Biodiesel from Hydrolyzed Waste Cooking Oil Using a S-ZrO$_2$/SBA-15 Super Acid Catalyst under Sub-Critical Conditions

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Abstract: Due to rapid changes in food habits, a substantial amount of waste fat and used oils are generated each year. Due to strong policies, the disposal of this material into nearby sewers causes ecological and environmental problems in many parts of the world. For efficient management, waste cooking oil, a less expensive, alternative and promising feedstock, can be used as a raw material for producing biofuel. In the present study, we produced a biodiesel from hydrolyzed waste cooking oil with a subcritical methanol process using a synthesized solid super acid catalyst, a sulfated zirconium oxide supported on Santa Barbara Amorphous silica (S-ZrO$_2$/SBA-15). The characterization of the synthesized catalyst was carried out using scanning electron microscopy (SEM), X-ray diffraction (XRD), and the Brunauer-Emmett-Teller (BET) method. The catalytic effect on biodiesel production was examined by varying the parameters: temperatures of 120 to 200 °C, 5–20 min times, oil-to-methanol mole ratios between 1:5 to 1:20, and catalyst loadings of 1–2.5%. The maximum biodiesel yield was 96.383%, obtained under optimum reaction conditions of 140 °C, 10 min, and a 1:10 oil-to-methanol molar ratio with a 2.0% catalyst loading. We successfully reused the catalyst five times without regeneration with a 90% efficiency. The fuel properties were found to be within the limits set by the biodiesel standard.

Keywords: biodiesel; heterogeneous acid catalyst; esterification; waste cooking oil; subcritical methanol

1. Introduction

Fossil resources have been treated as an easy source of useful energy for thousands of years. As a result, increasing rates of consumption threaten its reserves. Besides, problems associated with climate change and greenhouse gas (GHG) emissions have rendered their application a great global problem. Therefore, it is urgent to seek alternative energy sources to meet the demand of fuel energy [1]. In recent years, biodiesel has become an attractive alternative energy source, due to its fuel properties, cost-effectiveness, eco-friendliness, biodegradability, and renewability [2]. It consists of fatty acid monoalkyl (methyl or ethyl) esters, obtained from vegetable oils and animal fats by esterification and transesterification with alcohols in the presence of (acid/base) catalysts [3,4].

The feedstock sources are the most important aspect of biodiesel production. Both edible and non-edible oil feedstocks are widely studied to produce biodiesel. Food security, shortage of agricultural land and cost of production are mainly responsible for feedstocks not being used on a commercial scale. Thus, at present, waste oil and animal fat has become an attractive replacement for conventional biodiesel feedstock sources. Furthermore, investigations show that nearly 70% of the total production cost of biodiesel is related to these feedstock oils [5,6]. Moreover, using waste

cooking oil (WCO) as a source of fuel for commercial biodiesel production will not only reduce the raw material cost, but will also solve the problems related to its disposal in the environment [7,8].

The production-process optimization and improvement of biodiesel quality are other more salient issues that make it commercially viable. To get maximum biodiesel yields commercially, homogeneous acid/base catalysts have been commonly used for biodiesel production through transesterification processes. The two important factors for the wide use of homogeneous catalysts are the mild reaction condition and the fact that they are less energy intensive. However, this requires a superior quality of feedstocks to get high quality biodiesels with a maximum yield. When dealing with inferior grade feedstocks, the removal of the catalyst from the reaction mixture, soap formation, and downstream processing costs all limit their application [8,9]. To overcome this problem, a non-catalytic transesterification by supercritical methanol method (SCM) was used, that can handle feedstocks having impurities such as high free fatty acid (FFA) levels and moisture content. However, it involves a high capital cost, and requires an intensive temperature–pressure environment and a specialized alloyed reactor [10].

Recently, a two-step process, hydrolysis followed by non-catalytic esterification of FFA, has been revealed as an excellent way to use waste cooking oil. Very few studies have been performed in this process for managing WCO, and more work is still needed to achieve a better quality biodiesel with less effort. As a result, the exploration of the performance under the influence of a heterogeneous catalyst in the esterification step is required for the optimization of the reaction. The use of a heterogeneous acid catalyst plays an important role in the production of biodiesel from inferior grade feedstocks. Since these catalysts are fully separable, this ensures the avoidance of product contamination. Additionally, heterogeneous catalysts are regenerable and reusable several times with good efficiency [4,7,10]. Besides, solid acid catalysts have also gained attention as an alternative to heterogeneous base catalysts and classical homogeneous acid catalysts [10–12].

There is some studies that used some solid acid catalysts such as ion exchange resins, zeolites and zeotype materials in biodiesel production. The crucial advantage of using these catalysts is the elimination of the final biodiesel washing step. However, more work in the search for new solid acid catalysts for sustainable biodiesel production is required [13–15].

Sulfate-incorporated metal oxides, which belong to the category of solid superacids, are now receiving more attention, with the aim of replacing the conventional homogeneous base catalysts which are highly corrosive, hazardous, and environmentally polluting. Solid superacids have an advantage in the strength and type (Brönsted or Lewis) of their acidity [16]. In addition, nowadays, functionalized mesoporous silica-based catalysts have been used in the esterification process because of their extremely large surface area, uniformity, stability, and large pore size, all of which are very beneficial in reactions involving bulky molecules [17,18].

To date, several heterogeneous acid catalysts have been developed for biodiesel production by transesterification of waste cooking oil, such as ZS/Si, SO_4^{2-}/TiO_2-SiO_2, carbon-based catalysts derived from starch and Zeolyte (Y756) [19–22]. However, further study on solid acid catalysts and process optimization are still required.

In this study, we investigated how the application of a mesoporous superacid catalyst sulfated zirconium oxide supported on SBA-15 (S-ZrO_2/SBA-15) is expected to enhance the reaction rate and will be beneficial to the reaction involving bulky molecules. We also expected that this catalyst will be environmentally friendly, because of its good separation from the reaction mixture.

To the best of our knowledge, no work has yet used the S-ZrO_2/SBA-15 catalyst in biodiesel production through an esterification from hydrolyzed waste cooking oil. In this work, a heterogeneous solid superacid catalyst S-ZrO_2/SBA-15 was synthesized and applied to biodiesel production under subcritical methanol process conditions. The impact of the reaction parameters—methanol-to-oil mole ratio, temperature, time, and catalyst loading—were studied to optimize the esterification method to obtain high yields of biodiesel. The reusability of the catalyst was examined, to investigate the stability of the catalyst in the reaction.

2. Research Methodology

2.1. Chemicals

Deionized water was obtained from a Milli-Q reverse osmosis purification system (Fisher Scientific, Bedford, MA, USA). Anhydrous sodium sulfate 98.5% was purchased from Samchun Pure Chemical Co., Ltd. (Pyeongtaek, Korea). Reagent grade ethyl alcohol (C_2H_6O, anhydrous 99.9%), diethyl ether (($C_2H_5)_2O$, >99.0%), and potassium hydroxide (KOH, >85.0%) were purchased from Daejung Chemical & Metals Co., Ltd. (Gyeonggi-do, Korea). All chemicals were of analytical grade and used without further purification. For the catalyst preparation, hydrochloric acid (HCl) and Pluronic P123 ($HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20H}$) were obtained from Sigma-Aldrich Co., (St. Louis, MS, USA). The zirconium oxide precursor was purchased from Daejung Chemical & Metals Co., Ltd. Tetraethyl orthosilicate ($C_8H_{20}O_4Si$) $\geq$ 98%) was purchased from ACROS Organics Co., (Morris, NJ, USA). These were reagent grade chemicals.

2.2. Raw Materials

Waste cooking oil (WCO) was collected from restaurants and shops within Sangji University, Wonju City, South Korea, and processed by vacuum filtration to remove inorganic residues. Following this, it was heated at the water boiling point for half an hour to evaporate any remaining water, and a drying step using sodium sulfate was performed. Until the FFA production, the WCO was stored under ambient conditions, after which its properties were analyzed (Table 1).

Table 1. Properties of waste cooking oil.

Properties	Experimental Value	Test Method	Materials and Equipment
Acid value (mgKOH/g of oil)	2.92	Titrimetric [2,23]	
Iodine value (gI_2 100 g^{-1})	107.13	Titrimetric [24]	
Density	0.89	Measurement [23]	Burette, pipette, volumetric flask, thermometer, measuring cylinder
Viscosity (mm^2/s) at 15 °C	58.62	Ball drop method [25]	
Saponification value (mg KOH/g of oil)	188.39	Titrimetric [23]	

2.3. Catalyst Preparation

Sulfonated zirconium oxide supported by SBA-15 (S-ZrO_2/SBA-15) was synthesized by direct impregnation of the synthesized SBA-15 with the desired amount of zirconium hydroxide, according to the following method: Pluronic P123 was dissolved in deionized water, followed by 2 M HCl solution, and stirred for 3 h at 40 °C. After full dissolution, $Zr(OH)_2$ was added and stirred for 24 h at 40 °C. Then, the silica source tetraethyl orthosilicate (TEOS) was added to the mixture, which was stirred for 30 min at 40 °C. The product was transferred to a Teflon lined bottle, and aged in the oven for 24 h at 80 °C under static conditions. After this, the product was filtered with Whatman micro filter paper, and washed with deionized water, and dried at 105 °C for 24 h. The product was calcined for 6 h at 540 °C. Then, the calcined product was sulfated with 1.0 M H_2SO_4 (15.0 mL/g) at room temperature for 1 h. Finally, the sulfated material was filtered, dried at 105 °C for 24 h, and calcined again at 550 °C for 4 h.

2.4. Processing into Biodiesel

2.4.1. Hydrolysis of Feedstock Oil

A 350 mL 316 stainless steel batch reactor vessel with a glass liner was used for both the hydrolysis and esterification reactions (Hanwoul Eng. Co., Ltd., Model HR-8302, Gyeonggi-do, Korea). Usually, 150 g substrate was charged into the reaction vessel for each run at 275 °C for 45 min, and the rate of agitation was 500 rpm. For hydrolysis, water was taken into the reaction vessel according to the (WCO/water) 1:1.006 ratio (weight basis). After hydrolysis, the reaction mixture was extracted with diethyl ether. The products were separated into two different phases (FFA and glycerol) in a separating

funnel. The ether was evaporated to leave an oil consisting of the hydrolyzed free fatty acids (FFA), and a dry wash was performed using anhydrous sodium sulfate to absorb the remaining water. Following this, to determine the acid value, saponification value, and the degree of hydrolysis, the extracted FFA was taken for a volumetric titration procedure.

2.4.2. Esterification of Hydrolyzed Free Fatty Acid

The extracted FFA was taken for methyl esterification under subcritical conditions. After this, a similar experimental procedure as described above was followed. A reaction under non-catalytic conditions was also performed, to compare it with the catalytic process during the esterification of FFA.

The conversion rate for the esterification process was calculated with the following formula:

$$\text{biodiesel yield (\%)} = M - N/M \tag{1}$$

where M = acid value of free fatty acid (FFA) and N = acid value of produced biodiesel.

2.4.3. Purification of Biodiesel

After completing the reaction, catalysts were separated from the reaction mixture by a filtration process. Then, the reaction mixture was placed in a separating funnel. The reaction mixture was heated to recover the non-reacted methanol for further use. Some amount of sodium sulfate was taken in a funnel to perform dry wash; this was to absorb the water, produced from the reaction, present in the biodiesel. Finally, the product was taken in order to analyze its various fuel properties.

2.4.4. Experiment Design for Esterification of Waste Cooking Oil to Optimize Biodiesel Yield

The statistical design selected for the optimization of biodiesel production from the waste cooking oil was defined by a custom full factorial design using the Minitab18 software (Eretec Inc., Gunpo-Si, Gyunggi-Do, Korea). The biodiesel yield was selected as a response for this method. The experimental range and levels of the studied factors are listed in Table 2.The experimental matrix for the factorial design and results are shown in Table 3. The experimental range and levels of the studied factors were chosen according to the previous work in this laboratory [2]. The experimental range of the studied factors were established via an error and trial method.

Table 2. Design of experiment.

Factor	Levels	Values
Catalyst concentration (wt %)	4	1.0, 1.5, 2.0, 2.5
Temperature (°C)	5	120, 140, 160, 180, 200
Methanol/oil molar ratio	4	5, 10, 15, 20
Time (min)	4	5, 10, 15, 20

Table 3. Experiment matrix of four factors and experiment results.

Run	Point Type	Blocks	Temperature (°C)	Catalyst Concentration (wt %)	Methanol/Oil Molar Ratio	Time (min)	Biodiesel Yield (%)
1	1	1	140	1.0	10	20	86.0411
2	1	1	140	1.5	10	20	89.3791
3	1	1	140	2.0	10	20	92.3590
4	1	1	140	2.5	10	20	83.2312
5	1	1	160	1.0	5	20	82.5393
6	1	1	160	1.0	10	20	93.7367
7	1	1	160	1.0	15	20	94.3497
8	1	1	160	1.0	20	20	94.5014
9	1	1	120	1.0	20	15	84.8747
10	1	1	140	1.0	20	15	87.6919

Table 3. *Cont.*

Run	Point Type	Blocks	Temperature (°C)	Catalyst Concentration (wt %)	Methanol/Oil Molar Ratio	Time (min)	Biodiesel Yield (%)
11	1	1	160	1.0	20	15	94.3497
12	1	1	180	1.0	20	15	96.6802
13	1	1	200	1.0	20	15	97.8880
14	1	1	140	2.0	10	5	90.1924
15	1	1	140	2.0	10	10	96.3828
16	1	1	140	2.0	10	15	95.8730
17	1	1	140	2.0	10	20	92.3590
18	1	1	140	1.0	10	20	86.0411
19	1	1	140	1.5	10	20	89.3791
20	1	1	140	2.0	10	20	92.3590
21	1	1	140	2.5	10	20	83.2312

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. Brunauer-Emmett-Teller (BET) Surface Area

The N_2 adsorption and desorption isotherms of the synthesized support SBA-15 and catalyst were measured with an ASAP 2020 V3.04B automatic analyzer (Micrometrics, Norcross, GA, USA) at liquid N_2 temperature (Figure 1). The surface area, pore volume, and pore size of support and catalyst are reported in Table 4. It can be observed that the surface area, pore volume, and size decreased when ZrO_2 was loaded on the supports. The decrease in the surface area, pore volume, and pore size is due to the gradual accumulation of a large amount of metal oxide species on the pores of the support during the preparation.
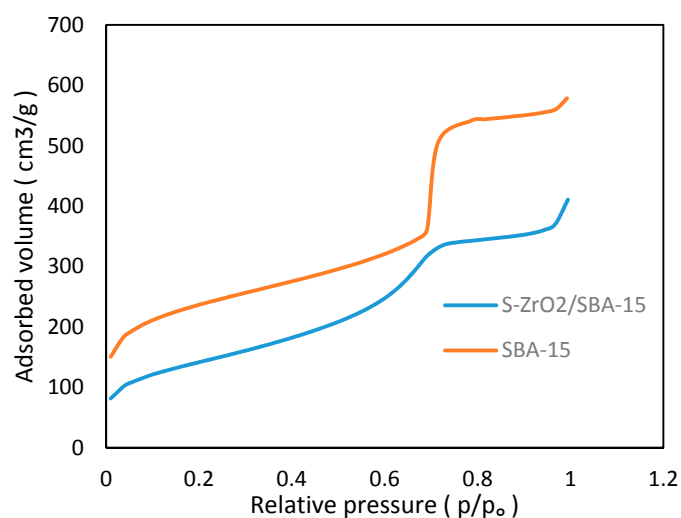

Figure 1. N_2 adsorption and desorption of the isotherms of the support SBA-15 and catalyst S-ZrO$_2$/SBA-15.

Table 4. Physiochemical properties of the catalysts.

Sample	SBET Surface Area (m²/g^{-1})	Pore Size (nm)	Pore Volume (cm³/g)	Surface Acidity (mmol/g)
SBA-15	833.80	5.38	0.13	-
S-ZrO$_2$/SBA-15	509.24	4.98	0.08	0.36

3.1.2. Low and Wide-Angle X-ray Diffraction

X-ray Diffraction (XRD) patterns of the support and catalyst were measured using an X-ray diffractometer system (D/MAX-2500V, Rigaku, Japan). A low-angle XRD analysis is a very effective probe for understanding mesostructured materials. Figure 2A shows the low-angle XRD patterns of the SBA-15 support and S-ZrO$_2$/SBA-15 catalyst. It can be seen that both samples exhibited XRD patterns with one very intense diffraction peak at d$_{100}$, and two weak peaks at d$_{110}$ and d$_{200}$, which are characteristic of a 2D hexagonal (P6mm) structure with excellent textural uniformity. From the results, it can be concluded that the S-ZrO$_2$/SBA-15 catalyst retains the mesoporous structure of SBA-15.
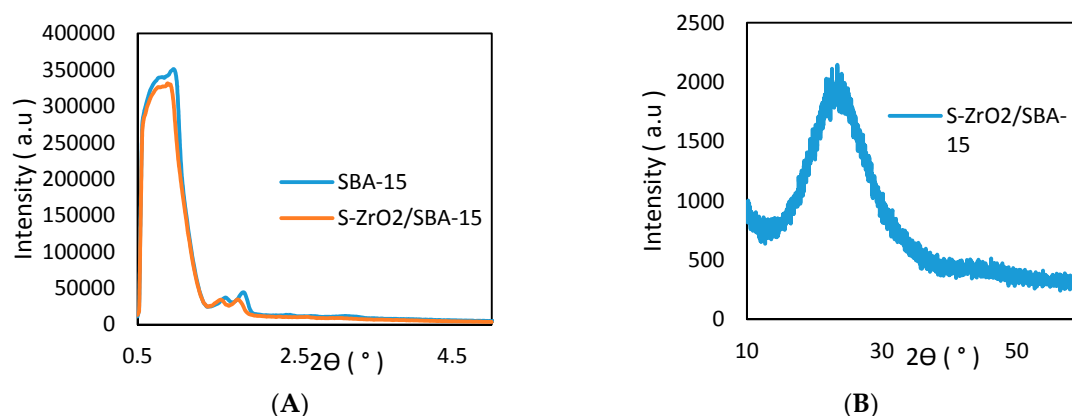
Figure 2. (**A**) Small-angle patterns of the SBA-15 support and catalyst S-ZrO$_2$/SBA-15; (**B**) The large-angle X-ray diffraction (XRD) patterns of the S-ZrO$_2$/SBA-15 catalyst.

From Figure 2B, only one broad peak appearing between 20° and 30° can be seen, which is characteristic of amorphous silica SBA-15 [15]. There are no more peaks related with ZrO$_2$ in the patterns. The results indicate that the ZrO$_2$ was finely dispersed on the SBA-15.

3.1.3. Acidity Test

The concentration of the acidic sites on the catalyst surface (surface acidity) was measured using an acid-base neutralization titration technique [26]. Catalyst sample (0.12 g) was mixed in 25 mL of 0.02 M NaOH solution and stirred slowly at room temperature for 48 h. The mixture was filtered off using filter paper and the alkali filtrate solution was titrated against 0.02 M HCl solution. The amount of surface acidity of the catalyst has been presented in Table 4. The surface acidity of the prepared catalyst S-ZrO$_2$/SBA-15 played the key role in the esterification of the waste cooking oil.

3.2. Statistical Analysis

A statistical design was chosen for the optimization of biodiesel production from waste cooking oil using a custom full factorial design. The application of this methodology requires a response, and also factors and levels. The biodiesel yield was selected as the response, and the range and levels of the investigated factors are listed in Table 3. The factors were the temperature, catalyst concentration, methanol-to-oil molar ratio, and time.

The experimental matrix for the factorial design and results have been shown in Table 3. A statistical analysis was carried out with the experimental values and the main effects of the factors were calculated. Table 5 shows the analysis of the main effects in the form of an analysis of variance (ANOVA) for the selected response with a statistical analysis test, a two-sided test with a 95% confidence level.

Table 5. Analysis of variance (ANOVA) for the linear model.

Source	DF	Adj. SS	Adj. MS	F-Value	p-Value
cat	3	135.732	45.2440	100.97	0.000
temp	4	199.079	49.7699	111.08	0.000
mole	3	176.465	58.8217	131.28	0.000
time	3	24.774	8.2581	18.43	0.000
Error	9	4.033	0.4481		
Lack-of-Fit	2	4.033	2.0163		
Pure Error	7	0.000	0.0000		
Total	22	547.405			

Standard deviation = 0.669; R^2 = 99.26%; Adj R^2 = 98.20%; DF = degree of freedom; Adj. SS = adjusted sum of squares; Adj. MS = adjusted mean of squares; F = probability distribution; p = probability.

The p-values were taken to check the significance of the corresponding coefficient. The smaller the p-values are, the bigger the significance of the corresponding coefficient. The significance of each coefficient was confirmed by the p-value ($p < 0.05$). The significance and regression models were proven by ANOVA as shown in Table 6. Furthermore, the coefficient determination value with 99.26% (R^2) and 98.20% as the adjusted coefficient value (Adj. R^2) indicated a high correlation and close performance of the model [8,27]. The significance of each coefficient was determined by T-values and p-values, which are listed in Table 6. The larger the T-values and smaller the p-values, the more significant the corresponding coefficient is. Once the model was identified, the catalyst was the most important factor in determining the biodiesel yield. The temperature was the second contributor toward the biodiesel yield followed by both the methanol-to-oil molar ratio and time.

Table 6. Regression coefficient estimation for the biodiesel yield from the waste cooking oil.

Term	Coefficient	SE Coeff	T-Value	p-Value
Constant	90.695	0.492	184.28	0.000
cat				
1.0	−1.812	0.369	−4.92	0.001
1.5	1.537	0.401	3.83	0.004
2.0	4.886	0.333	14.67	0.000
temp				
120	−7.644	0.594	−12.87	0.000
140	−4.803	0.454	−10.57	0.000
160	2.915	0.420	6.94	0.000
180	4.162	0.594	7.01	0.000
mole				
5	−8.469	0.433	−19.57	0.000
10	2.740	0.392	6.98	0.000
15	3.342	0.547	6.11	0.000
time				
5	−3.325	0.560	−5.94	0.000
10	2.865	0.560	5.12	0.001
15	1.249	0.462	2.70	0.024

Once the experiment was done, the response variable (biodiesel yield) was fitted to a general linear model in order to correlate the response variable to the studied factors, and the following linear regression equation was obtained:

%Yield = 90.695 − 1.812 cat 1.0 + 1.537 cat 1.5 + 4.886 cat 2.0 − 4.611 cat2.5 − 7.644 temp 120 − 4.803 temp_140 + 2.915 temp 160 + 4.162 temp 180 + 5.370 temp 200 − 8.469 mole 5 + 2.740 mole 10 + 3.342 mole 15 + 2.387 mole 20 − 3.325 time 5 + 2.865 time 10 + 1.249 time 15 − 0.789 time 20   (2)

3.3. Effect of Reaction Parameter in the Esterification

3.3.1. Effect of Temperature on Biodiesel Conversion

The temperature is one of the important reaction parameters affecting the reaction rate and, consequently, the production of biodiesel. In our study, the effects of the temperature on biodiesel production from hydrolyzed waste cooking oil using the S-ZrO$_2$/SBA-15 catalyst, were investigated at a fixed methanol-to-oil mole ratio and catalyst concentration. Figure 3 shows that the conversion of biodiesel increased as the temperature increased, and the maximum conversion was obtained at 200 °C. When the temperature is increased, the collision among the reactants also increases, which accelerates the chemical reaction, thereby enhancing the miscibility and mass transfer [28].
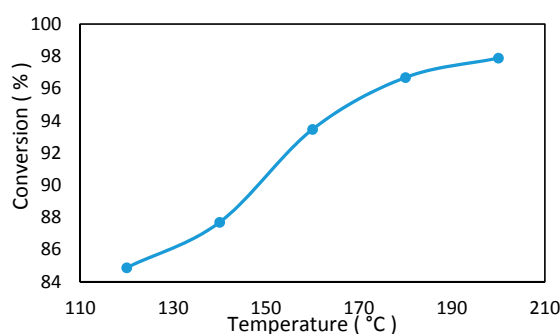
Figure 3. Effect of temperature on biodiesel production (t = 20 min, catalyst = 1.0 mass %, methanol/oil molar ratio = 20:1).

3.3.2. Effects of Methanol-to-Oil Mole Ratio on Biodiesel Production

The molar ratio is one of the important parameters which affects the conversion of biodiesel. Besides, esterification is a reversible reaction for which extra methanol is needed to drive biodiesel production. The effect of the molar ratio was investigated in the range of 5:1 to 20:1 in 20 min, using 1.0 wt % catalyst loading at 160 °C. Figure 4 shows that the conversion of biodiesel increased with the increase of the molar ratio. From Figure 4, we can see that the biodiesel conversion increased very sharply when the molar ratio increased from 8:1 to 10:1. However, there was no significant change when the methanol-to-oil mole ratio increased from 10:1 to 20:1. Thus, 1:10 was taken as the optimization point for other parameters.
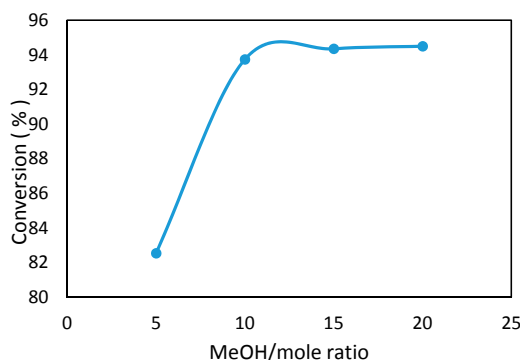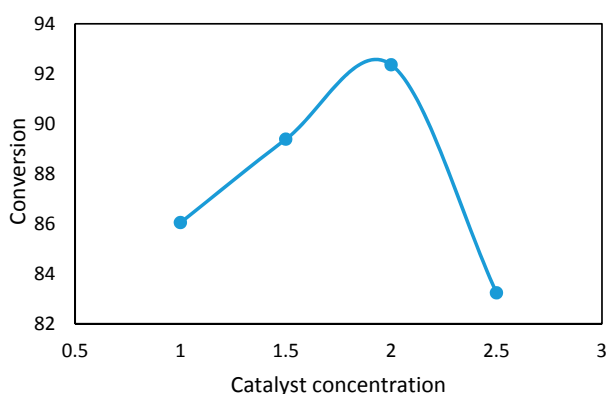

Figure 4. Effect of methanol to free fatty acid (FFA) mole ratio on biodiesel production.

3.3.3. Effect of Catalyst Concentration on Biodiesel Production

Catalyst concentration plays a significant role in the conversion of FFA to methyl ester. The effect of the catalyst loading concentration was investigated according to the mass of hydrolyzed oil. Figure 5 shows that with the increase of the catalyst concentration, the conversion of biodiesel increases. The maximum conversion was obtained at 2.0 wt %. However, when it was further increased beyond the optimum value 2.0 wt %, the yield of biodiesel started to decrease. Thus, the 2.0 wt % catalyst loading was taken as the optimization point. At high concentrations of catalyst loading, the reaction mixtures become more viscous, so some amount of catalyst may be left unused, which lowers the yield of biodiesel. Catalysts may even accumulate into the wall of the reaction vessel. Therefore, the catalyst could not be well diffused in the reaction, which also, in turn, lowers the activity of the catalyst [18,29].

Figure 5. Effect of catalyst concentration on biodiesel production (t = 20 min, T = 140 °C, methanol/oil molar ratio = 10:1).

### 3.3.4. Effect of Time on Biodiesel Production

The reaction time also plays a key role in the conversion to biodiesel from hydrolyzed oil. The effects of the reaction time were studied in order to get suitable times for the biodiesel conversion. The research was done at a range between 5 and 20 min, using a 2.0% catalyst concentration at 140 °C, and a methanol-to-oil mole ratio 10:1. Figure 6 shows that with increasing time the conversion to biodiesel also increased. At the beginning, from 5 to 10 min, the conversion rate increased drastically. However, upon further increasing the time, the production rate was reduced, due to the reverse reaction of the esterification, resulting in a loss of ester, as well as the production of free fatty acid [30]. Thus, 10 min was taken as the optimization point.
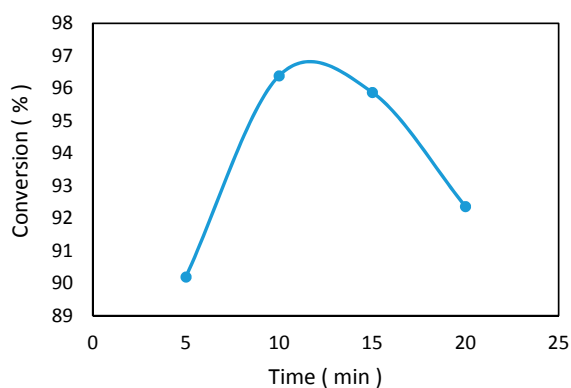
Figure 6. Effect of time on biodiesel production.

3.4. Comparison of the Non-Catalytic and Catalytic Processes

In this study, an esterification reaction was carried out for both catalytic and non-catalytic reaction processes under the same reaction conditions. The comparison was carried out with the use of a S-ZrO$_2$/SBA-15 heterogeneous solid acid catalyst. The esterification was done at a temperature of 140 °C, 2.0 wt % of the catalyst, the molar ratio of methanol and free fatty acid (FFA) was 10:1, and time was 10 min. The comparison of the non-catalytic and catalytic processes for the biodiesel conversion is shown in Figure 7 at optimum conditions where the temperature was at 140 °C, the time was 10 min, the catalyst loading was 2%, and the methanol/oil mole ratio was 10:1. The conversion of biodiesel using the S-ZrO$_2$/SBA-15 catalyst was much higher compared to the support SBA-15 because of the surface acid density of the catalyst. The SBA-15 support itself did not have acidity. However, after the incorporation of ZrO$_2$ into the support SBA-15, the acid concentration increased, as presented in Section 3.1.1. So, it can be concluded that the surface acid density played significant role in the esterification of the waste cooking oil.
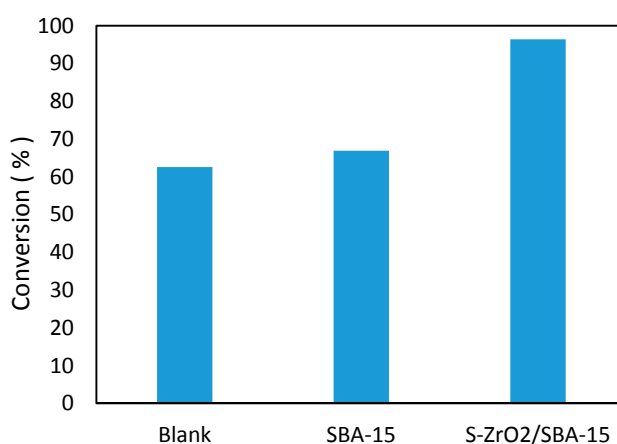
Figure 7. Comparison of the non-catalytic and catalytic processes on biodiesel content at optimum conditions.

3.5. Catalytic Activity of S-ZrO$_2$/SBA-15 Solid Acid Catalyst in Esterification and Comparison with Homogenous Catalyst Transesterification

Commercially, homogeneous-catalyzed transesterification is used for biodiesel production in order to obtain a high yield. However, homogeneous base catalysts are more sensitive to FFA and water when compared to acid catalysts. Consequently, low grade feedstock oil with a high FFA content cannot be used for biodiesel production using a homogeneous base catalyst. In such cases, highly refined oil must be used, and this will increase production costs. Furthermore, both homogeneous acid and base catalysts are corrosive and toxic. They are very difficult to separate from the reaction mixture and need several water washings which generate a large amount of waste water.

In this study, we developed a heterogeneous acid S-ZrO$_2$/SBA-15 catalytic route for biodiesel production in order to overcome the drawbacks caused by a homogeneous catalyst. We observed that the yield of biodiesel that uses a S-ZrO$_2$/SBA-15 solid catalyst was higher than that of a homogeneous catalyst (Table 7). However, the disadvantage of this solid acid catalyzed esterification is that it needs higher temperatures compared to homogeneous-catalyzed reactions. Nevertheless, prepared solid acid catalysts S-ZrO$_2$/SBA-15 are easily separable from the reaction mixture and are reusable several times.

Table 7. Comparison of the catalytic performance between a heterogeneous S-ZrO$_2$/SBA-15 acid catalyst and homogeneous catalysts.

Catalyst	Reaction Temperature (°C)	Catalyst Load (%)	Methanol to Oil Mole Ratio	Reaction Time (min)	Biodiesel Yield (%)	Reference
NaOH	60	1.1	7:1	20	88.8	[10]
KOH	87	6	9:1	60	87	[3]
H$_2$SO$_4$	95	4	20:1	1200	>90%	[31]
S-ZrO$_2$/SBA-15	140	2	10:1	10	96.383	This study

3.6. Reusability of the Catalyst

From an economic perspective, reuse, recycling and regeneration (3R) plays a significant role for industrialized applications. The reusability of the catalyst was studied under optimum conditions (Figure 8): 140 °C temperature, time 10 min, catalyst loading 2%, and methanol/oil mole ratio 10:1. After recovering the catalyst, it was washed with *n*-hexane and dried for reutilization. The catalyst was reused successfully five times with a 90% efficiency. The reduction of the biodiesel conversion could be explained by the deposition of carbon and non-reacted oil. Another possible reason could be attributed to the presence of biodiesel or glycerol on the active site of the catalyst. The decay in catalyst activity could also be due to the leaching of active sites into the reaction [32].
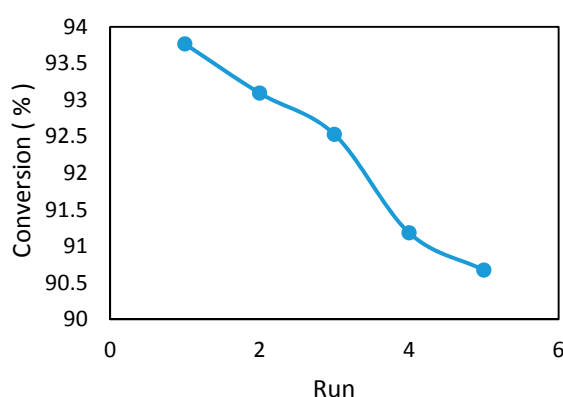
Figure 8. Effect of reusability of catalyst on biodiesel conversion at optimum conditions.

3.7. Fuel Properties of Synthesized Biodiesel

The biodiesel properties, such as density, kinematic viscosity, cloud point, pour point, and iodine value of the final product, are obtained in optimum conditions: temperature 140 °C, time 10 min, catalyst loading 2%, and methanol-to-oil mole ratio (10:1). After this, these properties were compared with standards. The fuel properties were in accordance with other investigations and with European standards (Table 8). This therefore proves that the WCO used in this study has immense potential to be used in large scale biodiesel productions with a suitable catalytic system.

Table 8. Properties of synthesized biodiesel from waste cooking oil and comparison with biodiesel standard.

Properties	Produced Biodiesel	Reference [7,27]	EN 14214	Test Method
Density at 27 °C (gm/cm^3)	0.87	0.860–0.894	0.860–0.900	Measurement
Viscosity (mm^2/S) at 40 °C	5.8	1.9–6.0	3.50–4.02	Ball drop method
Iodine value (gI$_2$ 100 g^{-1})	116.59		120 max	Titrimetric
Saponification value (mg KOH/g oil)	194.94			Titrimetric

4. Conclusions

The analytical results of BET, XRD and SEM confirmed the formation of a newly synthesized heterogeneous S-ZrO$_2$/SBA-15 catalyst. The synthesized S-ZrO$_2$/SBA-15 superacid catalyst showed very efficient and sustained catalytic activity for biodiesel production from low-grade waste cooking oil under subcritical methanol conditions. The surface acidity of the prepared catalyst influences the catalyst activity. The effect of the esterification reaction parameters was studied by ANOVA based on a custom full factorial design method. The catalyst was the most important factor in determining the biodiesel yield. The temperature was the second contributor toward the biodiesel yield followed by both the methanol-to-oil molar ratio and the time. The biodiesel yield reached 96.383% under optimum conditions (reaction temperature 140 °C, catalyst concentration 2.0%, methanol-to-oil mole ratio 10:1, and reaction time 10 min). The catalyst was recycled five times with a 90% activity, which proves that the S-ZrO$_2$/SBA-15 catalyst maintains a high catalytic activity during the recycling of the catalyst. A washing step for the purification of the biodiesel was avoided, which will reduce the generation of wastewater and the disposal costs. This heterogeneous acid catalytic method is capable of replacing the conventional homogeneous-catalyzed transesterification of waste cooking oil.

Author Contributions: The contributions of each author are as follows: Muhammad Nobi Hossain Synthesized the catalysts, produced free fatty acids (FFA) and biodiesel (FAME), collected experimental data, analyzed the numerical results, drafted the manuscript; Md Sufi Ullah Siddik Bhuyan contributed to the experimental design; Abul Hasnat Md Ashraful Alam helped to collect the experimental data and synthesis of catalysts; and Yong Chan Seo checked and edited the manuscript.

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