catalysts

Article

Nano-Magnetic CaO/Fe_2O_3/Feldspar Catalysts for the Production of Biodiesel from Waste Oils

Maryam Hanif [1], Ijaz Ahmad Bhatti [1], Muhammad Asif Hanif [1], Umer Rashid [2,3,*], Bryan R. Moser [4], Asma Hanif [5] and Fahad A. Alharthi [6]

[1] Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan; drmaryamhanifchemist@gmail.com (M.H.); ijazchem@gmail.com (I.A.B.); drmuhammadasifhanif@gmail.com (M.A.H.)
[2] Institute of Nanoscience and Nanotechnology (ION2), Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia
[3] Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals (CBRC), Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[4] Bio-Oils Research Unit, National Center for Agricultural Utilization Research, United States Department of Agriculture, Agricultural Research Service, Peoria, IL 61604, USA; bryan.moser@usda.gov
[5] Department of Chemistry, Government College Women University, Faisalabad 38000, Pakistan; asmarana_hanif@yahoo.com
[6] Chemistry Department, College of Science, King Saud University, Riyadh 1145, Saudi Arabia; fharthi@ksu.edu.sa
* Correspondence: umer.rashid@upm.edu.my or dr.umer.rashid@gmail.com; Tel.: +60-3-97697393

Abstract: Production of biodiesel from edible vegetable oils using homogenous catalysts negatively impacts food availability and cost while generating significant amounts of caustic wastewater during purification. Thus, there is an urgent need to utilize low-cost, non-food feedstocks for the production of biodiesel using sustainable heterogeneous catalysis. The objective of this study was to synthesize a novel supported nano-magnetic catalyst (CaO/Fe_2O_3/feldspar) for the production of biodiesel (fatty acid methyl esters) from waste and low-cost plant seed oils, including *Sinapis arvensis* (wild mustard), *Carthamus oxyacantha* (wild safflower) and *Pongamia pinnata* (karanja). The structure, morphology, surface area, porosity, crystallinity, and magnetization of the nano-magnetic catalyst was confirmed using XRD, FESEM/EDX, BET, and VSM. The maximum biodiesel yield (93.6–99.9%) was achieved at 1.0 or 1.5 wt.% catalyst with methanol-to-oil molar ratios of 5:1 or 10:1 at 40 °C for 2 h. The CaO/Fe_2O_3/feldspar catalyst retained high activity for four consecutive cycles for conversion of karanja, wild mustard, and wild safflower oils. The effective separation of the catalyst from biodiesel was achieved using an external magnet. Various different physico-chemical parameters, such as pour point, density, cloud point, iodine value, acid value, and cetane number, were also determined for the optimized fuels and found to be within the ranges specified in ASTM D6751 and EN 14214, where applicable.

Keywords: biodiesel; nano-magnetic catalyst; feldspar; transesterification; waste oils

check for updates

Citation: Hanif, M.; Bhatti, I.A.; Hanif, M.A.; Rashid, U.; Moser, B.R.; Hanif, A.; Alharthi, F.A. Nano-Magnetic CaO/Fe_2O_3/Feldspar Catalysts for the Production of Biodiesel from Waste Oils. *Catalysts* **2023**, *13*, 998. https://doi.org/10.3390/catal13060998

Academic Editors: José María Encinar Martín and Sergio Nogales Delgado

Received: 18 April 2023
Revised: 30 May 2023
Accepted: 4 June 2023
Published: 13 June 2023

Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Energy plays a critical role in economic growth and modern society. Moreover, economic development greatly depends on the long-term availability, security, and affordability of energy. Over the last 30 years there has been a dramatic increase in world-wide energy demand due to the emergence of developing economies and continued population growth [1]. The ever-increasing use of nonrenewable energy is not sustainable due to the irregular geographic distribution of resources as well as environmental, climatic, geopolitical, and economic concerns associated with their continued use [2]. In addition, the combustion of fossil fuels releases greenhouse gases that renders nonrenewable energy unsustainable and environmentally damaging [3].

Biodiesel represents a renewable, sustainable, and environmentally friendly alternative to petroleum diesel for combustion in compression-ignition (diesel) engines. Biodiesel is composed of fatty acid methyl (or ethyl) esters prepared from plant oils, waste lipids, used cooking oils, or other triglycerides and is typically prepared by alkaline-catalyzed transesterification. Biodiesel is a clean burning fuel with low exhaust emissions, high biodegradability, and minimal heteroatom residues. Biodiesel is an important alternative energy source because of its safe and renewable nature. Biodiesel has significantly reduced emissions of sulfates, particulate matter, unburnt hydrocarbons, and polycyclic aromatic hydrocarbons relative to petroleum diesel. In addition, net CO_2 emissions are not increased through the combustion of biodiesel because greenhouse gases are recycled as CO_2 by plants during photosynthesis [4]. Biodiesel is more environmentally friendly because it significantly reduces net CO_2 emissions versus petroleum diesel and is biodegradable and non-toxic [5].

In the biodiesel industry, the choice of raw material is extremely vital, as 80% of the cost to prepare biodiesel is associated with feedstock cost [6]. Edible feedstocks compete with food uses, deplete freshwater supplies, and crucially require large areas of fertile land [7]. In addition, production costs have increased 70–92% due to escalate in the cost of edible oils. These factors have stimulated interest in biodiesel production from non-edible oils [8]. Lately, low-cost waste oils have been under consideration as a potential feedstock alternative for BD production. In the current study, biodiesel was produced from waste/low-cost plant seed oils, including *Carthamus oxyacantha* (wild safflower), *Sinapis arvensis* (wild mustard) and *Pongamia pinnata* (karanja).

Predominantly, homogeneous catalysts are normally used for the industrial production of biodiesel due to their high catalytic activities and low cost. However, these catalysts cannot be reused, and the removal of dissolved homogeneous catalysts is tedious. Additionally, numerous processing steps are necessary, such as neutralization, washing, and dehydration. Thus, the major disadvantages of homogeneous catalysis are wastewater generation, extensive post-processing, and incompatibility with low-quality, low-cost feedstocks [9].

Heterogeneous catalysts have important advantages over homogeneous catalysts because they catalyze important chemical reactions associated with green chemistry that are environmentally friendly and economically favorable [10]. However, they often require high reaction temperatures and pressures, and catalytic performance is generally lower than homogeneous catalysts. Furthermore, coking, leaching, poisoning, and sintering may result in the deactivation of heterogeneous catalysts over time.

Nanomaterials have served as ideal supports for the preparation of solid acid catalysts because they possess large surface areas and can minimize mass transfer resistance [11]. Unfortunately, for small-size solid catalysts, their recovery and reutilization through the commonly used filtration or centrifugation approaches is difficult, especially with high-viscosity reaction systems (generally soybean oil has high viscosity). In such cases, a large amount of catalyst is lost during separation. Magnetic heterogeneous nano-catalysts are of interest because they have a higher surface area, which imparts greater catalytic activity relative to lower-surface-area solid catalysts. In addition, magnetic catalysts can be easily separated from reaction mixtures without the generation of large amounts of caustic wastewater [12,13].

Various common ferromagnetic materials, such as Fe_3O_4 and γ-Fe_2O_3, can be used as magnetic catalysts or catalyst supports. After modification and functionalization, they not only retain their magnetic properties but can also be quickly and easily separated when an external magnetic field is applied. Ferrites have considerable porosity, good chemical properties, high contact area, and high thermal stability, culminating in a more effective catalyst for the production of biodiesel [11]. Agglomeration in magnetite synthesis is very difficult to avoid, because of its magnetism. Thus, the selection of a suitable catalytic support has been of immense interest. Typically, a solid support with a high surface area is used to attach catalysts. Supports prevent the sintering and agglomeration of small catalyst particles, revealing additional surface area [14]. Most catalytic supports are zirconium dioxide, aluminum oxides, alumino silicates, magnesium oxide, silica gel, and titanium oxide [15]. Clay materials, compared to other supports, have the advantages of high quantity, low-priced, environmental compatibility, high selectivity, reusability, and operational simplicity [16].

The primary objective of this study was the synthesis of the novel supported nano-magnetic catalyst CaO/Fe_2O_3/Feldspar to produce biodiesel from waste/low-cost plant seed oils, including *Carthamus oxyacantha* (wild safflower), *Sinapis arvensis* (wild mustard) and *Pongamia pinnata* (karanja). The novel catalytic support which is low-cost feldspar (a clay mineral) was also prepared and characterized. Other objectives included the optimization of the transesterification reaction and characterization of the resulting biodiesel and catalytic materials.

2. Results and Discussion

2.1. Characterization of CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar Nano-Magnetic Catalyst

2.1.1. XRD Analysis

The XRD patterns of the nano-magnetic catalyst CaO/Fe_2O_3/feldspar and CaO/Fe_2O_3 are depicted in Figure 1. The results indicated that the CaO/Fe_2O_3/feldspar has several peaks at different angles, which indicated a crystalline structure. The prominent peaks were observed at 2θ = 30°, 32.34°, 35.55°, 37.36°, 43.5°, 53.61°, 63.15°, and 64.27°, which was attributed to the crystalline phases of (220), (111), (311), (200), (422), (511), (440), and (311), respectively (ICSD File No. 00-006-0711 and 00-032-0168) [17] [Maryam et al. 2021]. These indicated that Fe_2O_3 and CaO were present in the structure of the catalyst [16]. The intense sharp diffraction peaks within 2θ = 25–30° and the specifically intense peak at 27.4° suggested the presence of feldspar [18], which possessed a uniform structure and pore diameter. The narrow peaks showed the single phase of a highly ordered structure, which was indicated in the FESEM analysis as well (Figure 2). The crystal size of CaO/Fe_2O_3/feldspar nanoparticles calculated from the Scherrer equation was 45.73 nm.

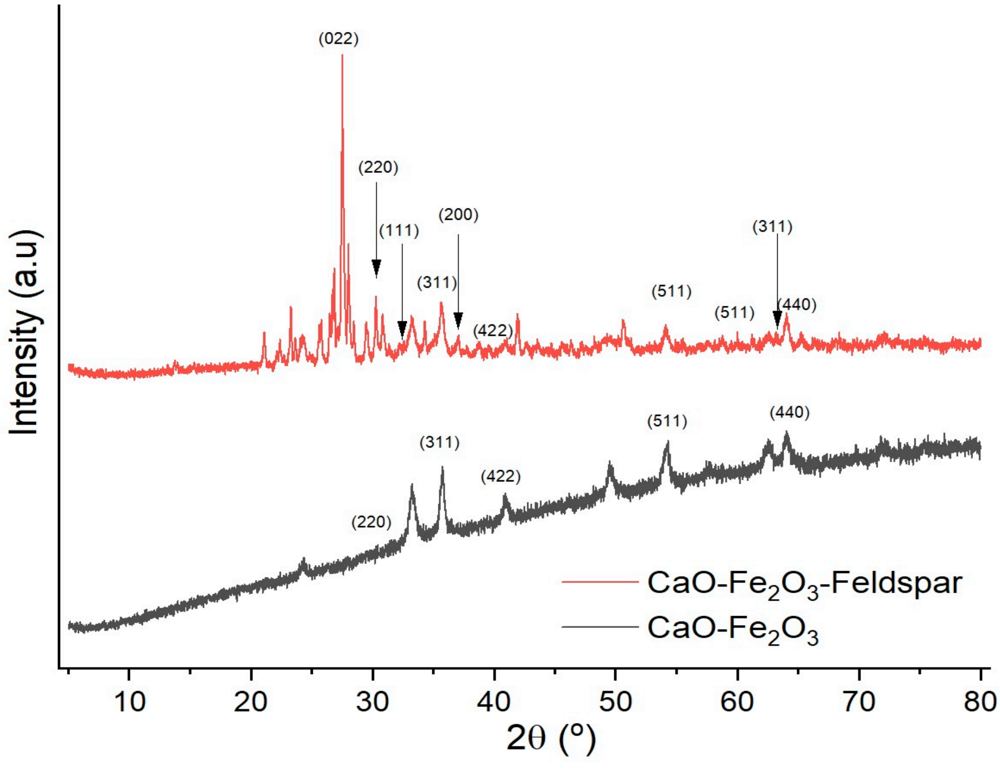
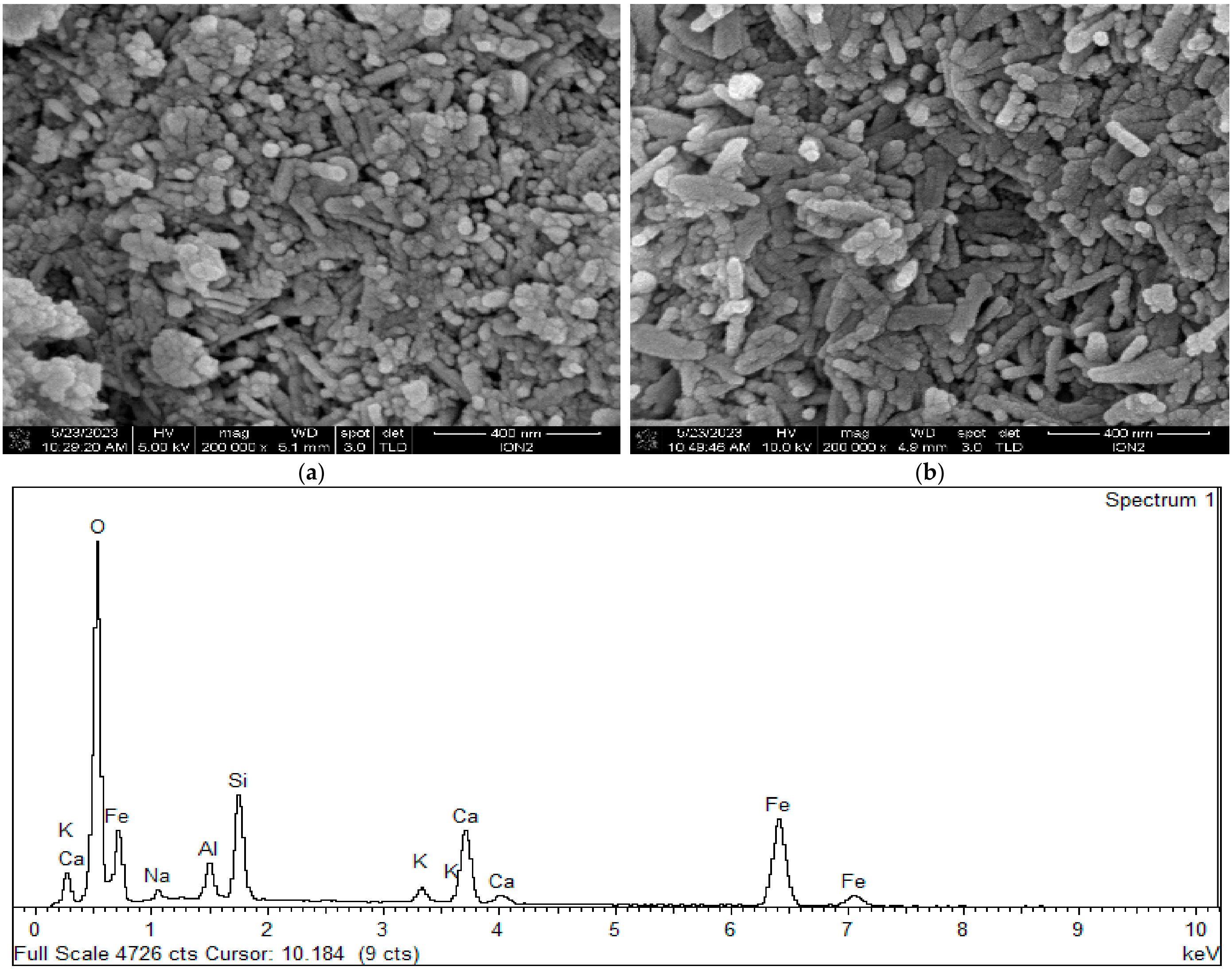


Figure 1. XRD analysis of CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar.



(**a**) (**b**)

(**c**)

Figure 2. FESEM images of (**a**) CaO/Fe_2O_3, (**b**) CaO/Fe_2O_3/feldspar and (**c**) EDX analysis of CaO/Fe_2O_3/feldspar.

2.1.2. FESEM and EDX Analysis

Figure 2a,b depict different surface roughness, particle sizes, and arrangement of particles, which is very important for the conversion of oil into biodiesel. Figure 2a shows the agglomeration and coral-like shape, whereas the CaO-Fe_2O_3 composite attached to the surface of feldspar (Figure 2b) indicates a morphology of well-arranged small platelets laced with pores. The surface morphology by SEM thus confirmed the successful synthesis of the CaO-Fe_2O_3 nano-catalyst supported on the feldspar, which was also indicated by the EDX analysis. A close inspection of the spectra revealed an exact wt.% of O (43.46%), Na (0.99%), Al (2.18%), Si (6.69%), K (1.34%), Ca (8.66%), and Fe (36.68%) elements in the CaO/Fe_2O_3/feldspar catalyst, as presented in Table 1. Based on the EDX analysis, the CaO-Fe_2O_3 was rich in Fe with a 59.82 wt.% composition. The large amount of O (37.12 wt.%) and Ca (3.06 wt.%) indicated that the CaO/Fe_2O_3 was pure. The results confirmed that the CaO-Fe_2O_3 was efficiently supported on the feldspar matrix without distorting the elemental ratio. The quantitative data derived from the EDX analysis for the CaO/Fe_2O_3/feldspar is presented in Figure 2c.

Table 1. EDX analysis of CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar.

Catalyst	**Element (wt.%)**							
	O	**Na**	**Al**	**Si**	**K**	**Ca**	**Fe**	**Total**
CaO/Fe_2O_3	37.12	-	-	-	-	3.06	59.82	100
CaO/Fe_2O_3/feldspar	43.46	0.99	2.18	6.69	1.34	8.66	36.68	100

2.1.3. Porosity and Surface Area Analysis

Results indicating the surface area, pore volume, and average pore size of the CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar are presented in Table 2. The CaO/Fe_2O_3 displayed a surface area of 68.680 m^2/g, pore volume of 0.189 cm^3/g, and average pore size of 7.670 nm. After the synthesis of the CaO/Fe_2O_3/feldspar, the surface area was 19.523 m^2/g with a pore volume of 0.060 cm^3/g and an average pore size of 7.911 nm. After the doping of feldspar, the surface area and pore volume of the CaO/Fe_2O_3/feldspar catalyst were higher than those of K-feldspar [17]. When the CaO/Fe_2O_3 was doped with feldspar, the surface area was reduced due to a blockage of pores by feldspar. Figure 3 illustrates the nitrogen adsorption–desorption isotherms of the CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar. The N_2 adsorption–desorption isotherms exhibited a typical type IV adsorption–desorption isotherm of CaO/Fe_2O_3/feldspar [19]. The mesoporous pore size of the CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar were consistent, as shown in Figure 3.

Table 2. Surface property analysis of CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar.

Catalyst	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Size (nm)**
CaO/Fe_2O_3	68.680	0.189	7.670
CaO/Fe_2O_3/feldspar	19.523	0.060	7.911

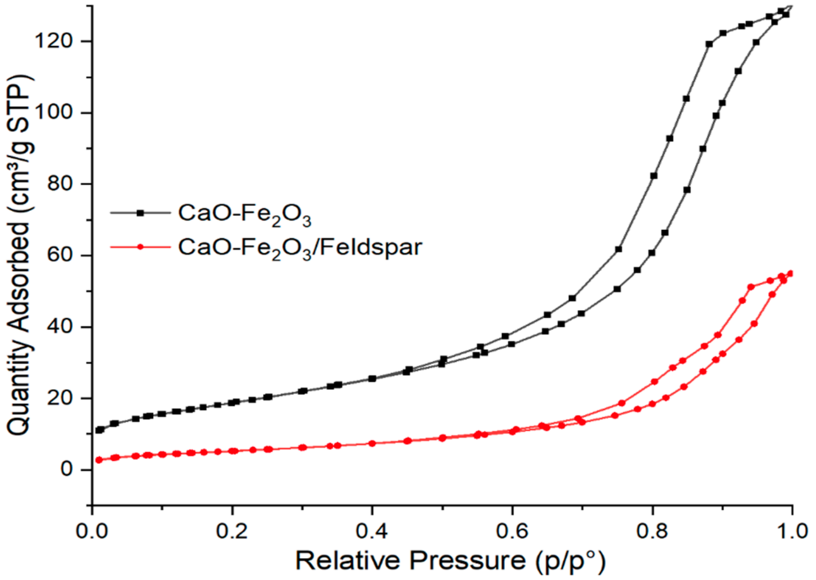


Figure 3. N_2 adsorption–desorption isotherms of CaO/Fe_2O_3 and CaO/Fe_2O_3 /feldspar.

2.1.4. VSM Analysis

The magnetic properties of the CaO/Fe_2O_3/feldspar catalyst were determined using VSM, as presented in Figure 4. The VSM results revealed that the M-H loop of the produced nano-magnetic catalysts had a magnetization of 22.15 emu/g. The VSM curve for the CaO/Fe_2O_3/feldspar in the absence of hysteresis curves is representative of normal super-paramagnetic behavior at room temperature. These results confirmed that the iron-containing feldspar catalysts can be easily separated from the reaction mixture by using an external magnet.

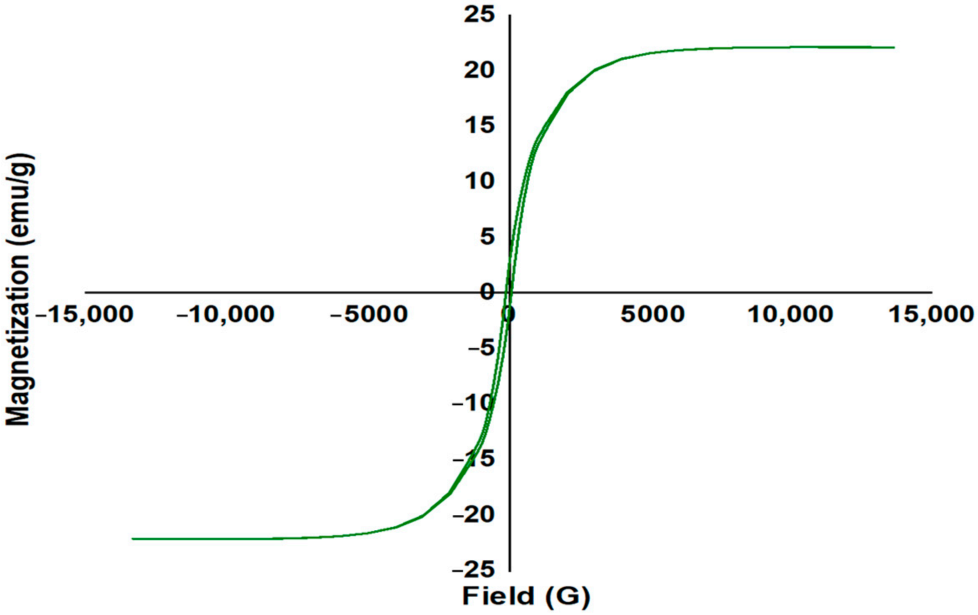


Figure 4. VSM analysis of CaO/Fe_2O_3/feldspar.

2.2. Optimization of Transesterification Reaction Process Parameters

The impact of two important operational reaction parameters i.e., catalyst concentration and methanol-to-oil molar ratio on the biodiesel yield of non-edible oils (wild safflower, wild mustard and karanja) in the presence of the CaO/Fe_2O_3/feldspar nano-magnetic catalyst is summarized in Table 3. The other reaction parameters were fixed at: a reaction temperature of 40 °C and a reaction time of 2 h. For karanja and wild mustard, the optimal catalyst concentration was 1.0%, which produced a maximum ester content of 89.1 ± 0.8% and 93.6 ± 0.3%, respectively. For wild safflower, a CaO/Fe_2O_3/feldspar concentration of 1.5% was adequate to complete the conversion of triglycerides into methyl esters. The utmost yield of biodiesel was obtained from wild safflower was 99.3 ± 0.7 at 1.5% catalyst concentration. Wild mustard and wild safflower oils gave highest biodiesel yields of 93.6 ± 0.3 and 99.3 ± 0.7, respectively, at a 5:1 methanol-to-oil molar ratio. Karanja oil conferred the highest biodiesel yield of 99.9 ± 0.9% at a 10:1 methanol-to-oil molar ratio. Certain levels of catalyst and methanol were required to obtain the maximum BD yield. The optimized catalyst concentration amount not only depended upon the category of catalyst used but was also dependent on the type of the feedstock oil under investigation. In addition, low catalyst levels were not sufficient to give a high conversion to methyl esters. However, increasing the catalyst concentration or the methanol-to-oil molar ratio ahead of the optimized levels resulted in decreased yields of biodiesel due to the formation of a viscous emulsion in the reaction mixture [20].

2.3. Proposed Mechanism of CaO/Fe_2O_3/Feldspar Catalyst for Transesterification

The initial step in the transformation of fatty oil into biodiesel involves the removal of a proton from methanol by the basic catalyst, resulting in the formation of a methoxide anion and a catalyst that has been protonated as shown in Figure 5. The methoxide anion then performs a nucleophilic attack on the carbonyl group of the triglyceride, leading to the formation of a tetrahedral intermediate. This intermediate subsequently produces a methyl ester and the corresponding anion of the diglyceride. The catalyst is restored in situ through proton abstraction from the catalyst by the diglyceride anion. Following the same mechanism, diglycerides and monoglycerides are consecutively converted into biodiesel and glycerol.

Table 3. Optimization reaction parameters for karanja, wild mustard, and wild safflower seed oils using CaO/Fe_2O_3/feldspar nano-magnetic catalyst.

Feedstock	Catalyst Conc. (%)	Methanol-to-Oil Ratio	Biodiesel Yield (%)
Karanja	0.5	5:1	85.0 ± 0.5
	1	5:1	89.1 ± 0.8
	1.5	5:1	87.5 ± 0.7
	2	5:1	86.0 ± 0.6
	2.5	5:1	85.6 ± 0.5
	1	10:1	99.9 ± 0.9
	1	15:1	88.1 ± 0.7
	1	20:1	85.6 ± 0.8
	1	25:1	83.7 ± 0.5
Wild mustard	0.5	5:1	85.0 ± 0.7
	1	5:1	93.6 ± 0.3
	1.5	5:1	84.7 ± 0.9
	2	5:1	82.9 ± 0.5
	2.5	5:1	81.8 ± 0.8
	1	10:1	85.4 ± 0.6
	1	15:1	83.2 ± 0.3
	1	20:1	80.5 ± 0.9
	1	25:1	79.8 ± 0.4
Wild safflower	0.5	5:1	85.0 ± 0.5
	1	5:1	85.9 ± 0.7
	1.5	5:1	99.3 ± 0.7
	2	5:1	86.5 ± 0.5
	2.5	5:1	85.0 ± 0.6
	1.5	10:1	86.0 ± 0.3
	1.5	15:1	84.5 ± 0.9
	1.5	20:1	82.3 ± 0.8
	1.5	25:1	80.4 ± 0.6

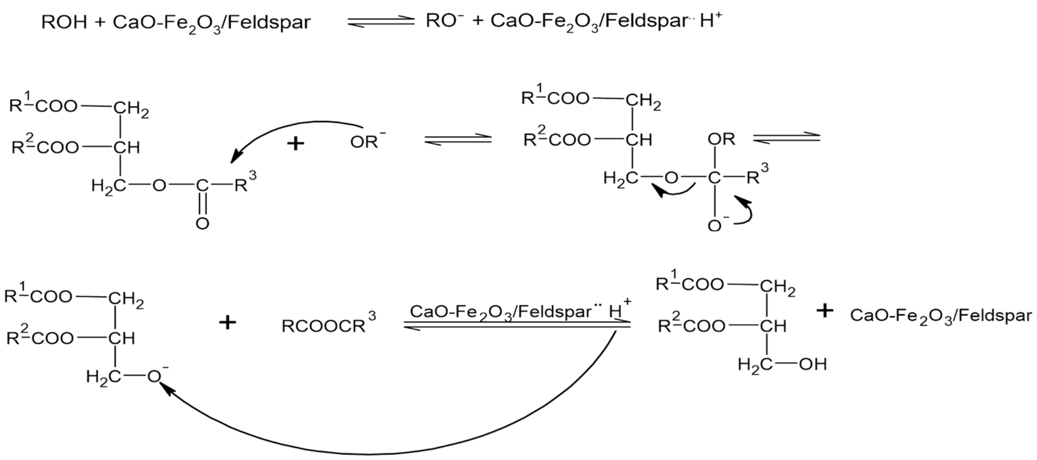


Figure 5. The proposed mechanism of CaO/Fe_2O_3/feldspar catalyst for transesterification of karanja, wild mustard, and safflower seed oil to biodiesel.

2.4. Comparison of Catalytic Activity with Published Literature Reported on Magnetic Catalysts

Table 4 summarizes results obtained from previous studies on the utilization of magnetic catalysts for the production of biodiesel. For example, Hazmi et al. [21] obtained a high FAME yield of 98.60% when applying a methanol-to-oil molar ratio of 12:1, although a higher reaction temperature of 75 °C and higher amount of catalyst loading (4 wt.%) were utilized in comparison to the current work. In another study, Ibrahim et al. [22] reported that an 18:1 methanol-to-oil molar ratio with 3 wt.% catalyst loading gave a FAME yield of 98.30%. Xie et al. [23] observed a 99.20% conversion rate; however, this was at a high methanol-to-oil molar ratio and reaction time of 8 h compared to the present study (2 h). Krishnan et al. [24] obtained a FAME yield of 87.32% with a catalyst loading of 10 wt.%, which was very high in comparison to the present study. Ali et al. [25] also achieved a higher esters yield but the reaction conditions were higher than our study (Table 4). Overall, the FAME yield is primarily impacted by the methanol-to-oil ratio and catalyst loading. Previous studies also noted a typical increase in biodiesel production when the reaction time and temperature were increased [21,23].

Table 4. Comparison study of different magnetic catalysts for biodiesel production.

Types of Catalyst	Experimental Reaction Conditions	Esters Yield (%)	References
RHC/K_2O-20%/Fe-5%	Methanol-to-oil ratio = 12:1, temp. = 75 °C, time = 4 h, catalyst loading = 4 wt.%	98.60	[21]
CaO-Fe_2O_3/AC	Methanol-to-oil ratio = 18:1, temp. = 65 °C, time = 3 h, catalyst loading = 3 wt.%	98.30	[22]
Fe_3O_4/MCM-41 composites	Methanol-to-oil ratio = 25:1, time = 8 h, catalyst loading = 3 wt.%	99.20	[23]
EFB supported magnetic solid acid catalyst	Catalyst loading = 10 wt.%	87.32	[24]
Magnetically recyclable $CuFe_2O_4$	Methanol-to-oil ratio = 18:1, temp. = 60 °C, time = 0.5 h, catalyst loading = 3 wt.%	90.24	[25]
CaO/Fe_2O_3/feldspar	Methanol-to-oil ratio = 10:1, catalyst loading = 1 wt.% (karanja oil) Methanol-to-oil ratio = 5:1, catalyst loading = 1 wt.% (wild mustard oil) Methanol-to-oil ratio = 5:1, catalyst loading = 1.5 wt.% (safflower oil)	99.9 93.6 99.3	Present study

2.5. CaO/Fe_2O_3/Feldspar Catalyst Reusability for Karanja, Wild Mustard, and Safflower Seed Oil

A catalytic test was carried out to assess the reusability of the CaO/Fe_2O_3/feldspar for repeated use without further treatment. The optimized set of conditions for each oil was chosen because it led to better performance in catalytic activity and comparison using the same catalyst. The reaction was performed five times and the respective ester yields were measured, as depicted in Figure 6.

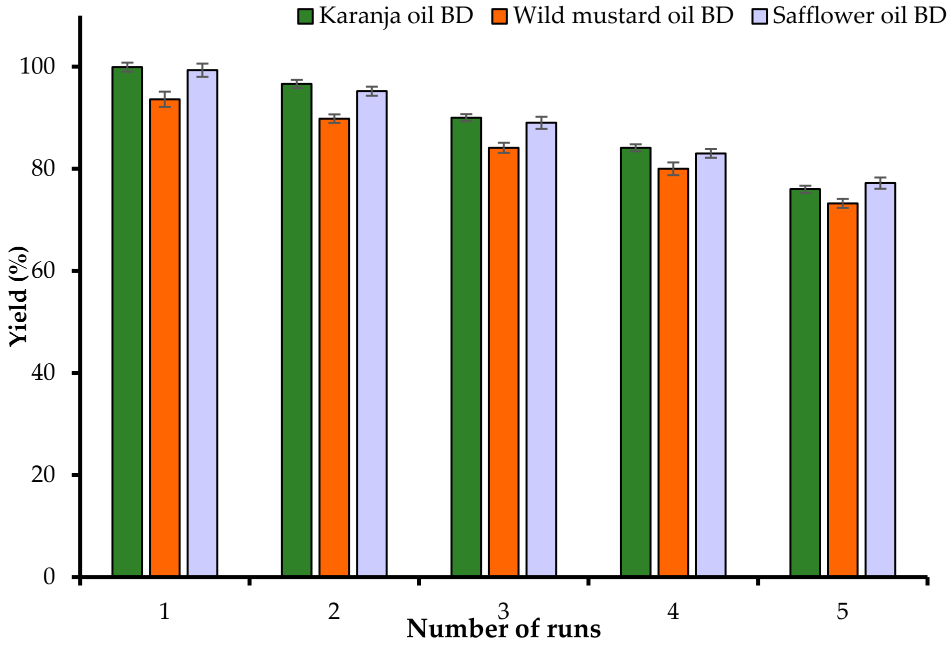


Figure 6. The reusability performance of CaO/Fe_2O_3/feldspar catalyst for karanja, wild mustard, and safflower seed oil.

The results indicated that after the fourth run of karanja, wild mustard, and safflower seed oils, ester yields of 76%, 73.2%, and 77.2% were obtained, respectively. It was found that the biodiesel yield was maintained at more than 80% when the catalyst was used consecutively four times. Thus, it can be concluded that the CaO/Fe_2O_3/feldspar catalyst does not merely show preferable catalytic performance throughout the transesterification reaction but is also highly suitable for repeated use for the studied oils. The results showed that the CaO/Fe_2O_3/feldspar catalyst has potential for industrial applications due to its effective reusability, absence of wastewater production, and easy removability from the reaction mixture using an external magnet.

2.6. Physicochemical Properties

The physicochemical properties of karanja, wild mustard, and wild safflower seed oil biodiesels using the optimized reaction conditions is summarized in Table 5. Biodiesel with a high density can contribute to the combustion issues while a low-density fuel could be substantially explosive. The American biodiesel standard, ASTM D6751, does not define a density limit [26]. The specified range of density of EN 14214:2003, the European biodiesel standard, lies between 0.86–0.90 g/mL. The densities of all the biodiesel samples were within the range specified in EN 14214 for karanja, wild mustard, and wild safflower. The acid value (AV) indicates the amount of free fatty acids present in biodiesel, with higher numbers indicating a higher acid content [27]. According to American (ASTM) and European (EU) standard requirements, the limit allowed level of AV in pure biodiesel is 0.50 mg KOH g^{-1} [28]. The AVs of the biodiesel fuels prepared from karanja, wild mustard, and wild safflower seed oils were 0.15, 0.46, and 0.15 mg KOH g^{-1}, respectively. The conversion of triglycerides by reaction with aqueous alkali into glycerol and soap is called the saponification reaction. The saponification value (SV) is the indication of the amount of saponifiable units per unit weight of oil. A low SV indicates a higher proportion of high-molecular-weight fatty acids in the fat/oil or vice versa [28]. The saponification values of karanja, wild mustard, and wild safflower oil biodiesels were 180.04, 175.04, and 196.58 mg KOH g^{-1} oil, respectively. The comparatively low SV for the wild mustard biodiesel was attributed to its high content of higher-molecular-weight erucic acid (Table 5). The iodine value (IV) is a measure of the degree of unsaturation in a fat or oil and is an important indicator of oxidative stability, as oxidative stability is dependent on the number and type of double bonds present in biodiesel. According to EN14214, a maximum IV of 120 g I_2/100 g is specified [29]. ASTM D6751 does not specify limits for IV. The IVs of the biodiesel produced from karanja, wild mustard, and wild safflower seed oils were 82.05, 86.65, and 69.44 g I_2/100 g, respectively. The low temperature operability of biodiesel is measured by CP and PP, which give an indication of when biodiesel will solidify and clog fuel filters and lines as ambient temperatures decrease. As seen in Table 5, the CPs and PPs of biodiesel produced from karanja, wild mustard, and wild safflower oils were in the range of 0.8–4.0 °C and −3.9, –1.1 °C, respectively. The cetane number (CN) is a dimensionless parameter that indicates ignition delay and fuel quality. Fuels with a higher CN auto ignite in shorter times after injection to the combustion chamber. Biodiesel CN increases with degree of saturation and chain length of fatty acids. The minimum specifications for CN in ASTM D6751 and EN 14214 are 47 and 51, respectively [30]. The CNs of karanja, wild mustard, and wild safflower seed oil biodiesels were 58.05, 57.98, and 58.44, respectively.

2.7. Fatty Acid Profile

The major fatty acids identified in karanja [31], wild mustard [32], and wild safflower [33] seed oils were oleic acid (51.92%), erucic acid (41.43%), and linoleic acid (75.17%), respectively, as shown in Table 6. Other fatty acids of significance included linoleic (11.03%) and palmitic (10.33%) acids in karanja oil, oleic (23.11%), linoleic (15.75%), and eicosanoic (12.83%) acids in wild mustard oil, and oleic acid (12.98%) in wild safflower oil. Lastly, all three oils contained low levels ($\leq$3.15%) of trienoic linolenic acid as well as shorter chain capric ($\leq$0.15%), lauric ($\leq$0.22%), and myristic ($\leq$0.93%) acids. IV can be calculated from the fatty acid profile following the American Oil Chemists' Society's official method Cd 1c-85. The calculated IV of karanja, wild mustard, and wild safflower oil biodiesels were 78.9, 81.0, and 141.5 g I_2/100 g, respectively. The higher value for safflower oil biodiesel was attributed to its high content of linoleic acid (75.17%) relative to the other methyl ester samples. Biodiesel fuels with higher levels of polyunsaturated fatty acid methyl esters will exhibit higher IV, as IV is a measure of total unsaturation within the sample.

Table 5. Comparison of fuel properties of biodiesel prepared from karanja, wild mustard, and wild safflower with ASTM D6751.

Fuel Parameters	Karanja	Wild Mustard	Wild Safflower	ASTM D6751 Limits
Density (g/mL)	0.85	0.86	0.88	Not specified
Cloud point (°C)	4.0	2.1	0.8	Report
Pour point (°C)	−1.1	−1.6	−3.9	Not specified
Acid value (mg KOH/g)	0.15	0.46	0.15	0.50 max
Iodine value (g I_2/100 g)	82.5	86.65	69.44	Not specified
Saponification value (mg KOH g^{-1} oil)	180.04	175.04	196.58	Not specified
Cetene number	58.05	57.98	58.44	47 minimum

Table 6. Fatty acid composition of karanja, wild mustard, and wild safflower seed oils.

Fatty Acid	Molecular Formula	Fatty Acid Amount (%)		
		Karanja Oil	Wild Mustard Oil	Wild Safflower Oil
Capric acid	$C_{10}H_{20}O_2$	0.11	0.15	0.13
Lauric acid	$C_{12}H_{24}O_2$	0.22	0.12	0.09
Myristic acid	$C_{14}H_{28}O_2$	0.93	0.18	0.16
Palmitic acid	$C_{16}H_{32}O_2$	10.33	3.63	7.73
Linolenic acid	$C_{18}H_{30}O_2$	3.15	0.09	0.32
Linoleic acid	$C_{18}H_{32}O_2$	11.03	15.75	75.17
Oleic acid	$C_{18}H_{34}O_2$	51.92	23.11	12.98
Stearic acid	$C_{18}H_{36}O_2$	4.66	1.15	0.89
Eicosanoic acid	$C_{20}H_{40}O_2$	9.76	12.83	0.11
Erucic acid	$C_{22}H_{42}O_2$	-	41.43	-

3. Materials and Methods

3.1. Materials and Chemical Reagent

P. pinnata (karanja), *S. arvensis* (wild mustard), and *C. oxyacantha* (wild safflower) seeds were collected from wild areas of Pakistan. Oil was extracted from the ground seeds (20 kg) using a VOSOCO automatic screw press machine. The extracted oil was filtered using a vacuum filtration assembly to remove residual solids. The acid values of karanja oil (3.75 mg KOH/g), wild mustard oil (2.30 mg KOH/g), and safflower seed oil (1.95 mg KOH/g) were determined before the transesterification reaction. Feldspar (clay mineral) was taken from the northern area of Pakistan. All chemicals used were of analytical grade and came from Sigma Aldrich.

3.2. Preparation of Supported Nano-Magnetic Catalyst

Calcium nitrate (0.05 g) was dissolved into 100 mL of deionized water, after which 3.5 g of ferric oxide was added. This solution was agitated for 10 min at 1500 rpm, followed by ultrasonication for 15 min to achieve a well-dispersed suspension. Then, a 2M solution of sodium hydroxide was added dropwise under constant stirring at 1500 rpm until a pH of 12 was reached. The suspension was then stirred overnight at 1500 rpm. The precipitates were washed with deionized water until a pH of 7 was obtained. The solid was then dried overnight in an oven at 80 °C. The product was then ground into a fine powder by a mortar and pestle. Finally, the powder underwent calcination at 550 °C for 1 h in a furnace. A total of 23.5 g of catalyst was produced from 25 g of starting material [34,35].

Initially, 0.5 g of CaO/Fe_2O_3 and 0.75 g of feldspar as a support were dissolved in distilled water via precipitation. The material was stirred for one hour at room temperature, filtered, washed three times with distilled water, and then dried for 0.5 h at 150 °C. The resulting powder underwent calcination at 550 °C for 1 h in a furnace. The supported nano-magnetic catalyst (CaO/Fe_2O_3/feldspar) was then ground using a mortar and pestle. Finally, nano-sieving was used to collect the nano-sized particles.

3.3. Characterization of Catalyst and Esters

X-ray diffraction (XRD) was used to obtain information regarding the structure, crystalline phase change, and degree of crystallinity of the magnetic feldspar catalyst. The structures of nano-catalysts were studied using a Rigaku SmartLab powder x-ray diffractometer (XRD, 40 kV, 30 mA, Rigaku Corporation, Tokyo, Japan) of Hypix-400 monochromatic CuKα (λ = 1.5406 Å), which radiated in the range of 5° to 60°. The crystalline phases of the CaO/Fe_2O_3 and CaO/Fe_2O_3/feldspar were determined.

The structural properties of nanoparticles were characterized using FESEM (JFC-1600, JEOL, Tokyo, Japan), while the elemental analysis for major elements in the samples were determined using an EDX spectrometer model EX-230BU from JEOL (Tokyo, Japan) with an emission current of 15.00 kV and 8.00 mm WD.

The total surface areas of the samples were measured using the Brunauer–Emmett–Teller (BET) method. The BET analyses were conducted using a Thermo–Finnigan Sorpmatic 1990 series (Thermo Finnigan LLC, San Jose, CA, USA) by using nitrogen adsorption–desorption analysis.

The magnetic properties of the nano-magnetic catalyst (CaO/Fe_2O_3/feldspar) were determined using a Lakeshore 7404 Series VSM instrument (Lake Shore Cryotronics, Westerville, OH, USA). During the test, the sample was placed on a rod in an external magnetic field and vibrated via connection with a vibrator. Furthermore, the magnetization as a function of the applied magnetic field (M–H loop) was measured. The electromotive induction method was used to quantify the induced electromotive force generated by flux changes.

The fatty acid compositions of the oils were determined by gas chromatography equipped with a flame ionization detector (GC-FID) utilizing an Agilent 7890A equipped with a capillary column (BPX-70, 60 m × 0.25 mm × 0.25 µm, Trajan Scientific, Victoria, Australia). The H_2 carrier gas was fixed at a flow rate of 40 mL/min and the temperature program was set to increase from 100 to 250 °C at 10 °C/min. Peaks were identified by comparison to reference standards.

3.4. Transesterification and Physiochemical Properties Evaluation

The extracted oil (50 g) was added to a 250 mL conical flask. Then, the waste oils, methanol and CaO/Fe_2O_3/feldspar nano-magnetic catalyst were each transesterified at 60 °C for 2 h on a temperature-controlled hotplate fitted with a magnetic stirrer. After the reaction, the magnetic catalyst was separated using an external magnet. The CaO/Fe_2O_3/feldspar catalyst and glycerol created during the transesterification reaction were separated from the biodiesel phase using separatory funnel. The biodiesel phase was washed with excess hot (75–80 °C) distilled water. The percentage biodiesel yield was calculated using Equation (1) [35].

$$Biodiesel\ yield\ (\%) = \frac{Weight\ of\ biodiesel\ (g)}{Weight\ of\ Oil\ (g)} \times 100 \quad (1)$$

The effect of different reaction parameters, such as the catalyst amount (0.5%, 1%, 1.5%, 2% and 2.5%) and methanol-to-oil molar ratio (5:1, 10:1, 15:1, 20:1 and 25:1), were optimized to give the highest yield of fatty acid methyl esters.

The physiochemical parameters of the resulting biodiesel, such as density, cloud point, (CP), pour point (PP), acid value (AV), cetane number (CN), iodine value (IV) and saponification value (SV), were measured according to the methods and instrumentation described previously [30].

3.5. CaO/Fe_2O_3/Feldspar Catalyst Reusability Test

The reusability experiments of the CaO/Fe_2O_3/feldspar catalyst in repeated transesterification reaction cycles were conducted for karanja, wild mustard, and wild safflower oils. The CaO/Fe_2O_3/feldspar catalyst was used under optimum reaction conditions without undergoing a regeneration process. After each run, the spent catalyst was washed using hexane then by methanol and dried at 100 °C for 6 h before further experiments. The produced biodiesel was analyzed by GC for fatty acid conversion of each oil.

3.6. Statistical Analysis

Each sample was analyzed in triplicate and data presented as mean ± SD.

4. Conclusions

The transesterification of waste and low-cost oils was investigated using a novel CaO/Fe_2O_3/feldspar catalyst. The morphology (FESEM), phase and crystallize size (XRD), surface area (BET), and magnetic properties (VSM) were measured. It was found that magnetic separation not only facilitated separation but also avoided material loss and increased fatty acid methyl ester yields. The highest biodiesel yield for karanja, wild mustard, and wild safflower oils were 99.9 ± 0.9, 93.6 ± 0.3, and 99.3 ± 0.7%, respectively. These yields were obtained after optimization of the catalyst concentration and methanol-to-oil molar ratio. For the karanja and wild mustard oils, the optimal catalyst concentration was 1.0%, whereas 1.5% was the optimum amount for wild safflower oil. The wild mustard and wild safflower oils gave a maximum biodiesel yields at a 5:1 methanol-to-oil molar ratio. Karanja gave the highest yield at a 10:1 methanol-to-oil molar ratio. The reusability study depicted that the CaO/Fe_2O_3/feldspar catalyst is capable of good reusability (>70%) for karanja, wild mustard, and safflower seed oils. The resulting fuel properties of the optimized methyl esters indicated their acceptability for use as biodiesel fuels in compression-ignition engines. This information is valuable in biodiesel production from inexpensive feedstocks with high acid value. Overall, the present study clearly offered a cheap and environmentally beneficial technique for efficient catalysts synthesis and its efficient application for biodiesel production with higher yield. In the current investigation, it demonstrated that CaO/Fe_2O_3/feldspar nano-magnetic catalysts can be used as a low-cost and naturally safe material for producing biodiesel as compared to traditionally employed homogeneous catalysts.

Author Contributions: Conceptualization, M.H., M.A.H. and U.R.; methodology, M.H., U.R., M.A.H. and B.R.M.; software, U.R. and F.A.A.; validation, I.A.B., M.A.H., A.H., U.R. and B.R.M.; formal analysis, M.H. and A.H.; investigation, M.H., resources, I.A.B., U.R., F.A.A. and B.R.M.; data curation, M.H.; writing—original draft preparation, M.H., A.H., I.A.B. and M.A.H.; writing—review and editing, U.R., F.A.A. and B.R.M.; visualization, M.H., M.A.H. and U.R.; supervision, I.A.B.; project administration, I.A.B., F.A.A. and U.R.; funding acquisition, F.A.A. and B.R.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research work obtained financial support under Geran Putra Berimpak from Universiti Putra Malaysia (Kod Project: UPM/800–3/ 3/1/GPB/2019/9679700). This research was funded (in part) by the U.S. Department of Agriculture, Agricultural Research Service.

Data Availability Statement: All the data is contained within the article.

Acknowledgments: Authors extend their thanks to the Researchers Supporting Project (RSP2023R160), King Saud University (Riyadh, Saudi Arabia).

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

Disclaimer: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

References

1. Ali, A.; Mushtaq, A. Do biofuels really a need of the day: Approaches, mechanisms, applications and challenges. *Int. J. Chem. Biochem. Sci.* **2023**, *23*, 219–226.
2. Sanjid, A.; Masjuki, H.; Kalam, M.; Abedin, M.; Rahman, S.A. Experimental investigation of mustard biodiesel blend properties, performance, exhaust emission and noise in an unmodified diesel engine. *APCBEE Procedia* **2014**, *10*, 149–153. [CrossRef]
3. Siddique, H.S.; Nadeem, F.; Inam, S.; Kazerooni, E.A. Recent production methodologies and advanced spectroscopic characterization of biodiesel: A review. *Int. J. Chem. Biochem. Sci.* **2020**, *18*, 134–144.
4. Lokman, I.M.; Rashid, U.; Yunus, R.; Taufiq-Yap, Y.H. Carbohydrate-derived solid acid catalysts for biodiesel production from low-cost feedstocks: A review. *Catal. Rev. Sci. Eng.* **2014**, *56*, 187–219. [CrossRef]
5. Jamil, F.; Al-Haj, L.; Al-Muhtaseb, A.H.; Al-Hinai, M.A.; Baawain, M.; Rashid, U.; Ahmad, M.N.M. Current scenario of catalysts for biodiesel production: A critical review. *Rev. Chem. Eng.* **2018**, *34*, 267–297. [CrossRef]
6. Srivastava, N.; Srivastava, M.; Gupta, V.K.; Manikanta, A.; Mishra, K.; Singh, S.; Singh, S.; Ramteke, P.; Mishra, P. Recent development on sustainable biodiesel production using sewage sludge. *3 Biotech* **2018**, *8*, 245. [CrossRef]
7. Abomohra, A.E.-F.; Elsayed, M.; Esakkimuthu, S.; El-Sheekh, M.; Hanelt, D. Potential of fat, oil and grease (FOG) for biodiesel production: A critical review on the recent progress and future perspectives. *Prog. Energy Combust. Sci.* **2020**, *81*, 100868. [CrossRef]
8. Aslam, K.; Mushtaq, A.; Nadeem, F.; Ghnia, J.B.; Rafique, M.; Sillanpää, M. Economic feasibility of non-edible oils as biodiesel feedstock: A brief. *Int. J. Chem. Biochem. Sci.* **2020**, *18*, 145–150.
9. Irshad, F.; Mushtaq, A. Biomass-derived Materials and their Commercial Applications. *Int. J. Chem. Biochem. Sci.* **2020**, *23*, 202–211.
10. Ikram, M.M.; Hanif, M.A.; Khan, G.S.; Rashid, U.; Nadeem, F. Significant seed oil feedstocks for renewable production of biodiesel: A review. *Curr. Org. Chem.* **2019**, *23*, 1509–1516. [CrossRef]
11. Xie, W.; Li, J. Magnetic solid catalysts for sustainable and cleaner biodiesel production: A comprehensive review. *Renews* **2023**, *171*, 113017. [CrossRef]
12. Xie, W.; Wang, H. Immobilized polymeric sulfonated ionic liquid on core-shell structured Fe_3O_4/SiO_2 composites: A magnetically recyclable catalyst for simultaneous transesterification and esterifications of low-cost oils to biodiesel. *Renew. Energy* **2020**, *145*, 1709–1719. [CrossRef]
13. Xie, W.; Wan, F. Basic ionic liquid functionalized magnetically responsive Fe_3O_4@HKUST-1 composites used for biodiesel production. *Fuel* **2018**, *220*, 248–256. [CrossRef]
14. Xie, W.; Wang, H. Grafting copolymerization of dual acidic ionic liquid on core-shell structured magnetic silica: A magnetically recyclable Brönsted acid catalyst for biodiesel production by one-pot transformation of low-quality oils. *Fuel* **2021**, *283*, 118893. [CrossRef]
15. Hanif, M.A.; Nisar, S.; Rashid, U. Supported solid and heteropoly acid catalysts for production of biodiesel. *Catal. Rev.* **2017**, *59*, 165–188. [CrossRef]
16. Xue, B.; Guo, H.; Liu, L.; Chen, M. Preparation, characterization and catalytic properties of yttrium-zirconium-pillared montmorillonite and their application in supported Ce catalysts. *Clay Miner.* **2015**, *50*, 211–219. [CrossRef]
17. Keshavarz, M.; Papari, R.F.; Bulgariu, L.; Esmaeili, H. Synthesis of CaO/Fe_2O_3 nanocomposite as an efficient nanoadsorbent for the treatment of wastewater containing Cr (III). *Sep. Sci. Technol.* **2021**, *56*, 1328–1341. [CrossRef]
18. Ali, B.J.; Othman, S.S.; Harun, F.W.; Jumal, J.; Rahman, M.B.A. Immobilization of enzyme using natural feldspar for use in the synthesis of oleyl oleate. In *AIP Conference Proceedings*; AIP Publishing LLC: Melville, NY, USA, 2018; p. 030018.
19. Lokman, I.M.; Rashid, U.; Taufiq-Yap, Y.H. Production of biodiesel from palm fatty acid distillate using sulfonated-glucose solid acid catalyst: Characterization and optimization. *Chin. J. Chem. Eng.* **2015**, *23*, 1857–1864. [CrossRef]
20. Kusumaningtyas, R.D.; Pristiyani, R.; Dewajani, H. A new route of biodiesel production through chemical interesterification of jatropha oil using ethyl acetate. *Int. J. ChemTech Res.* **2016**, *9*, 627–634.
21. Hazmi, B.; Rashid, U.; Taufiq-Yap, Y.H.; Ibrahim, M.L.; Nehdi, I.A. Supermagnetic nano-bifunctional catalyst from rice husk: Synthesis, characterization and application for conversion of used cooking oil to biodiesel. *Catalysts* **2020**, *10*, 225. [CrossRef]
22. Ibrahim, N.A.; Rashid, U.; Hazmi, B.; Moser, B.R.; Alharthi, F.A.; Rokhum, S.L.; Ngamcharussrivichai, C. Biodiesel production from waste cooking oil using magnetic bifunctional calcium and iron oxide nanocatalysts derived from empty fruit bunch. *Fuel* **2022**, *317*, 123525. [CrossRef]
23. Xie, W.; Han, Y.; Wang, H. Magnetic Fe_3O_4/MCM-41 composite-supported sodium silicate as heterogeneous catalysts for biodiesel production. *Renew Energy* **2018**, *125*, 675–681. [CrossRef]
24. Krishnan, S.G.; Pua, F.; Syed Jaafar, S.N. Synthesis and characterization of local biomass supported magnetic catalyst for esterification reaction. *Mater. Today Proc.* **2020**, *31*, 161–165. [CrossRef]
25. Ali, R.M.; Elkatory, M.R.; Hamad, H.A. Highly active and stable magnetically recyclable $CuFe_2O_4$ as a heterogenous catalyst for efficient conversion of waste frying oil to biodiesel. *Fuel* **2020**, *268*, 117297. [CrossRef]
26. Saeed, A.; Hanif, M.A.; Hanif, A.; Rashid, U.; Iqbal, J.; Majeed, M.I.; Moser, B.R.; Alsalme, A. production of biodiesel from *Spirogyra elongata*, a common freshwater green algae with high oil content. *Sustainability* **2021**, *13*, 12737. [CrossRef]

27. Ijaz, B.; Hanif, M.A.; Rashid, U.; Zubair, M.; Mushtaq, Z.; Nawaz, H.N.; Choong, T.S.Y.; Nehdi, I.A. High vacuum fractional distillation (HVFD) approach for quality and performance improvement of *Azadirachta indica* biodiesel. *Energies* **2020**, *13*, 2858. [CrossRef]
28. Ismail, S.A.-E.A.; Ali, R.F.M. Physico-chemical properties of biodiesel manufactured from waste frying oil using domestic adsorbents. Science and technology of advanced materials. *Sci. Technol. Adv. Mater.* **2015**, *16*, 034602. [CrossRef]
29. Folayan, A.J.; Anawe, P.A.L.; Aladejare, A.E.; Ayeni, A.O. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass. *Energy Rep.* **2019**, *5*, 793–806. [CrossRef]
30. Sakthivel, R.; Ramesh, K.; Purnachandran, R.; Shameer, P.M. A review on the properties, performance and emission aspects of the third generation biodiesels. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2970–2992. [CrossRef]
31. Islam, A.K.M.A.; Chakrabarty, S.; Yaakob, Z.; Ahiduzzaman, M.; Islam, A.K.M.M. Koroch (*Pongamia pinnata*): A promising unexploited resources for the tropics and subtropics. In *Forest Biomass-From Trees to Energy*; IntechOpen: London, UK, 2021.
32. Hanif, M.; Bhatti, H.N.; Hanif, M.A.; Rashid, U.; Hanif, A.; Moser, B.R.; Alsalme, A. A novel heterogeneous superoxide support-coated catalyst for production of biodiesel from roasted and unroasted *Sinapis arvensis* seed oil. *Catalysts* **2021**, *11*, 1421. [CrossRef]
33. Murthy, I.; Anjani, K. Fatty acid composition in *Carthamus* species. In Proceedings of the 7th International Safflower Conference, Wagga Wagga, Australia, 3–6 November 2008; Australian Oilseeds Federation: Sydney, Australia, 2007.
34. Ali, M.A.; Al-Hydary, I.A.; Al-Hattab, T.A. Nano-magnetic catalyst CaO-Fe_3O_4 for biodiesel production from date palm seed oil. *Bull. Chem. React. Eng. Catal.* **2017**, *12*, 460–468. [CrossRef]
35. Shi, M.; Zhang, P.; Fan, M.; Jiang, P.; Dong, Y. Influence of crystal of Fe_2O_3 in magnetism and activity of nanoparticle CaO@ Fe_2O_3 for biodiesel production. *Fuel* **2017**, *197*, 343–347. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.