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Bifunctional Heterogeneous Catalyst for Biodiesel Production from Waste Vegetable Oil

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Abstract: Bifunctional solid catalysts facilitate the esterification of free fatty acids (FFA) into alkyl esters alongside the transesterification reaction, which allows for the use of waste vegetable oils with high water and FFA contents for biodiesel production. This makes the process economically viable and greener, as the waste fats and oils are readily available. The concurrent esterification and transesterification of waste palm oil (WPO) and waste sunflower oil (WSO) with methanol was investigated in the presence of calcium oxide on alumina catalyst in a conventional batch process. The catalyst characterization showed the existence of calcium oxide aluminates (calcined at 750 °C), which exhibited crystalline phases with porous/spongy-like particles. The high concentration of CaO in CaO/Al₂O₃ was a favorable support material in the heterogeneously-catalyzed transesterification reactions. The optimum catalyst parameters for the production of fatty acid methyl esters (FAMEs) were observed at 65 °C for 4 h with a methanol-to-oil ratio of 9:1, 60% (waste palm oil, or WPO) and 80% (waste sunflower oil, or WSO), CaO/Al₂O₃ (% wt/wt) catalyst ratio as well as 4% CaO/Al₂O₃ concentration (% wt.) for WSO and WPO. The simultaneous esterification/transesterification reactions at optimum conditions on WPO and WSO led to high yield of FAMEs of 89, 61 and 55% for WPO and 54, 75 and 98% for WSO at catalyst ratios (wt %) of 60, 70 and 80% respectively. The use of bifunctional heterogeneous catalyst (CaO/Al₂O₃) with waste vegetable oil can result in high performance and the upscaling of biodiesel production.

Keywords: CaO/Al₂O₃; biodiesel; waste palm oil; waste sunflower oil

1. Introduction

The ever-growing rate of energy production and consumption with its attendant release of greenhouse gases cause ever-increasing adverse environmental effects, which in turn affect the well-being of humans [1]. The majority of the energy consumed globally originates from petroleum, charcoal, and natural gas. Nevertheless, these sources are limited and could possibly be depleted in the next centuries [2,3]. Therefore, the decline in global fossil energy resources will result in an increase in the crude oil prices and make renewable and sustainable energy sources more attractive. There is a necessity to find clean and renewable energy supplies, which is environmentally benign, to substitute current fossil energy sources. Biodiesel produced from the transesterification of triglycerides molecules in vegetable oils, animal fats, and waste oils such as yellow grease and soybean soapstock is a promising alternative energy source because of its lower emissions of particulate matter and greenhouse gases [4].

The first generation of biodiesel was produced using oils obtained from oil-bearing crops, leading to the food-for-fuel debate. Plant feedstock majorly made up of lignocellulosic materials (second-generation), though abundant and cheaper than food crops, are still considered to be costly for large-scale production of biodiesel. The growing interest in waste vegetable oils and waste animal fats is being fueled by the fact that it offers a cost-effective way to deal with the growing global generation of waste vegetable oils and its considerably lower cost compared to virgin oils [4].

The production of fatty acid methyl esters (FAME) can be mediated by homogeneous and heterogeneous catalysts. Homogeneous catalysts exist in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts are in a different phase, generally as a solid [1]. Homogeneous base and acid catalysts are widely used owing to their simplicity in application, good performance, and cost effectiveness. Alkaline catalysts such as KOH and NaOH are mostly utilized apart from sodium or potassium carbonates and alkoxides because of their high solubility in methanol (forming potassium and sodium methoxide [KCH_3O and CH_3NaO]) and the high yield of methyl ester that can be obtained under mild conditions when quality feedstock [< 1 FFA (wt %) and < 0.5 moisture (wt %)] are utilized [5,6], although this may demand a number of hours for the reaction to complete. However, homogeneous acid catalysts have a longer reaction time, higher temperature (80–100 °C), and unwanted technical equipment failure, which are disadvantageous to its application. Furthermore, to increase triglyceride conversion, an excessive quantity of methanol, for example, a molar ratio of methanol/oil higher than 12:1, is required [7], whereas the reaction is conventionally performed at a temperature of 60–65 °C under atmospheric pressure with a molar ratio of alcohol/oil at 6:1. An acid catalyst is mostly taken as a pretreatment stage in order to reduce the time of reaction when converting free fatty acids (FFA) to esters, which is followed by the addition of a base catalyst for the transesterification step to convert triglyceride into esters. The homogeneous-catalyzed transesterification method is costly, especially in the separation of the catalyst from the reaction mixture, the purification of methyl esters, high energy consumption, and corrosiveness.

Heterogeneously-catalyzed transesterification methods have been applied for methyl ester production [8,9]. This process requires simple purification steps and no neutralization. Moreover, heterogeneous catalysts are more environmentally friendly, sustainable, and neither involve catalyst recovery nor aqueous treatment stages. The inorganic solid catalysts that can be utilized for the transesterification reaction are the basic character, acidic character, and bifunctional (acidic–basic character); the latter are efficiently able to catalyze esterification and transesterification simultaneously. Heterogeneous bifunctional catalysts (solid base–solid acid) are very advantageous as they can be recycled, reused, and regenerated, with less energy consumption, and do not form soaps. They also simplify the glycerol purification and can be easily separated from the reaction products. Since they are used in powder form or in pellets, they also give better FAME yields in shorter reaction time and temperatures, in addition to being tolerant to FFAs and water in the feedstock [3,8,10]. Transesterification reactions with basic heterogeneous catalysts are mostly used for methyl ester or biodiesel production, and it is essential to use feedstock such as animal fats or vegetable oils, which contains low amounts of FFA [7,10]. Free fatty acids and water have less of an effect on solid-acid catalysts; hence, they do not dissolve in the feedstock, as well as in the alcohol, and they can be easily separated through filtration and reuse. Such catalysts are efficient for the esterification of FFA and triglycerides [3,11]. When the feedstock has a high content of FFAs or water, the alkali catalyst may react with the FFAs to generate soaps, while the water hydrolyzes the triglycerides to produce diglycerides and more FFAs [3,10]. The formation of soap during reactions causes catalyst consumption, a reduction in ester yield, and prevents the separation of glycerol from methyl ester [12].

Studies have reported the use of solid heterogeneous catalysts such as metal oxides of alkaline earth metals (Ba, Be, Ca, Mg, Sr), γ -alumina, hydrotalcites, mixed oxides, and zeolites [13]. CaO, a solid basic catalyst, is economical and mostly utilized because of its high activity and strength with a long lifespan [14]. A strong acid catalyst such as hydrochloric, sulfuric, or phosphoric acid, heteropoly acid impregnated on various supports (zirconia, silica, activated carbon, and alumina), Nafion-NR50,

$\text{WO}_3\text{-ZrO}_2$, and $\text{SO}_4\text{-ZrO}_2$ are used for transesterification because of their possession of sufficient acid sites on the surfaces with diverse strengths of Lewis acidity [15,16]. As an alternative to the use of solid-acid catalysts for FFA esterification and solid-basic catalysts for the transesterification of triglycerides, the use of a solid catalyst with an acidic–basic character has been suggested. Bifunctional catalysts act as a base and an acid at once and can mediate simultaneous (esterification and transesterification) reactions for methyl ester production [17]. Other currently developed catalysts for the production of methyl esters are biomass pyrolysis by-products, which include biochar, fly ash, sugars, etc. [18].

In this study, a two-step catalytic FAME production from waste palm oil (WPO) and waste sunflower oil (WSO) was performed using calcium oxide (solid base) impregnated on alumina (solid acid) catalyst. Alumina (Al_2O_3) was selected as a support because of its large pore size and pore volume, high specific surface area, and thermal and mechanical stability. The main focus of the study was to determine the optimum reaction conditions and the effect of different catalyst loading of $\text{CaO}/\text{Al}_2\text{O}_3$ after calcination on the FAME yield during the transesterification of WSO and WPO. Therefore, it is plausible that the use of a bifunctional heterogeneous catalyst such as $\text{CaO}/\text{Al}_2\text{O}_3$, which is reusable in the transesterification of readily available WSO and WPO, can result in the enhancement and optimization of economically viable biodiesel (FAMEs).

2. Materials and Methods

2.1. Materials

Analytical grade chemicals and reagents were used in this study. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, Merck, KGaA, Darmstadt, Germany)), sodium hydroxide pellets (NaOH , 98% (Merck, KGaA, Darmstadt, Germany)), and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kimix, 98%, Merck, KGaA, Darmstadt, Germany)) were used as starting materials. Deionized water (DIW; Labotec, Cape Town, South Africa) was used as the solvent. These reagents were used without further purification for catalyst synthesis. The FAME production reaction was carried out with the use waste palm oil (WPO) and waste sunflower oil (WSO) (collected from Suppa Oil Company, Cape Town), together with methanol (>99.9% pure, Sigma Aldrich, KGaA, Darmstadt, Germany) in the presence of prepared calcium oxide impregnated on alumina at catalyst ratios ($\text{CaO}/\text{Al}_2\text{O}_3$ wt %) of 60, 70 and 80%. The batch process was carried out in a 500 mL glass reactor with stirring at 700 rpm and constant temperature (65 °C).

2.2. Preparation of Calcium Oxide/Alumina Catalysts

A $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst was synthesized via the co-precipitation method. The CaO and Al_2O_3 were formed using sodium hydroxide (NaOH) to co-precipitate the oxyhydroxides from a solution with the right proportion of the respective metal nitrates. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, 99%) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kimix, 98%) were dissolved in a 2 L flask containing deionized water to give a $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of 80% $\text{CaO}/20\%\text{Al}_2\text{O}_3$ (wt %) and stirred vigorously using a high-power Dragon Lab OS20-S overhead stirrer setup. The solution was simultaneously heated at 100 °C over a Heidolph MR 3001K hot plate fitted with a thermocouple (Heidolph EKT 3001) temperature control system. The NaOH solution (Merck 98%, 4 M) at 78–80 °C was added drop-wise to the boiling nitrate solutions. The milky suspension/solution was maintained at 100 °C (pH 7.0–8.0) and stirred continuously for about 30 min to stimulate the nucleation–dissolution processes. The overhead stirrer (Dragon Lab OS20-S) was initially set at a speed of 1000 rpm and gradually increased to 2200 rpm as the solution viscosity rises due to nucleation. The milky solution was allowed to cool at room temperature for 20 min; it was then filtered in a Buckner filter setup, and the precipitates [$\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$] were washed repeatedly with warm distilled water to get rid of the nitrate (NaNO_3) and dried overnight in an oven at a temperature of 100 °C. The calcination process (crystallization, re-crystallization, thermal decomposition, and sintering) was carried out to remove H_2O , CO_2 , and other volatiles from the precursor by means of a Kiln Contracts furnace in a fluidized bed reactor set at 750 °C (6 h) through

atmospheric heated air (10 °C/ min) prior to testing of the solid catalyst (CaO/Al₂O₃) powder [19]. A more detailed description of the catalyst synthesis with respect to varying basic to acidic oxides ratios is provided elsewhere [20].

2.3. Catalyst Characterization

2.3.1. Thermal Gravimetric Analysis

The thermal behavior of the catalyst was evaluated using a bench model thermal gravimetric analyzer (Perkin Elmer TGA7), as the sample (20 g) was heated at 900 °C in high flow of nitrogen (100 mL/min) with a ramp of 20 °C per min. The weight change was recorded as related to water removal, possible carbon burning, and metal oxidation using Equations (1) and (2):

2.3.2. Morphological Characterization

A high-resolution scanning electron microscope (Hitachi S-3000N Standard VP-SEM, High Technologies, Schaumburg, IL, USA) equipped with a scatter electron detector (BSED) and a thermoionic electron source, which allows for imaging in the compositional, 3D, and topographic modes from each segment of the detector, was used to conduct this test. The VP-SEM contained an energy-dispersive X-ray spectrometer (ISIS 300 EDX), which offered a speed map point and an area analysis that facilitated the investigation of the macroscopic distribution of the oxides crystallites and the quantitative analysis of the metals in the catalyst. The sample was prepared by pressing the powder on an aluminium sample holder coated with graphite glue, which was utilized to conduct electrons, thus stopping the charge build up. A desk II gold sputter cathode unit (Denton Vacuum, Moorestown, NJ, USA) was used to clean the surface and to deposit an ultra-thin layer of a heavy metal conductive coating (Au) on the sample. The morphology and porosity of the catalyst samples were confirmed and measured by transmission electron microscopy (Standard TEM Hitachi kF-3300 300 kV). The solid catalyst was homogeneously dispersed in a pure acetone using a water bath (54 °C) and then deposited in a copper grid to allow the evaporation of solvent under atmospheric air before analysis.

2.3.3. Brunauer–Emmett–Teller (BET) Characterization

The BET surface area and pore volume of the catalysts were determined using a Gemini 2375 adsorption equipment (Micromeritics ASAP 2000 analyzer, Instruments Corp., Dallas, TX, USA) at liquid nitrogen temperature after the pretreatment of the catalysts at 100 °C under the flow of helium for 1 h.

2.3.4. X-ray Diffraction

The X-ray diffraction measurement of CaO on Al₂O₃ catalysts was performed on a Multiflex X-ray diffractometer (Rigaku America Corporation, The Woodlands, TX, USA) using Cu-K α radiation with a wavelength of 1.540 Å at 40 kV and 20 mA. The scan range was 15°–85° at a rate of 1 °/min. The diffraction pattern was recorded in the continuous scan mode utilizing a sample of 0.04°. Diffraction peaks of crystalline phases were contrasted with those of standard compounds reported in the International Centre for Diffraction Data (ICDD).

2.4. Fatty Acids Methyl Esters Production

2.4.1. Pretreatment and Assay for Total Free Fatty Acid Content of the Feedstock

The waste vegetable oil (WVO) was vacuum-filtered to remove all the suspended solid materials, phospholipids, and other impurities prior to transesterification by base–acid catalysts. The filtered oil was heated at 110 °C for 30 min to evaporate the water present [21]. The total free fatty acid (FFA) content in the oil was determined to avoid saponification, the formation of gels, and the formation of foam as well as to ease glycerol and catalyst separation [22]. The free fatty acid (FFA) content in the oils was determined using the titration method. The standard solution was made of 1 g KOH or NaOH diluted in 1 L of distilled water. The standard solution was added slowly to a mixture of 10 mL isopropyl alcohol and four drops of phenolphthalein until the solution turned pink. The volume of the standard solution (V_1) was recorded and subsequently (V_2) after the addition of oil (1 mL). The total free fatty acids content in the oil was determined by using the following Equation (3) [23]:

$$\text{FFA} \left(\frac{\text{mg}}{\text{g}} \right) = (V_2 - V_1) \times \frac{1.4}{\rho_{\text{oil}}} \quad (3)$$

2.4.2. Production of Fatty Acid Methyl Esters

WPO (50 mL) was maintained at a constant temperature of 65 °C in a water bath. The reactor used was equipped with a mechanical agitator set at a speed of 700 rpm and a condenser that was connected to the mouth of the reactor vessel for the heat transfer and cooling system. An illustration of the experimental setup is shown in Figure 1.

Figure 1. Simultaneous esterification and transesterification setup.

The mixture of $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst (4 wt %) and methanol (450 mL) was carefully added to the WPO (methanol/oil ratio of 9:1) in a glass reactor and allowed to react for 4 h. After cooling at room temperature, the mixture was transferred to a separating funnel where the glycerol and catalyst were separated from the solution by gravity overnight in order to facilitate the separation of FAME and glycerol/solid catalyst phase. The glycerol phase (bottom layer) was removed, and the methyl ester phase (upper layer) was washed with water to remove the vestige of methanol, catalyst, and glycerol. The procedure was repeated for WSO at different combinations of CaO /alumina ratios (by varying the CaO ratio as 60, 70 and 80%). The methanol-to-oil molar ratio of 9:1 and 4 wt % of the

catalyst concentration based on the oil were kept constant. The methyl esters phase was weighed and analyzed using a gas chromatography-mass spectrometry (GC-MS) after separation to determine the oil conversion and FAME yield.

2.5. Product Analyses

FAME is produced via the transesterification reaction of the WVO with methanol in the presence of a catalyst; and in this study, a bifunctional heterogeneous catalyst was used to form methyl esters of the triglycerides. The product stream was analyzed for the presence of FAME, unreacted feedstock (triglycerides), residual methanol, and glycerol. The composition and quantity of fatty acids (FAs) in the WVOs and in the synthesized FAME were determined using gas chromatograph-mass spectrometry (GC-MS). A sample was injected into the GC using a 7980B Agilent Technologies Injector with a CTC CombiPAL auto-sampler and Agilent 5975B MS. The oven was programmed at 150 °C (1 min), 180 °C (4 min), and 325 °C (20 min) before Ramp1 (25 °C/min) and Ramp2 (4 °C/min). Pure helium was used as the carrier gas at an injection volume of 1 µL (Mode ratio, 15:1), a flow rate of 1 mL/min, and an injection temperature set at 280 °C (40–550 *m/z*, Energy: 70 eV). Heptadecanoic acid (C17:0; C₁₇H₃₄O₂ or margaric acid) was used as the internal standard, and the FAME yield was calculated. This proved to be a reliable technique as heptadecanoic acid methyl ester is a saturated ester and does not participate in the reaction. The FA profile was compared with the literature values to authenticate the determination. The FA was compared with the fraction of the total peak area attributed to each by the GC-MS mass spectrum libraries and normalized to the heptadecanoic acid methyl ester peak. In calculating the FAME produced, the concentration of the internal standard was multiplied by the peak ratio of the FAME to the internal standard. The yield of FAME was expressed as illustrated in Equation (4) [24]:

$$\text{FAME Yield (\%)} = \frac{\text{Weight of FAME produced (g)}}{\text{Weight of oil used (g)}} \times 100 \quad (4)$$

where the weight of oil was 50 g and the FAME produced from each run was acquired from the GC-MS results.

2.6. Catalyst Reusability

The ability of the solid catalysts to carry out similar catalytic activity repeatedly was assessed by means of performing experimental runs right after the first batch at the same optimum conditions attained for the maximum FAME yield. The solid catalyst was recovered and washed using n-hexane and methanol to get rid of any remains of oil and/or glycerol that is adsorbed to the surface after the first reaction. Afterwards, it was filtered and dried in an oven for 12 h, followed by calcination in air at 750 °C, after which it was used for second consecutive transesterification runs in a new reaction cycle at the same conditions using WSO and WPO to obtain FAME.

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. Thermal Behavior

Thermal gravimetric analysis performed on the heterogeneous catalysts to obtain the optimum calcination temperature and to remove the poisoning species—mainly H₂O and carbonate as well as to expose the basic sites—revealed that there was a minimal weight loss until 300 °C. The decrease noticed between 300 and 500 °C can be attributed to the removal of H₂O, as shown in Figure 2. The 40% reduction in weight at 750–900 °C (Figure 2) was as a result of the generation of calcium and aluminium oxides owing to the surface hydroxides decomposition [25].

Figure 2. Thermal gravimetric analysis of 80% calcium hydroxide/aluminium hydroxide filtrate.

3.1.2. Ultrastructure and Morphological Analysis

The morphology of the catalyst was studied using SEM-EDX (scanning electron microscopy with energy dispersive X-Ray) analysis. This showed the formation of aggregated (interconnected) particles of a calcined sample (750 °C) [20]. The elemental composition of the areas examined on 80%CaO/Al₂O₃ catalyst sample is shown in Table 1. The analysis of the catalyst confirmed the presence of Ca (CaO) and Al (Al₂O₃). The elemental composition of the 80%CaO/Al₂O₃ catalyst revealed that the percentage of Ca (41.41 wt %) and O (49.62 wt %) were higher than that of Al (8.97 wt %). The catalysts demonstrated analogous morphology, and there was no specific shape that can be derived from the image except for the rough surfaces of the solid materials [20]. Ca particles were distributed on Al. Hence, it can be concluded that the presence of Al₂O₃ contributed significantly to the high catalytic activity observed during the transesterification of WPO and WSO. This also revealed that there was a significant homogeneity of the CaO/Al₂O₃ catalyst, which was visible from the value of Al and Ca acquired from the EDX analysis (Table 1). The morphology of the 80%CaO/Al₂O₃ catalyst particles from TEM further revealed that most of the particles were in the range of 10–100 nm of porosity and confirmed as the rectangular shape [20], which was in accordance with the study performed by Yalman [26], and these are relatively uniformly distributed. The catalyst particles exhibited high efficacy during the transesterification of triglyceride, irrespective of the FFA present in the WPO and WSO.

3.1.3. Brunauer–Emmett–Teller (BET) Characterization

The textural properties of the solid base–acid catalysts at a calcination temperature of 750 °C were observed through BET measurement with the surface area of pure CaO and Al₂O₃ recorded as 3.8624 m²/g and 539.2541, respectively (Table 2). The surface area of the CaO/Al₂O₃ catalyst increased to 8.5683 m²/g after its preparation via co-precipitation and thermal activation. Nevertheless, a significant reduction of pore volume of Al₂O₃ was observed. Calcination at high temperature is necessary to thermally activate metal hydroxides into an active metal oxides catalyst for transesterification reaction [4].

Table 1. EDX analysis of the selected areas (weight %) of 80%CaO/Al₂O₃.

Samples	Al	Ca	O
1	10.73	36.33	52.94
2	8.38	40.32	51.31
3	9.06	46.54	44.4
4	8.04	45.76	46.2
5	10.05	33.68	56.27
6	10	38.29	51.71
7	7.8	41.35	50.85
8	8.63	32.28	59.09
9	10.36	45.8	43.84
10	6.7	53.73	39.57
Minimum	6.7	32.28	39.57
Maximum	10.73	59.09	53.73
Std. Dev.	1.3	6.63	6.03
Mean	8.97	41.41	49.62

Table 2. Catalysts' Brunauer–Emmett–Teller (BET) properties.

Parameters	CaO	Al ₂ O ₃	80%CaO/Al ₂ O ₃
Area, m ² /g	3.8624	539.2541	8.5683
Total pore volume, cm ³ /g	0.019392	1.297447	0.045008
Average Pore size, Å	200.8361	96.2401	210.1157

3.1.4. Bulk Phase of the Catalyst

The diffraction patterns of CaO/Al₂O₃ at catalyst ratios (wt %) of 60, 70 and 80% showed the CaO crystalline phases ranging from 20.0° to 40.0° (2θ) [20]. This corroborates the vast distribution of CaO particles in all CaO on Al₂O₃ catalysts. Pasupulety et al. [27] observed similar characteristics of a crystalline CaO phase at a 2θ range of 30.0–37.0° for 20% CaO/Al₂O₃. This disparity in the location of the peaks could be attributed to the equipment settings and/or catalyst preparation technique used in the study. Moreover, the samples were open to atmospheric conditions, prior to and during the XRD measurements. A high dispersion of CaO on Al₂O₃ gave rise to high activity and bulk particle formation by the crystallization of CaO, which may cause the decrease of active sites, leading to the reduction of activity.

3.2. Characterization of Oil Samples

The profiles of the WVOs used in the current study are presented in Tables 3–5. The samples were composed mostly of triglycerides including palmitic acid, stearic acid, as well as a high quantity of unsaturated FA, especially oleic and linoleic acids (Table 4). The WPO contained 18.68% saturated and 17.52% unsaturated FAs with a high quantity of short-carbon chains of palmitic (16.56%) and oleic (14.11%) acids (Table 3), while WSO consisted mostly of oleic (17.04%) and stearic (5.93%) acids (Table 4). This was in line with the findings reported by Saifuddin et al. [28], where the major FAs present in the waste oils were palmitoleic, palmitic, linoleic, oleic, and stearic acid. The analysis of WSO indicated the presence of nine types of FA, specifically palmitic acid, margaric acid, linolelaidic acid, oleic acid, stearic acid, linoleic acid, arachidic acid, behenic acid, and hexadecadienoic acid; with linolelaidic acid being present in significant amounts (48.56%) followed by oleic acid (25.64%) compared to other FA (Table 4). Whereas for WPO, four FA types were identified: oleic acid, stearic acid, palmitic acid, and linoleic acid. WPO showed high levels of palmitic acid (40.52%) and oleic acid (40.89%) when compared to other FA (Table 5). The total FAs content of WSO was lower (29.18%) compared to WPO (36.2%) (Table 3). Thus, WSO has a better potential as a feedstock for FAME production. The WSO and WPO samples were characterized by FFA contents of 0.3825 mg/g and 76.96 mg/g, respectively. High FFA content (>1% w/w) during the transesterification of glycerides with alcohol in the presence

of a catalyst can cause saponification and challenge in the products separation, and consequently a low yield of FAME [3,6,10]. Therefore, it is crucial to determine the FFA content of the oil prior to use. Different kinds of vegetable oils contain a diverse composition of FAs, which may lead to distinct activities during the transesterification reactions [29].

Table 3. Analysis of total fatty acid (FA) content of the waste vegetable oil (WVOs). WPO: waste palm oil, WSO: waste sunflower oil.

Fatty Acids	WSO (Mass %)	WPO (Mass %)
Palmitic acid (C16:0)	5.99	16.56
Stearic acid (C18:0)	5.93	1.91
Arachidic acid (C20:0)	0.22	0.21
Lignoceric acid (C24:0)	0	0
Palmitoleic (C16:1)	0	0
Oleic acid (C18:1c)	17.04	14.11
Linoleic acid (C18:2c)	0	3.41
Total	29.18	36.2

Table 4. Characterization of WSO.

Fatty Acids	wt %
Heptane, 2,2,4,6,6-pentamethyl	0.1808
4-Methyldecane	0.277
Hexane, 3,3-dimethyl	0.4396
3,6-Dimethyldecane	0.2217
Octane, 5-ethyl-2-methyl	0.1093
Dodecane, 2-phenyl-	0.3037
Indanol-5	0.3677
2,4-Dimethylheptane	0.2818
Pentadecane	0.3578
Diethyl Phtalate	0.6016
Nonadecane	0.2484
Phenol, 2,4-bis(1,1-dimethylethyl)	1.4815
n-Pentacosane	0.3449
triacontane	0.2417
Hexadecanoic acid or Palmitic acid	7.6173
Heptadecanoic acid or Margaric acid	0.8198
9,12-Octadecadienoic acid or Linolelaidic acid	48.5629
9-Octadecenoic acid or Oleic acid	25.6451
Octadecanoic acid or Stearic acid	7.6528
Linoleic acid	1.0534
5-Dodecyne	0.2022
Eicosanoic acid or Arachidic acid	0.2815
Docosanoic acid or Behenic acid	1.4139
Hexadecadienoic acid	1.2934

3.3. Yield of Fatty Acid Methyl Esters

According to the previous studies, a methanol-to-oil molar ratio of 9:1 is satisfactory for a high yield and complete conversion of triglycerides to methyl esters [28,30]. The optimum catalyst loading of 4 wt % was selected for the transesterification of both waste oils. Farooqa et al. [31] reported that an increase in catalyst loading above 5 wt % leads to an increase in the mixture viscosity and a decrease in the yield of FAME. The effect of the catalyst ratio on the yield of FAME was investigated by varying the CaO ratio at a range of 60–80%. The purification process was effective, as no traces of glycerol were observed in the FAMES produced. The maximum FAME yield of 98% was achieved at 80%CaO/Al₂O₃ when WSO was used, while a maximum yield of 89% was obtained at a 60%CaO/Al₂O₃ catalyst ratio

for WPO. Details are provided elsewhere [20]. This could be attributed to the fact that WPO consisted of a higher amount of FFAs (76.96 mg/g) compared to WSO (0.3825 mg/g), thus requiring a higher quantity of acidic sites (Al_2O_3) to esterify the FFAs and facilitate the conversion of triglycerides to FAME in conjunction with the basic sites (CaO) and thus achieve a high FAME yield. This decrease in FAME yield with increased CaO loading could also be an indication of the impact of external mass transfer constraints originated by the generation of products, for instance the FAME and by-product (e.g., glycerol).

Table 5. Characterization of of WPO.

Fatty Acids	wt %
2,2,4,6,6-Pentamethylheptane	0.223
n-Nonadecane	0.3331
S-Butylbenzene	0.2269
n-Octadecane	0.4567
2,4-Di-tert-butylphenol	1.9877
n-Docosane	0.4907
Hexadecanoic acid or Palmitic acid	40.5223
Heptadecanoic acid or Margaric acid	0.8483
11,14-Octadecadienoic acid or Linoleic acid	7.689
8-Octadecenoic acid or Oleic acid	40.8909
Octadecanoic acid or Stearic acid	6.3312

According to Yalman [25], such constraints are only avoidable at a higher stirring speed of approximately 1300 rpm. There was no stirrer with the capability of more than 1000 rpm readily available for use. This decrease in yield could also be attributed to the variation in the particle size of the $\text{CaO}/\text{Al}_2\text{O}_3$ catalysts, which might have caused a decrease in its catalytic activity during the reaction systems. Lee et al. [4] reported that the activity of a catalyst is dependent on the particle size. Thus, smaller catalyst particles are supposed to demonstrate a higher reaction rate owing to an increase in the external surface area available. On the other hand, the bigger the particle size of a solid, the smaller the surface area available for the reaction to take place, and the reduction in the number of collisions between the molecules (solid–liquid phase) during the reaction.

The further applicability of the FAME produced in the current study, for the production of surfactants for enhanced oil recovery, has been reported elsewhere [20].

3.4. Reusability

The economic potential of $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst was evaluated via the reusability tests, which represents its capacity to perform the same catalytic activity conducted on WSO and WPO. The methanol-to-oil molar ratio of 9:1 and 4 wt % catalyst loading at 65 °C for 4 h utilized to achieve the initial FAME yield was sustained. Figure 3 shows the reusability of the $\text{CaO}/\text{Al}_2\text{O}_3$ catalysts. It was observed that the FAME yield displayed a descending trend due to the influence of deactivation or a decrease in the number of catalyst active sites as well as the reduction in the weight of the catalyst as a result of process operations, which is common to heterogeneous catalysts [30,32]. The maximum FAME yields of 98 and 80% were attained in the use of WSO for the first and second run, respectively. Conversely, for WPO, the first and second maximum FAME yields of 89 and 77% were recorded respectively. The active sites' deactivation with time could be due to various possible phenomena, such as coking, sintering, poisoning or leaching [30,33]. The blockage of the active sites by poisoning is evident when the process involves used oils with impurities in the form of pigments, food debris, oxidized fats, non-hydratable lecithins and various other non-lipid substances [33]. The loss of catalytic activity can also be attributed to leaching during the process, which increases the contamination of the product and the operational cost on account of substituting the catalyst [30,32,34].

Figure 3. Reusability of CaO/Al₂O₃ catalysts at optimum reaction conditions.

4. Conclusions

Numerous categories of heterogeneous catalysts have been investigated for transesterification. Nevertheless, there is still a need for meticulous studies to be conducted on feedstock containing high amounts of FFA. In this study, the use of bifunctional catalyst in the transesterification of waste vegetable oil was successful, notwithstanding the presence of free fatty acids. The optimum reaction conditions of temperature (65 °C), oil-to-methanol molar ratio (1:9), catalyst/oil loading (4 wt %), and reaction time (4 h) employed resulted in high FAME yield (89% for WPO and 98% for WSO). The results showed that 60% CaO/40% alumina by weight catalyst, calcined at high temperature of 750 °C for activation into metal oxides and transesterification reaction, effectively mediated the transesterification of WPO ([FFA] = 76.96 mg/g). However, due to the lower FFA content in WSO (0.3825 mg/g), a lower ratio of the acidic oxide was required, 80% CaO/20% alumina by weight catalyst. As shown in this study, an active bifunctional catalyst with high CaO dispersion could be prepared via the co-precipitation method as confirmed by the SEM analysis. However, the basic–acidic oxide ratio to be employed is dependent on the type of WVO and its FFAs content. The FFAs content of WSO was 29.18% compared to 36.2% for WPO, which gave WSO better potential as a feedstock for FAME production. The esterification/transesterification reactions of WPO and WSO with CaO/Al₂O₃ bifunctional catalyst resulted in the high yield of FAMES: 89% for WPO and 98% for WSO at catalyst ratios (wt %) of 60% and 80% respectively. The WVO have great potential as an alternative source of marketable FAME, which is an environmentally friendly and cheap energy to replace fossil fuel.

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