 .CaO catalysts

Catalysts	CaO (wt.%)	V_2O_5 (wt.%)
CaO	99.98	-
2% V_2O_5 -CaO	98.01	1.99

The XRD analysis determines the type and crystal structure of catalysts (see Figure 1). The CaO diffractogram exhibits 2 θ peaks at 28.70°, 29.4°, 31.50°, 35.99°, 37.37°, 39.42°, 43.19°, 47.54°, 48.53°, 50.82°, 53.92°, 57.43°, 60.70°, 62.70° and 64.69°, that indicate the diffraction line of CaO (Ezzah-Mahmudah *et al.*, 2016; Istadi *et al.*, 2015). Both CaO and 2% V_2O_5 .CaO catalysts resulting diffraction lines at $2\theta = 18.01$ and 34.16 indicating the presence of a certain amount of $\text{Ca}(\text{OH})_2$ (JCPDS No. 00-084-1267) (Chen *et al.*, 2016). This result is consistent with the findings of Wang *et al.* (2018), who discovered a small amount of $\text{Ca}(\text{OH})_2$ in the Ca-B catalyst diffraction pattern at $2\theta = 18.2^\circ$ and 34.2° , due to absorption of water by the CaO catalyst (Wang *et al.*, 2018). Calcined CaO at 900°C also produced low intensity peaks at $2\theta = 29.01^\circ$ (JCPDS No. 00-183-1762), corresponded to CaCO_3 (Widiarti *et al.*, 2021). CaO is an alkaline crystal, and because it is exposed to carbon dioxide at ambient temperature, its stability is limited. Calcium carbonate will be formed as a result of the reaction between calcium oxide and carbon dioxide (Hadiyanto *et al.* 2016; Zul *et al.*, 2021). The diffraction intensity of the 2% V_2O_5 .CaO catalyst at $2\theta = 28.70^\circ$ was lower than the diffraction intensity of the CaO catalyst. It caused by partial substitution of Ca^{2+} ions by the impurities (V^{5+} ions) in the parent lattice (Borah *et al.*, 2019). This fact is also in accordance with research of Ngaosuwan *et al.* (2021), which stated that the incorporation of La_2O_3 into CaO with the physical mixing method also reduced the intensity of the diffraction pattern of CaO. Mulyatun and Prasetyoko (2011) stated that the V_2O_5 catalyst with an orthorhombic crystal structure contributed peaks with high intensity at 2θ of 20.28°, 26.15° and 34.31°. From Figure 1, it is known that 2% V_2O_5 .CaO catalyst has a similar diffraction pattern to CaO catalyst. It means that the crystal character of V_2O_5 metal oxide is not seen in the diffractogram of the synthesized 2% V_2O_5 .CaO using the physical mixing method. This circumstance may be due to the lower metal oxide content in the catalyst, making it hard to detect the V_2O_5 character. The catalyst with a V_2O_5 content of < 25% had no crystalline vanadia in its X-ray diffraction pattern, indicating that vanadium oxide was uniformly disseminated on its surface (Chary *et al.*, 2004; Sun *et al.*, 2007; Zhao *et al.*, 2018).

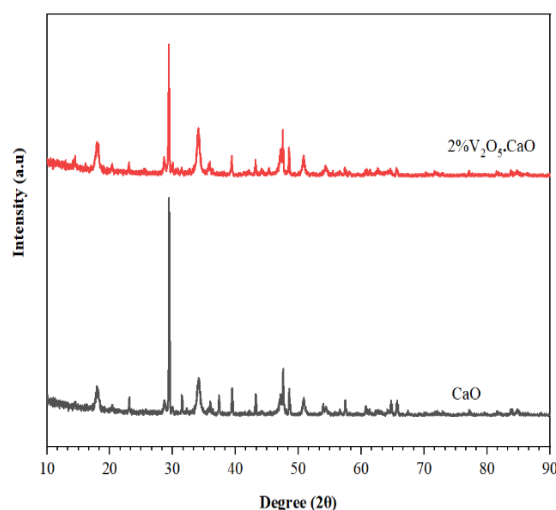


Fig. 1 XRD diffractogram of CaO and 2% V_2O_5 .CaO catalysts

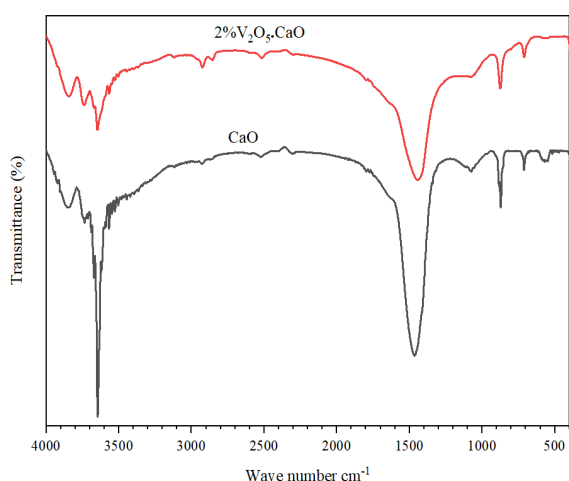


Fig. 2 FT-IR spectra of 2%V₂O₅.CaO and CaO catalysts

The FT-IR spectra of 2%V₂O₅.CaO and CaO catalysts are displayed in Figure 2., it known that weak absorption band at 878 cm⁻¹ corresponding to the C–O symmetric stretching mode of carbonate ion (CO₃²⁻), indicating the presence of CaCO₃ in the catalysts (Maneerung *et al.*, 2016). CaCO₃ could be formed due to the high affinity of the Ca–O structure, which reacted with CO₂ after calcination, forming CaCO₃ on the catalyst surface (Kesserwan *et al.*, 2020). The bending vibration of the O–Ca–O group at 1430 cm⁻¹ proves that CaO was formed (Boro *et al.*, 2014). The spectra in the range of 3300–3600 cm⁻¹ reveal the stretching vibration of hydroxyl group (O–H) for Ca(OH)₂, both of which were formed by adsorbed interlayer of water molecules on the surface of the catalyst (Maneerung *et al.*, 2016). Ca(OH)₂ was formed during the nitrate decomposition process, followed by a reaction with water. The presence of metal-oxide bonding vibration is detected by FT-IR spectroscopy on 600–700 cm⁻¹ wavenumber range (Syamsuddin & Hameed, 2016). Infrared spectra of 2%V₂O₅.CaO catalyst showed no characteristic peak of the crystalline 2%V₂O₅ phase. It is caused by the low content of V₂O₅ in 2%V₂O₅.CaO. Ngaosuwan *et al.* (2021) stated that IR spectroscopy could not detect La₂O₃ in the La₂O₃/CaO samples due to the low vibration intensity of pure La₂O₃ compared to CaO. The characteristic peak of V₂O₅ was only observed when the V₂O₅ content reached 30% in CaO. This result is supported by Sun *et al.* (2007) which stated that the peak caused by V₂O₅ was not observed in the infrared spectra of the V₂O₅/NbP catalyst with low V₂O₅ content (Sun *et al.*, 2007). The characteristic peak of V₂O₅ was only observed when the V₂O₅ content reached 25%. This result suggests that the addition of

V₂O₅ did not change the structure of CaO significantly, meaning that the CaO framework stayed stable even with the addition of V₂O₅.

Table 3 illustrates the physico-chemical properties of the BET surface area, average pore size and pore volume, total acid and base sites density of CaO and 2%V₂O₅.CaO catalysts. The surface area of the CaO is 10.367 mm²/g, while the 2%V₂O₅.CaO catalyst has a surface area of 12.382 mm²/g. The porosity of the CaO surface was a consequence of released CO₂ in the high temperature calcination, which caused higher surface area in the 2%V₂O₅.CaO catalyst compared to the CaO catalyst. The addition of metal oxide (2%V₂O₅) to the CaO base catalyst also caused an increase in the surface area of the 2%V₂O₅.CaO catalyst. This is evidenced by Kaur *et al.* (2014) who synthesized Zr/CaO catalysts with various Zr concentration (10–20 wt.%). They found that the addition of zirconium to the CaO catalyst increased in surface area proportional to the increasing zirconium loading on the CaO catalyst (Kaur & Ali, 2014). In this study, a simple physical mixing method was used to make the 2%V₂O₅.CaO catalyst. It has a larger surface area than the bifunctional catalyst made by the previous researchers.

TPD-NH₃ and TPD-CO₂ analyses were carried out to determine the acidity and basicity degrees of a catalyst. The data could also provide the amount of acidic and basic sites on the bifunctional catalysts to help explain the relationship of catalyst activity in one-pot esterification-transesterification reaction (Lee *et al.*, 2015). In TPD analysis, the peaks desorbed at high temperature regions indicate a high bonding strength on the active sites of the support. On the other hand, the peaks desorbed at lower temperature zones suggest a low bonding strength in the active sites, resulting in a low acidity or basicity. The peaks that are desorbed at temperatures below 300 °C are considered to have a low acid or base strength. The peaks that are desorbed at temperatures between 400 and 500 °C are considered to have a moderate acid or base strength, and the peaks that are observed at temperatures above 500 °C are considered to have a high acidic or base strength (Rabiah Nizah *et al.*, 2014).

From Figure 3, it can be observed that the prepared 2%V₂O₅.CaO catalysts have a higher total basicity than the CaO catalyst. Furthermore, the addition of 2%V₂O₅ on the CaO catalyst caused the total base site density of the catalyst to increase slightly from 4.7481 mmol/g to 5.8652 mmol/g. The dual interaction of the V₂O₅ surface lattice oxygen and the Ca species prompt a synergetic effect that assists strong basic sites formation. The presence of V⁵⁺ acts as an electron donor, facilitating the interaction between the reactant molecules and the catalyst.

Table 3

The physico-chemical properties of the BET surface area, average pore size and pore volume, total acid and base sites density of CaO and 2%V₂O₅.CaO catalysts

Catalyst	Method of synthesis	Average surface area (m ² /g)	Average pore size (nm)	Average pore volume (cm ³ /g)	Total number of acid sites (mmol/g)	Total number of base sites (mmol/g)	References
CaO	Coprecipitation	10.367	2.391	0.013	-	4.7481	This study
2%V ₂ O ₅ .CaO	Physical Mixing	12.382	2.169	0.014	2.7464	5.8652	This study
W _{0.6} -Mo _{0.4} /CaO	Wet Impregnation	9.400	2.841	0.058	3.738	1.365	(Mansir et al., 2017)
7%Fe ₂ O ₃ /CaO	Impregnation	8.880	9.75	0.030	4.93	4.69	(Ezzah-Mahmudah et al., 2016)
Ca-B	Impregnation	5.86	16.6	0.024	2.67	1.69	(Wang et al., 2018)

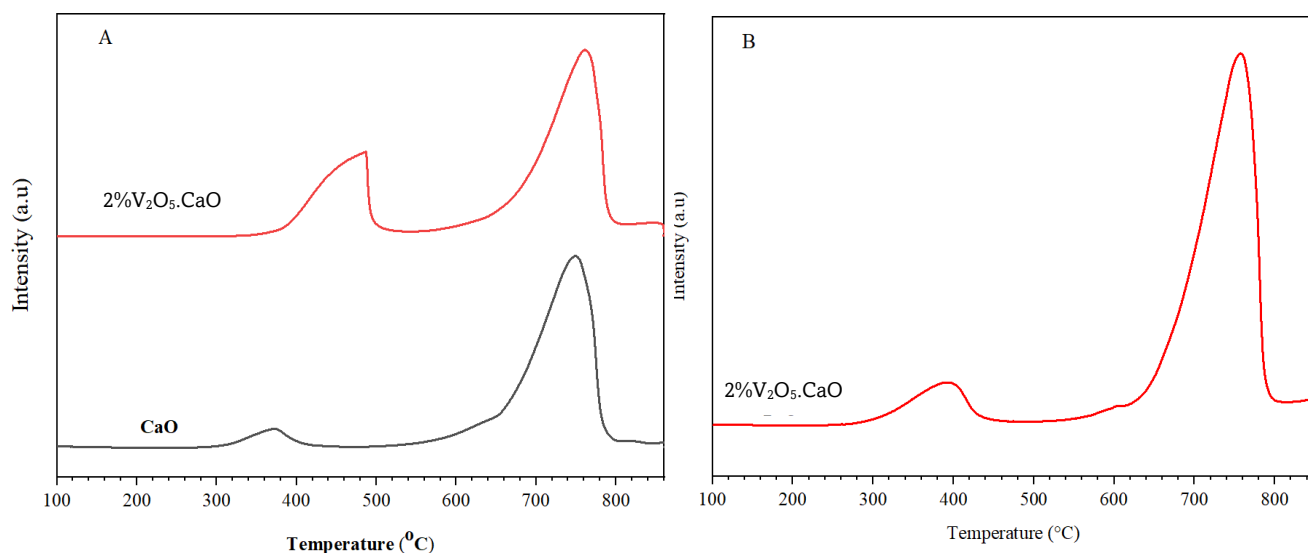


Fig. 3 TPD-CO₂ (A) and TPD-NH₃ (B) of CaO and 2%V₂O₅.CaO catalysts

Figure 3 (A) depicts the fundamental property of the synthesized catalyst samples (as assessed by TPD-CO₂). The TPD-CO₂ profiles of the samples (CaO and 2%V₂O₅.CaO) revealed peaks of CO₂ desorption at a temperature range of 350-800°C. This indicates that all the sample catalysts (CaO and 2%V₂O₅.CaO) desorb their CO₂ peaks at strong and moderate basicity sites. On the catalyst 2%V₂O₅.CaO, strong basicity sites exhibit a desorption peak at temperatures ranging from 625–800 °C, while moderate basicity sites exhibit a desorption peak at temperatures ranging from 350–480°C. The synthesized 2%V₂O₅.CaO catalyst has a higher basicity strength than the CaO catalyst. It can be seen from the desorption peak of CO₂ in Figure 3(A), where the desorption peak of CaO at strong moderate basicity site has a lower temperature than the catalyst of 2%V₂O₅.CaO.

Figure 3(B) displays the results of the TPD-NH₃ analysis, which determined the acidity strength of the 2%V₂O₅.CaO catalyst. Based on Figure 3 (B), the addition of metal oxide V₂O₅ causes the appearance of an acid side to the 2%V₂O₅.CaO catalyst with a total acid site density of 2.7464 mmol/g. The TPD-NH₃ profile of 2%V₂O₅.CaO catalyst illustrates the NH₃ desorbed peaks at a variety of temperature zones, including 350-450 °C and 650-800 °C, respectively. The profile peaks NH₃ desorbed in the temperature zones ranging from 350-450 °C can be attributed to a medium acidity strength. In addition, the sharp peaks in the NH₃ desorption curve at 600-800 °C are also indicate high acid strength (Borgna, 2015). The 2% V₂O₅ metal oxide contributed to the acid site formation in the CaO catalyst, which favored the esterification reaction in biodiesel production from WCO. Both the Lewis and Brønsted acid sites were found in V₂O₅ metal oxides (Mulyatun & Prasetyoko, 2011). This result is also obtained by Almeida *et al.* (2016), whom stated that V₂O₅ addition to SiO₂ catalyst formed Brønsted and Lewis acid sites for soybean oil-based biodiesel production. Based on the TPD-NH₃ and TPD-CO₂, the synthesized 2%V₂O₅.CaO catalyst using simple physical mixing had both acidic and alkaline sides with high strength.

3.2 The Catalytic Activity of V₂O₅.CaO esterification and transesterification simultaneously

Catalytic activity of the physically mixed 2%V₂O₅.CaO catalyst was evaluated by WCO-based biodiesel production with 20:1 methanol to WCO molar ratio and 1%wt catalyst loading at 60 °C for 3 hours. The analysis of the fatty acid methyl

ester (FAME) of the biodiesel component performed by GC-MS. The composition of FAME based on GCMS results is as follows: Methyl laurate, Methyl myristate, Methyl palmitoleate, Methyl palmitate, Methyl linoleate, Methyl oleate, Methyl stearate, and Methyl arachate. The WCO-based biodiesel component in this study is the same as the biodiesel component produced from waste cooking oil catalyzed by TiO₂-MgO mixed oxides (Wen *et al.*, 2010).

This study was done in order to determine whether the 2%V₂O₅.CaO catalyst showed higher activity than the CaO catalyst. Figure 4 illustrates how catalytic activity of different materials affects biodiesel synthesis. It can be seen that the biodiesel yields of CaO were all less than 35.79%. In contrast, the 2%V₂O₅.CaO catalyst demonstrated good catalytic activity, resulting in a high biodiesel yield (51.30%) over same reaction conditions for the CaO catalyst. These findings suggest that the acidity, basicity, and surface area of the catalyst play a supportive role in the improved biodiesel yield that was achieved at a very mild reaction temperature of 60 °C.

Figure 4 demonstrates that the total number of acid-base sites and surface area characteristics of the catalysts are the primary factors that determine the catalytic performance. It is found that the yield of FAME and FFA conversion is proportional to the total number of acid-base sites and the surface area of the catalyst. The 2%V₂O₅.CaO catalyst shows better catalytic activity than the CaO catalyst. This is shown by the FAME yield (%) and FFA conversion in the production of WCO-based biodiesel (Figure 4). The 2%V₂O₅.CaO catalyst shows a higher total number of acid-base sites and surface area compared to the CaO catalyst. It causes the yield of FAME and FFA conversion from the 2% V₂O₅.CaO catalyst to be higher than the CaO catalyst. The 2%V₂O₅.CaO catalyst is a catalyst that has both acidic and basic sides due to the addition of metal oxide V₂O₅, which has Lewis and Brønsted acid sites on the CaO base catalyst. The acid site (V₂O₅) of the catalyst is responsible for the FFA esterification reaction, while the basic site (CaO) of the catalyst helps the triglyceride transesterification reaction in the production of WCO-based biodiesel. The CaO catalyst only has a basic side, so it will be difficult to convert free fatty acids (FFA) into FAME in the production of WCO-base biodiesel. The feedstock's free fatty acids (FFA) and water content directly alter CaO catalysts' catalytic activity. CaO becomes inert when it reacts with FFA (Zul *et al.*, 2021).

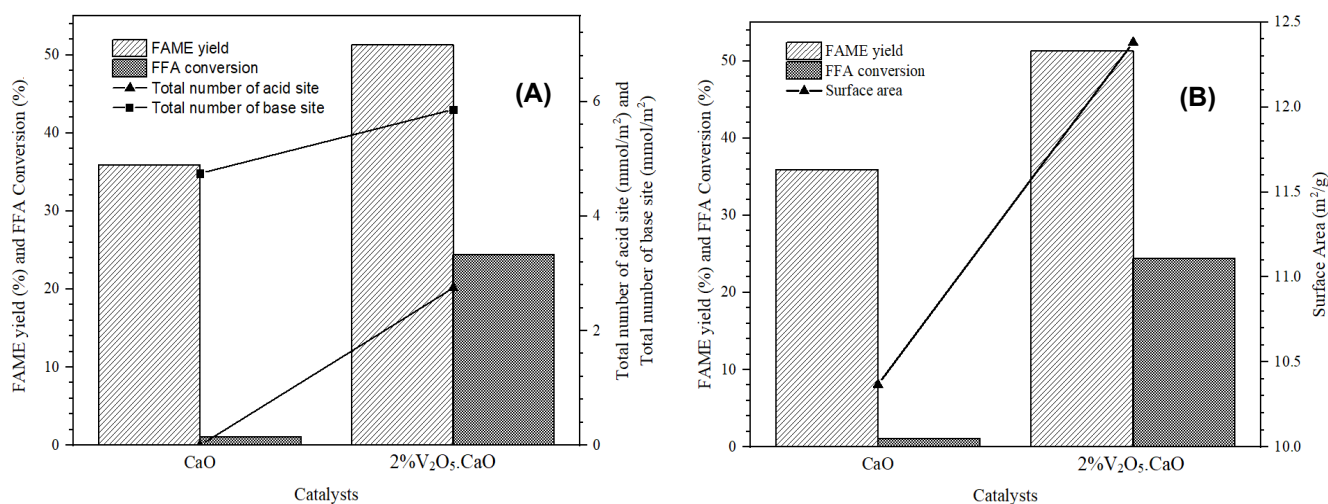


Fig. 4 Influence of total number of Acid-base sites (A) and surface area (B) of catalysts on the FAME yield (%) and FFA Conversion (%)

Base strength and the total number of base-site catalysts affect transesterification catalytic activity. Figure 4(A) illustrates series catalytic trend with total number of base sites. Catalytic trends paralleled the total number of base sites basicity variability. The acidity of 2%V₂O₅.CaO catalyst may contribute to its catalytic activity, together with its basic active site. The addition of 2% V₂O₅ metal oxide to the CaO catalyst contributed to the appearance of the acid sites of the CaO base catalyst. The metal oxide V₂O₅ has both Brønsted and Lewis acid sites (Mulyatun & Prasetyoko, 2011). The inclusion of these sites at 2%V₂O₅.CaO would increase the selectivity and activity of the catalyst, giving greater acidity strength and more active sites, hence aiding the important free fatty acid esterification in the manufacture of biodiesel from non-food feedstocks. It is in line with the results of the TPD-NH₃ analysis, which show that the 2%V₂O₅.CaO catalysts displayed a pronounced desorption peak of NH₃ at temperatures above 500°C, indicating strong acid sites. In biodiesel synthesis, acidic materials improve esterification catalytic performance. The esterification reaction is significantly affected by the addition of acid sites (V₂O₅) to the surface of CaO catalysts, as shown by the lower FFA conversion of CaO (1.11%) when compared to 2% V₂O₅.CaO (24.42%) catalysts. FFA conversion rate also depends on the synthesized catalyst's acidity. Due to anionic surface, Brønsted acid sites can share protons, while Lewis acid sites can take electron-pairs. High total number of acid site catalysts capture more FFAs in the active site.

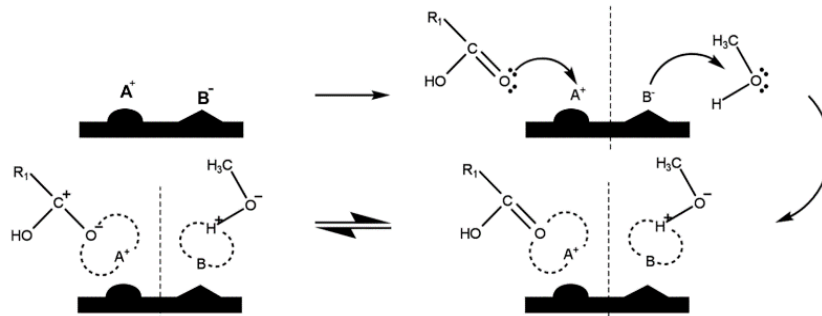
It was thought that the existence of acid site (V₂O₅) and basic sites (CaO) in the catalyst would promote its activity as a catalyst for the simultaneous esterification-transesterification of WCO containing high FFA. Furthermore, both esterification-transesterification can be catalyzed simultaneously because of the acid and base sites in the 2%V₂O₅.CaO catalyst. Abukhadra *et al.* (2019) proposed acid and basic catalyst sites for simultaneous esterification and transesterification. These findings give further evidence that the total amount of acid-base sites and surface area of the catalyst take an extremely important part in manufacturing biodiesel from feedstock that has higher FFA. The 2%V₂O₅.CaO catalyst which had the great levels of both total number of acid-base sites and surface area, was the catalyst that produced the largest amount of FAME yield. In conclusion, the stability of acidic groups was extremely significant for the conversion of FFAs and assisted in the resistance of FFAs on basic groups. Both active sites (acid and base site) contributed to biodiesel production.

The catalytic activity of bifunctional catalysts in biodiesel production is strongly influenced by the total number of acid-

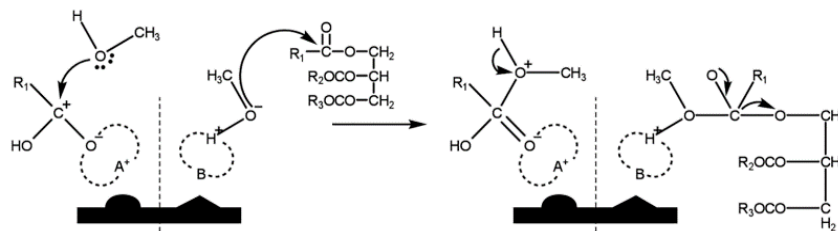
base species and surface area of the catalyst (Ngaosuwan *et al.*, 2021). Figure 4(B) depicts the effect of the catalyst's surface area on its catalytic activity. The 2%V₂O₅.CaO catalyst has a larger surface area than the CaO catalyst. It causes the catalytic activity of the V₂O₅.CaO catalyst to be higher than that of the CaO catalyst, both in the esterification and transesterification reaction. In catalysis applications, mesoporous catalysts' surface area has been improved via much effort. Surface area is affected by synthesis technique, support type and amount, and calcination temperature (Soltani *et al.*, 2017). The results show that a mesoporous catalyst with a larger surface area improves catalytic activity. The catalyst's mass interaction with reactants can enhance with a larger surface area. This is also in accordance with research by Wang *et al.* (2018), which states that the incorporation of Ca-B (700°C) causes the addition of an acid site and surface area to the CaO catalyst, resulting in an increase in catalytic activity. Ngaosuwan *et al.* (2021) synthesized La₂O₃/CaO catalyst with various synthesis methods, including impregnation and physical mixing. It was found that the total basicity and surface area greatly determine the catalytic activity of the La₂O₃/CaO catalyst (Ngaosuwan *et al.*, 2021). The 5%La₂O₃/CaO_{phy} catalyst synthesized by the physical mixing method has the best catalytic activity in biodiesel production from palm oil because this catalyst has a large surface area and total acid-base sites. According to these findings, the concentration of acid-base site and surface area catalysts has an influence, at least partially, on the yield of FAME produced from waste cooking oil.

The proposed mechanism of FFA esterification by V₂O₅ metal oxide in acid site and transesterification of TG by CaO catalyst in basic site is shown in Figure 5 (Wan Omar & Amin, 2011). In step 1: In order to initiate the process of physical adsorption of reactants, the carbonyl group in the free fatty acid and methanol in the bulk solution must first diffuse to the catalyst surface. Adsorption of carbonyl group belonging to the FFA in the acid site takes place, while methanol would be absorbed in the basic site, forming a methoxide. Step 2: A tetrahedral intermediate would be formed as a result of a subsequent nucleophilic attack on the acid site's carbocation (esterification) and the oxygen anions of the methanol -OH group along with the triglyceride carbonyl group at the basic site (transesterification). Step 3: Desorption of the -OH group (OH bond breakage) and alkyl triglycerides (C-O bond breakage) resulting in FAME along with water and glycerol as by-products.

Step 1 : Methanol and FFA adsorbed on basic site respectively



Step 2 : Nucleophilic attack



Step 3 : Desorption

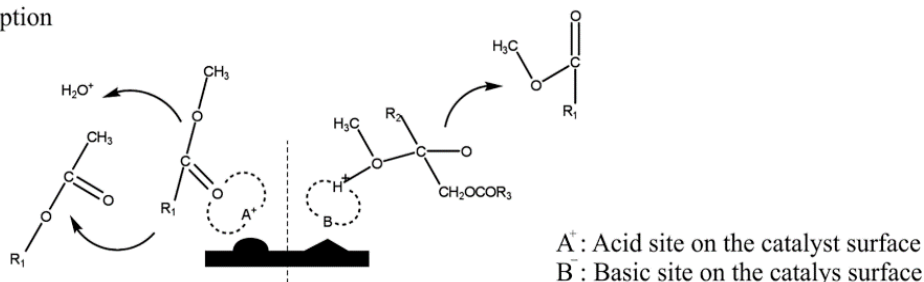


Fig 5. Suggested reaction mechanism of esterification and transesterification with acid-base sites of $V_2O_5 \cdot CaO$ [Reprinted (adapted) with permission from ref (Wan Omar & Amin, 2011). Copyright 2011, Elsevier].

4. Conclusion

The metal oxide with CaO catalyst, namely $2\%V_2O_5 \cdot CaO$ catalyst has been synthesized via the physical mixing method for converting WCO to biodiesel. The obtained FAME yield when using the $2\%V_2O_5 \cdot CaO$ catalyst was higher than when using the CaO catalyst. $2\%V_2O_5 \cdot CaO$ catalyst has a larger specific surface area, a higher total number of acid-base, a stronger basicity and acidity than CaO. It solves the saponification issue and concurrently catalyzes the FFA esterification and TG transesterification, raising the catalytic activity for biodiesel synthesis. Therefore, the prepared $2\%V_2O_5 \cdot CaO$ via the physical mixing method is a suitable catalyst for supporting simultaneous esterification-transesterification, and it is prospective for making biodiesel derived from WCO with high FFA.

Acknowledgments

The authors are grateful to the Material Laboratory, Universitas Islam Negeri Walisongo Semarang, Indonesia for all support throughout the research

Author Contributions: M. Mulyatun: Conceptualization, methodology, formal analysis, writing—original draft., I.Istadi: supervision, writing—review, resources, validation., W.Widayat: supervision, writing—review, resources, validation. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Directorate General of Higher Education Ministry of National Education Indonesia 345-30/UN7.6.1/PP/2022.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Abukhadra, M. R., Ibrahim, S. M., Yakout, S. M., El-Zaidy, M. E., & Abdeltawab, A. A. (2019). Synthesis of Na^+ trapped bentonite/zeolite-P composite as a novel catalyst for effective production of biodiesel from palm oil; Effect of ultrasonic irradiation and mechanism. *Energy Conversion and Management*, 196 (May), 739–750. <https://doi.org/10.1016/j.enconman.2019.06.027>
- Ali, R. M., Elkatory, M. R., & Hamad, H. A. (2020). Highly active and stable magnetically recyclable $CuFe_2O_4$ as a heterogenous catalyst for efficient conversion of waste frying oil to biodiesel. *Fuel*, 268 (February), 117297. <https://doi.org/10.1016/j.fuel.2020.117297>
- Almeida, T. A., Rodrigues, I. A., Estrela, T. S., Nunes, C. N. F., Machado, L. L., Leão, K. V., Barros, I. C. L., Amorim, F. A. C., & Braga, V. S. (2016). Synthesis of ethyl biodiesel from soybean oil, frying oil and chicken fat, using catalysts based on vanadium pentoxide. *Energy*, 97, 528–533. <https://doi.org/10.1016/j.energy.2015.12.085>
- Asikin-mijan, N., Lee, H. V., & Taufiq-yap, Y. H. (2015). Chemical Engineering Research and Design Synthesis and catalytic activity of hydration – dehydration treated clamshell derived CaO for biodiesel production. *Chemical Engineering Research and*

- Design, 102, 368–377. <https://doi.org/10.1016/j.cherd.2015.07.002>
- Borah, M. J., Das, A., Das, V., Bhuyan, N., & Deka, D. (2019). Transesterification of waste cooking oil for biodiesel production catalyzed by Zn substituted waste egg shell derived CaO nanocatalyst. *Fuel*, 242 (May 2018), 345–354. <https://doi.org/10.1016/j.fuel.2019.01.060>
- Borgna, A. (2015). Bifunctional $\text{Mo}_3\text{VO}_7/\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{Al}_2\text{O}_3$ Catalysts for One-step Conversion of Glycerol to Acrylic Acid: Catalyst Structural Evolution and Reaction Pathways. *Elsevier B.V.* <https://doi.org/10.1016/j.apcatb.2015.02.032>
- Boro, J., Konwar, L. J., & Deka, D. (2014). Transesterification of non edible feedstock with lithium incorporated egg shell derived CaO for biodiesel production. *Fuel Processing Technology*, 122, 72–78. <https://doi.org/10.1016/j.fuproc.2014.01.022>
- Buasri, A., Ksapabutr, B., Panapoy, M., & Chaiyut, N. (2012). Process Optimization for Ethyl Ester Production in Fixed Bed Reactor Using Calcium Oxide Impregnated Palm Shell Activated Carbon (CaO/PSAC). *International Journal of Renewable Energy Development*, 1(3), 81-86; <https://doi.org/10.14710/ijred.1.3.81-86>
- Chary, K. V. R., Reddy, K. R., Kumar, C. P., Naresh, D., Rao, V. V., & Mestl, G. (2004). Characterization and reactivity of molybdenum oxide catalysts supported on $\text{Nb}_2\text{O}_5\text{-TiO}_2$. *Journal of Molecular Catalysis A: Chemical*, 223(1–2), 363–369. <https://doi.org/10.1016/j.molcata.2004.01.029>
- Chen, G. Y., Shan, R., Yan, B. B., Shi, J. F., Li, S. Y., & Liu, C. Y. (2016). Remarkably enhancing the biodiesel yield from palm oil upon abalone shell-derived CaO catalysts treated by ethanol. *Fuel Processing Technology*, 143, 110–117. <https://doi.org/10.1016/j.fuproc.2015.11.017>
- Das, H. P., Neeharika, T. S. V. R., Sailu, C., Srikanth, V., Kumar, T. P., & Rani, K. N. P. (2017). Kinetics of amidation of free fatty acids in jatropha oil as a prerequisite for biodiesel production. *Fuel*, 196, 169–177. <https://doi.org/10.1016/j.fuel.2017.01.096>
- Ezzah-Mahmudah, S., Lokman, I. M., Saiman, M. I., & Taufiq-Yap, Y. H. (2016). Synthesis and characterization of $\text{Fe}_2\text{O}_3/\text{CaO}$ derived from Anadara Granosa for methyl ester production. *Energy Conversion and Management*, 126, 124–131. <https://doi.org/10.1016/j.enconman.2016.07.072>
- Faruque, M. O., Razzak, S. A., & Hossain, M. M. (2020). Application of heterogeneous catalysts for biodiesel production from microalgal oil—a review. *Catalysts*, 10 (9), 1–25. <https://doi.org/10.3390/catal10091025>
- Hadiyanto, H., Lestari, S. P., & Widayat, W. (2016). Preparation and Characterization of Anadara Granosa Shells and CaCO_3 as Heterogeneous Catalyst for Biodiesel Production. *Bulletin of Chemical Reaction Engineering & Catalysis*, 11(1), 21-26. <https://doi.org/10.9767/bcrec.11.1.402.21-26>
- Istadi, I., Prasetyo, S. A., & Nugroho, T. S. (2015). Characterization of $\text{K}_2\text{O}/\text{CaO}-\text{ZnO}$ Catalyst for Transesterification of Soybean Oil to Biodiesel. *Procedia Environmental Sciences*, 23(Ictcred 2014), 394–399. <https://doi.org/10.1016/j.proenv.2015.01.056>
- Jeon, Y., Chi, W. S., Hwang, J., Kim, D. H., Kim, J. H., & Shul, Y. G. (2019). Core-shell nanostructured heteropoly acid-functionalized metal-organic frameworks: Bifunctional heterogeneous catalyst for efficient biodiesel production. *Applied Catalysis B: Environmental*, 242, 51–59. <https://doi.org/10.1016/j.apcatb.2018.09.071>
- Kaur, N., & Ali, A. (2014). Kinetics and reusability of Zr/CaO as heterogeneous catalyst for the ethanolysis and methanolysis of Jatropha curcas oil. *Fuel Processing Technology*, 119, 173–184. <https://doi.org/10.1016/j.fuproc.2013.11.002>
- Kesserwan, F., Ahmad, M. N., Khalil, M., & El-Rassy, H. (2020). Hybrid $\text{CaO}/\text{Al}_2\text{O}_3$ aerogel as heterogeneous catalyst for biodiesel production. *Chemical Engineering Journal*, 385, 123834. <https://doi.org/10.1016/j.cej.2019.123834>
- Krishnamurthy, K. N., Sridhara, S. N., & Ananda Kumar, C. S. (2020). Optimization and kinetic study of biodiesel production from *Hydnocarpus wightiana* oil and dairy waste scum using snail shell CaO nano catalyst. *Renewable Energy*, 146, 280–296. <https://doi.org/10.1016/j.renene.2019.06.161>
- Kung, H. H. (1989). Transition Metal Oxides - Surface Chemistry and Catalysis. In *Studies in Surface Science and Catalysis* (Vol. 45). Elsevier B.V. [https://doi.org/10.1016/S0167-2991\(08\)60921-0](https://doi.org/10.1016/S0167-2991(08)60921-0)
- Lee, H.V., Juan, J.C. & Taufiq-Ya, Y. H. (2015). Preparation and application of binary acid-base $\text{CaO}-\text{La}_2\text{O}_3$ catalyst for biodiesel production. *Renewable Energy*, 74, 124–132. <https://doi.org/10.1016/j.renene.2014.07.017>
- Li, J., Xu, H., Fei, Z. A., Liu, H., Qiao, D. R., & Cao, Y. (2012). CaO/NaA combined with enzymatic catalyst for biodiesel transesterification. *Catalysis Communications*, 28, 52–57. <https://doi.org/10.1016/j.catcom.2012.07.025>
- Li, X., Liu, S., Na, Z., Lu, D., & Liu, Z. (2013). Adsorption, concentration, and recovery of aqueous heavy metal ions with the root powder of *Eichhornia crassipes*. *Ecological Engineering*, 60, 160–166. <https://doi.org/10.1016/j.ecoleng.2013.07.039>
- Maneerung, T., Kawi, S., Dai, Y., & Wang, C. H. (2016). Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energy Conversion and Management*, 123, 487–497. <https://doi.org/10.1016/j.enconman.2016.06.071>
- Mansir, N., Hwa Teo, S., Lokman Ibrahim, M., & Yun Hin, T. Y. (2017). Synthesis and application of waste egg shell derived CaO supported W-Mo mixed oxide catalysts for FAME production from waste cooking oil: Effect of stoichiometry. *Energy Conversion and Management*, 151, 216–226. <https://doi.org/10.1016/j.enconman.2017.08.069>
- Mulyatun, M., & Prasetyoko, D. (2011). Vanadium Contribution to the Surface Modification of Titanium Silicalite for Conversion of Benzene to Phenol. *IPTEK The Journal for Technology and Science*, 22(2). <https://doi.org/10.12962/j20882033.v22i2.58>
- Ngaosuwan, K., Chaiyariyakul, W., Inthong, O., Kiatkittipong, W., Wongsawaeng, D., & Assabumrungrat, S. (2021). $\text{La}_2\text{O}_3/\text{CaO}$ catalyst derived from eggshells: Effects of preparation method and La content on textural properties and catalytic activity for transesterification. *Catalysis Communications*, 149, 106247. <https://doi.org/10.1016/j.catcom.2020.106247>
- Piker, A., Tabah, B., Perkas, N., & Gedanken, A. (2016). A green and low-cost room temperature biodiesel production method from waste oil using egg shells as catalyst. *Fuel*, 182, 34–41. <https://doi.org/10.1016/j.fuel.2016.05.078>
- Rabiah Nizah, M. F., Taufiq-Yap, Y. H., Rashid, U., Teo, S. H., Shajaratun Nur, Z. A., & Islam, A. (2014). Production of biodiesel from non-edible *Jatropha curcas* oil via transesterification using $\text{Bi}_2\text{O}_3\text{-La}_2\text{O}_3$ catalyst. *Energy Conversion and Management*, 88, 1257–1262. <https://doi.org/10.1016/j.enconman.2014.02.072>
- Rahman, N. J. A., Ramli, A., Jumbri, K., & Uemura, Y. (2019). Tailoring the surface area and the acid-base properties of ZrO_2 for biodiesel production from *Nannochloropsis* sp. *Scientific Reports*, 9(1), 1–12. <https://doi.org/10.1038/s41598-019-52771-9>
- Rezania, S., Oryani, B., Park, J., Hashemi, B., Yadav, K. K., Kwon, E. E., Hur, J., & Cho, J. (2019). Review on transesterification of non-edible sources for biodiesel production with a focus on economic aspects, fuel properties and by-product applications. *Energy Conversion and Management*, 201(July), 112155. <https://doi.org/10.1016/j.enconman.2019.112155>
- Roy, T., Sahani, S., & Chandra Sharma, Y. (2020). Study on kinetics-thermodynamics and environmental parameter of biodiesel production from waste cooking oil and castor oil using potassium modified ceria oxide catalyst. *Journal of Cleaner Production*, 247, 119166. <https://doi.org/10.1016/j.jclepro.2019.119166>
- Shatesh Kumar, Shamsuddin, M. R., Farabi, M. S. A., Saiman, M. I., Zainal, Z., & Taufiq-Yap, Y. H. (2020). Production of methyl esters from waste cooking oil and chicken fat oil via simultaneous esterification and transesterification using acid catalyst. *Energy Conversion and Management*, 226 (May), 113366. <https://doi.org/10.1016/j.enconman.2020.113366>
- Shobhana-Gnanaserkhar, Asikin-Mijan, N., AbdulKareem-Alsultan, G., Sivasangar-Seenivasagam, Izham, S. M., & Taufiq-Yap, Y. H. (2020). Biodiesel production via simultaneous esterification and transesterification of chicken fat oil by mesoporous sulfated Ce supported activated carbon. *Biomass and Bioenergy*, 141, 105714. <https://doi.org/10.1016/j.biombioe.2020.105714>
- Soltani, S., Rashid, U., Al-Resayes, S. I., & Nehdi, I. A. (2017). Recent progress in synthesis and surface functionalization of mesoporous acidic heterogeneous catalysts for esterification of free fatty acid feedstocks: A review. *Energy Conversion and Management*, 141, 183–205. <https://doi.org/10.1016/j.enconman.2016.07.042>

- Sun, Q., Fang, D., Wang, S., Shen, J., & Auroux, A. (2007). Structural, acidic and redox properties of V_2O_5/NbP catalysts. *Applied Catalysis A: General*, 327(2), 218–225. <https://doi.org/10.1016/j.apcata.2007.05.016>
- Syamsuddin, Y., & Hameed, B. H. (2016). Synthesis of glycerol free-fatty acid methyl esters from Jatropha oil over Ca-La mixed-oxide catalyst. *Journal of the Taiwan Institute of Chemical Engineers*, 58, 181–188. <https://doi.org/10.1016/j.jtice.2015.06.041>
- Wan Omar, W. N. N., & Amin, N. A. S. (2011). Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Processing Technology*, 92 (12), 2397–2405. <https://doi.org/10.1016/j.fuproc.2011.08.009>
- Wang, A., Li, H., Zhang, H., Pan, H., & Yang, S. (2018). Efficient catalytic production of biodiesel with acid-base bifunctional rod-like Ca-B oxides by the sol-gel approach. *Materials*, 12(1). <https://doi.org/10.3390/ma12010083>
- Wen, Z., Yu, X., Tu, S. T., Yan, J., & Dahlquist, E. (2010). Biodiesel production from waste cooking oil catalyzed by TiO_2 -MgO mixed oxides. *Bioresource Technology*, 101(24), 9570–9576. <https://doi.org/10.1016/j.biortech.2010.07.066>
- Widayat, W., Hadiyanto, H., Wardani, P. W. A., Zuhra, U. A., & Prameswari, J. (2020). Preparation of KI/hydroxyapatite catalyst from phosphate rocks and its application for improvement of biodiesel production. *Molecules*, 25(11). <https://doi.org/10.3390/molecules25112565>
- Widiarti, N., Bahruji, H., Holilah, H., Ni'mah, Y. L., Ediati, R., Santoso, E., Jilil, A. A., Hamid, A., & Prasetyoko, D. (2021). Upgrading catalytic activity of NiO/CaO/MgO from natural limestone as catalysts for transesterification of coconut oil to biodiesel. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-021-01373-5>
- Xie, W., & Zhao, L. (2013). Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Conversion and Management*, 76, 55–62. <https://doi.org/10.1016/j.enconman.2013.07.027>
- Yadav, G. D., & Nair, J. J. (1999). Sulfated zirconia and its modified versions as promising catalysts for industrial processes. *Microporous and Mesoporous Materials*, 33(1–3), 1–48. [https://doi.org/10.1016/S1387-1811\(99\)00147-X](https://doi.org/10.1016/S1387-1811(99)00147-X)
- Zhao, X., Yan, Y., Mao, L., Fu, M., Zhao, H., Sun, L., Xiao, Y., & Dong, G. (2018). A relationship between the V4+/V5+ ratio and the surface dispersion, surface acidity, and redox performance of V_2O_5 - WO_3 /TiO₂ SCR catalysts. *RSC Advances*, 8(54), 31081–31093. <https://doi.org/10.1039/c8ra02857e>
- Zul, N. A., Ganesan, S., Hamidon, T. S., Oh, W. Da, & Hussin, M. H. (2021). A review on the utilization of calcium oxide as a base catalyst in biodiesel production. *Journal of Environmental Chemical Engineering*, 9(4), 105741. <https://doi.org/10.1016/j.jece.2021.105741>



© 2023. The Author(s). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution-ShareAlike 4.0 (CC BY-SA) International License (<http://creativecommons.org/licenses/by-sa/4.0/>)