

Article

Comprehensive Comparison of Hetero-Homogeneous Catalysts for Fatty Acid Methyl Ester Production from Non-Edible *Jatropha curcas* Oil

Khawer Khan¹, Noaman Ul-Haq^{2,*}, Wajeeh Ur Rahman², Muzaffar Ali², Umer Rashid^{3,*}, Anwar Ul-Haq¹, Farrukh Jamil², Ashfaq Ahmed^{2,4}, Faisal Ahmed², Bryan R. Moser⁵ and Ali Alsalmeh⁶

¹ Department of Basic Sciences, Riphah International University, Islamabad 44000, Pakistan; khawerkhan357.kk@gmail.com (K.K.); anwar.haq@riphah.edu.pk (A.U.-H.)

² Department of Chemical Engineering, Lahore Campus, COMSATS University Islamabad, Lahore 54000, Pakistan; w.rehman0109@gmail.com (W.U.R.); muzaffaraliuet@gmail.com (M.A.); fjamil@cuilahore.edu.pk (F.J.); ashfaqengr97@gmail.com (A.A.); faisalahmed@cuilahore.edu.pk (F.A.)

³ Institute of Nanoscience and Nanotechnology (ION2), Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia

⁴ Institute for Sustainable Industries and Liveable Cities, Victoria University, Melbourne 8001, Australia

⁵ Bio-Oils Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, Peoria, IL 61604, USA; bryan.moser@usda.gov

⁶ Chemistry Department, College of Science, King Saud University, Riyadh 1145, Saudi Arabia; aalsalme@ksu.edu.sa

* Correspondence: noamanulhaq@cuilahore.edu.pk (N.U.-H.); umer.rashid@upm.edu.my or dr.umer.rashid@gmail.com (U.R.); Tel.: +60-3-9769-7393 (U.R.)



Citation: Khan, K.; Ul-Haq, N.; Rahman, W.U.; Ali, M.; Rashid, U.; Ul-Haq, A.; Jamil, F.; Ahmed, A.; Ahmed, F.; Moser, B.R.; et al. Comprehensive Comparison of Hetero-Homogeneous Catalysts for Fatty Acid Methyl Ester Production from Non-Edible *Jatropha curcas* Oil. *Catalysts* **2021**, *11*, 1420. <https://doi.org/10.3390/catal11121420>

Academic Editors: Hwai Chyuan Ong, Chia-Hung Su and Hoang Chinh Nguyen

Received: 30 September 2021
Accepted: 1 November 2021
Published: 23 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 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/>).

Abstract: The synthesis of biodiesel from *Jatropha curcas* by transesterification is kinetically controlled. It depends on the molar ratio, reaction time, and temperature, as well as the catalyst nature and quantity. The aim of this study was to explore the transesterification of low-cost, inedible *J. curcas* seed oil utilizing both homogenous (potassium hydroxide; KOH) and heterogenous (calcium oxide; CaO) catalysis. In this effort, two steps were used. First, free fatty acids in *J. curcas* oil were reduced from 12.4 to less than 1 wt.% with sulfuric acid-catalyzed pretreatment. Transesterification subsequently converted the oil to biodiesel. The yield of fatty acid methyl esters was optimized by varying the reaction time, catalyst load, and methanol-to-oil molar ratio. A maximum yield of 96% was obtained from CaO nanoparticles at a reaction time of 5.5 h with 4 wt.% of the catalyst and an 18:1 methanol-to-oil molar ratio. The optimum conditions for KOH were a molar ratio of methanol to oil of 9:1, 5 wt.% of the catalyst, and a reaction time of 3.5 h, and this returned a yield of 92%. The fuel properties of the optimized biodiesel were within the limits specified in ASTM D6751, the American biodiesel standard. In addition, the 5% blends in petroleum diesel were within the ranges prescribed in ASTM D975, the American diesel fuel standard.

Keywords: biodiesel; calcium oxide; fatty acid methyl esters; *Jatropha curcas*; transesterification

1. Introduction

Energy demands have been consistently increasing worldwide alongside the increasing human population and industrialization. Natural gas, petroleum, and coal (fossil fuels) are the traditional and common non-renewable sources of energy, and these sources are depleting rapidly due to huge energy consumption. The potential shortage of energy in the future and rising prices of non-renewable fuels have prompted interest in alternative renewable energy sources and energy security [1–4]. Moreover, fossil fuels have many environmental issues, cause atmospheric pollution, and are a major contributor to anthropogenic greenhouse gas emissions. Combustion of fossil fuels emits CO_x, SO_x, NO_x, hydrocarbons, and many carcinogenic compounds into the atmosphere that may lead

to global warming and negative effects on human health [5]. Biodiesel prepared from animal fats, vegetable oils, and other renewable lipids has been promoted as a sustainable alternative to conventional petroleum diesel (petrodiesel) due to its environmental benefits.

Currently, one third of vehicles sold in Europe and the United States (US) are diesel powered. Biodiesel is a potential alternative fuel for these diesel vehicles, and biodiesel demand has been increasing since 2005 in the US [3,6,7]. Biodiesel is defined as the mono-alkyl esters of fatty acids derived from plant oils or animal fats [8]. Biodiesel has several advantages over petrodiesel such as reduced CO₂ emissions, derivation from renewable sources, a high cetane number (CN), inherent lubricity, easy and efficient production, and no need for drilling or a petroleum refinery, as well as the fact that it can be produced locally, is biodegradable, has a higher flash point (FP) for safer handling, and has negligible toxicity [2–4,8–11].

There are numerous potential sources for biodiesel, which include used cooking oils, vegetable oils, animal fats, and others. Animal fats and used cooking oils are generally not feasible for direct biodiesel production because inherent impurities cause problems during processing [6,12]. Hence, vegetable oils are the most promising feedstocks for biodiesel production, especially low-cost, inedible oils that do not compete with food production and can be grown on marginal lands. Examples of inedible feedstocks include jatropha (*Jatropha curcas*), polanga (*Calophyllum inophyllum*), and karanja (*Pongamia pinnata*). Jatropha is one of the most promising sources because it has many advantages for biodiesel production in terms of economic, agronomic, and environmental considerations [13–16].

Many methods have been developed for biodiesel production from oils, such as microemulsion, thermal cracking, and transesterification [1]. However, biodiesel produced by microemulsion and thermal cracking may lead to incomplete combustion because of its low CN [14]. Thus, transesterification to yield fatty acid methyl esters (FAME) is the most common and simple method to produce biodiesel from vegetable oils and generally yields superior fuel properties compared to microemulsion and cracking, including the CN, FP, kinematic viscosity (KV), lubricity, oxidative stability, and low temperature performance [2,13].

In the present work, we investigated the alkaline catalysts calcium oxide (CaO) and potassium hydroxide (KOH) for transesterification of low-cost, inedible jatropha oil and compared their catalytic performances under various conditions. The transesterification parameters of the methanol-to-oil molar ratio, catalyst load, and reaction time were optimized using heterogeneous CaO nanoparticles and homogenous KOH. The fuel properties (cetane index (CI), cloud point (CP), FP, KV, and specific gravity) of FAME produced from both KOH and CaO were measured and compared to the American biodiesel standard, ASTM D6751. In addition, the fuel properties of a 5 vol.% (B5) blend of FAME in petrodiesel were evaluated against the American petrodiesel standard, ATM D975.

2. Results and Discussion

2.1. Catalyst Characterization

The heterogeneous CaO nano-catalyst was prepared by calcination, while the homogenous KOH catalyst was pretreated under high temperature but below its melting point. The morphologies of CaO and KOH were then analyzed by XRD and SEM. In XRD analysis, the peak width with the highest intensity provided an average crystalline size for the catalysts, which was 20–60 nm. CaO nanoparticles afforded significantly smaller crystal sizes than KOH. Furthermore, SEM images (Figure 1) revealed a morphology consisting of agglomerated spherical grains for both catalysts.

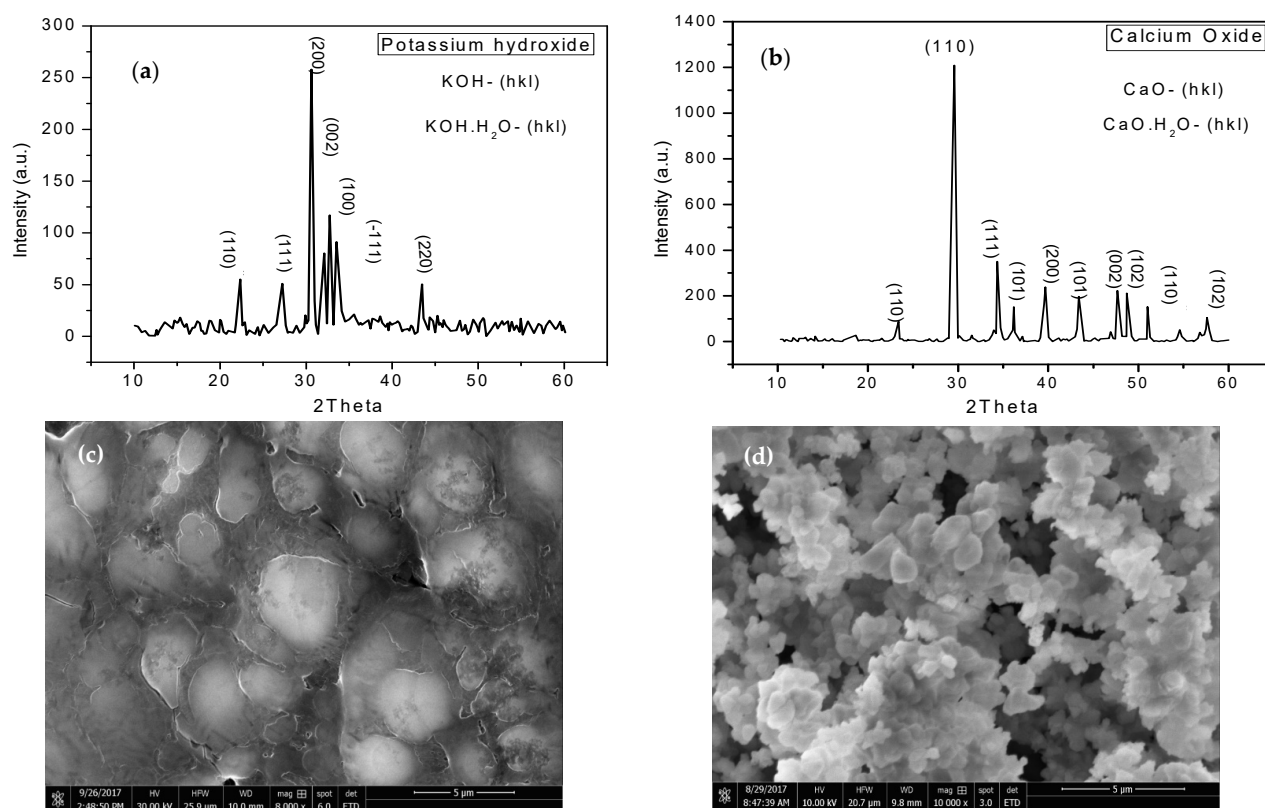


Figure 1. XRD analysis of (a) KOH and (b) CaO. SEM images of (c) KOH and (d) CaO.

2.2. FTIR Analysis of Biodiesel

The functional groups identified in the FTIR spectra of FAME, synthesized using KOH (denoted as BD-K) and CaO (denoted as BD-C) catalysts, are shown in Table 1. The absorption peaks observed in the spectra of BD-C and BD-K were nearly identical, which indicated that similar functional groups were present in each sample. These peaks indicated the presence of alkane moieties, as confirmed by C–H stretching vibrations at around 2852 and 2921 cm^{-1} . In addition, the strong peaks at 1742 cm^{-1} (C=O vibration) and 1163 cm^{-1} (C–O vibrations) clearly indicated the presence of the ester moiety, thus confirming that transesterification had occurred with both catalysts. Thus, from these results, it is concluded that FAME were formed in each case.

Table 1. Functional groups identified in the FTIR spectra of BD-C (from CaO) and BD-K (from KOH).

Peak	Possible Functional Group	Type of Vibration	Absorption Range (cm^{-1})	BD-C	BD-K
1	–CH ₂ –	Stretching	2850–2950	2922	2921
2	–CH ₂ –	Stretching	2850–2950	2853	2852
3	C=O	Stretching	1730–1750	1742	1742
4	–CH ₃	Stretching	1350–1475	1462	1462
5	C–O	Stretching	1000–1300	1163	1162

2.3. Yield of Biodiesel

The yield of biodiesel achieved using CaO was 96%, which was comparable to yields reported elsewhere from other heterogeneous catalysts [17–19]. The yield obtained from KOH was only 92%, which is lower than the values reported in the literature [20–22]. The lower yield observed for KOH was attributed to the increased basicity of KOH (pKa 15.7) relative to CaO (pKa 12.8), which promoted reactions such as hydrolysis and saponification on FAME, which, in turn, lowered the yield. In addition, the smaller particle sizes of

CaO may have provided an increased surface area for catalytic activity to occur, thereby enhancing the yield relative to KOH.

Acid-catalyzed pretreatment was conducted prior to transesterification to lower the amount of FFA in the oil from 12.4 to less than 1 wt.%. During pretreatment, FFA were esterified to FAME in the presence of excess methanol. Pretreatment was performed because FFA can cause catalyst deactivation, soap formation, and yield loss when alkaline catalysts are utilized for transesterification.

2.4. Effect of Reaction Parameters on Biodiesel Yield

2.4.1. Effect of Methanol-to-Oil Molar Ratio

The effect of the methanol-to-oil molar ratio on the FAME yield from CaO- and KOH-catalyzed transesterifications was studied. Ratios of interest included 3:1, 6:1, 9:1, 12:1, 15:1, and 18:1, as illustrated in Figure 2. A molar ratio of 3:1 is the theoretical minimum stoichiometric amount. Lower ratios would lead to incomplete conversion due to insufficient methanol. Molar ratios in excess of 3:1 thus utilized a stoichiometric excess of methanol in an effort to drive the equilibria toward the desired FAME products. All optimization reactions were conducted at 60 °C, utilizing 1.0 wt.% of the catalyst for 1.5 h.

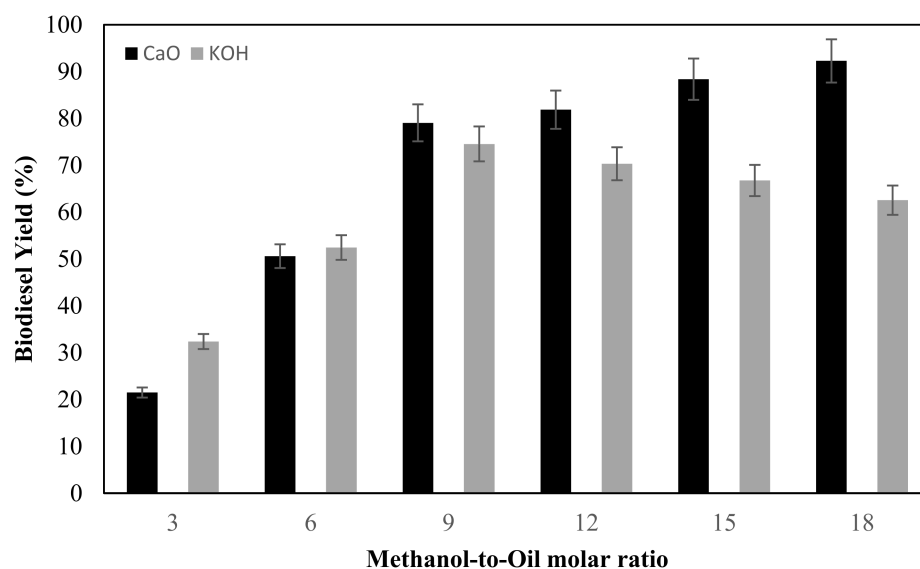


Figure 2. Effect of methanol/oil molar ratio on biodiesel yield.

As seen in Figure 2, the yield increased rapidly with both catalysts, up to a molar ratio of 9:1, with KOH and CaO providing yields of 73% and 79%, respectively. Beyond this amount of methanol, the yield gradually increased with CaO but decreased with KOH. In the case of KOH, the yield dropped to 63% as a result of difficulties encountered in the separation of the biodiesel from the glycerol and catalyst due to increased solubility caused by the larger amount of methanol. With regard to CaO, the yield increased to 92% as the molar ratio reached 18:1. This increase was attributed to oil dispersion caused by excess methanol, which improved the miscibility and enhanced the yield [23]. Given these results, the optimum molar ratios chosen for CaO- and KOH-catalyzed transesterifications were 18:1 and 9:1, respectively. These ratios were utilized hereafter for optimization of the catalyst load and reaction time.

2.4.2. Effect of Catalyst Load

The influence of the catalyst load on the FAME yield from CaO- and KOH-catalyzed transesterifications was investigated. Catalyst loads of interest ranged from 1 to 9 wt.%, as shown in Figure 3. All optimization reactions were conducted at 60 °C with molar ratios of methanol to oil of 18:1 and 9:1 for CaO and KOH, respectively.

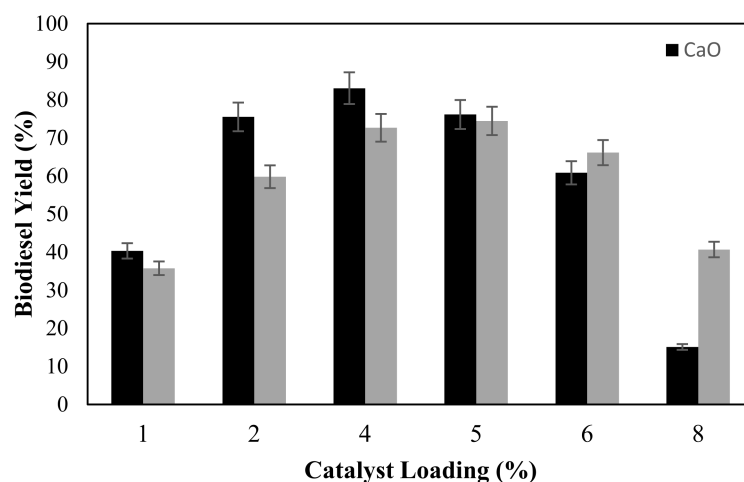


Figure 3. Effect of catalyst loading on biodiesel yield.

In the case of CaO, the yield increased from 40% to 86% up to a loading of 4 wt.%. However, further increases in the catalyst load from 5 to 9 wt.% returned lower yields, as production of FAME decreased to 15% at 9 wt.%. As reported previously, excessive catalyst loading can cause difficulty during mixing of a heterogeneous catalyst, oil, and methanol. Furthermore, excessive catalyst loads can adsorb some quantity of FAME, which suppresses the overall yield [24]. In addition, high dosages of the catalyst (>5 wt.%) caused phase separation and increased saponification of triglycerides and FAME, which produced soaps. These soaps became coated on the catalyst surface and hindered biodiesel separation during purification. Therefore, 4 wt.% catalyst loading was concluded to be the optimum amount for CaO-catalyzed transesterification.

With regard to KOH, the yield was enhanced significantly from 36% to 72% when the catalyst load was increased from 1 to 5 wt.%. Yields decreased with further increases in the load due to the formation of thick slurries that hindered the reaction. These thick slurries depressed the yield by disrupting adequate mixing of the catalyst, oil, and methanol [25]. Additionally, excessive catalyst loadings may have promoted saponification that further depressed the yield. Thus, a load of 5 wt.% of KOH was determined to be the optimum level.

2.4.3. Effect of Reaction Time

The influence of the reaction time on the biodiesel yield from CaO- and KOH-catalyzed transesterifications was studied. Reaction times of interest ranged from 2 to 7 h, as shown in Figure 4. All optimization reactions were conducted at 60 °C. Molar ratios of methanol to oil of 18:1 and 9:1, and catalyst loads of 4 and 5 wt.% were used for CaO and KOH, respectively.

When CaO was used as a catalyst, yields were low (7%) for the first 2 h of the reaction. These results were attributed to the immiscibility of the reactants and the poor diffusion of the heterogeneous CaO catalyst at the initial stages of the reaction. This phenomenon has been reported elsewhere [26]. As the reaction proceeded further, the yield climbed rapidly to 96% by 5.5 h. Such a dramatic increase may be attributed to activation of CaO by methanol. Methanol activates CaO by converting small amounts of CaO into $\text{Ca}(\text{OCH}_3)_2$, which acts as an initiating agent and exhibits higher catalytic activity than the nonactivated catalyst [26]. In fact, it has been postulated that $\text{Ca}(\text{OCH}_3)_2$ is the key active species that drives transesterification [27,28]. However, after 5.5 h, the yield of FAME gradually decreased, which was probably due to hydrolysis and/or saponification caused by prolonged exposure to the catalyst. Thus, based on these results, the optimum reaction time for CaO-catalyzed transesterifications was 5.5 h.

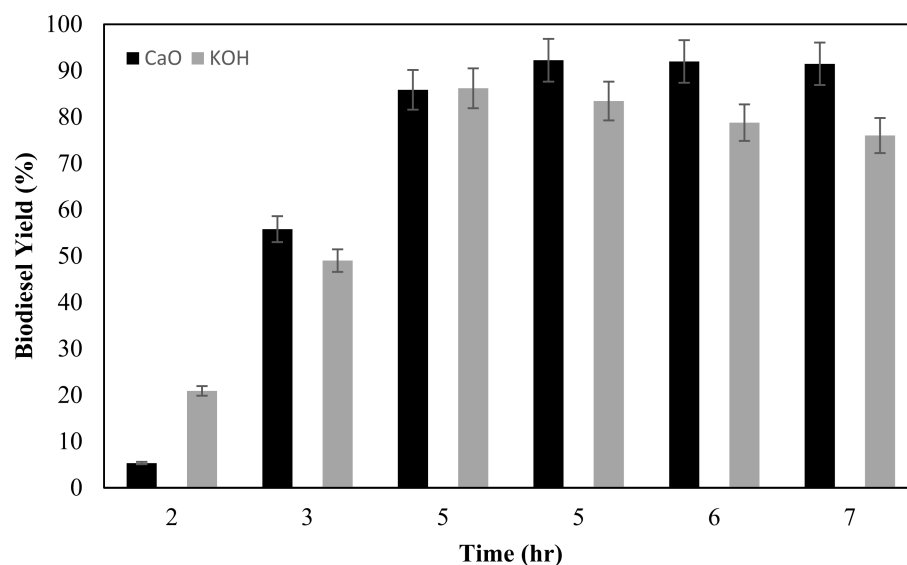


Figure 4. Effect of reaction time on biodiesel production.

In the case of KOH, the yield of FAME increased to 87% as the reaction time was increased to 3.5 h. However, as the reaction progressed beyond 3.5 h, the yield fell to 76%, which represented a larger decrease than observed for CaO. The lower yield obtained with KOH relative to CaO at longer reaction times was attributed to the increased basicity of KOH, which more vigorously promoted yield-reducing hydrolysis and/or saponification reactions caused by prolonged exposure to the catalyst. Therefore, the optimum reaction time for KOH-catalyzed transesterifications was 3.5 h, based on these results.

Arias et al. [29] reported that microreactors can significantly improve the mixing between reactants and phases, enhance the transfer rates, and, consequently, increase biodiesel yields in a shorter reaction time. This type of micro-scale system can be used for investigations of heterogeneous catalysts to improve the reaction time.

2.5. Biodiesel Fuel Properties

The fuel properties of FAME (B100; 100% biodiesel) prepared from jatropha oil using the optimized reaction conditions elucidated previously are shown in Table 2. Fuel properties of interest included CI, CP, FP, KV, and SG. These results were compared to the American biodiesel standard, ASTM D6751. A B5 (5% biodiesel in petrodiesel) blend was also analyzed and compared to the American petrodiesel standard, ASTM D975, which allows for blends of biodiesel of up to 5%.

The FP is a measure of the lowest temperature at which vapors will ignite if given an ignition source and has important implications for the storage and handling of flammable or combustible materials. Fuels such as gasoline have an FP below 37.8 °C and are thus flammable, whereas petrodiesel and biodiesel are combustible since they have an FP above 37.8 °C. As expected, B100 provided a much higher FP than the corresponding B5 blends due to the higher FP of biodiesel relative to petrodiesel. The FPs of BD-K and BD-C were 288 °C and 293 °C, respectively, which were well above the minimum level specified in ASTM D6751. In addition, the B5 blends provided FPs of 84 (BD-K) and 83 °C (BD-C), which were above the lower limit prescribed in ASTM D975.

Table 2. Fuel properties of biodiesel (B5 and B100 blends) produced by KOH (BD-K) and CaO (BD-C) catalysts, and comparison to ASTM D6751 (B100) and ASTM D975 (B5).

Biodiesel	Property	ASTM Method	B5	B100	ASTM D6751	ASTM D975
BD-K	FP (°C)	D93	84	288	93 minimum	52 minimum
	CP (°C)	D2500	1	7	Not specified	Not specified
	KV (40 °C; mm ² /s)	D445	2.05	4.40	1.9–6.0	1.9–4.1
	CI	D976	53.7	47.3	47 minimum	40 minimum
	SG (15.6 °C)	D1298	0.851	0.896	Not specified	Not specified
BD-C	FP (°C)	D93	83	293	93 minimum	52 minimum
	CP (°C)	D2500	4	9	Not specified	Not specified
	KV (40 °C; mm ² /s)	D445	2.12	4.50	1.9–6.0	1.9–4.1
	CI	D976	53.9	49.7	47 minimum	40 minimum
	SG (15.6 °C)	D1298	0.853	0.899	Not specified	Not specified

The CP is the temperature at which growing crystals first become visible when a fuel is cooled. Once the CP is reached, the tendency of fuels to plug filters or small orifices increases until the pour point (PP) is reached, which is the temperature at which the fuel ceases to pour. In all cases, the PP occurs at a lower temperature than the CP. The CPs of BD-K and BD-C were 7 and 9 °C, respectively, which, as expected, were considerably higher than the values for the corresponding B5 blends (1 °C and 4 °C, respectively). It is well known that petrodiesel generally has lower CP values than biodiesel, and these results confirm that trend. Neither ASTM D6751 (B100) nor ASTM D975 (B5) contains specific limits for the CP. The relatively high CP of the B100 samples revealed that they are most suitable for high- and moderate-temperature climates or for summer use in colder climates.

KV is important because it influences the flow characteristics and atomization of fuels. Fuels with high KV have lower flow rates and poor atomization, which contributes to coking and deposition and subsequently decreases engine life. The KVs (40 °C) of BD-K and BD-C were 4.40 and 4.50 mm²/s, respectively, which were well within the range specified in ASTM D6751. In addition, the B5 blends provided KVs of 2.05 (BD-K) and 2.12 mm²/s (BD-C), which were within the limits prescribed in ASTM D975.

The CN is an indicator of the combustion speed of diesel fuel and plays a similar role for diesel as the octane rating for gasoline. Thus, the CN is important for determining the ignition quality of diesel fuel. A high CN indicates rapid ignition upon injection into the combustion chamber and is thus more desirable. However, if the CN is too high, then ignition occurs too rapidly without proper mixing with air, which increases smoke emissions and reduces engine power. In this study, the CI was used as a substitute for the CN and is calculated based on the fuel's density and distillation range. The CIs of BD-K and BD-C were 47.3 and 49.7, respectively, which were above the minimum CN limit specified in ASTM D6751. In addition, the B5 blends provided CIs of 53.7 (BD-K) and 53.9 (BD-C), which were above the minimum limit for the CN prescribed in ASTM D975.

SG is the ratio of the density of a substance to the density of water at a given temperature. If SG is less than 1, then the substance is less dense than water and vice versa. Because SG is related to density, it influences fuel economy, as fuels with higher SG will contain more energy per unit volume than those with lower SG. The SGs (15.6 °C) of BD-K and BD-C were 0.896 and 0.899, respectively, which were higher than the values for the corresponding B5 blends (0.851 and 0.853, respectively). It is well documented that petrodiesel has lower SG than biodiesel, and these results confirm that trend. Neither ASTM D6751 (B100) nor ASTM D975 (B5) contains specifications for SG.

3. Materials and Methods

3.1. Materials

Jatropha oil was purchased from a local market in Islamabad, Pakistan. Methanol (99.5%), chloroform (GC grade), potassium hydroxide (KOH; 98.9%), calcium carbonate (CaCO₃; 98.5%), and sulfuric acid (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals and reagents were of analytical grade and used as received.

3.2. Preparation of Catalysts

For the preparation of the calcium oxide (CaO) nano-catalyst, 2.0 g of finely ground CaCO₃ was calcined at 900 °C for 3 h. KOH was ground into fine a powder and pretreated at 300–400 °C for 3 h.

3.3. Characterization of Catalysts and Biodiesel

Catalyst morphology was determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Functional group analysis of FAME was performed using Fourier transform infrared spectrometry (FTIR) and confirmed by GC-MS. Crystallography was accomplished utilizing a Bruker D8 X-ray diffractometer (Billerica, MA, USA) and equipped with a Cu anode. X-rays were generated by a horizontal HyPix-400 with Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. The sample was dispersed on a glass holder as a compact layer with a smooth surface. The scan was set over $2\theta = 5\text{--}80^\circ$ with a $5^\circ/\text{min}$ scan. Diffractograms were compared to the standard JCPDS (Joint Committee on Powder Diffraction Standards). SEM images were captured using a JOEL (Peabody, MA, USA) JSM-5910 SEM at 20,000 magnification under high vacuum to avoid interruption of the electron beam that created the secondary and backscattered electrons used for imaging. Prior to capturing images, all samples were dispersed evenly on an aluminum plate covered with carbon tape. The catalysts were sputtered with gold using a model JFT-1600 JEQL sputter coater to create a conductive layer to prevent charging, minimize thermal damage, and enhance the secondary signal. FTIR spectra were collected with a Thermo Nicolet 7000 FTIR spectrometer from Thermo Fisher Scientific (Waltham, MA, USA). Samples were evenly dispersed on a diamond ATR crystal. A total of 200 scans were performed at 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3.4. Pretreatment and Transesterification of Jatropha Oil

Transesterification was conducted in a two-necked round-bottom flask equipped with a magnetic stirrer and reflux condenser. The reaction temperature varied between 50 and 55 °C and was controlled using a water bath. The reaction was carried out in two steps: pretreatment followed by transesterification. In the first step, methanol and oil (6:1 molar ratio) were mixed with sulfuric acid (1%) and heated at 50 °C for 1.5 h to convert free fatty acids (FFA) in the oil to FAME. Then, 0.5% (w/w %) of the catalyst (CaO or KOH) was added, and the mixture was heated under constant stirring for 1 h. The reaction was equipped with a reflux condenser to reduce methanol loss, and the weight change by the end of the reaction was <0.5%, meaning the overall methanol-to-oil ratio was maintained. After the reaction, excess methanol was removed under reduced pressure by rotary evaporation, and, after equilibration to room temperature, centrifugation yielded three phases. The upper phase contained biodiesel, the middle phase was glycerol, and the bottom phase consisted of the catalyst and traces of glycerol. The upper phase was collected and washed with hot distilled water until a neutral pH was achieved.

3.5. Fuel Properties and Yield of Jatropha Oil-Based Biodiesel

The fuel properties of FAME were measured in triplicate, and mean values were reported. The cloud point (CP) was determined following ASTM D2500. Kinematic viscosity (KV) was determined at 40 °C in accordance with ASTM D445. The flash point (FP) was measured following ASTM D93. The cetane index (CI) was calculated according to ASTM D976. Specific gravity (SG) was measured following ASTM D1298.

3.6. GC-MS Analysis of Biodiesel

Gas-chromatographic mass spectrometric (GC-MS) analysis was conducted to quantify the FAME content. Analyses were performed using a Perkin-Elmer (Richmond, CA, USA) Clarus 500 model GC-MS equipped with a capillary column (HP-1, 30 m \times 0.25 mm \times 0.25 μm) and coupled to a Perkin-Elmer Clarus 500C MS. The sample injection tool was placed at an oven temperature of 50 °C and was held at that temperature for 1 min. The

oven temperature was then increased to 325 °C at a heating rate of 10 °C/min and held for 2 min. Helium (99.99%) with a constant flow rate of 1.2 mL/min was used as a carrier gas. Finally, the yield of biodiesel was calculated according to the following equation [30]:

$$\text{Yield (\%)} = \frac{\Sigma A - A_{meh}}{A_{meh}} \times \frac{C_{meh} \times V_{meh}}{Wt} \times 100 \quad (1)$$

where

ΣA (mm²): total area of peaks;

A_{meh} (mm²): peak area of methyl heptadecanoate;

C_{meh} (ppm): concentration of methyl heptadecanoate;

V_{meh} (mL): volume of methyl heptadecanoate;

Wt (g): weight of product.

3.7. Blending Biodiesel with Petrodiesel

The blend was prepared at room temperature by pipetting a precisely measured volume of biodiesel into petrodiesel followed by agitation of the contents to ensure homogeneity. Properties were measured at the B5 (5 volume % biodiesel in petrodiesel) blend level. Petrodiesel was obtained from a local gas station in Islamabad, Pakistan.

4. Conclusions

Both CaO and KOH provided FAME in high yield after transesterification of *J. curcas* seed oil. However, yields employing CaO were higher (96%) compared to KOH (92%). The lower yield of KOH was attributed to the increased basicity that promoted unwanted hydrolysis and saponification reactions. In addition, the smaller crystalline sizes of CaO, as determined by XRD, provided a higher surface area for enhanced catalytic activity. Pretreatment was conducted with catalytic sulfuric acid prior to transesterification to lower the FFA content of *J. curcas* seed oil from 12.4 to less than 1 wt.%. Pretreatment was necessary because reactions of excessive FFA with alkaline catalysts such as CaO and KOH result in catalyst deactivation, soap formation, and lower yields.

The optimum reaction conditions elucidated for heterogeneously catalyzed CaO transesterifications were an 18:1 molar ratio of methanol to oil, 4 wt.% catalyst load, and a reaction time of 5.5 h. The optimum reaction conditions for homogeneously catalyzed KOH transesterifications were a molar ratio of methanol to oil of 9:1, 5 wt.% catalyst load, and a reaction time of 3.5 h. All optimization studies were performed at 60 °C.

The fuel properties such as the CI, CP, FP, KV, and SG of biodiesel prepared from CaO and KOH under optimum conditions were within the limits specified in ASTM D6751, where applicable. The relatively high CP of the B100 samples revealed that they were best suited for high- and moderate-temperature climates or for summer use in colder climates. In addition, the fuel properties of B5 blends of jatropha oil-based biodiesel in petrodiesel were within the ranges prescribed in ASTM D975, where appropriate.

These results indicate that low-cost, inedible *J. curcas* seed oil is readily convertible to FAME utilizing heterogeneous CaO nanoparticles. The resulting biodiesel as well as its B5 blend with petrodiesel exhibited fuel properties that were within the limits prescribed in international fuel standards. These results also indicate that CaO nanoparticles are an effective heterogeneous catalyst for the production of biodiesel. In summary, the work described herein provides new insights into potential commercial applications of heterogeneously catalyzed transesterification of *J. curcas* seed oil, which will be useful to biodiesel producers.

Author Contributions: Conceptualization, N.U.-H., A.U.-H., F.J. and U.R.; methodology, K.K., N.U.-H., U.R. and W.U.R.; validation, F.J., U.R. and B.R.M.; formal analysis, W.U.R., A.A. (Ashfaq Ahmad), F.A., M.A. and A.U.-H.; investigation, K.K., A.A., F.A., U.R. and A.U.-H.; resources, A.U.-H., N.U.-H., U.R. and A.A. (Ali Alsalmeh); data curation, K.K., F.A. and A.A. (Ashfaq Ahmed); writing—original draft preparation, K.K., N.U.-H., F.J., M.A. and F.A.; writing—review and editing, U.R., A.A. (Ali

Alsalmeh) and B.R.M.; supervision, A.U.-H. and N.U.-H.; project administration, A.U.-H., N.U.-H., U.R. and A.A.; funding acquisition, A.A. (Ali Alsalmeh) and U.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Researchers Supporting Project (Ref: RSP-2021/78), King Saud University (Riyadh, Saudi Arabia). This research was funded (in part) by the U.S. Department of Agriculture, Agricultural Research Service.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to thank Tariq Mahmood, Nano Sciences and Technology Department, National Centre for Physics, Quaid-i-Azam University (Islamabad, Pakistan), for providing his facilities for this work. The authors also thank Ibne Sina at the Institute for Science and Technology for SEM structural analysis.

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. Agarwal, D.; Agarwal, A.K. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. *Appl. Therm. Eng.* **2007**, *27*, 2314–2323. [[CrossRef](#)]
2. Jain, S.; Sharma, M. Prospects of biodiesel from Jatropha in India: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 763–771. [[CrossRef](#)]
3. Jayed, M.; Masjuki, H.H.; Saidur, R.; Kalam, M.A.; Jahirul, M.I. Environmental aspects and challenges of oilseed produced biodiesel in Southeast Asia. *Renew. Sustain. Energy Rev.* **2009**, *13*, 2452–2462. [[CrossRef](#)]
4. Robles-Medina, A.; González-Moreno, P.A.; Esteban-Cerdán, L.; Molina-Grima, E. Biocatalysis: Towards ever greener biodiesel production. *Biotechnol. Adv.* **2009**, *27*, 398–408. [[CrossRef](#)] [[PubMed](#)]
5. El Diwani, G.; Attia, N.; Hawash, S. Development and evaluation of biodiesel fuel and by-products from jatropha oil. *Int. J. Environ. Sci. Technol.* **2009**, *6*, 219–224. [[CrossRef](#)]
6. Kulkarni, M.G.; Dalai, A.K. Waste cooking oil an economical source for biodiesel: A review. *Ind. Eng. Chem. Res.* **2006**, *45*, 2901–2913. [[CrossRef](#)]
7. Pahl, G. *Biodiesel: Growing a New Energy Economy*; Chelsea Green Publishing: Hartford, VT, USA, 2008.
8. Su, E.; Wei, D. Improvement in lipase-catalyzed methanolysis of triacylglycerols for biodiesel production using a solvent engineering method. *J. Mol. Catal. B Enzym.* **2008**, *55*, 118–125. [[CrossRef](#)]
9. Nie, K.; Xie, F.; Wang, F.; Tan, T. Lipase catalyzed methanolysis to produce biodiesel: Optimization of the biodiesel production. *J. Mol. Catal. B Enzym.* **2006**, *43*, 142–147. [[CrossRef](#)]
10. Shah, S.; Sharma, S.; Gupta, M. Biodiesel preparation by lipase-catalyzed transesterification of Jatropha oil. *Energy Fuels* **2004**, *18*, 154–159. [[CrossRef](#)]
11. Vieira, A.d.A.; Silva, M.D.; Langone, M. Biodiesel production via esterification reactions catalyzed by lipase. *Lat. Am. Appl. Res.* **2006**, *36*, 283–288.
12. Hanif, M.A.; Nisar, S.; Rashid, U. Supported solid and heteropoly acid catalysts for production of biodiesel. *Catal. Rev. Sci. Eng.* **2017**, *59*, 165–188. [[CrossRef](#)]
13. Helwani, Z.; Othman, M.R.; Aziz, N.; Kim, J.; Fernando, W.J.N. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Appl. Catal. A Gen.* **2009**, *363*, 1–10. [[CrossRef](#)]
14. Leung, D.Y.; Wu, X.; Leung, M. A review on biodiesel production using catalyzed transesterification. *Appl. Energy* **2010**, *87*, 1083–1095. [[CrossRef](#)]
15. Parawira, W. Biotechnological production of biodiesel fuel using biocatalysed transesterification: A review. *Crit. Rev. Biotechnol.* **2009**, *29*, 82–93. [[CrossRef](#)]
16. Pinzi, S.; Garcia, I.L.; Lopez-Gimenez, F.J.; Luque de Castro, M.D.; Dorado, G.; Dorado, M.P. The ideal vegetable oil-based biodiesel composition: A review of social, economical and technical implications. *Energy Fuels* **2009**, *23*, 2325–2341. [[CrossRef](#)]
17. Endalew, A.K.; Kiros, Y.; Zanzi, R. Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO). *Energy* **2011**, *36*, 2693–2700. [[CrossRef](#)]
18. Elkady, M.F.; Zaatout, A.; Balbaa, O. Production of biodiesel from waste vegetable oil via KM micromixer. *J. Chem.* **2015**, *2015*, 630168. [[CrossRef](#)]
19. Tyagi, O.S.; Atray, N.; Kumar, B.; Datta, A. Production, characterization and development of standards for biodiesel—A review. *MAPAN* **2010**, *25*, 197–218. [[CrossRef](#)]
20. Mathiyazhagan, M.; Ganapathi, A. Factors affecting biodiesel production. *Res. Plant Biol.* **2011**, *1*, 1–5.

21. Cao, F.; Chen, Y.; Zhai, F.; Li, J.; Wang, J.; Wang, X.; Wang, S.; Zhu, W. Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropoly acid. *Biotechnol. Bioeng.* **2008**, *101*, 93–100. [[CrossRef](#)]
22. Kartika, I.A.; Yani, M.; Ariono, D.; Evon, P.; Rigal, L. Biodiesel production from jatropha seeds: Solvent extraction and in situ transesterification in a single step. *Fuel* **2013**, *106*, 111–117. [[CrossRef](#)]
23. Ngamcharussrivichai, C.; Wiwatnimit, W.; Wangnoi, S. Modified dolomites as catalysts for palm kernel oil transesterification. *J. Mol. Catal. A Chem.* **2007**, *276*, 24–33. [[CrossRef](#)]
24. Hawash, S.; El Diwani, G.; Abdel Kader, E. Optimization of biodiesel production from jatropha oil by heterogeneous base catalysed transesterification. *Int. J. Eng. Sci. Technol.* **2011**, *3*, 5242–5251.
25. Chen, G.-Y.; Shan, R.; Shi, J.-F.; Yan, B.-B. Transesterification of palm oil to biodiesel using rice husk ash-based catalysts. *Fuel Process. Technol.* **2015**, *133*, 8–13. [[CrossRef](#)]
26. Sakai, T.; Kawashima, A.; Koshikawa, T. Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. *Bioresour. Technol.* **2009**, *100*, 3268–3276. [[CrossRef](#)]
27. Gangadhara, R.; Prasad, N. Studies on optimization of transesterification of certain oils to produce biodiesel. *Chem. Int.* **2016**, *2*, 59.
28. Mumtaz, M.W.; Mukhtar, H.; Dilawer, U.A.; Hussain, S.M.; Hussain, M.; Iqbal, M.; Adnan, A.; Nisar, J. Biocatalytic transesterification of *Eruca sativa* oil for the production of biodiesel. *Biocatal. Agric. Biotechnol.* **2016**, *5*, 162–167. [[CrossRef](#)]
29. Arias, E.L.M.; Martins, P.F.; Munhoz, A.L.J.; Gutierrez-Rivera, L.; Filho, R.M. Continuous synthesis and in situ monitoring of biodiesel production in different microfluidic devices. *Ind. Eng. Chem. Res.* **2012**, *51*, 10755–10767. [[CrossRef](#)]
30. 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](#)]