

Article

Heterogeneous Biodiesel Catalyst from Steel Slag Resulting from an Electric Arc Furnace

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Abstract: Biodiesel is one of the most environmentally friendly and renewable fuels, as it is a non-polluting fuel and is made from living resources, such as vegetable oils. The steel industry generates a variety of solid wastes, including electric arc furnace slag (EAFS). The synthesis of biodiesel from waste sunflower cooking oil was examined in this study, utilizing EAFS as a catalyst, which mainly contains ferric and ferrous oxides, calcium oxide, and silica. To evaluate their impact on biodiesel production, four independent variables were chosen: temperature (50–70 °C), catalyst loading (1–5%), methanol-to-oil (M:O) molar ratio (5–20), and time (1–4 h). The response surface methodology (RSM) was used to examine the impact of independent variables on reaction response, which is the biodiesel yield. This process was carried out using a design expert program by central composite design (CCD). A model was constructed, and showed that the biodiesel yield was directly proportional to all independent reaction parameters. The predicted model's adequacy was investigated using analysis of variance (ANOVA), which showed that it is an excellent representative of the results. The optimization of reaction conditions was investigated in order to maximize biodiesel yield at minimal reaction temperature and time, achieving a 94% biodiesel yield at a 20:1 M:O molar ratio, 5% catalyst loading, 55.5 °C reaction temperature, and 1 h reaction time.

Keywords: electric arc furnace slag; biodiesel; optimization; response surface methodology



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1. Introduction

Population growth and industrialization activities increase the demand for energy resources. Scientists are encouraged to develop sustainable and renewable fuels in response to global warming concerns. Biofuels, such as biodiesel, are a type of renewable energy that is primarily made up of methyl or ethyl esters, with properties similar to diesel fuel. Biodiesel is appealing because it reduces greenhouse gas emissions and is biodegradable and nontoxic [1,2]; it is produced by the transesterification of vegetable oil and animal fat. Many types of low-cost feedstock can be used for the production of biodiesel, such as waste edible oil, waste cooking oil, animal fats, and vegetable oils [3,4]. When food is cooked or fried, waste cooking oil (WCO) is produced, posing disposal issues [5,6]. When using a homogeneous catalyst that cannot be separated or reused, this reaction is fast and has a high conversion rate. The use of heterogeneous catalysts is more attractive than the use of homogeneous catalysts, because it makes catalyst separation more simple [4,7].

During the transesterification of palm seed oil, Ali et al. used a catalyst made of CaO nanoparticles on Fe₃O₄—which is a magnetic particle—as a biodiesel catalyst. The yield of the resultant biodiesel was 69.7% when the reaction temperature was 65 °C, the reaction duration was 300 min, the molar ratio was 20 methanol/oil, and the catalyst loading was 10 wt%. [8]. For the transesterification reaction using soybean oil, Liu et al. employed carbide slag loaded with ferric oxide (CS/Fe₂O₃) as a biodiesel catalyst. The fuel produced was biodiesel, according to the determined physical and chemical parameters [9]. To generate biodiesel from seed oil, Panchal investigated using an iron oxide Nano-catalyzed transesterification reaction. Using optimal operational settings such as the dimethyl-carbonate-to-oil

molar ratio (5:1), iron oxide Nano-catalyst (50 mg percent based on oil weight), agitation speed of 150 rpm, and 60 °C temperature for 5 h reaction time, biodiesel generation (96%) was obtained [10]. Rengasamy et al. made biodiesel with iron nanoparticles. Producing biodiesel using a synthesized nano-catalyst made of iron is a possible alternative to regular diesel fuel [11]. As a biodiesel catalyst, Widayat et al. employed alpha Fe₂O₃; the yield of biodiesel produced was 86.781% [12]. Khodary et al. used electric arc furnace dust as a heterogonous solid waste as a catalyst for biodiesel production; the resulting biodiesel had a 96% yield at 57 °C, a methanol-to-oil ratio of 20:1, a 1 h processing time, and a 5% catalyst loading [13].

The electric arc furnace (EAF) is a type of furnace used in the steelmaking industry, and it is regarded as the basic alternative to the blast furnace/basic oxygen furnace (BF/BOF) route. The most important scrap recycling process is EAF [14]. Electric arc furnace slag is a side product of the steelmaking industry that is created after the melting and acid refining of molten steel [15]. Electric arc furnace slag contains heavy metals such as iron, which is recognized to cause a first-class hazard, and its disposal necessitates large surfaces, so many studies have been conducted to recycle this solid waste in many industries [16]. This paper shows the possibility of biodiesel synthesis from waste sunflower cooking oil, utilizing EAF slag as a solid heterogeneous catalyst in the transesterification reaction between the methanol and the oil. Different process conditions were used to get the best process conditions that resulted from the optimization process using a design expert program to attain an economical process with a high production rate.

2. Experimental Methodology

2.1. The Raw Materials Used to Produce Biodiesel

The reaction was catalyzed by electric arc furnace slag (EAFS) supplied from an Egyptian steel factory in Ain El-Sokhna. Waste sunflower cooking oil was collected from Egyptian restaurants. Tables 1 and 2 show the chemical composition and physicochemical properties of waste cooking sunflower, respectively. Morgan Chemical Ltd., El Obour, Egypt, provided 99% methanol (MeOH).

Table 1. Waste sunflower cooking oil chemical composition.

Fatty Acid	%
Oleic acid	32.54
Heptadecanoic acid	34.62
Palmitic acid	19.03
Linolenic acid	3.21
n-Pentadecanoic acid	1.51
Linoleic acid	1.51
Arachidic acid	1.71
Myristic acid	0.75
Eicosadienoic acid	0.66
Lauric acid	0.17
Palmitoleic acid	0.21
Others	4.08

Table 2. Waste sunflower cooking oil physicochemical properties.

Property	Value	Reference
Molecular weight	820.7806	[17,18]
Density of 25 °C (kg/m ³)	895	ASTM D 1298-99 [19]
Viscosity at 40 °C	35.8	ASTM D 445-04 [20]
Acid value (mg of KOH/g of oil)	1.8	ASTM D 974-02 [21]
Saponification value (mg of KOH/g of oil)	206.85	ASTM D 94-002 [22]

2.2. Catalyst Preparation

EAFS was collected from a steel factory; it was crushed and then ground using a grinding mill.

2.3. Assessment of EAFS

For elemental analysis of EAFS, X-ray fluorescence was used to determine the concentrations of various elements. The test was carried out at a temperature of 22 ± 1 °C and a humidity of $44 \pm 1\%$. This test was based on ASTM (C114-18) [23].

The phases present in the material were indicated by X-ray diffraction (XRD). The identification of the most probable phases was carried out using a PANalytical computer-certificated program (X'Pert High Score Software 2006—Licensed modules: PW3209) with the aid of the International Center of Diffraction Database (ICDD) received with the X-ray diffraction equipment (X'Pert Pro PANalytical; Manufactured by Panalytical B.V. Company, Almelo, The Netherlands (ISO 9001/14001 KEMA-0.75160). The scan type was continuous and the anode material was copper. The general setting was 30 mA and 40 KV.

The standard sieving procedure described in ASTM D 422/2007 [24] was used to determine the particle size distribution. The sieves used complied with ASTM E 11/2009 [25].

2.4. Waste Sunflower Cooking Oil Collection and Preparation

For this investigation, waste sunflower cooking oil (WFO) was collected from Egyptian restaurants. To eliminate any suspended materials and/or burned food particles, the WFO was centrifuged and filtered. The oil sample was heated at 105 °C for 2 h to remove any unwanted water via evaporation.

2.5. Production of Biodiesel

A batch glass reactor equipped with a reflux condenser for methanol condensation and a thermocouple for temperature measurement was used for the transesterification reaction, as shown in Figure 1. The waste sunflower cooking oil was heated using a magnetic heat stirrer. Once the desired temperature was achieved, it was blended with EAFS and methanol, and then at the end of the reaction time the product was filtered to remove the waste powder. After cooling, the mixture was transferred to a separating funnel for separating the glycerol from the biodiesel. After 2 h of settling, the resulting mixture was sufficiently separated. Unreacted methanol was removed from the biodiesel by heating it for 30 min at 80 °C. The resulting biodiesel was weighed according to the following relationship for conversion calculations:

$$\text{Biodiesel Conversion, \%} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of Sunflower Oil}} \times 100 \quad (1)$$

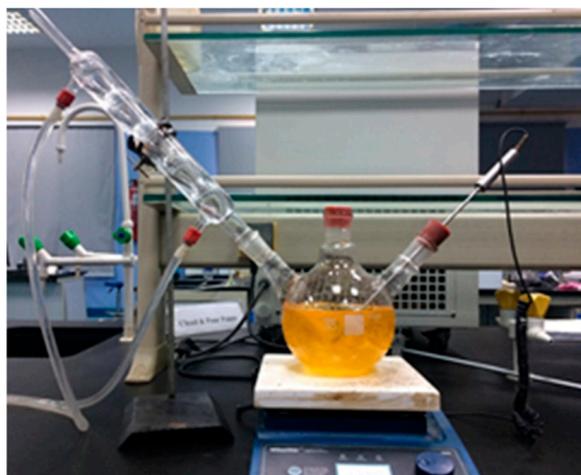


Figure 1. Experimental setup.

2.6. Experimental Design

The design Expert 13 software was utilized to generate and produce a comprehensive examination of how the yield of biodiesel changes with the process variables [26]. As shown in Table 3, four independent variables were chosen. Factors to consider included EAFS catalyst loading concentration, methanol-to-oil molar ratio (M:O), reaction time, and reaction temperature.

Table 3. Transesterification reaction parameters.

Reaction Parameter	Ranges		Reaction Parameter	Ranges	
	Minimum	Maximum		Minimum	Maximum
Methanol-to-oil molar ratio (M:O)	5	20	Reaction time (h)	1	4
Reaction temperature (°C)	50	70	EAFS concentration, %	1	5
Stirring rate, RPM	750				

The M:O molar ratio is an important variable for biodiesel production. According to the stoichiometric equation of the transesterification reaction, 3 moles of methanol are required to convert 1 mole of triglyceride (TG) to 3 moles of fatty acid methyl ester (FAME or biodiesel). This illustrates the importance of excess methanol, which plays an important role in maintaining the reaction at a constant rate and enhancing the forward reaction. Consequently, the M:O molar ratio must be greater than 3:1. Here, it was chosen within a range of 5:1 to 20:1 to investigate the effect of a wide range of excess methanol on the biodiesel yield. From 50 to 70 °C, increasing temperature had a direct increasing effect on biodiesel yield. This might be attributed to the decrease in oil viscosity. However, at temperatures above 70 °C, this effect is negligible.

According to the results of the experiments performed at a reaction time of 4 h, a methanol-to-oil ratio of 20, a catalyst loading of 5%, and a temperature of 70 °C, the resultant biodiesel yield was recorded to be 97.7%, so these conditions were considered to be the ultimate limit for this analysis. Increasing the process conditions further would not result in a significant change in the yield value. According to the results of experiments conducted at a reaction time of 1 h, a methanol-to-oil ratio of 5, a catalyst loading of 1%, and a temperature of 50 degrees Celsius, the resultant biodiesel yield was recorded to be 69.2%, so these conditions were considered to be the lower limit. Decreasing the values for the reaction conditions by less than this would decrease the conversion to unacceptable values.

The choice of the reaction parameters was chosen based on the work of El Sheltawy et al., Ling et al., Refaat, and Sulaiman and Talha [2,27–30]. Table 4 shows the number of trials conducted utilizing the central composite design (CCD) methodology. Thirty experimental

runs were performed. The experimental runs 25 to 30 share the same conditions, which are considered to be the design's center point. Economic and environmental concerns influenced the selection of the recommended optimization objectives—minimizing biodiesel production costs by reducing reaction conditions, and lowering energy costs while maximizing biodiesel output.

Table 4. Experimental runs.

Run No.	Catalyst Loading, %	Methanol/Oil Ratio	Reaction Time, h	Temperature, °C
1	1	5	1	50
2	1	5	4	50
3	1	20	1	50
4	1	20	4	50
5	5	5	1	50
6	5	5	4	50
7	5	20	1	50
8	5	20	4	50
9	1	5	1	70
10	1	5	4	70
11	1	20	1	70
12	1	20	4	70
13	5	5	1	70
14	5	5	4	70
15	5	20	1	70
16	5	20	4	70
17	3	12.5	0.5	60
18	3	12.5	5.5	60
19	3	3	2.5	60
20	3	27.5	2.5	60
21	0.5	12.5	2.5	60
22	7	12.5	2.5	60
23	3	12.5	2.5	40
24	3	12.5	2.5	80
25–30	3	12.5	2.5	60

2.7. Optimal Biodiesel Sample Evaluation

The optimized biodiesel sample's physicochemical parameters were evaluated and compared to the ASTM D6751 [31] Biodiesel International Standard and the EN 14214 [32] Biodiesel Standard. Gas chromatography was used to examine the optimal biodiesel sample. The total FAME and methyl linoleate content of the generated biodiesel were determined using the EN 14103 [33] technique. The EN 14105 [34] method was also used to test triglycerides, free glycerol, and total glycerol in the biodiesel.

2.8. Reusability of EAFS

Solid particles were filtered out of the optimal biodiesel sample, and then methanol was used to extract the glycerol, and it was dried to remove the methanol. The resulting EAFS was used to catalyze the transesterification reaction under the same optimized

reaction conditions. The conversion was calculated after each transesterification reaction to examine the catalyst's strength and efficiency.

3. Experimental Results

3.1. Assessment Results of EAFS

3.1.1. Chemical Composition of EAFS

The chemical composition of EAFS is shown in Table 5. The majority of solid waste was composed of CaO, FeO/Fe₂O₃, Al₂O₃, MgO, and SiO₂ oxides. According to earlier studies, these oxides are strong biodiesel catalysts [7,9,10,35–39]. The metal oxides are used as catalysts during the transesterification reaction, as the reaction takes place on them. The metal oxides consist of two parts: the first is the positive metal ions (cations or Lewis acids), which act as electron acceptors, while the second is negative oxygen ions (anions), which act as proton acceptors and, thus, act as Brønsted bases. The reaction mechanism can be described as follows:

- The (O-H) bonds of the methanol are broken down rapidly into methoxide anions and hydrogen cations. Surface O²⁻ removes H⁺ from CH₃OH to produce surface CH₃O⁻, which is very basic and catalytic in the transesterification reaction;
- The methyl esters are formed when the methoxide anions combine with triglyceride molecules. The carbonyl carbon atom of the triglyceride molecule attracts a methoxide anion from the metal oxide's surface to generate a tetrahedral intermediate, which absorbs H⁺ from the metal oxide's surface. The tetrahedral intermediate can react with methanol to produce methoxide anions. Finally, the tetrahedral intermediate can be rearranged to produce biodiesel [29,40].

EAF slag has a low loss on ignition, as its moisture content and impurities (organic matter, sulfates, and carbonates) are vaporized at the high processing temperature of the molten steel, which ranges between 1500 and 1600 °C.

Table 5. Chemical analysis of EAFS.

Oxides	%
CaO	26.51
FeO/Fe ₂ O ₃	33.21
SiO ₂	20.73
Al ₂ O ₃	8.77
MgO	3.55
MnO	4.13
Cr ₂ O ₃	1.22
Loss on ignition	0.01

3.1.2. Phases Present in EAFS

EAFS, as shown in Figure 2, is mostly made up of gehlenite (Al₂O₃·2CaO·SiO₂), larnite (2CaO·SiO₂), hematite (Fe₂O₃), and wüstite (FeO) phases, according to the mineralogical analysis, which was the result of X-ray fluorescence or chemical analysis.

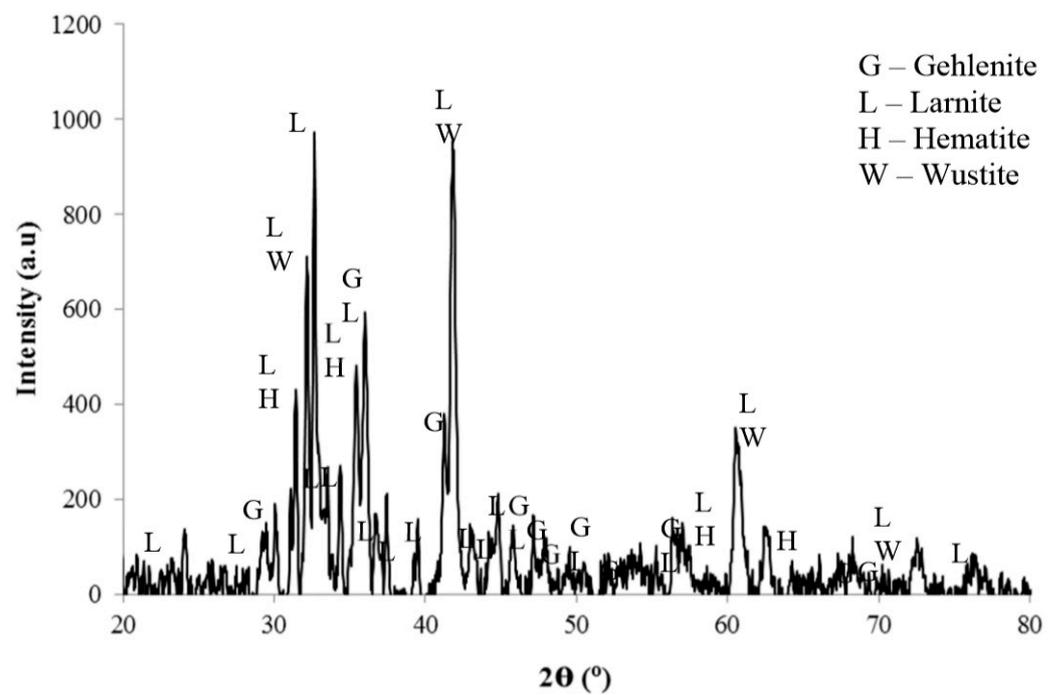


Figure 2. Mineralogical analysis of EAFS.

3.1.3. Particle Size Analysis of EAFS

Figure 3 indicates the particle size distribution of EAFS. The waste powder is very fine, as shown in this diagram; 537 nm is the average particle size of the waste powder. Small particle size means large surface area of the catalyst and more active centers available for the chemical reaction, so the used catalyst will result in a high reaction conversion.

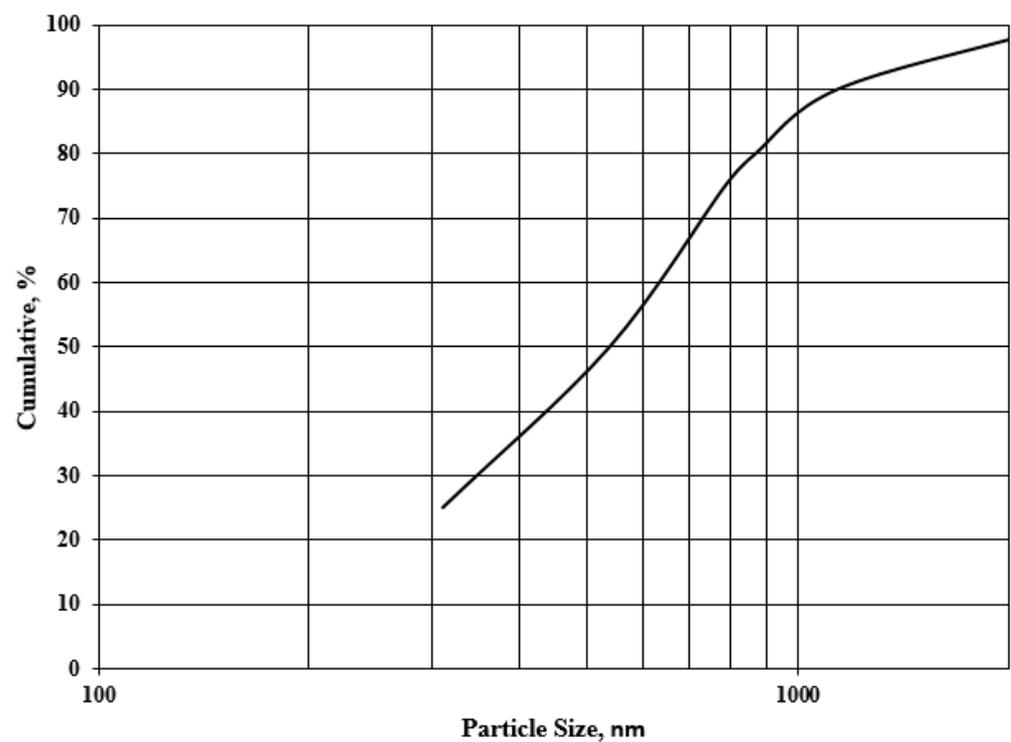


Figure 3. Particle size distribution of EAFS.

3.2. Analysis of Variance (ANOVA) on the Resulting Biodiesel

The results of the biodiesel conversion in each experimental run were as follows: A design expert was used to develop the regression equation using ANOVA, which was used to assess the resulting model at a 95% confidence level. The p -values must be less than 0.05 to meet the significance level, which was set at 5%. To validate the model, the F-test and p -value were utilized. Using the ANOVA analysis technique, the design expert software suggested that the quadratic model was the preferred model. The findings of the ANOVA performed by the design expert software are shown in Table 6. The correlation between biodiesel conversion and reaction conditions is shown in the equation below.

$$Y = 0.918 A + 3.653 B + 0.476 C + 4.623 D - 0.039 BD - 0.024 B^2 - 0.029 D^2 - 96.584 \quad (2)$$

where Y represents biodiesel yield, A represents reaction time in hours, B represents the methanol-to-oil ratio, C represents the catalyst loading (wt%), and D represents the reaction temperature ($^{\circ}\text{C}$).

The predicted values were compared to the biodiesel conversion experiment results, which showed an excellent agreement, as shown in Figure 4, so the resulting model was perfect.

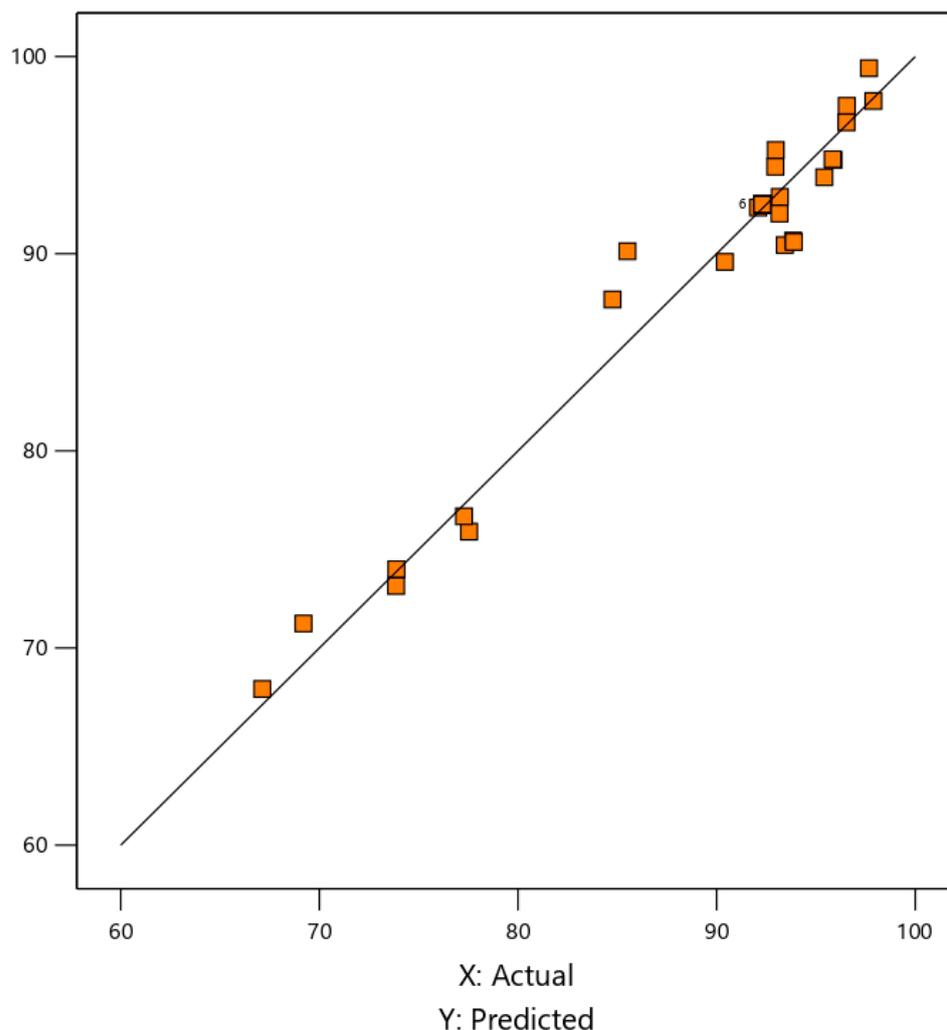


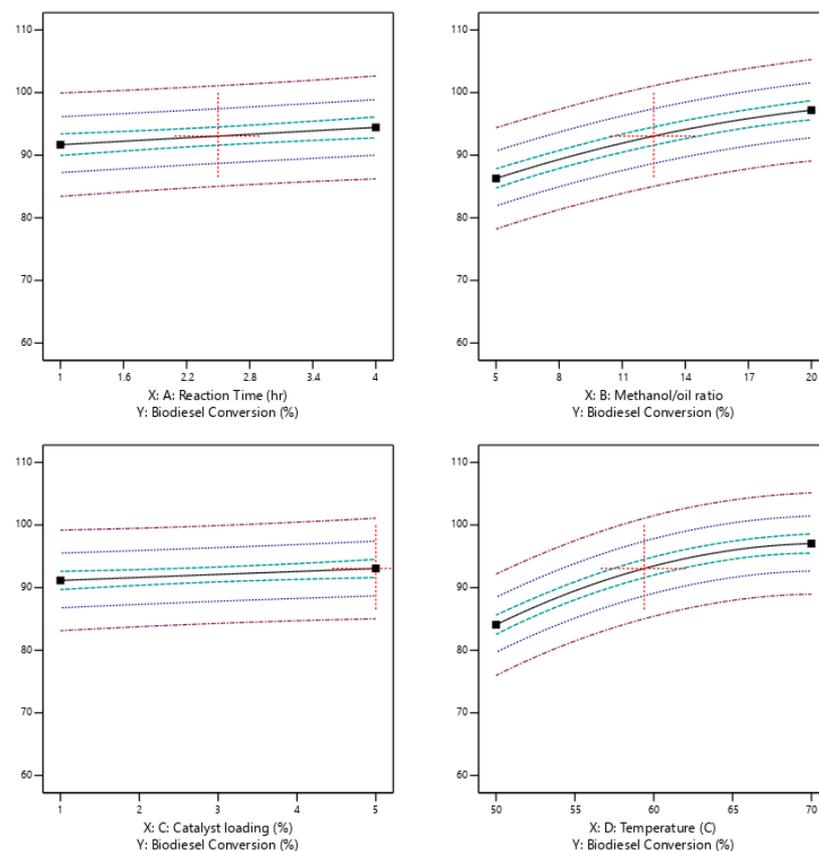
Figure 4. Relationship between biodiesel yield predictions and experimental data.

Table 6. ANOVA Analysis for Biodiesel Results.

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	Significant
Model	2153.19	7	307.60	78.12	<0.0001	
A—Reaction time	41.25	1	41.25	10.48	0.0038	
B—Methanol/oil ratio	665.39	1	665.39	168.99	<0.0001	
C—Catalyst loading	21.78	1	21.78	5.53	0.0280	
D—Temperature	1010.65	1	1010.65	256.68	<0.0001	
BD	139.65	1	139.65	35.47	<0.0001	
B ²	49.74	1	49.74	12.63	0.0018	
D ²	239.25	1	239.25	60.76	<0.0001	
Residual	86.62	22	3.94			
Lack of fit	86.62	17	5.10			
Pure error	0.0000	5	0.0000			

3.3. Reaction Condition's Impact on the Conversion of Biodiesel

Figure 5 proved that the methanol-to-oil ratio and temperature of the reaction have the greatest impacts on the conversion of biodiesel. Increasing any reaction parameter while keeping the others constant increases the biodiesel yield, so all reaction parameters are directly proportional to biodiesel conversion. Increasing the reaction time will result in giving more time for the reaction to take place. Increasing the amount of catalyst will result in increasing the surface area and the number of active centers provided for the reaction. Increasing the methanol-to-oil ratio will result in an increase in the rate of forward direction, as will increasing the temperature of the reaction. There are different lines as each line represent the relation between on reaction parameter while keeping the others constant.

**Figure 5.** Impact of reaction parameters on the conversion of biodiesel.

3.4. Impact of Reaction Parameters on the Conversion of Biodiesel

The impact of reaction variable interactions on biodiesel conversion is depicted in the surface and contour graphs. The contour and 3D plot in Figure 6 describe the correlation between the reaction temperature and M:O ratio, reaction temperature interactions (BD), and the conversion of biodiesel. BD interactions have a significant effect on the biodiesel yield.

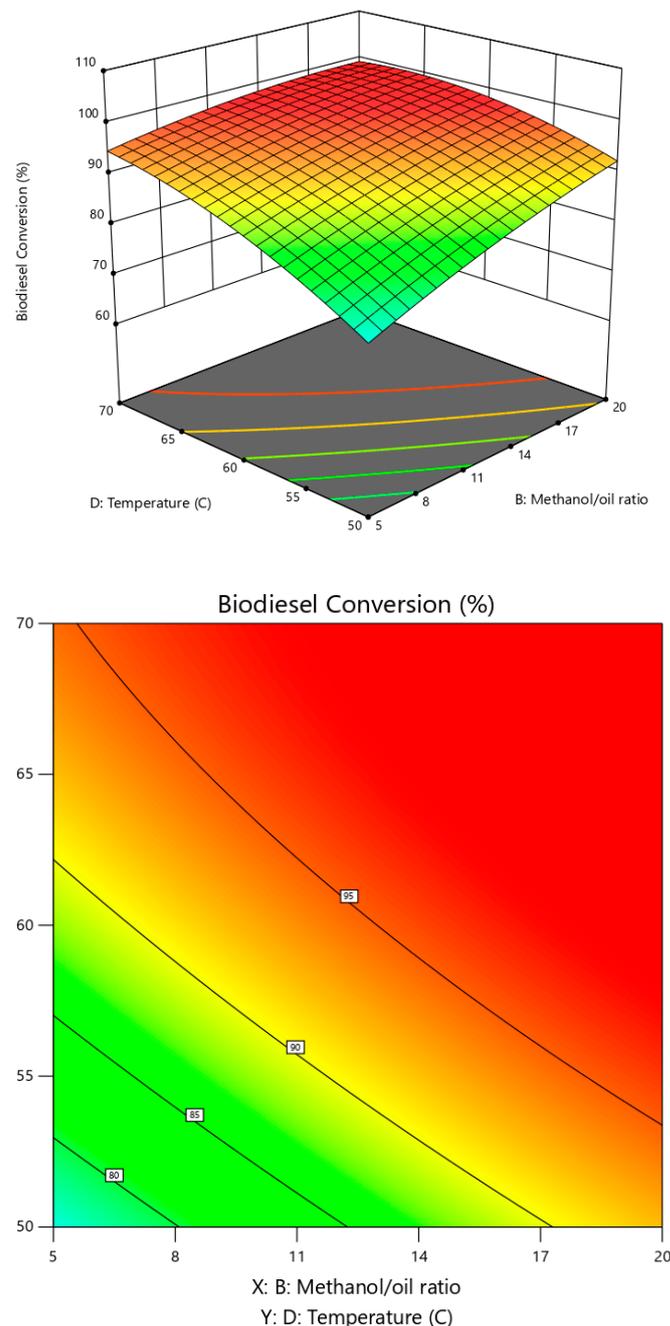


Figure 6. Contour and surface graph representing the relationship between biodiesel conversion, M:O ratio, and reaction temperature.

3.5. Optimization of Reaction Variables

The optimal conditions were found to be a M:O molar ratio of 20:1, a catalyst loading of 5%, a reaction temperature of 55.5 °C, a reaction period of 1 h, and a stirring rate of 750 rpm, which provided a biodiesel conversion of approximately 94%. Tables 7 and 8 represent an overview of the optimization constraints, as well as some of the program's

results and the desirability of each solution. Table 9 shows a comparison between the results of the present work and those of other recent papers. It should be noted that the biodiesel resulting from this work used low reaction temperature and time, so it used less energy compared with the other works; in addition, it used solid waste without any chemical preparation steps, unlike the others, and it gave a higher conversion of approximately 94%, so this production process has low energy and cost, while at the same time it produced biodiesel with high purity and yield. The reason behind this phenomenon was the use of solid waste catalysts composed of different types of solid oxides with different reactivity, structure, shape, and active ingredients, which have a better impact on the reaction than when using a single pure solid oxide as a catalyst. This work used a high methanol-to-oil ratio—in other words, excess methanol, which was separated from the resulting biodiesel via distillation to recycle it and reuse it again after adding additional methanol.

Table 7. Optimization constraints.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A: Reaction time	Minimize	1	4	1	1	5
B: Methanol/oil ratio	Within range	5	20	1	1	3
C: Catalyst loading	Within range	1	5	1	1	3
D: Temperature	Minimize	50	70	1	1	5
Biodiesel conversion	Maximize	67.129	97.8914	3	1	5

Table 8. Design expert's obtained solutions.

Number	Reaction Time	Methanol/Oil Ratio	Catalyst Loading	Temperature	Biodiesel Conversion	Desirability	Selected
1	1.000	20.000	5.000	55.501	93.850	0.780	
2	1.000	20.000	5.000	55.360	93.759	0.780	
3	1.000	19.999	5.000	55.242	93.685	0.780	
4	1.000	20.000	5.000	55.782	94.017	0.780	
5	1.000	20.000	4.984	55.528	93.855	0.780	
6	1.000	20.000	5.000	56.070	94.187	0.780	
7	1.000	19.997	4.963	55.519	93.838	0.780	
8	1.000	20.000	4.959	55.204	93.642	0.779	
9	1.000	20.000	4.951	55.734	93.965	0.779	
10	1.000	20.000	5.000	56.227	94.277	0.779	

Table 9. Comparison between the results obtained in this paper and the results obtained from recent papers.

Used Catalyst	Catalyst Preparation	Methanol/Oil Ratio	Catalyst Loading	Reaction Temperature	Reaction Time	Biodiesel Conversion	Reference
Enhanced eggshell-derived CaO nanocatalyst	Needs preparation steps before usage	12:1	2.5 wt%	60 °C	2 h	94%	[41]
α -Fe ₂ O ₃	Needs preparation steps before usage	12:1	6 wt%	80 °C	3 h	92%	[42]
Beach sand	Needs preparation steps before usage	9:1	2.5 wt%	70 °C	2 h	93.89%	[43]
EAF slag	Used as delivered after crushing and grinding steps	20:1	5 wt%	55 °C	1 h	93.850%	(Present work)

3.6. Optimal Biodiesel Sample Analysis

The physicochemical parameters and their standard limitations are shown in Table 10; all of the properties are consistent with both EN 14214 [32] and ASTM D 6751 [31].

The final optimized biodiesel sample generated from waste sunflower cooking oil was examined. The findings of the gas chromatography (GC) investigations for the best biodiesel sample are shown in Table 11. It is obvious that the biodiesel generated met the necessary specifications for the European standards EN 14104, EN 14103 [33], and EN 14105 [34]. The concentrations of total and free glycerol were 0.016 and 0.022% (m/m), respectively [34]. In comparison to EN 14105 [34], the concentrations of triglyceride, diglyceride, and monoglyceride were 0.0065, 0.0091, and 0.0728% (*w/w*), respectively. Using EN 14103, total FAME concentration was equal to 97.2% [33].

Table 10. Optimal biodiesel sample physicochemical properties.

Physical Properties	Standard Method	Produced Biodiesel	ASTM	Biodiesel
Kinematic viscosity at 40 °C (cSt)	ASTM D-445 [20]	4.1	1.9–6.0	3.5–5.0
Calorific value (MJ/kg)	ASTM D-5865 [44]	39.126		>32.9
Density at 15 °C (g/cm ³)	ASTM D-4052 [45]	0.862		0.86–0.9
Pour point (°C)	ASTM D-97 [46]	−20		
Cloud point (°C)	ASTM D-97 [46]	−10		<−4
Flash point (°C)	ASTM D-93 [47]	155	>130	>101

Table 11. Results of gas chromatography.

Test	Results	Specification		Units
		Min	Max	
Total glycerol	0.022		0.25	%
Free glycerol	0.016		0.02	%
Triglycerides	0.0728		0.20	%
Diglycerides	0.0091		0.20	%
Monoglycerides	0.0065		0.80	%
Total FAME	97.2	96.5		%

3.7. EAFS Reusability

The biodiesel yield declined from 94 to 70% after the second reaction, then to approximately 49% by the third. The glycerol contamination on the catalyst's active center is one of several explanations for the catalyst's decreased activity. The second explanation is catalyst leaching, which is defined as the loss of active species from a solid due to its change into a liquid medium, and this quick drop is related to the high concentration of CaO in solid waste, as shown in Figure 7. The findings revealed that EAFS can only be used one or two times before needing to be replaced with a new catalyst.

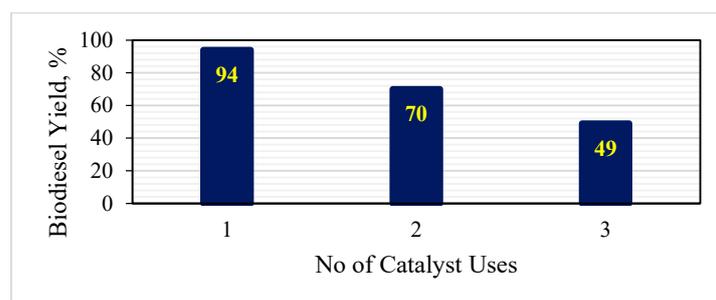


Figure 7. EAFS Reusability.

4. Conclusions

The use of steel slag from electric arc furnaces (EAFs) as a heterogeneous solid catalyst in the manufacture of biodiesel from waste sunflower cooking oil was investigated. According to the chemical analysis, EAFs solid waste is mostly made up of $\text{Fe}_2\text{O}_3/\text{FeO}$, CaO , Al_2O_3 , MgO , and SiO_2 oxides, which is a favorable sign that it can be employed as a biodiesel catalyst. To determine their impact on biodiesel generation, four independent reaction parameters were chosen: methanol-to-oil (M:O) molar ratio, reaction temperature, catalyst loading, and reaction time. A response surface approach was used to assess the impact of all reaction factors on biodiesel output. A model representing the impact of all reaction parameters on biodiesel conversion was constructed. The reaction temperature and M:O ratio had the greatest impact on biodiesel conversion. Within the desired limits, the design expert program provided the top 100 solutions, including reducing the cost of biodiesel production and increasing the quantity of biodiesel output. The best conditions were discovered to be an M:O molar ratio of 20:1, a catalyst loading of 5%, a reaction temperature of 55.5 °C, a reaction period of 1 h, and a stirring rate of 750 rpm, yielding a biodiesel conversion of 94%. The produced biodiesel met the required standard specifications. The reusability test revealed that EAFs can only be used two times at most before using a new catalyst.

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Data Availability Statement: All data generated or analyzed during this study are available in this article.

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Conflicts of Interest: The author declare that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Al-Sakkari, E.G.; El-Sheltawy, S.T.; Abadir, M.F.; Attia, N.K.; El-Diwani, G. Investigation of cement kiln dust utilization for catalyzing biodiesel production via response surface methodology. *Int. J. Energy Res.* **2017**, *41*, 593–603. [[CrossRef](#)]
2. Mukhtar, A.; Saqib, S.; Lin, H.; Hassan Shah, M.U.; Ullah, S.; Younas, M.; Rezakazemi, M.; Ibrahim, M.; Mahmood, A.; Asif, S.; et al. Current status and challenges in the heterogeneous catalysis for biodiesel production. *Renew. Sustain. Energy Rev.* **2022**, *157*, 112012. [[CrossRef](#)]
3. Zhang, Y.; Duan, L.; Esmaeili, H. A review on biodiesel production using various heterogeneous nanocatalysts: Operation mechanisms and performances. *Biomass Bioenergy* **2022**, *158*, 106356. [[CrossRef](#)]
4. Yaashikaa, P.R.; Kumar, P.S.; Karishma, S. Bio-derived catalysts for production of biodiesel: A review on feedstock, oil extraction methodologies, reactors and lifecycle assessment of biodiesel. *Fuel* **2022**, *316*, 123379. [[CrossRef](#)]
5. Abdullah, M.O.; Nolasco-hipolito, C. Biodiesel Production using Calcium Oxide as Catalyst: A Review. In Proceedings of the EnCon 2014, 7th Engineering Conference on Advances in Process Engineering & Green Energy, Kuching, Malaysia, 19–22 August 2014. [[CrossRef](#)]
6. Topare, N.S.; Jogdand, R.I.; Shinde, H.P.; More, R.S.; Khan, A.; Asiri, A.M. A short review on approach for biodiesel production: Feedstock's, properties, process parameters and environmental sustainability. *Mater. Today Proc.* **2021**, *in press*. [[CrossRef](#)]
7. Dai, Y.-M.; Chen, K.-T.; Wang, Y.-J.; Chen, C.-C. Application of Peanut Husk Ash as a Low-Cost Solid Catalyst for Biodiesel Production. *Int. J. Chem. Eng. Appl.* **2014**, *5*, 276–280. [[CrossRef](#)]
8. Ali, M.A.; Al-Hydary, I.A.; Al-Hattab, T.A. Nano-magnetic catalyst $\text{CaO-Fe}_3\text{O}_4$ for biodiesel production from date palm seed oil. *Bull. Chem. React. Eng. Catal.* **2017**, *12*, 460–468. [[CrossRef](#)]
9. Liu, M.; Huang, Y.; Liu, Q.; Hu, X.; Liu, Q.; Chen, H.; Dong, Y.; Zhao, Y.; Niu, S. Ferric oxide as a support of carbide slag for effective transesterification of triglycerides in soybean oil. *Energy Convers. Manag.* **2019**, *198*. [[CrossRef](#)]
10. Panchal, B. Biodiesel Synthesis with Iron Oxide Nano-Catalyst Catalyzed Pongamia Pinnata Seed Oil and Dimethyl Carbonate. *Am. J. Energy Eng.* **2018**, *6*, 21. [[CrossRef](#)]
11. Rengasamy, M.; Mohanraj, S.; Vardhan, S.H.; Balaji, R. Transesterification of castor oil using nano-sized iron catalyst for the production of biodiesel. *J. Chem. Pharm. Sci.* **2014**, *974*, 2115.
12. Widayat; Putra, D.A.; Nursafitri, I. Synthesis and catalytic evaluation of hematite ($\alpha\text{-Fe}_2\text{O}_3$) magnetic nanoparticles from iron sand for waste cooking oil conversion to produce biodiesel through esterification-transesterification method. In *Materials Science and Engineering Conference Series*; IOP Publishing: Bristol, UK, 2019; p. 509. [[CrossRef](#)]

13. Khodary, K.E.; Naeem, M.M.; Roushdy, M.H. Utilization of electric arc furnace dust as a solid catalyst in biodiesel production. *Clean Technol. Environ. Policy* **2021**, *1*, 1–11. [[CrossRef](#)]
14. Cavaliere, P. *Clean Ironmaking and Steelmaking Processes*; Springer: Cham, Switzerland, 2019.
15. Arribas, I.; Santamaría, A.; Ruiz, E.; Ortega-López, V.; Manso, J.M. Electric arc furnace slag and its use in hydraulic concrete. *Constr. Build. Mater.* **2015**, *90*, 68–79. [[CrossRef](#)]
16. Rastovčan-Mioč, A.; Sofilić, T.; Mioč, B. Application of electric arc furnace slag. In Proceedings of the MATRIB, Korčula, Croatia, 24–26 June 2009; pp. 436–444.
17. Zhu, H.; Wu, Z.; Chen, Y.; Zhang, P.; Duan, S.; Liu, X.; Mao, Z. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. *Chin. J. Catal.* **2006**, *27*, 391–396. [[CrossRef](#)]
18. Xu, H.; Miao, X.; Wu, Q. High quality biodiesel production from a microalga *Chlorella protothecoides* by heterotrophic growth in fermenters. *J. Biotechnol.* **2006**, *126*, 499–507. [[CrossRef](#)] [[PubMed](#)]
19. Rand, S.J. Astm D1298 Density. *ASTM Int.* **2003**, *5*, 221.
20. Astm, D. Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity). In *Manual on Hydrocarbon Analysis*, 6th ed.; ASTM International: West Conshohocken, PA, USA, 2008; pp. 1–10.
21. Drews, A.W. Standard Test Method for Acid and Base Number by Color-Indicator Titration. In *Manual on Hydrocarbon Analysis*, 6th ed.; ASTM International: West Conshohocken, PA, USA, 2008; Volume 91, pp. 543–545. [[CrossRef](#)]
22. Methods, T.; Products, P.; Products, P.; Laboratories, L.T. *Standard Test Methods for Saponification Number of Petroleum Products 1*; ASTM International: West Conshohocken, PA, USA, 2002; pp. 1–9.
23. *ASTM C114-18*; Standard Test Methods for Chemical Analysis of Hydraulic Cement. ASTM International: West Conshohocken, PA, USA, 2018; pp. 1–33. [[CrossRef](#)]
24. *ASTM D422*; Particle Size Analysis—ASTM D422 Particle Size Analysis. ASTM International: West Conshohocken, PA, USA, 2017; pp. 70–138.
25. *ASTM E 11-09*; Standard Specification for Woven Wire Test Sieve Cloth and Test Sieves. ASTM International: West Conshohocken, PA, USA, 2010; p. 9.
26. Montgomery, D.C. *Montgomery Design and Analysis of Experiments*, 8th ed.; Arizona State University: Tempe, AZ, USA, 2013; Volume 2009, p. 2001.
27. El-Sheltawy, S.T.; Al-Sakkari, E.G. Recent Trends in Solid Waste Utilization for Biodiesel Production. *J. Solid Waste Technol. Manag.* **2016**, *42*. [[CrossRef](#)]
28. Ling, J.S.J.; Tan, Y.H.; Mubarak, N.M.; Kansedo, J.; Saptoru, A.; Nolasco-Hipolito, C. A review of heterogeneous calcium oxide based catalyst from waste for biodiesel synthesis. *SN Appl. Sci.* **2019**, *1*, 810. [[CrossRef](#)]
29. Refaat, A.A. Biodiesel production using solid metal oxide catalysts. *Int. J. Environ. Sci. Technol.* **2011**, *8*, 203–221. [[CrossRef](#)]
30. Talha, N.S.; Sulaiman, S. Overview of catalysts in biodiesel production. *ARPN J. Eng. Appl. Sci.* **2016**, *11*, 439–442.
31. ASTM. *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*; ASTM International: West Conshohocken, PA, USA, 2010; Volume i, pp. 1–11.
32. En, V.A. *Liquid Petroleum Products—Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications—Requirements and Test Methods*; European Committee for Standardization: Brussels, Belgium, 2018; p. 14538.
33. Biodiesel, A.-I.-O. *Application note EN 14103 Determination of Total FAME and Linolenic Acid Methyl Ester in FAME with AC Biodiesel All in One Solution*; PAC: Houston, TX, USA, 2011; pp. 1–3.
34. Biodiesel, A.-I.-O.; Glycerol, T. *Application Note EN 14105 Determination of Free and Total Glycerol and mono-, di-,—triglycerides in Fatty Acid Methyl Esters (FAME)*; PAC: Houston, TX, USA, 2011; pp. 2–4.
35. Banerjee, S.; Rout, S.; Banerjee, S.; Atta, A.; Das, D. Fe₂O₃ nanocatalyst aided transesterification for biodiesel production from lipid-intact wet microalgal biomass: A biorefinery approach. *Energy Convers. Manag.* **2019**, *195*, 844–853. [[CrossRef](#)]
36. Correia, L.M.; Saboya, R.M.A.; de Sousa Campelo, N.; Cecilia, J.A.; Rodríguez-Castellón, E.; Cavalcante, C.L.; Vieira, R.S. Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sunflower oil. *Bioresour. Technol.* **2014**, *151*, 207–213. [[CrossRef](#)]
37. El Shimi, H.I.; Attia, N.K.; El Diwani, G.I.; El Sheltawy, S.T. Investigation of silicates as a catalyst in biodiesel production: A review. *Int. J. Energy Res.* **2016**, *40*, 1743–1756. [[CrossRef](#)]
38. Puspa, N.; Agustina, D.; Sari, P.; Poedjojono, B. Utilization of Waste Cooking Oil for Biodiesel Production Using Alumina Supported base Catalyst. In Proceedings of the 3rd International Conference on Biological, Chemical and Environmental Sciences, Kuala Lumpur, Malaysia, 21–22 September 2015; pp. 21–25. [[CrossRef](#)]
39. Rasouli, H.; Esmaeili, H. Characterization of MgO nanocatalyst to produce biodiesel from goat fat using transesterification process. *3 Biotech* **2019**, *9*, 1–11. [[CrossRef](#)]
40. Koberg, M.; Gedanken, A. *Using Microwave Radiation and SrO as a Catalyst for the Complete Conversion of Oils, Cooked Oils, and Microalgae to Biodiesel*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 209–227.
41. Erchamo, Y.S.; Mamo, T.T.; Workneh, G.A.; Mekonnen, Y.S. Improved biodiesel production from waste cooking oil with mixed methanol–ethanol using enhanced eggshell-derived CaO nano-catalyst. *Sci. Rep.* **2021**, *11*, 6708. [[CrossRef](#)]
42. Ajala, E.O.; Ajala, M.A.; Ayinla, I.K.; Sonusi, A.D.; Fanodun, S.E. Nano-synthesis of solid acid catalysts from waste-iron-filling for biodiesel production using high free fatty acid waste cooking oil. *Sci. Rep.* **2020**, *10*, 13256. [[CrossRef](#)]

43. de Oliveira, K.G.; de Lima, R.R.S.; de Longe, C.; de Bicudo, T.C.; Sales, R.V.; de Carvalho, L.S. Sodium and potassium silicate-based catalysts prepared using sand silica concerning biodiesel production from waste oil. *Arab. J. Chem.* **2021**, *15*, 103603. [[CrossRef](#)]
44. ASTM. *Standard Test Method for Gross Calorific Value of Coal and Coke*; ASTM International: West Conshohocken, PA, USA, 2013; pp. 1–19.
45. ASTM. *Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter*; ASTM International: West Conshohocken, PA, USA, 2013; pp. 1–8. [[CrossRef](#)]
46. ASTM International. Final Draft Uganda Standard, FDUS 1730. In *Standard Test Method for Pour Point of Petroleum Products*; ASTM International: West Conshohocken, PA, USA, 2013.
47. ASTM International. *ASTM D93 Flash Point*; ASTM International: West Conshohocken, PA, USA, 2004; Volume 5, p. 80112.