

Article

Optimization of Biodiesel Production from Waste Cooking Oil Using S-TiO₂/SBA-15 Heterogeneous Acid Catalyst

Muhammad Nobi Hossain, Md Sufi Ullah Siddik Bhuyan, Abul Hasnat Md Ashraful Alam and Yong Chan Seo *

Department of Environmental Engineering, Sangji University, 83 Sangjidae-gil, Wonju-si, Gangwon-do 26339, Korea; mnhossain.8911@gmail.com (M.N.H.); siddikdcc@gmail.com (M.S.U.S.B.); hasnat_38@yahoo.com (A.H.M.A.A.)

* Correspondence: ycseo@sangji.ac.kr; Tel.: +82-33-730-7525; Fax: +82-33-730-0444

Received: 10 December 2018; Accepted: 4 January 2019; Published: 10 January 2019



Abstract: The aim of this research was to synthesize, characterize, and apply a heterogeneous acid catalyst to optimum biodiesel production from hydrolyzed waste cooking oil via an esterification reaction, to meet society's future demands. The solid acid catalyst S-TiO₂/SBA-15 was synthesized by a direct wet impregnation method. The prepared catalyst was evaluated using analytical techniques, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and the Brunauer–Emmett–Teller (BET) method. The statistical analysis of variance (ANOVA) was studied to validate the experimental results. The catalytic effect on biodiesel production was examined by varying the parameters as follows: temperatures of 160 to 220 °C, 20–35 min **reaction** time, methanol-to-oil mole ratio between 5:1 and 20:1, and catalyst loading of 0.5%–1.25%. The maximum biodiesel yield was $94.96 \pm 0.12\%$ obtained under the optimum reaction conditions of 200 °C, 30 min, and 1:15 oil to methanol molar ratio with 1.0% catalyst loading. The catalyst was reused successfully three times with 90% efficiency without regeneration. The fuel properties of the produced biodiesel were found to be within the limits set by the specifications of the biodiesel standard. This solid acid catalytic method can replace the conventional homogeneous catalyzed transesterification of waste cooking oil for biodiesel production.

Keywords: analysis of variance; biodiesel; esterification; heterogeneous acid catalyst; optimization; waste cooking oil

1. Introduction

The demand for alternative energy sources has increased due to the depletion of fossil fuels. Recently, biodiesel has become the most promising alternative energy source to address the energy and global warming crises because of its cost effectiveness, eco-friendliness, and renewability [1]. Biodiesel is composed of fatty acid mono alkyl esters and is synthesized by esterification or transesterification of vegetable oils [2], animal fats [3,4], or waste oils with methanol in the presence or absence of acid, base, or enzyme catalyst [5–7].

In general, biodiesel is produced via a transesterification reaction in the presence of a homogeneous or heterogeneous catalyst [8–10]. However, to get the maximum biodiesel yield, most commercial biodiesel is produced through a transesterification reaction in the presence of a homogeneous acid or base catalyst, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sulfuric acid (H₂SO₄), or phosphoric acid (H₃PO₄). A homogeneous catalytic transesterification reaction proceeds more rapidly in mild reaction conditions than do those using the other types of catalysts [10–12].

However, homogeneous catalysts possess some disadvantages: they are corrosive, toxic, hygroscopic, and easily soluble in reaction mixtures, causing poor product quality [13]. Homogeneous acid/base catalysts are very sensitive to a high content of free fatty acids (FFAs) in feedstocks. Moreover, when these catalysts are used, saponification products can be formed, which require washing by considerable amounts of fresh water; this, in turn, causes a loss of biodiesel yield and generates a large amount of wastewater. Besides this, these catalysts cause unavoidable reactor corrosion and are very hard to recover, thus increasing the overall production cost. In this case, biodiesel can be produced from FFA by an esterification reaction using a heterogeneous acid catalyst; a schematic of this esterification reaction is presented in Figure 1 [13–15].

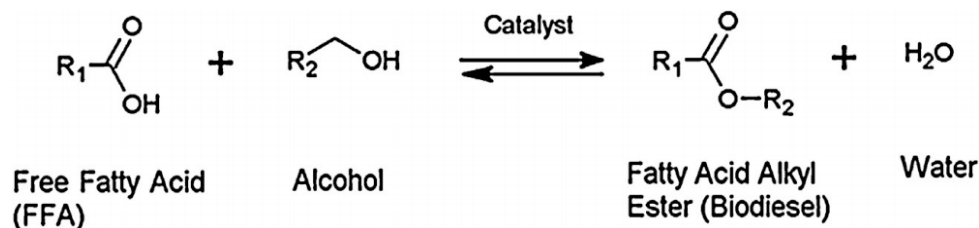


Figure 1. A schematic representation of the esterification reaction [13].

Biodiesel production by noncatalytic transesterification at supercritical conditions can resolve the difficulties resulting from homogeneous catalytic transesterification as it can handle impurities in the oil sample, such as high FFA or moisture content. However, it involves high production cost and requires high reaction conditions (high temperature and pressure) and a special alloyed reactor [2,16]. Therefore, to overcome these drawbacks, the focus of the current advancements in heterogeneous catalysis research is to develop a reusable heterogeneous solid acid catalyst. Solid acid catalysts can be separated more easily from the reaction mixtures and can also be reused more efficiently [17]. As a result of the reuse of these catalysts, biodiesel synthesis could be more economical. Also, solid acid catalysts are insensitive to moisture and the high FFA content of low-grade oil, which would lead to cheaper production without any pretreatment [15,18].

Some research has been done using solid acid catalysts, such as ion exchange resin, zeolites, and zeotype materials. However, more work is still needed in the search for new solid acid catalysts for sustainable biodiesel production [15,19,20]. In recent years, mesoporous silica-supported catalysts have been used in the esterification process because of their high surface area, uniformity, nonporous channel, stability, and large pore size, which make them helpful to reactions involving large molecules [2,20].

The aim of this work was to synthesize and characterize a highly efficient supported solid acid catalyst by a direct wet impregnation catalytic method, and to optimize biodiesel production from waste cooking oil using the prepared catalyst. The activity of the prepared solid catalyst was evaluated for biodiesel production from high-FFA-content raw material, and the performance of the catalyst was compared with that of other solid acid catalysts. Although several kinds of solid catalysts have been used for biodiesel production, the directly synthesized catalyst (S-TiO₂/SBA-15) is expected to reduce the severe reaction conditions. The prepared catalyst was characterized using surface area analysis (BET: Brunauer–Emmett–Teller), XRD (X-ray diffraction), and an acid–base neutralization method. The reusability of the prepared catalyst was also observed.

2. Results and Discussion

2.1. Characterization of the Prepared Catalyst

2.1.1. Physical Properties of the Catalyst

The porosity of the prepared S-TiO₂/SBA-15 catalyst was evaluated from N₂ adsorption isotherms (Figure 2). The surface characteristics of the synthesized catalyst and support, including surface area,

pore volume, and pore size, are reported in Table 1. It can be seen that the surface area, pore volume, and pore size of the catalyst decreased as TiO_2 loading increased on the SBA-15 support. The decrease in the surface area, pore volume, and pore size are due to the gradual accumulation of the metal oxide species blocking some of the pores of the support during preparation. However, the decrease in the surface area is very small, suggesting that the active sulfated metal oxide species are highly dispersed on the surface of the support [2,4].

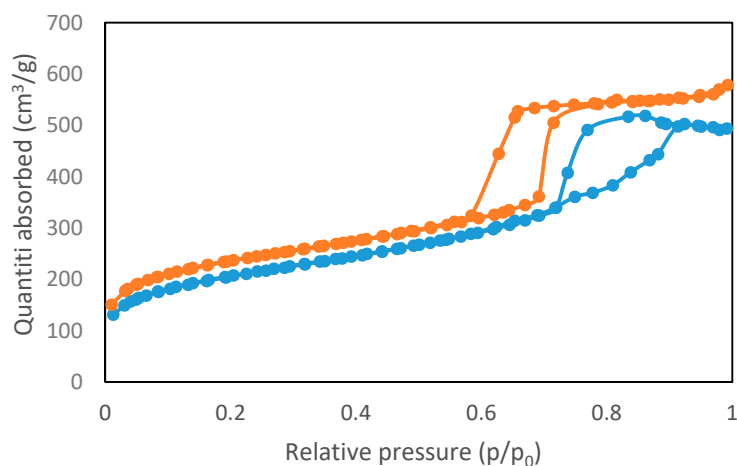


Figure 2. N_2 physisorption isotherm of the SBA-15 support and the S- TiO_2 /SBA-15 catalyst.

Table 1. Surface area, pore size, and pore volume of the catalyst.

Sample	Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)	Surface Acidity (mmole/g)
SBA-15 [2]	833.80	5.38	0.13	-
S- TiO_2 /SBA-15	733.98	5.10	0.09	0.18

2.1.2. Low- and Wide-Angle X-ray Diffraction

Figure 3 shows the XRD patterns of the support and catalyst as measured using an X-ray diffractometer system (D/MAX-2500V). Low-angle XRD analysis is a very effective probe to understand mesostructured materials. Figure 4A shows the small-angle XRD patterns of the SBA-15 support and the S- TiO_2 /SBA-15 catalyst. The SBA-15 support and the S- TiO_2 /SBA-15 catalyst both exhibited XRD diffraction patterns with one very intense diffraction peak and two small peaks. The intense peak was indexed as d_{100} , and the smaller peaks were indexed as d_{110} and d_{200} , which are characteristic of the 2-D hexagonal ($p6mm$) ordered mesoporous structure of the SBA-15 with excellent textural uniformity [2]. From this finding, it can be concluded that the S- TiO_2 /SBA-15 catalyst retains the mesoporous structure of the SBA-15 support.

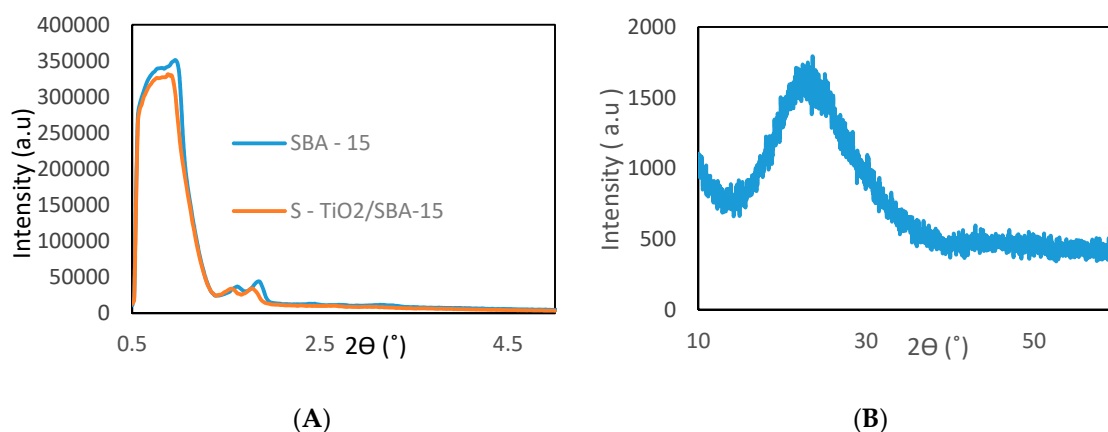


Figure 3. (A) Small-angle patterns of the SBA-15 support and the S-TiO₂/SBA-15 catalyst; (B) Wide-angle patterns of the S-TiO₂/SBA-15 catalyst.

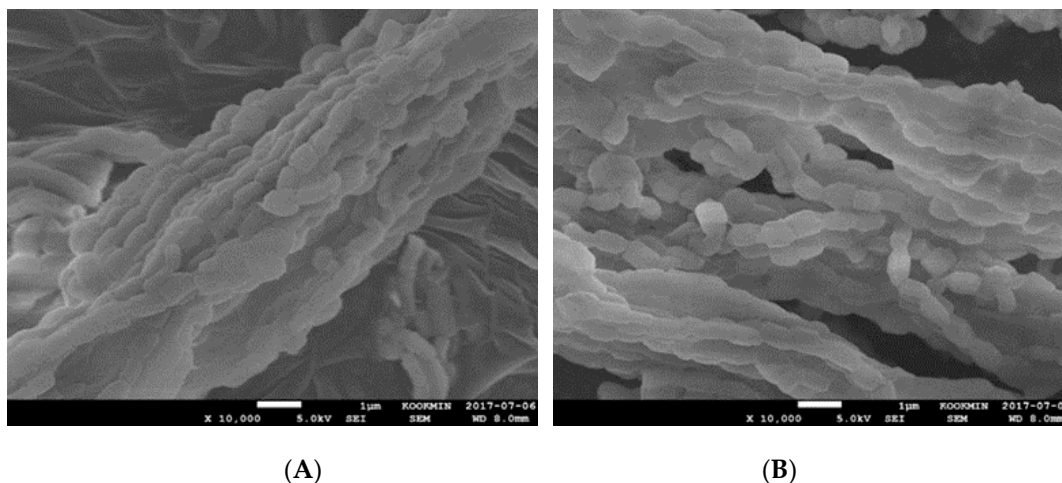


Figure 4. FE-SEM images of (A) pure SBA-15 silica and (B) the synthesized S-TiO₂/SBA-15 catalyst.

Figure 3B shows the large-angle XRD patterns of the S-TiO₂/SBA-15 catalyst. Only one broad peak appeared between 20° and 30°. This is characteristic of the SBA-15 silica [21]. There were no additional peaks related to TiO₂ in the patterns. The results indicated that TiO₂ was finely dispersed on the SBA-15.

2.1.3. Scanning Electron Microscopy

The morphology of pure SBA-15 (A) and the S-TiO₂/SBA-15 (B) catalyst was characterized by SEM, as shown in Figure 4. The well-ordered hexagonal mesoporous structure of the SBA-15 template was preserved after the impregnation of metal oxide in the SBA-15 support. The micrographs (Figure 4) revealed that the S-TiO₂/SBA-15 retained the well-defined wheat-like macrostructure of pure SBA-15. The SEM images in Figure 5 indicate that the hexagonal shape of SBA-15 remained unchanged after being incorporated with S-TiO₂, which was also shown by XRD in Figure 3.

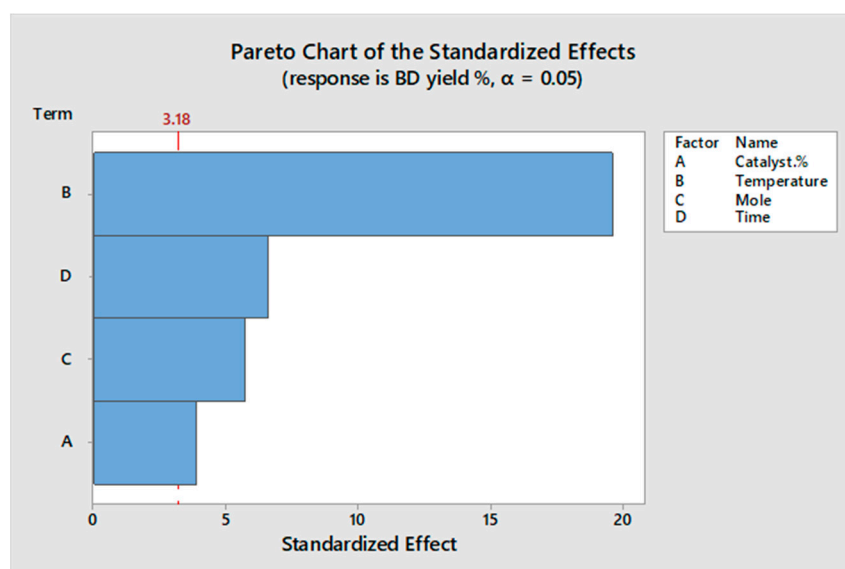


Figure 5. Pareto chart of the standardized effects on biodiesel yield.

2.1.4. Acid–Base Neutralization Technique

The concentration of acidic sites on the catalyst surface (surface acidity) was measured by means of a neutralization titration technique [2,17]. The surface acidity of the catalyst is presented in Table 2. The surface acidity of the prepared S–TiO₂/SBA-15 catalyst plays a key role in the esterification of waste cooking oil.

Table 2. Experimental design matrix with experimental and predicted values of biodiesel yield.

Std Order	Run Order	Blocks	Pt Type	Catalyst %	Temperature	Mole	Time	Biodiesel Yield %	Predicted
1	1	1	1	1.00	160	20	20	75.35	78.03
2	2	1	1	1.00	180	20	20	80.49	83.17
3	3	1	1	1.00	200	20	20	89.04	90.76
4	4	1	1	1.00	220	20	20	96.03	98.35
5	5	1	1	0.50	220	20	20	91.83	94.51
6	6	1	1	0.75	220	20	20	93.80	96.48
7	7	1	1	1.00	220	20	20	96.03	98.35
8	8	1	1	1.25	220	20	20	95.99	98.67
9	9	1	1	1.00	200	5	20	83.15	85.83
10	10	1	1	1.00	200	10	20	85.36	88.04
11	11	1	1	1.00	200	15	20	88.68	91.41
12	12	1	1	1.00	200	20	20	87.83	90.76
13	13	1	1	1.00	200	15	20	89.50	91.41
14	14	1	1	1.00	200	15	25	90.65	93.33
15	15	1	1	1.00	200	15	30	95.18	97.85
16	16	1	1	1.00	200	15	35	95.36	98.04

2.2. Statistical Analysis

The optimization of biodiesel production from waste cooking oil was performed using a custom full factorial design. The process factors (catalyst loading, temperature, methanol-to-oil mole ratio, and reaction time) and their results are presented in Table 2. The biodiesel yield was selected as a response in the experimental design.

A statistical analysis of variance (ANOVA) was performed to emphasize the acceptability and significance of the experimental data obtained from investigations of the effect of the process parameters on biodiesel production using the S–TiO₂/SBA-15 heterogeneous acid catalyst (Table 3). The coefficient of determination (R^2) and adjusted coefficient of determination ($\text{adj } R^2$) were used to

evaluate the adequacy of the model. The F values and p values were also used to check the significance of the corresponding coefficient. If the p value was lower than 0.005, then the given model was considered to be significant and the process factors to contribute significantly to the responses [22].

Table 3. Analysis of variance (ANOVA).

Source	DF	Adj SS	Adj MS	F Value	p Value
Model	12	560.380	46.698	131.90	0.001
Linear	12	560.380	46.698	131.90	0.001
Catalyst %	3	14.234	4.745	13.40	0.030
Temperature	3	344.069	114.690	323.93	0.000
Mole	3	29.986	9.995	28.23	0.011
Time	3	40.033	13.344	37.69	0.007
Error	3	1.062	0.354		
Total	15	561.443			

$S = 0.5950$, $R^2 = 0.998$, $\text{Adj } R^2 = 0.995$; where SD = standard deviation, DF = degrees of freedom, Adj SS = adjusted sum of square, Adj MS = adjusted means of square, F = Probability distribution, p = probability.

According to the ANOVA results (Table 3), it can be seen that the p value of the model is 0.001, which indicates that model is very suitable. The significance of the coefficients of process factors were also confirmed by their p values ($p < 0.005$). In addition, the adequacy of the model was proven by the coefficient of determination R^2 (0.998) and the adjusted coefficient of determination $\text{adj } R^2$ (0.995). The larger the F value and smaller the p value, the more significant the corresponding coefficient of the studied factor. According to the p values (Table 3), the order of significance of the studied factors on the biodiesel yield is temperature first, followed by time, mole, and catalyst; this was also confirmed by the Pareto chart (Figure 5).

2.3. Effect of Process Parameters and Optimization

The effect of each process parameter on the response variable (biodiesel yield) at their different level is shown in Figure 6. In each plot of performance parameters, the maximum biodiesel yield indicates the optimum condition for an individual parameter. From Figure 6, it can be seen that the maximum biodiesel yield was obtained at 1 wt % catalyst loading. However, the biodiesel yield started to decrease when the catalyst loading exceeded 1 wt %. This is because excess catalyst can disturb the reaction mixture, causing diffusion problems [23]. Hence, 1 wt % catalyst loading was selected as the optimum level. In the case of the effect of temperature, from Figure 6, it can be observed that with increasing temperature, the biodiesel yield increases as the reacting molecules collide very frequently [12]. The maximum biodiesel yield was obtained at 220 °C. Since our target was higher biodiesel yield at lower temperature, 200 °C was selected as optimum reaction temperature. Since the esterification reaction is reversible in nature, an excess amount of methanol is needed to shift the reaction equilibrium to the right-hand side with greater formation of methyl ester (biodiesel yield). The maximum biodiesel yield was obtained when the methanol-to-oil mole ratio was increased up to 15:1. On the other hand, from Figure 6, when the methanol-to-oil mole ratio was beyond 15:1, the biodiesel yield decreased. Performing the reaction at a higher methanol-to-oil mole ratio favors the reverse reaction and decreases the biodiesel yield [12,24]. The reaction time also played an important role in increasing biodiesel yield in the acid-catalyzed esterification process. Figure 6 shows that with increasing reaction time, the biodiesel yield also increased. Biodiesel yield sharply increased when the reaction time was increased from 25 to 30 min. However, when the reaction time was increased from 30 min to 35 min, there was no significant change. Therefore, a reaction time of 30 min was taken to be the optimum point.

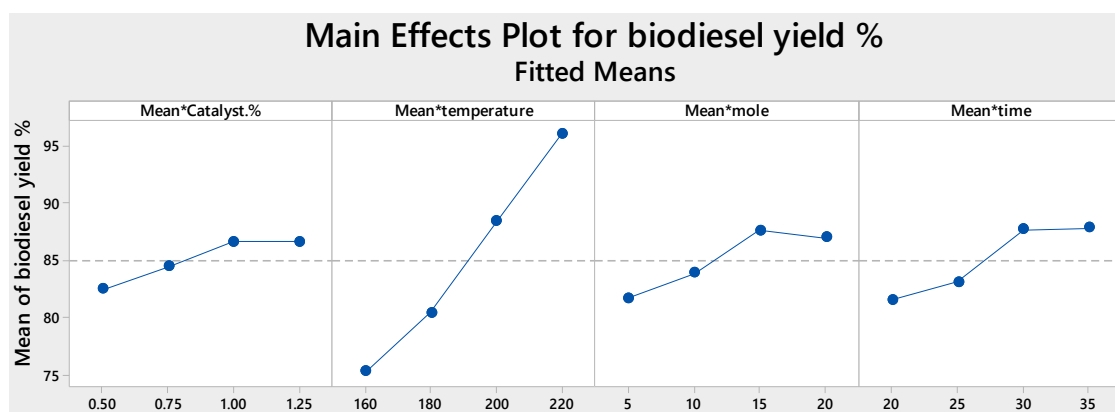


Figure 6. Effect of process parameters on biodiesel yield.

The optimum conditions for biodiesel yield are catalyst loading of 1 wt %, reaction temperature of 200 °C, methanol-to-oil mole ratio of 15:1, and reaction time of 30 min. An experimental confirmation test was carried out at optimum conditions to verify the results obtained from the experimental design. The confirmation test was run in duplicate, and the optimum biodiesel yield obtained was $94.96 \pm 0.12\%$ at optimum conditions.

2.4. Catalytic Activity of S-TiO₂/SBA-15 Solid Acid Catalyst in Esterification and Comparison with Other Solid Acid Catalysts in Transesterification

To investigate the performance of the catalyst, a comparison study was carried out between catalytic and noncatalytic esterification reactions for biodiesel production. A comparison of reaction conditions and the performance of various solid acid catalysts used in biodiesel production from waste cooking oil is presented in Table 4. The results presented in Table 4 indicate that the production of biodiesel using the S-TiO₂/SBA-15 catalyst was much higher than that using the noncatalytic process and higher than that using the SBA-15 support. This is due to the acid density on the surface of the catalyst influencing the catalytic activity in the esterification of waste cooking oil [2]. It also can be seen in Table 4 that a yield above 95% was achieved in more mild reaction conditions using our S-TiO₂/SBA-15 solid acid catalyst, compared to all other catalysts, except S-TiO₂/MCM-41. As shown in Table 4, 99.29% biodiesel yield was possible at the methanol supercritical temperature (240 °C) using S-TiO₂/SBA-15.

Table 4. Comparison of catalytic performance between heterogeneous S-TiO₂/SBA-15 acid catalyst and other heterogeneous acid catalysts.

Catalyst	Reaction Temp. °C	Catalyst Load %	Methanol-to-Oil Mole Ratio	Reaction Time min	Biodiesel Yield %	Reference
Blank	200		15:1	30	62.55	This study
SBA-15	200	1	15:1	30	71.96	This study
SO ₄ ²⁻ /SnO ₂ -SiO ₂	150	6	15:1	90	88.2	[25]
Carbon-based catalyst derived from starch	80	10	30:1	480	92	[26]
ZS/Si	200	3	18:1	300	98%	[27]
S-TiO ₂ /MCM-41	240	1	20:1	20	99.29	[4]
S-TiO ₂ /SBA-15	240	1	20:1	20	97.50	This study
S-TiO ₂ /SBA-15	200	1	15:1	30	94.96	This study

The aim of this study was to produce biodiesel at temperatures below the supercritical point. We can see in Table 4 that a 92% yield is possible at a low reaction temperature (80 °C) using a carbon-based catalyst derived from starch, but it needs not only large catalyst amount and methanol-to-oil mole ratio, but also a long reaction time, which can increase the production cost. Using the ZS/Si solid acid catalyst, a higher reaction yield was obtained compared to that using the S-TiO₂/SBA-15 synthesized catalyst. However, as can be seen in Table 4, the ZS/Si catalyst also needs a long reaction time and a large amount of catalyst compared to S-TiO₂/SBA-15. Hence, it can be concluded that S-TiO₂/SBA-15 is a promising alternative solid acid catalyst for biodiesel production.

2.5. Reusability and Stability of the Catalyst

In order to observe the activity and stability of the catalyst, the reusability of the catalyst was studied, as shown in Figure 7. From an economic point of view, the reusability of the catalyst is a very important feature for solid acid catalysts as it could make the post-reaction process simpler and reduce the production cost for the desired product. Another reason to select a solid superacid catalyst is for its easy removal from the final product and its environmental friendliness [28]. The reusability of the catalyst was investigated under the optimum reaction conditions. Upon completion of the reaction, the catalyst was recovered by filtration, washed with hexane, and finally dried at 105 °C. The catalyst was reused successfully three times with 90% efficiency and without significant loss in activity. The experimental results indicate that S-TiO₂/SBA-15 is a stable catalyst and can be reused several times.

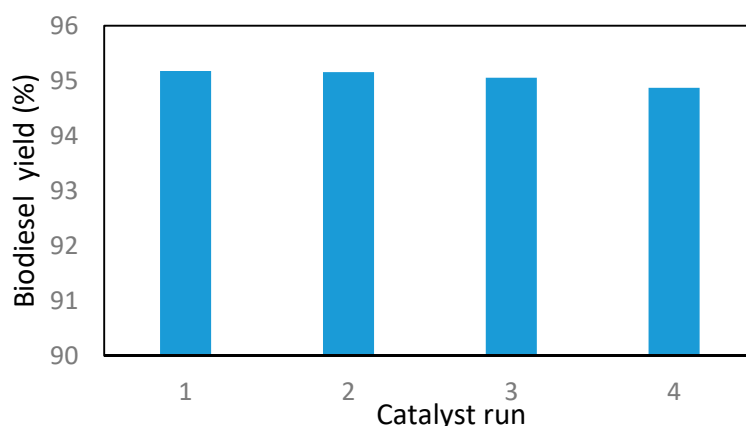


Figure 7. Reusability of the catalyst for biodiesel conversion in optimum conditions. T (temperature) = 200 °C, catalyst loading = 1%, methanol-to-oil mole ratio = 15:1, t = 30 min.

2.6. Properties of Biodiesel

The physiochemical properties of the produced biodiesel were analyzed and compared with ASTM [1,22] standard values. (Table 5). It was found that the properties of the obtained biodiesel are closely in accordance with the specifications of the biodiesel standard.

Table 5. Properties of biodiesel from waste cooking oil and comparison with the American biodiesel standard.

Properties	Produced Biodiesel	ASTM Test Values [1,22]	Test Method
Density at 15 °C (gm/cm ³)	0.876	0.860–0.894	measurement
Viscosity (mm ² /s) at 40 °C	5.8	1.9–6.0	ball drop method [29]
Iodine value (g I ₂ /100 g)	115.67		titrimetric
Pour point (°C)	−3.25	−15–10	ASTM D2500
Cloud point (°C)	7.6	−3–12	ASTM D97

2.7. Biodiesel Production from Various Sources by Heterogeneous Catalysis

Nowadays, biodiesel is considered a promising alternative to fossil fuels because of its environmental friendliness and due to the gradual depletion of natural resources. Various sources for biodiesel production using various heterogeneous catalysts are presented in Table 6.

Feedstocks for biodiesel production can be classified into vegetable oil (edible and nonedible), animal fats, and waste cooking oil. The main resources for biodiesel production around the world are edible oils. However, because of the high price and the reduction of food sources, the focus of biodiesel production could be shifted to the nonedible oils, which are comparatively low in price. However, a large amount of land space is needed for cultivating vegetable oil plants. Aside from vegetable oils, animal fats can be another option for biodiesel production which provides an economical advantage. From Table 6, it can also be seen that biodiesel from animal fats can also be produced at a higher rate compared to vegetable oils. However, due to the low availability of animal fats, it is not possible to meet the world's fuel demand solely from animal fats [30,31].

In this case, waste cooking oil (WCO) can be a very good choice as a feedstock for biodiesel production, and it is more widely available and cheaper than other vegetables oils, too. A large amount of WCO is generated around the world every day. Usually, WCO is dumped into a nearby river or sewer, disturbing the ecological and environmental balance [4,32]. It can be seen from Table 6 that the biodiesel yield from waste cooking oil can be higher than that from vegetables oils or animal fats, if a suitable catalytic method is applied. Therefore, not only can the disposal problem be solved but, also, the ecological and environmental balance can be protected by reusing waste cooking oil.

Table 6. Biodiesel production from various sources by heterogeneous catalysis.

Feedstocks (Oil)	Catalyst	Optimum Reaction Conditions	% Biodiesel Yield	References
Soybean	$\text{SO}_4^{2-}/\text{ZnO}$	Temperature = 65 °C, methanol-to-oil mole ratio = 6, Catalyst = 4 wt %, Reaction time = 4 h	80.19	[33]
Palm oil	Zirconia-supported activated natural zeolite	Temperature = 65 °C, methanol-to-oil mole ratio = 10, Catalyst = 10 wt %, Reaction time = 2 h	84.2	[34]
Jatropha	Montmorillonite KSF/1–20	Temperature = 160 °C, methanol-to-oil mole ratio = 12, Catalyst = 4.8 wt %, Reaction time = 6 h	68	[35]
<i>Cerbera odollam</i>	$\text{SO}_4^{2-}/\text{ZrO}_2$	Temperature = 180 °C, methanol-to-oil mole ratio = 8, Catalyst = 6 wt %, Reaction time = 3 h	84	[36]
<i>Moringa oleifera</i>	$\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}$	Temperature = 150 °C, methanol-to-oil mole ratio = 5, Catalyst = 19 wt %, Reaction time = 2.5 h	84	[37]
Chicken fat	Eggshell	Temperature = 57.5 °C, methanol-to-oil mole ratio = 13, Catalyst = 8.5 wt %, Reaction time = 5 h	92.29	[38]
Waste cooking oil	S-TiO ₂ /SBA-15	Temperature = 200 °C, methanol-to-oil mole ratio = 15, Catalyst = 1 wt %, Reaction time = 30 min	94.96	This study

3. Materials and Method

3.1. Materials

The suppliers and purities of the chemicals used are presented in Table 7.

Table 7. Suppliers and purities of chemicals used in the experiment.

Chemical	Supplier	Purity (Mass Percentage)
Anhydrous sodium sulfate	Samchun Pure Chemical Co., Ltd Pyeongtaek Korea	98.5%
Ethyl alcohol	Dae-Jung Chemical & Metals Co., Ltd., Gyeonggi-do Korea	99.9%
Methanol	Dae-Jung Chemical & Metals Co., Ltd., Gyeonggi-do Korea	99.9%
Diethyl ether	Dae-Jung Chemical & Metals Co., Ltd., Gyeonggi-do Korea	>99.0%
Hydrochloric acid	Dae-Jung Chemical & Metals Co., Ltd., Gyeonggi-do Korea	35~37%
Potassium hydroxide	Dae-Jung Chemical & Metals Co., Ltd., Gyeonggi-do Korea	>85.0%
Pluronic P123	Sigma-Aldrich. Co St. Louis, USA	>99.5%
Titanium sulfate solution $\text{Ti}(\text{SO}_4)_2$	Fisher Scientific, Loughborough, UK	>24%
Tetraethyl orthosilicate (TEOS)	ACROS Organics Co. (Morris, NJ, USA)	≥98%

3.2. Pretreatment of Waste Cooking Oil (WCO)

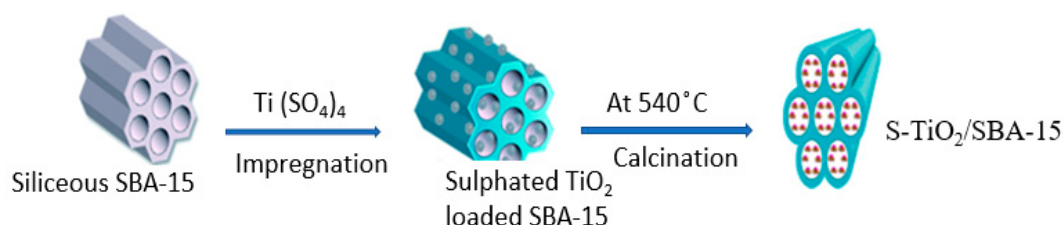
Waste cooking oil (WCO) was collected from a student restaurant and stored in ambient conditions for pretreatment. Solid particles and other impurities were removed from the WCO by a filtration technique. After the removal of impurities, the WCO was heated at 110 °C for one hour to evaporate any remaining water. A dry wash was performed using sodium sulfate. Sodium sulfate was recovered from the waste cooking oil by a filtration process. The samples were then stored in ambient conditions; their properties were measured and are shown in Table 8.

Table 8. Properties of waste cooking oil.

Properties	Experimental Value	Test Method
Acid value (mg KOH/g of oil)	2.92	titrimetric
Iodine value (g I ₂ /100 g)	107.13	titrimetric
Density (gm/cm ³)	0.891	measurement
Viscosity (mm ² /s) at 15 °C	58.62	ball drop method [29]
Saponification value (mg KOH/g of oil)	188.39	titrimetric

3.3. Catalyst Preparation

To synthesize the catalyst—sulfated titanium oxide supported on SBA-15 (S-TiO₂/SBA-15)—a solution of titanium sulfate was directly impregnated onto the prepared Santa Barbara amorphous-15 (SBA-15) silica composite (Figure 8). The catalyst was prepared by a direct wet impregnation method following a method from the literature with little modification [2]. Ti(SO₄)₂ was used as a precursor and TiO₂ source. The sulfation step was excluded here. The mole composition of the catalytic mixture was P123/TEOS/HCl/H₂O/Ti(SO₄)₂ = 1.0:3.75:1.64:434:2.54.

**Figure 8.** A schematic illustration of the synthesis process of the S-TiO₂/SBA-15 solid acid catalyst.

3.4. Experimental Procedure

The process of biodiesel production followed a similar procedure to that in our previous work with a different catalyst [2]. Both the hydrolysis and the esterification reaction were run in a 350 mL 316 stainless steel batch reactor vessel with a glass liner (Hanwol Eng. Co., Ltd. Model HR-8302, Gyeonggi-do, Korea). For the hydrolysis reaction, the required amount of WCO was placed into the batch reactor vessel at the molar ratio of 1:50 (WCO/water). Each hydrolysis reaction was carried out under the same reaction conditions (temperature at 275 °C for 45 min at a stirring speed of 500 rpm). Diethyl ether solvent was used for extracting the hydrolyzed product from the reaction mixture. The hydrolyzed products were separated into two different phases (FFA and glycerol) in a separator funnel. The diethyl ether was heated to its boiling point to evaporate and leave an oil consisting of the hydrolyzed free fatty acids (FFAs). Then, anhydrous sodium sulfate was used to absorb water from the FFAs. Finally, sodium sulfate was recovered by a filtration process. After extraction, the FFAs were transferred to the reaction vessel for the esterification reaction to produce biodiesel under subcritical conditions. The effect of the reaction parameters (methanol-to-oil molar ratio, reaction time, catalyst loading, and temperature) on the biodiesel yield was studied. The range of each parameter was chosen based on the available literature [2,4,12,20,39]. The conversion rate of FFAs to biodiesel during the esterification process was calculated using Equation (1) below [2,40–42]:

$$\% \text{ conversion FFA (biodiesel yield)} = AV_{\text{FFA}} - AV_{\text{BD}} / AV_{\text{FFA}}, \quad (1)$$

where AV_{FFA} is the acid value of the free fatty acid (FFA) and AV_{BD} is the acid value of the produced biodiesel.

3.4.1. Purification of Biodiesel

Once the reaction was over, the mixture was cooled down to room temperature before being transferred into a separator funnel and allowed to settle down overnight. The reaction mixture separated into three different layers. The upper layer was unreacted methanol, the middle layer was biodiesel, and the lower layer consisted of byproduct water and catalyst. The layers formed based on density differences. The biodiesel was separated and heated to recover the remaining methanol at its boiling point. The biodiesel was then treated with sodium sulfate (Na_2SO_4) as a dry wash to absorb any water that was produced from the reaction. Finally, sodium sulfate was removed by a filtration process.

3.4.2. Experiment Design for Optimization of the Biodiesel Yield

The design of the experiment to optimize the biodiesel production from used cooking oil was performed using a custom full factorial method using Minitab 18 statistical software. The reaction parameters of catalyst loading (wt %), temperature ($^{\circ}\text{C}$), methanol-to-oil mole ratio, and reaction time (min) were selected to study their effect on the percentage yield of biodiesel. The studied factors (reaction parameters) and their levels (ranges) are presented in Table 9.

Table 9. Factors and their levels for experimentation.

Factors	Levels	Values
Catalyst %	4	0.50, 0.75, 1.00, 1.25
Temperature	4	160, 180, 200, 220
Mole ratio	4	5, 10, 15, 20
Reaction time	5	20, 25, 30, 35

4. Conclusions

In this study, S-TiO₂/SBA-15 superacid catalyst was found to be an effective heterogeneous acid catalyst for the esterification of low-grade waste cooking oil feedstock at subcritical conditions. Confirmation of the catalyst structure and acidic nature of the catalyst was acquired using XRD, SEM, BET, and an acid–base neutralization technique. The acid density of the catalyst surface influences the catalytic activity and plays a significant role in the esterification reaction. A custom full factorial design was used to optimize biodiesel production from the waste cooking oil, and the design was followed to optimize the reaction parameters to determine the maximum biodiesel yield. The statistical analysis of variance (ANOVA) was also studied to validate the experimental results. The maximum biodiesel yield obtained using waste cooking oil was $94.96 \pm 0.12\%$ under optimum conditions (temperature of 200°C , catalyst loading of 1.0%, methanol-to-oil molar ratio of 15:1, and reaction time of 30 min). The catalyst was reused successfully three times with 90% efficiency, demonstrating that S-TiO₂/SBA-15 is a stable catalyst and maintains high catalytic activity for the esterification reaction. The fuel properties of the produced biodiesel were found to be closely in accordance with the biodiesel standard. The washing step for the purification of biodiesel is unnecessary with this catalyst, which will lessen the generation of wastewater and simplify the purification process. This heterogeneous acid catalytic method is capable of replacing conventional homogeneous catalyzed transesterification and other heterogeneous catalyzed transesterification reactions involving waste cooking oil.

Author Contributions: Conceptualization, M.S.U.S.B.; Data curation, M.N.H.; Formal analysis, M.N.H.; Investigation, M.N.H.; Methodology, M.N.H. and M.S.U.S.B.; Project administration, Y.C.S.; Resources, Y.C.S.; Supervision, Y.C.S.; Validation, M.S.U.S.B.; Visualization, A.H.M.A.A.; Writing—original draft, M.N.H.; Writing—review & editing, M.N.H., M.S.U.S.B. and Y.C.S.

Funding: This research work was financially supported by Korea Ministry of Environment (MOE) as “Knowledge-based environmental service (Waste to energy recycling) Human Resource Development Project”.

Acknowledgments: The authors would like to acknowledge the support provided by the department of environmental engineering, Sangji university, Republic of Korea.

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

References

- Pandit, P.R.; Fulekar, M.H. Egg shell waste as heterogeneous nanocatalyst for biodiesel production: Optimized by response surface methodology. *J. Environ. Manag.* **2017**, *198*, 319–329. [[CrossRef](#)]
- Hossain, M.N.; Bhuyan, M.S.U.S.; Alam, A.H.M.A.; Seo, Y.C. Biodiesel from Hydrolyzed Waste Cooking Oil Using a S-ZrO₂/SBA-15 Super Acid Catalyst under Sub-Critical Conditions. *Energies* **2018**, *11*, 299. [[CrossRef](#)]
- Goodrum, J.W.; Geller, D.P.; Adams, T.T. Rheological characterization of animal fats and their mixtures with #2 fuel oil. *Biomass Bioenergy* **2003**, *24*, 249–256.
- Bhuyan, M.S.U.S.; Alam, A.H.M.A.; Chu, Y.; Seo, Y.C. Biodiesel Production Potential from Littered Edible Oil Fraction Using Directly Synthesized S-TiO₂/MCM-41 Catalyst in Esterification Process via Non-Catalytic Subcritical Hydrolysis. *Energies* **2017**, *10*, 1290. [[CrossRef](#)]
- Farooq, M.; Ramli, A.; Subbarao, D. Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *J. Clean. Prod.* **2013**, *59*, 131–140. [[CrossRef](#)]
- Phan, A.N.P.T.M. Biodiesel production from waste cooking oils. *Fuel* **2008**, *87*, 3490–3496. [[CrossRef](#)]
- Wen, Z.; Yu, X.; Tu, Sh.; Yan, J.; Dahlquist, E. Biodiesel production from waste cooking oil catalyzed by TiO₂-MgO mixed oxides. *Bioresour. Technol.* **2010**, *101*, 9570–9576. [[CrossRef](#)] [[PubMed](#)]
- Gupta, A.R.; Yadav, S.V.; Rathod, V.K. Enhancement in biodiesel production using waste cooking oil and calcium diglyceride as a heterogeneous catalyst in presence of ultrasound. *Fuel* **2015**, *158*, 800–806. [[CrossRef](#)]
- Negi, N.A.; Sayed, G.H.; Yehia, F.Z.; Habib, O.I.; Mohamed, E.A. Biodiesel production from one-step heterogeneous catalyzed process of Castor oil and Jatropha oil using novel sulphonated phenyl silane montmorillonite catalyst. *J. Mol. Liq.* **2017**, *234*, 157–163.
- Soriano, N.U., Jr.; Venditti, R.; Argyropoulos, D.S. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* **2009**, *88*, 560–565. [[CrossRef](#)]
- Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z.; Sopian, K. Overview of the production of biodiesel from waste cooking oil. *Renew. Sustain. Energy Rev.* **2013**, *18*, 184–193. [[CrossRef](#)]
- Faruq, M.; Ramli, A.; Naeem, A. Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renew. Energy* **2015**, *76*, 362–368. [[CrossRef](#)]
- Haigh, K.F.; Vladislavljevic, G.T.; Reynolds, J.C.; Nagy, Z.; Saha, B. Kinetics of the pre-treatment of used cooking oil using Novozyme 435 for biodiesel production. *Chem. Eng. Res. Des.* **2014**, *9*, 713–719. [[CrossRef](#)]
- Negm, N.A.; Sayed, G.H.; Habib, O.I.; Yehia, F.Z.; Mohamed, E.A. Heterogeneous catalytic transformation of vegetable oils into biodiesel in one-step reaction using super acidic sulfonated modified mica catalyst. *J. Mol. Liq.* **2017**, *237*, 38–45. [[CrossRef](#)]
- Mansir, N.; Taufiq-Yap, Y.H.; Rashid, U.; Lokman, I.M. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Convers. Manag.* **2017**, *141*, 171–182. [[CrossRef](#)]
- Kusdiana, D.; Saka, S. Two-step preparation for catalyst-free biodiesel fuel production. *Appl. Biochem. Biotechnol.* **2004**, *115*, 781–791. [[CrossRef](#)]
- Khayoon, M.S.; Hameed, B.H. Synthesis of hybrid SBA-15 functionalized with molybdophosphoric acid as efficient catalyst for glycerol esterification to fuel additives. *Appl. Catal. A Gen.* **2012**, *433–434*, 152–161. [[CrossRef](#)]
- Tan, Y.H.; Abdullah, M.O.; Nolasco-Hipolito, C.; Taufiq-Yap, Y.H. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Appl. Energy* **2015**, *160*, 58–70. [[CrossRef](#)]
- Veillette, M.; Giroir-Fendler, A.; Fauchaux, N.; Heitz, M. Esterification of free fatty acids with methanol to biodiesel using heterogeneous catalysts: From model acid oil to microalgae lipids. *Chem. Eng. J.* **2017**, *308*, 101–109. [[CrossRef](#)]

20. Liu, L.; Li, H.; Zhang, Y. Mesoporous silica-supported chromium catalyst: Characterization and excellent performance in dehydrogenation of propane to propylene with carbon dioxide. *Catal. Commun.* **2007**, *8*, 565–570. [CrossRef]
21. Soltani, S.; Rashid, U.; Al-Resayes, S.I.; Nehdi, I.A. Recent progress in synthesis and surface functionalization of mesoporous acidic heterogeneous catalysts for esterification of free fatty acid feedstocks: A review. *Energy Convers. Manag.* **2017**, *141*, 183–205. [CrossRef]
22. Kılıç, M.; Uzun, B.B.; Pütün, E.; Pütün, A.E. Optimization of biodiesel production from castor oil using factorial design. *Fuel Process. Technol.* **2013**, *111*, 105–110. [CrossRef]
23. Sani, Y.M.; Daud, W.M.A.W.; Aziz, A.R.A. “Activity of solid catalysts for biodiesel production”: A critical review. *Appl. Catal. A Gen.* **2014**, *470*, 140–161. [CrossRef]
24. Wan, L.; Liu, H.; Skala, D. Biodiesel production from soyabean oil in subcritical methanol using MnCO_3/ZnO as catalyst. *Appl. Catal. B Environ.* **2014**, *152–153*, 352–359. [CrossRef]
25. Lam, M.K.; Lee, K.T. Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid acid sulfated tin oxide catalyst. *Fuel* **2010**, *89*, 3866–3870. [CrossRef]
26. Lou, W.Y.; Zong, M.H.; Duan, Z.Q. Efficient production of biodiesel from high free fatty acid containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresour. Technol.* **2008**, *99*, 8752–8758. [CrossRef]
27. Jacobson, K.; Gopinath, R.; Meher, L.C.; Dalai, A.K. Solid acid catalyzed biodiesel production from waste cooking oil. *Appl. Catal. B* **2008**, *85*, 86–91. [CrossRef]
28. Kaur, M.; Malhotra, R.; Ali, A. Tungsten supported Ti/SiO₂ nanoflowers as reusable heterogeneous catalyst for biodiesel production. *Renew. Energy* **2018**, *116*, 109–119. [CrossRef]
29. Available online: <https://www.scribd.com/document/343180251/Viscosity-of-Fluids-Lab-Ball-Drop-Method> (accessed on 10 December 2018).
30. Banković-Ilić, I.B.; Stamenković, O.S.; Veljković, V.B. Biodiesel production from non-edible plant oils. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3621–3647. [CrossRef]
31. Bobadilla, M.C.; Lorza, R.L.; García, R.E.; Gómez, F.S.; González, E.P.V. An Improvement in Biodiesel Production from Waste Cooking Oil by Applying Thought Multi-Response Surface Methodology Using Desirability Functions. *Energies* **2017**, *10*, 130. [CrossRef]
32. Bobadilla, M.C.; Martínez, R.F.; Lorza, R.L.; Gómez, F.S.; González, E.P.V. Optimizing Biodiesel Production from Waste Cooking Oil Using Genetic Algorithm-Based Support Vector Machines. *Energies* **2018**, *11*, 2995. [CrossRef]
33. Istadi, I.; Anggoro, D.D.; Buchori, L.; Rahmawati, D.A.; Intaningrum, D. Active acid catalyst of sulphated zinc oxide for transesterification of soybean oil with methanol to biodiesel. *Procedia Environ. Sci.* **2015**, *23*, 385–393. [CrossRef]
34. Hidayat, A.; Sutrisno, B. Free Fatty Acids Esterification on Palm Oil Sludge using Zirconia-supported Indonesian Natural Zeolite as Heterogeneous Catalyst. *OJCHEG* **2018**, *34*, 2464–2470.
35. Zanette, A.F.; Barella, R.A.; Pergher, S.B.; Treichel, H.; Oliveira, D.; Mazutti, M.A.; Silva, E.A.; Oliveira, J.V. Screening, optimization and kinetics of *Jatropha curcas* oil transesterification with heterogeneous catalysts. *Renew. Energy* **2011**, *36*, 726–731. [CrossRef]
36. Kansedo, J.; Lee, K.T.; Bhatia, S. Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production. *Fuel* **2009**, *88*, 1148–1150. [CrossRef]
37. Kafuku, C.; Lam, M.K.; Kansedo, J.; Lee, K.T.; Mbarawa, M. Heterogeneous catalyzed biodiesel production from *Moringa oleifera* oil. *Fuel Process. Technol.* **2010**, *91*, 1525–1529. [CrossRef]
38. Kirubakaran, M. Eggshell as heterogeneous catalyst for synthesis of biodiesel from high free fatty acid chicken fat and its working characteristics on a CI engine. *J. Environ. Chem. Eng.* **2018**, *6*, 4490–4503.
39. Uddin, M.R.; Ferdous, K.; Uddin, M.R.; Rahman, M.; Khan, R.; Salam, M.A. Synthesis of biodiesel from waste cooking oil. *Chem. Eng. Sci.* **2013**, *1*, 22–26. [CrossRef]
40. Zhang, Q.; Wu, J.; Ma, P.; Cai, J.; Zhang, Y. Acid Value Determination and Pre-Esterification of Crude *Euphorbia lathyris* L. Oil. *World J. Eng. Technol.* **2015**, *32*, 70–75. [CrossRef]

41. Corro, G.; Bañuelos, F.; Vidal, E.; Cebada, S. Measurements of surface acidity of solid catalysts for free fatty acids esterification in *Jatropha curcas* crude oil for biodiesel production. *Fuel* **2014**, *115*, 625–628. [[CrossRef](#)]
42. Wang, Y.; Ou, S.; Liu, P.; Xue, F.; Tang, S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. *J. Mol. Catal. A Chem.* **2006**, *252*, 107–112. [[CrossRef](#)]



© 2019 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 (<http://creativecommons.org/licenses/by/4.0/>).