energies

Article

Biodiesel Production from *Reutealis Trisperma* Oil Using KOH Impregnated Eggshell as a Heterogeneous Catalyst

Kusmiyati Kusmiyati [1,*], Didik Prasetyoko [2], Siwi Murwani [3], Muthiah Nur Fadhilah [3], Titie Prapti Oetami [2], Hadiyanto Hadiyanto [3,4,*], Widayat Widayat [5], Arief Budiman [6] and Achmad Roesyadi [7]

1 Department of Industrial Engineering, Faculty of Engineering, Universitas Dian Nuswantoro, Semarang 50241, Indonesia
2 Laboratory of Materials Chemistry and Energy, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institute Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia; didikp@gmail.com (D.P.); titie@gmail.com (T.P.O.)
3 Department of Chemical Engineering, Muhammadiyah of University Surakarta, Surakarta 57162, Indonesia; siwimurwani@gmail.com (S.M.); muthiah@gmail.com (M.N.F.)
4 School of Postgraduate Studies, Diponegoro University, Semarang 50275, Indonesia
5 Department of Chemical Engineering, Diponegoro University, Semarang 50275, Indonesia; yayat_99@yahoo.com
6 Department of Chemical Engineering, Gadjah Mada University, Yogyakarta 55281, Indonesia; abudiman@ugm.ac.id
7 Department of Chemical Engineering, Institute Teknologi Sepuluh November, Surabaya 60111, Indonesia; aroesyadi@its.ac.id
* Correspondence: kusmiyati@dsn.dinus.ac.id (K.K.); hadiyanto@live.undip.ac.id (H.H.)

Received: 4 August 2019; Accepted: 26 September 2019; Published: 28 September 2019

Abstract: This research paper describes the synthesis of a heterogeneous catalyst (Potassium hydroxide (KOH)-impregnated eggshell) from waste chicken eggshell using the wet impregnation technique. In this experiment, the catalyst was derived from eggshell that was calcined at 800 °C for 5 h. It was impregnated with KOH at various KOH concentrations (10%, 15%, 20%, and 25%). The best catalyst was obtained by eggshell impregnated with 20% KOH concentration. This result was supported by the analysis of the catalyst characterization using Fourier-transform infrared spectrometry (FT-IR), which showed that the catalyst contained $CaCO_3$ and CaOH groups. X-ray fluorescence analysis (XRF) was also used to analyze the types of mineral contained in the catalyst, including calcium, potassium, sulfur, and other impurities. It revealed that the optimum minerals were found in the KOH-impregnated eggshell (20%) catalyst of 94.42% calcium, 5.06% potassium, and a small amount of other impurities. These optimum minerals serve as active sites to increase the biodiesel yield. Scanning electron microscopy (SEM) showed that the catalyst samples appear as small, spherical, homogenous, and solid particles. The catalytic activity was investigated by the transesterification of *Reutalism trisperma* oil in various types of catalyst (KOH-impregnated eggshell, eggshell, and KOH-impregnated CaO), percentages of catalyst loading (weight of 1%, 3%, 5%, 7%, and 10%) and molar ratios (methanol to oil of 6:1, 8:1, 10:1, 12:1, and 15:1) for 60 min at 60 °C. The result indicated the optimum catalyst loading was 5 wt% with an 84.57% biodiesel yield. While the best molar ratio was 12:1 (methanol:oil) with a 97.95% biodiesel yield. The optimum condition was gained using a molar ratio of 12:1, 5 wt% catalyst loading, and KOH-impregnated eggshell with a 94% biodiesel yield.

Keywords: eggshell; heterogeneous catalyst; transesterification; biodiesel; *Reutalism trisperma* oil

1. Introduction

In 2014, the International Energy Agency (IEA) reported that approximately 81.7% of energy demand was supplied by fossil fuels and this demand will have increased by 53% by the end of 2030 [1]. There is a continuous decline in fossil fuel usage, and, therefore, an increase in the amount of research seeking alternative fuel sources to ensure energy security and environmental protection. Biodiesel is a prospective alternative fuel source because it is renewable, biodegradable, and environmentally friendly and has a lower emission contribution of gaseous pollutants [2]. According to the American Society for Testing and Materials (ASTM) standard, biodiesel is defined as liquid fuel derived from vegetable oils or animal fats and consists of long-chain fatty acids methyl ester for use in compression ignition (CI) engines [3].

However, the raw materials of biodiesel have a high manufacturing cost due to the complexity of the purification process [4]. Generally, biodiesel production with edible oils is more expensive than using non-edible oils. Recently, the use of various non-edible oils was explored to reduce the biodiesel production cost, including *Silybum marianum* L., *Datura stramonium*, *C. pentandra*, and *Cerbera odollam* [5].

Reutealis trisperma is a tree (10–15 m in height) that is endemic to the Philippines and is widely known as a timber species. The fruits of this tree are usually single-celled and each fruit contains one seed. The seed has a hard, brittle, and thick shell, while the shape is mostly oval and smooth with numerous small ridges. *Reutealis trisperma* has several advantages, including a high biodiesel yield, the ability to grow in adverse conditions and increase soil fertility, and a long production age. *Reutealis trisperma* has been recognized as having great potential for biodiesel production due to its non-edible oil [6].

The transesterification of *Reutealis trisperma* in biodiesel production is carried out through heterogeneous catalysts. Such catalysts have many advantages; they are reusable, environmentally friendly, and have a simple purification process and lower production cost [7]. Those advantages can be obtained by using catalysts derived from natural resources. Sanjay [8] reported a variety of heterogeneous catalysts derived from renewable resources for the synthesis of oils into biodiesel. Therefore, much attention has been focused on solid base catalysts because of their simplification in separation [9].

Recently, calcium oxide has been reported to be the best catalyst due to its easy separation and relatively low environmental impact [10]. In industries, the sources of calcium oxide are mainly from commercial precursors that have a high biodiesel production cost. Recently, an eggshell-derived catalyst was found to be a solution for biodiesel production problems by reducing the catalyst cost. Eggshell has received attention as a potential source of calcium oxide and, moreover, for its additional value as an abundantly available and inexpensive material. The most important constituent of the eggshell is pure $CaCO_3$ (94 wt%). Based on this composition, eggshell can be utilized as a heterogeneous catalyst resource. In addition to the abundant amount of eggshell, it has an intrinsic pore structure and high $CaCO_3$ content [11].

In a previous study, the esterification of soybean oil and methanol catalyzed by CaO derived from eggshell using potassium modification, which produced a biodiesel yield of 99.1%, was investigated. Meanwhile, the transesterification of biodiesel synthesis using commercial CaO with potassium hydroxide (KOH) modification produced a lower biodiesel yield (96.5%) [12]. Hence, it can be stated that eggshell modified with KOH as potassium loading can produce a higher biodiesel yield than commercial CaO with modified KOH.

According to Kumar and Chandrika [6], wet impregnation using KOH as a modifier can increase the biodiesel yield [6]. The active sites in the eggshell catalysts increase by increasing the potassium loading [9]. Therefore, this research focused on the preparation of KOH-impregnated CaO as a heterogeneous catalyst derived from eggshell in the synthesis of biodiesel from *Reutalism trisperma* oil.

2. Materials and Methods

2.1. Material

Reutealis trisperma oil was obtained from PT. Kemiri Sunan Drajat, consisting of 2.44% free fatty acid [13] while the catalyst material was prepared from eggshells obtained from bakery and food stalls in the area of Surakarta, Central Java. Eggshells were washed and rinsed and, subsequently, they were oven-dried at a temperature of 120 °C for 10 h. The dried eggshells were crushed and sieved to a particle size with a range of 100–150 mm [14].

2.2. Catalyst Preparation and Characterization

The CaO catalysts and potassium hydroxide impregnated with eggshell were prepared using the wet impregnation technique. In this experiment, the CaO catalyst was impregnated by 10–25 wt% KOH. For this purpose, 10 g of eggshell was impregnated with 30 mL of KOH solution and stirred with a magnetic stirrer for 5 h, dried at 120 °C for 10 h, and calcined at 800 °C for 5 h. Subsequently, the catalysts characterization was carried out [12]. The experiment preparation of the catalyst was carried out at the Energy Laboratory, Chemical Engineering Department, ITS Surabaya, while the biodiesel produced at the Center of Biomass and Renewable Energy(CBIORE), Diponegoro University.

The catalyst properties were characterized by FT-IR analyses to determine the active surface functional groups. The FT-IR spectra were performed on Shimadzu Instrument Spectrum One 8400S FT-IR, which was operated in the range of 400–4000 wavenumbers (cm^{-1}). The samples were prepared using a KBr technique standard. The catalyst samples were ground into a fine powder in a clean mortar and weighed (0.4 mg). Subsequently, the powder was mixed with 200 mg of KBr powder (99.99%). A pressure of 5 tons per square inch was used to press the mixture in order to make a transparent pellet of an approximate thickness of 0.1 mm, which was suitable for spectrophotometer [14].

The chemical composition was determined by energy-dispersive X-ray fluorescence (ED-XRF) spectrometer, model Minipal 4, operating at a voltage of 30 kV and a current of 300 μA, with a measurement time of 600 s, in the range of 500–1000 wavenumbers. The morphology of the catalyst was observed using scanning electron micrographs (SEM). The SEM micrographs were performed using EVO® MA 10 scanning electron micrographs (SEM) with magnification 5000 and 10,000×. Preparation of the samples was performed by cutting the samples and encompassing them for impregnation section and electron beam was set at 20 kV [15].

2.3. Transesterification of Reutalism Trisperma Oil

The esterification of *Reutalism trisperma* oil was carried out using 3.0 wt% H_2SO_4 as a catalyst to reduce the amount of free fatty acid and the weight ratio of methanol to oil was set at 1:3. The esterification was carried out in a round bottom flask equipped with a reflux condenser and a magnetic stirrer. The mixture of the methanol, oil, and catalyst was heated at 65 °C in an oil bath for 2 h. After the reaction was complete, two layers of the product formed and these layers were separated from the mixture using a separating funnel. The upper layer rich in FFA, methanol, and water fraction was discarded, while the lower part was taken for transesterification reaction.

The transesterification reaction was carried out using a methanol to oil molar ratio of 15:1, with a catalyst with 7 wt% oil weight and a reaction time of 1 h at 60 °C. The mixture was stirred at 900 rpm. After the reaction, the mixture was allowed to settle for about 60 min, and the glycerol at the bottom layer was separated from the *Reutalism trisperma* methyl esters. The amount of catalyst used varied from 1, 3, 5, 7, and 10 wt% and the effect of the reaction time was also investigated at a range of 15, 30, 45, 60, and 90 min. We also varied the methanol to oil molar ratio from 6:1 to 15:1. The yield of biodiesel was calculated in triplicates in order to determine the standard deviation of each measurement and a single factor analysis of variance (ANOVA) was employed to evaluate the significance of differences among the groups of variables.

The fatty acid composition was determined using gas chromatography (Hewlett Packard, Palo Alto, CA, USA, 6890 series, Agilent, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) at a temperature of 250 °C. A column (HP-INNOWax Polyethylene Glycol) had a maximum temperature of 240 °C, and 1 µm film thickness with a helium gas injector. The measurement by using gas chromatography (GC) was started by mixing the sample with a stabilizer and solvent hexane, placing it in the auto sampling cell for 15 min, and turning on the GC. Compounds in the sample were identified by comparing the mass spectra and retention time using the library data [16]. The analysis of the biodiesel product was carried out at UPT Laboratorium Terpadu Universitas Diponegoro Semarang.

3. Results and Discussion

3.1. Characterization of the Catalyst

The functional groups in the KOH-impregnated eggshell catalyst were analyzed with FT-IR spectroscopy as depicted in Figure 1. Almost all samples showed a strong peak at 3641 cm^{-1} and 1647 cm^{-1}, which were assigned to the OH group from $Ca(OH)_2$ [17]. This result was due to molecules derived from absorption of water on the surface of CaO, where CaO is known to be hygroscopic so moisture can easily be absorbed from the air. The stretching vibrations of O–C–O bonds of unidentate carbonate at the surface of calcined CaO are identified by IR bands at about 1458, 1057, and 864 cm^{-1} [18].

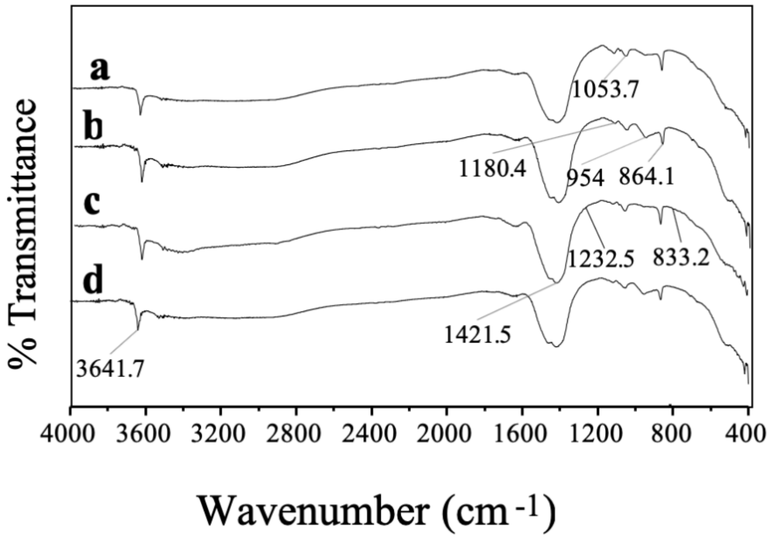

Figure 1. Fourier-transform infrared spectrometry (FT-IR) spectra of Potassium Hydroxide (KOH)-impregnated eggshell samples at various KOH concentrations (wt%): (**a**) 10%, (**b**) 15%, (**c**) 20%, and (**d**) 25% at 800 °C for 5 h.

The spectra of KOH-impregnated eggshell (20%), CaO-KOH and eggshell catalyst samples are presented in Figure 2. Almost all of the samples have four peaks of spectra, namely the OH group from $Ca(OH)_2$ at 3641 cm^{-1} and 1647 cm^{-1}; bands of carbonate ions (CO_3^{2-}) at 1458, 1057, and 864 cm^{-1} [9], and a band at 1390 cm^{-1} in the spectrum of the eggshell-KOH catalyst that was assigned to molecular CO_2. Furthermore, the reaction of KOH and $CaCO_3$ to calcination indicated the absence of a peak in the spectrum of the eggshell [12].

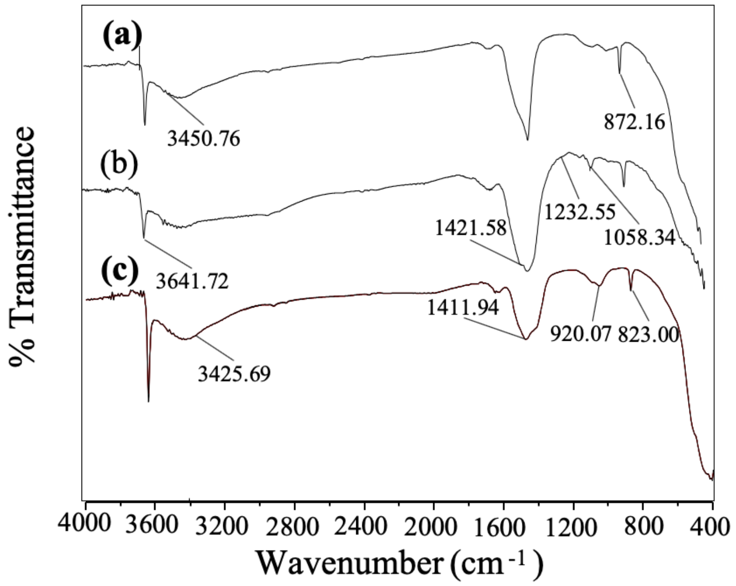

Figure 2. FT-IR spectra of (**a**) KOH-CaO, (**b**) KOH-impregnated eggshell, and (**c**) eggshell calcined at 800 °C for 5 h.

Table 1 depicts the chemical composition of KOH-impregnated eggshell at various concentrations, eggshell without impregnation, and CaO impregnation. The analysis of the eggshell revealed that a high amount of calcium, approximately 99.39 wt%, with potassium and sulfur, was found to be present in both the inner and outer eggshell membranes [19]. After impregnation, the percentage of calcium decreased, the lowest CaO of 94.42 wt% was found for KOH-impregnated eggshell (20%) due to the ion exchange between potassium and calcium. The percentage of potassium oxide increased from 0.4 to 5.06 wt% for the eggshell and KOH-impregnated eggshell (20%) catalysts, respectively. The results indicate the impregnation of KOH, which increases the potassium element, corresponds with the increase of KOH concentration.

Table 1. Chemical composition (wt%) of eggshell and KOH-impregnated eggshell.

Material	Oxide (%)					
	SO_3	K_2O	CaO	Fe_2O_3	CuO	SrO
KOH-impregnated Eggshell (10 wt%)	0.060	4.280	95.080	0.430	0.088	0.067
KOH-impregnated Eggshell (15 wt%)	0.000	4.300	95.000	0.290	0.240	0.180
KOH-impregnated Eggshell (20 wt%)	0.040	5.060	94.420	0.310	0.110	0.063
KOH-impregnated Eggshell (25 wt%)	0.000	12.000	87.600	0.130	0.170	0.120
Eggshell	0.010	0.400	99.390	0.130	0.048	0.026
CaO-KOH (20 wt%)	0.000	2.920	96.840	0.170	0.049	0.024

The ion exchange of Ca^{2+} and K^+ can form the new base site, namely K_2O, which can increase the base site of the catalyst as well as the catalytic activity of KOH-impregnated eggshell catalysts [20]. Moreover, the presence of a low amount of other elements (Cu, Fe, S, and Sr) is noticeable, which are considered as impurities of the catalyst. Due to its high calcium content, this catalyst is a promising material for biodiesel production [19].

Figures 3–5 show the SEM of CaO-KOH, eggshell, and KOH-impregnated eggshell catalysts, respectively. The eggshell has small, spherical, and homogenous solid particles with a smaller average size than particles of CaO-KOH and KOH-impregnated eggshell catalysts. KOH-impregnated eggshell appears as a clump of particles and clots forming obvious series with a larger size than the eggshell and CaO-KOH. Meanwhile, in CaO-KOH, the particles are not uniform but consisting of particles with random sizes [12].

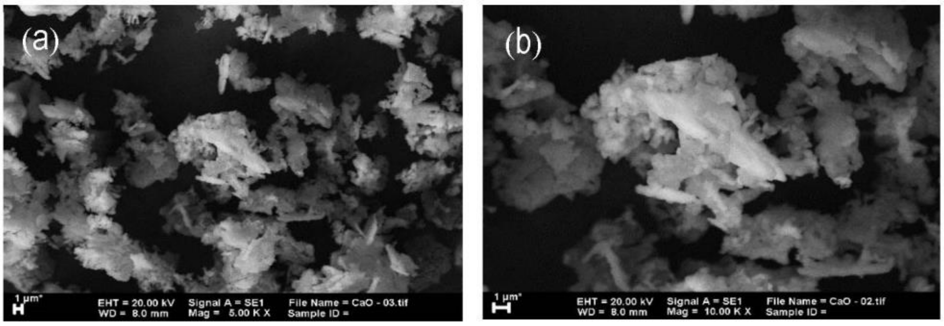

Figure 3. The SEM morphology of CaO-KOH catalysts powder with magnification of (**a**) 5000× (**b**) 10,000×.

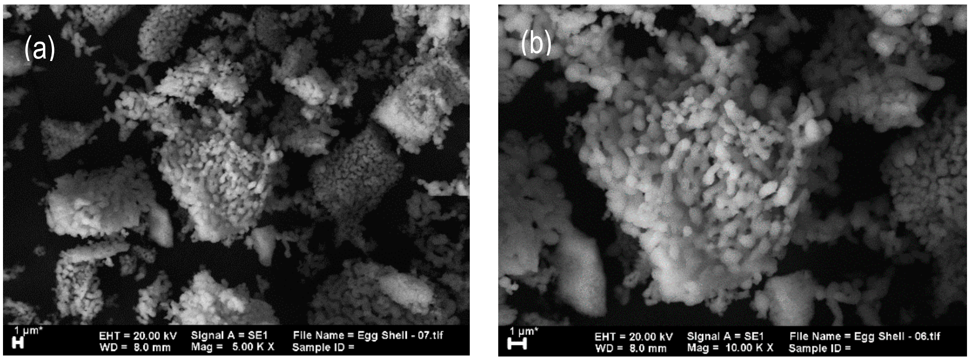

Figure 4. The SEM morphology of eggshell catalysts powder with magnification of (**a**) 5000× (**b**) 10,000×.

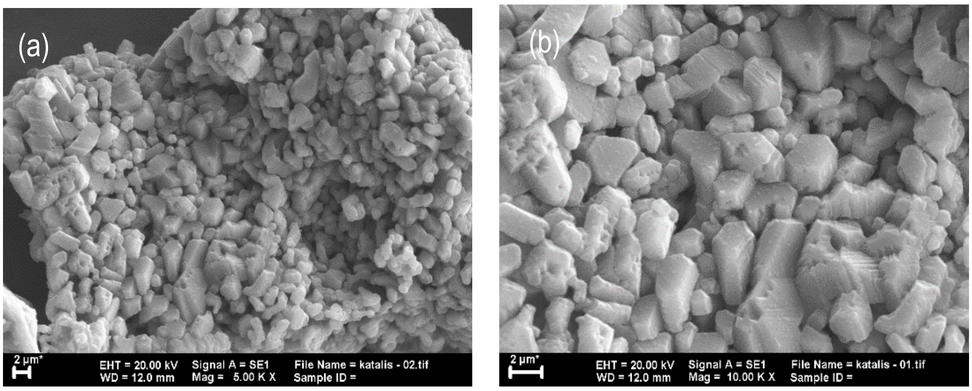

Figure 5. The SEM morphology of KOH-impregnated eggshell catalysts powder with magnification of (**a**) 5000× (**b**) 10,000×.

3.2. Effect of Methanol to Oil Molar Ratio

The effects of the molar ratio of the methanol to oil on biodiesel production with *Reutealis trisperma* oil were observed under a total reaction time of 60 min and temperature of 60 °C and the result is presented in Figure 6.

The ratios of methanol to oil molar in the reaction were varied, 6:1, 8:1, 10:1, 12:1, and 15:1. The biodiesel yield increased from 45% to 86% for the methanol to oil molar ratios of 6:1 to 12:1, and, on the contrary, decreased at 15:1 with a biodiesel yield of 68.59%. The highest biodiesel yield of 97.95% was observed in the methanol to oil molar ratio of 12:1. The maximum yield was obtained when using excess alcohol or removing one of the products since this shifted the equilibrium conversion of the reaction [21]. A significant increase in biodiesel yield is in accordance with an increase of the methanol to oil molar ratio ($p < 0.05$) [22]. Nevertheless, there is a limitation for certain methanol to oil ratios where the high methanol concentrations can cause the decline of biodiesel yield. The result was due to the interference in the reaction of the methanol with the reactants and dissolution of glycerol in the excess methanol [9]. Therefore, the appropriate methanol to oil molar ratio is 12:1 for the transesterification of *R. trisperma* oil with the KOH-impregnated eggshell catalyst.

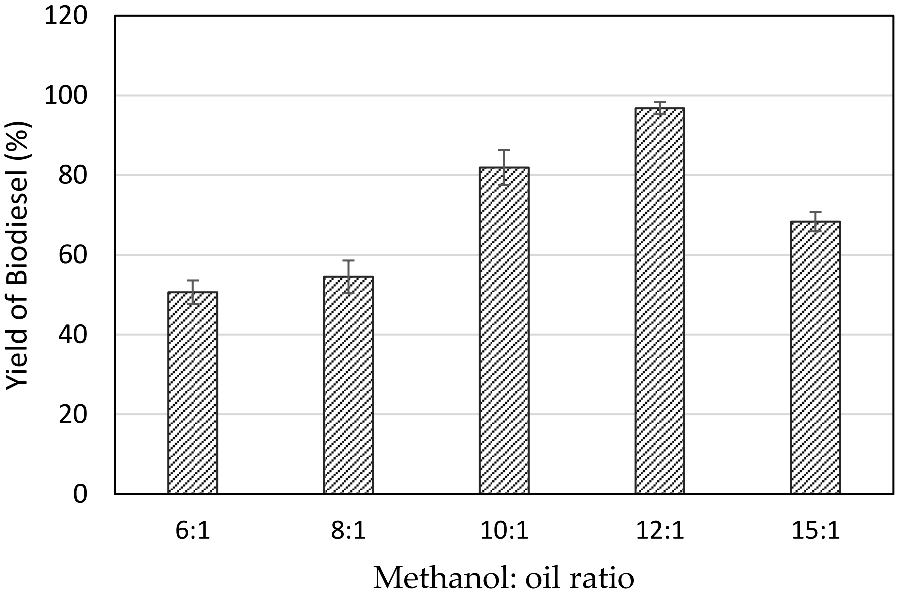

Figure 6. Effect of molar ratio on the biodiesel yield using KOH-impregnated eggshell (20 wt%) catalyst with a catalyst loading of 7 wt% at 60 °C for 60 min. The *p*-values of ANOVA test was 0.000 ($p < 0.05$).

3.3. Effect of Catalyst Loading

Figure 7 shows the effect of catalyst loading on the biodiesel yield with KOH-impregnated eggshell. The amount of catalyst was varied of 1.0, 3.0, 5.0, and 7.0 wt% in order to get the optimum biodiesel yield.

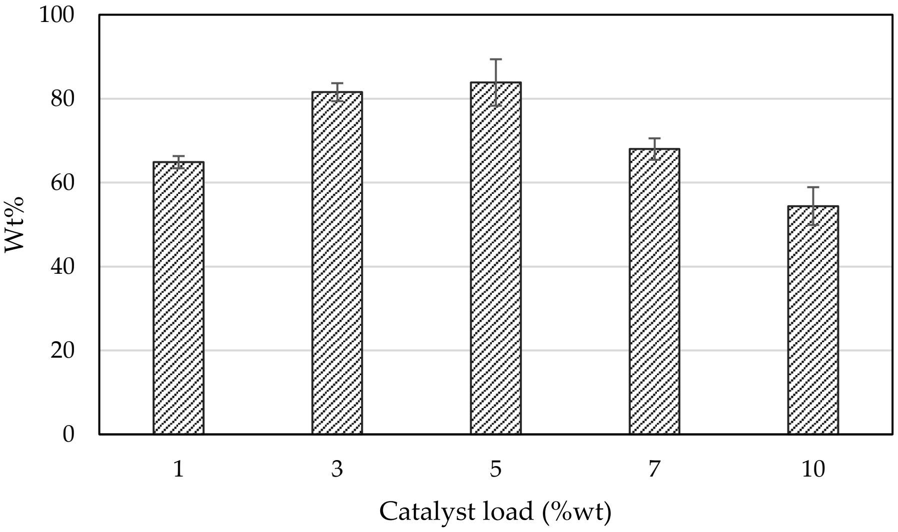

Figure 7. Effect of catalyst loading with KOH-impregnated eggshell (20%) on the biodiesel yield using methanol to oil molar ratio of 15:1 at 60 °C for 60 min. The *p*-values of ANOVA test was 0.000 ($p < 0.05$).

The highest biodiesel yield of 78% was obtained when 5 wt% of the catalyst was loaded. A significant increase in the amount of biodiesel yield from 56% to 78% was observed when the catalysts used in the reaction were increased from 1.0 wt% to 5.0 wt% ($p < 0.05$). However, a further increase of the amount of the catalyst up to 7 wt% and 10 wt% resulted in the significant decline of the biodiesel yield.

A higher amount of catalyst loading leads to higher mass transfer resistance because of the highly viscous mixture. Obadiah [23], Mahesh [9], and Wei [11] had similar findings on the transesterification of oil using CaO derived from waste eggshell as a catalyst, in which the increase of the catalyst caused a decrease of the methyl ester yield. Based on the result of this work, the optimum catalyst loading was 5 wt%, which had a biodiesel yield of 78%.

3.4. Properties of Biodiesel

The properties of the biodiesel produced from *R. Trisperma* oil were determined using the ASTM D56751 standards and the results are in Table 2. The results show that all of the properties were in the range of the standard limit. As compared to the reported previous data, biodiesel produced from *R. trisperma* has better biodiesel properties compared to yellow horn seed oil and *Silyburn maranum*, in terms of cetane number (62.5), density (890 kg/m^3), viscosity (6.0 cst), and acid value (0.8 mg KOH/g). Therefore, the biodiesel produced using *R. Trisperma* oil has better properties compared with other non-edible oils and can be used to serve as biodiesel feedstock.

Table 2. Properties of biodiesel based on ASTM D56751.

Properties	Method	Unit	ASTM D56751	*R. Trisperma*	*Yellow Horn Seed* [a]	*Silyburn Maranum* [b]
Density	ASTM D-1298	kg/m^3	860–900	890	-	914
Viscosity	ASTM D-445	mm^2/s (cst)	1.9–6.0	6.0	4.4	4.61
Acid Value	ASTM D-664	mg KOH/g	Max 0.8	0.5	0.06	0.08
Flash Point	ASTM D-93	°C	Min 130	148	165	230
Cetane Number	ASTM D-613	-	Min 47	62.5	56.1	34.04

Sources: [a] Yellow Horn Seed [24], [b] Silyburn Maranum [25].

3.5. Catalytic Activity

A chromatogram of biodiesel produced by the KOH-impregnated eggshell catalyst is presented in Figure 8. Four peaks were identified at a retention time of 9.716, 10.988, 19.303, and 20.875 min. They were assigned as methyl laurate, methyl myristate, methyl oleate, and methyl stearate. Unknown methyl ester peaks appear at a retention time of 12.468, 13.093, and 24.061 min. The highest peak at 19.303 min was attained for a methyl oleate compound.

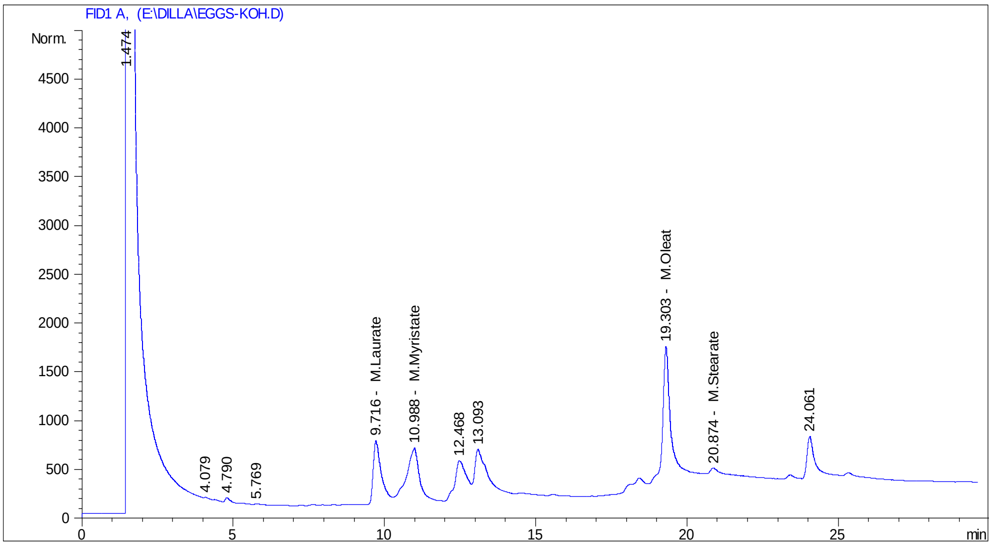

Figure 8. Chromatogram of biodiesel yield from transesterification of the KOH-impregnated eggshell.

Suprapto et al. [13] observed the chromatogram of biodiesel from *Reutalism trisperma* oil using CaO from limestone at different run time (17 min) analyses. Similarly, the results show the highest peak was found in methyl oleate at a retention time of 5.526 min. Other peaks were identified at a retention time of 3.687 and 5.780 min, and assigned as methyl palmitate and methyl stearate.

Figure 9 shows methyl oleate as the methyl ester content obtained by the transesterification reaction of *Reutealis trisperma* oil with various catalysts. It shows that 44% methyl ester was achieved with KOH-impregnated eggshell as the catalyst. Eggshell and CaO-KOH catalysts produced methyl oleate of 78% and 46%, respectively. The highest methyl oleate was obtained by using eggshell as the catalyst. These results are consistent with the XRF results, which show that the higher the CaO content in eggshell, the higher methyl ester content.

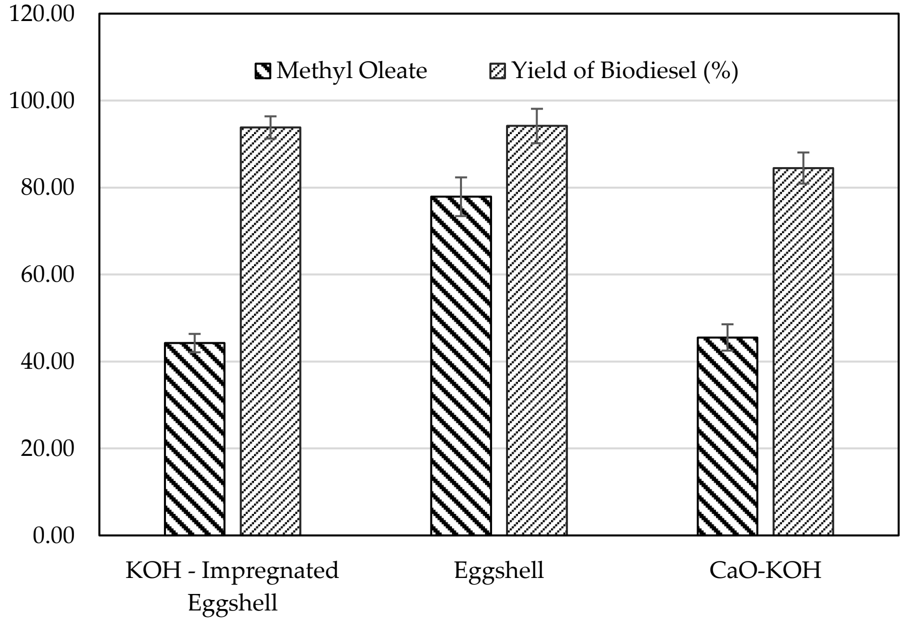

Figure 9. The yield of methyl ester produced by KOH-impregnated eggshell, eggshell, and CaO-KOH catalysts. The *p*-value of the ANOVA test was 0.000 ($p < 0.05$).

Meanwhile, the highest yield of 94% was obtained with KOH-impregnated eggshell as the catalyst due to the presence of K_2O as a new base site that can significantly increase ($p < 0.05$) the catalytic activity in the transesterification reaction of *Reutealis trisperma* oil [20]. Meanwhile, the lowest yield of 84% was obtained with CaO-KOH as the catalyst. There is no significant increase in biodiesel yield when eggshell without impregnation was used as the catalyst since the content of the active site (K_2O and CaO) according to XRF results is almost the same as the KOH-impregnated eggshell.

4. Conclusions

Biodiesel fuel was developed from a novel feedstock of *Reutalism trisperma* oil using KOH-impregnated eggshell. A CaO catalyst was successfully synthesized from eggshell. The KOH-impregnated eggshell calcined at 800 °C with a catalyst with CaO content as the main composition and with K_2O as a new base site. The KOH-impregnated eggshell catalysts demonstrated higher catalytic activity in the transesterification reaction of *Reutealis trisperma* oil. It can be concluded that the highest biodiesel yield of 94% was obtained with optimum reaction conditions; a reaction time of 60 min, temperature of 60 °C, methanol to oil molar ratio of 12:1, and catalyst loading of 5%. These optimum reaction conditions were obtained using KOH-impregnated eggshell (20%) as a catalyst due to the higher stable amount of active sites (K_2O and CaO) as compared with other catalysts.

Author Contributions: K.K. and H.H. contributed to design and conception, drafting the article, and final approval of the article. D.P. prepared and characterized the catalyst; S.M. conducted biodiesel production and catalyst test; T.P.O. and M.N.F. contributed to collecting the references, drafting the article, preparing all figures and all tables, and the discussion. W.W., A.B., and A.R., contributed to help data analysis and discussion.

Funding: This research was funded by the Ministry of Research, Technology and Higher Education (KEMENRISTEKDIKTI) Republic of Indonesia through Riset Konsorsium Unggulan Perguruan Tinggi program in 2018–2019.

Acknowledgments: The authors would like to express their appreciation for the support from the Ministry of Research, Technology and Higher Education (KEMENRISTEKDIKTI) through Hibah Konsorsium Riset Unggulan Perguruan Tinggi (KRUPT) No 451-01/UN-7.P4.3/PP/2019 under title of grant: Production of multi-feedstock biodiesel with high flexibility to support national energy security. This research was also supported by Center of Biomass and Renewable Energy (CBIORE), Diponegoro University.

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

References

1. Yadav, M.; Singh, V.; Sharma, Y.C. Methyl Transesterification of Waste Cooking Oil Using a Laboratory Synthesized Reusable Heterogeneous Base Catalyst: Process Optimization and Homogeneity Study of Catalyst. *Energy Convers. Manag.* **2017**, *148*, 1438–1452. [CrossRef]
2. Farooq, M.; Ramli, A. Biodiesel Production from Low FFA Waste Cooking Oil Using Heterogeneous Catalyst Derived from Chicken Bones. *Renew. Energy* **2015**, *76*, 362–368. [CrossRef]
3. Pasupulety, N.; Gunda, K.; Liu, Y.; Rempel, G.L.; Ng, F.T.T. Production of Biodiesel from Soybean Oil on CaO/Al_2O_3 Solid Base Catalysts. *Appl. Catal. A Gen.* **2013**, *452*, 189–202. [CrossRef]
4. Kusmiyati, K.; Pratiwi, T.R.; Wulandari, T. Waste Fish Oil Biodiesel Production and Its Performance in Diesel Engine. *ARPN J. Eng. Appl. Sci.* **2016**, *11*, 1040–1044.
5. Holilah, H.; Prasetyoko, D.; Oetami, T.P.; Santosa, E.B.; Zein, Y.M.; Bahruji, H.; Ediati, R.; Juwari, J. The Potential of Reutealis Trisperma Seed as a New Non-Edible Source for Biodiesel Production. *Biomass Convers. Biorefin.* **2014**, *5*, 347–353. [CrossRef]
6. Kumar, K.R.; Chandrika, K. Biodiesel Production and Characterization from Non-Edible Oil Tree Species Aleurites Trisperma Blanco. *Biomass Convers. Biorefin.* **2014**, *5*, 287–294. [CrossRef]
7. Hadiyanto, H.; Lestari, S.P.; Widayat, W. Preparation and Characterization of Anadara Granosa Shells and $CaCO_3$ as Heterogeneous Catalyst for Biodiesel Production. *Bull. Chem. React. Eng. Catal.* **2016**, *11*, 21–26. [CrossRef]
8. Sanjay, B. Heterogeneous Catalyst Derived from Natural Resources for Biodiesel Production: A Review. *Res. J. Chem. Sci.* **2013**, *3*, 95–101.
9. Sneha, E.M.; Ramanathan, A.; Begum, K.M.M.S.; Narayanan, A. Biodiesel Production from Waste Cooking Oil Using KBr Impregnated CaO as Catalyst. *Energy Convers. Manag.* **2015**, *91*, 442–450.
10. Lesbani, A.; Tamba, P.; Mohadi, R. Preparation Of Calcium Oxide From Achatina Fulica As Catalyst For Production Of Biodiesel From Waste Cooking Oil. *Indones. J. Chem* **2013**, *13*, 176–180. [CrossRef]
11. Wei, Z.; Xu, C.; Li, B. Application of Waste Eggshell as Low-Cost Solid Catalyst for Biodiesel Production. *Bioresour. Technol.* **2009**, *100*, 2883–2885. [CrossRef] [PubMed]
12. Zeng, D.; Zhang, Q.; Chen, S.; Liu, S.; Chen, Y.; Tian, Y.; Wang, G. Preparation and Characterization of a Strong Solid Base from Waste Eggshell for Biodiesel Production. *J. Environ. Chem. Eng.* **2015**, *3*, 560–564. [CrossRef]
13. Suprapto, S.; Fauziah, T.R.; Sangi, M.S.; Oetami, T.P.; Qoniah, I.; Prasetyoko, D. Calcium Oxide from Limestone as Solid Base Catalyst in Transesterification of Reutealis Trisperma Oil. *Indones. J. Chem.* **2016**, *16*, 208–213. [CrossRef]
14. Liao, C.C.; Chung, T.W. Optimization of Process Conditions Using Response Surface Methodology for the Microwave-Assisted Transesterification of Jatropha Oil with KOH Impregnated CaO as Catalyst. *Chem. Eng. Res. Des.* **2013**, *91*, 2457–2464. [CrossRef]
15. Turco, F.; Davit, P.; Cossio, R.; Agostino, A.; Operti, L. Accuracy Improvement by Means of Porosity Assessment and Standards Optimization in SEM-EDS and XRF Elemental Analyses on Archaeological and Historical Pottery and Porcelain. *J. Archaeol. Sci. Rep.* **2017**, *12*, 54–65. [CrossRef]

16. Bahadur, S.; Goyal, P.; Sudhakar, K. Ultrasonic Assisted Transesterification of Neem Oil for Biodiesel Production. *Energy Sources Part A Recovery Util. Environ. Eff.* **2015**, *37*, 1921–1927. [CrossRef]
17. Mar, W.W.; Somsook, E. Methanolysis of Soybean Oil over KCl/CaO Solid Base Catalyst for Biodiesel Production. *Sci. Asia* **2012**, *38*, 90–94. [CrossRef]
18. Granados, L.M.; Poves, Z.M.D.; Alonso, M.D.; Mariscal, R.; Galisteo, C.F.; Tost, M.R.; Santamaria, J.; Fierro, G.L.J. Biodiesel from Sunflower Oil by Using Activated Calcium Oxide. *Appl. Catal. B Environ.* **2007**, *73*, 317–326. [CrossRef]
19. Correia, L.M.; Cecilia, J.A.; Castellón, E.R.; Cavalcante, C.L., Jr.; Vieira, R.S. Relevance of the Physicochemical Properties of Calcined Quail Eggshell (CaO) as a Catalyst for Biodiesel Production. *J. Chem.* **2017**, *2017*, 1–12. [CrossRef]
20. Meher, L.C.; Kulkarni, M.G.; Dalai, A.K.; Naik, S.N. Transesterification of Karanja (*Pongamia Pinnata*). *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 389–397. [CrossRef]
21. Padhi, S.K.; Singh, R.K. Non-Edible Oils as the Potential Source for the Production of Biodiesel in India: A Review. *J. Chem. Pharm. Res.* **2011**, *3*, 39–49.
22. Dehkordi, A.M.; Ghasemi, M. Transesterification of Waste Cooking Oil to Biodiesel Using Ca and Zr Mixed Oxides as Heterogeneous Base Catalysts. *Fuel Process. Technol.* **2012**, *97*, 45–51. [CrossRef]
23. Obadiah, A.; Swaroopa, G.A.; Kumar, S.V.; Jeganathan, K.R. Biodiesel Production from Palm Oil Using Calcined Waste Animal Bone as Catalyst. *Bioresour. Technol.* **2012**, *116*, 512–516. [CrossRef] [PubMed]
24. Li, J.; Fu, Y.J.; Qu, X.J.; Wang, W.; Luo, M.; Zhao, C.J.; Zu, Y.G. Biodiesel Production from Yellow Horn (*Xanthoceras Sorbifolia* Bunge.) Seed Oil Using Ion Exchange Resin as Heterogeneous Catalyst. *Bioresour. Technol.* **2012**, *108*, 112–118. [CrossRef] [PubMed]
25. Fadhil, A.B.; Ahmed, K.M.; Dheyab, M.M. *Silybum Marianum* L. seed Oil: A Novel Feedstock for Biodiesel Production. *Arab. J. Chem.* **2012**, *10*, 683–690. [CrossRef]