

Article

# Biodiesel and Crude Glycerol from Waste Frying Oil: Production, Characterization and Evaluation of Biodiesel Oxidative Stability with Diesel Blends

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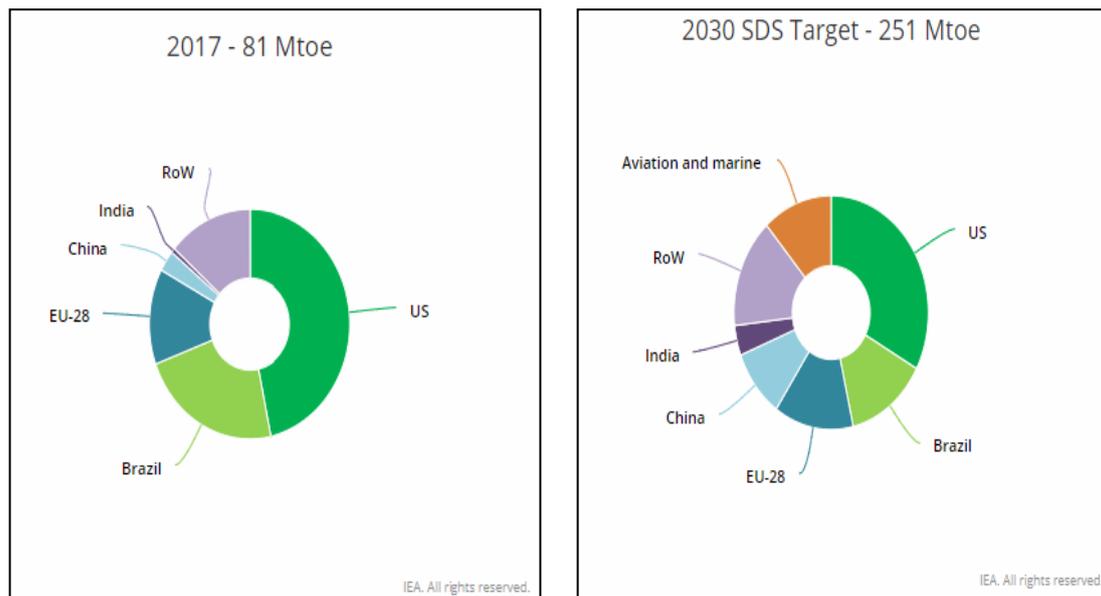
**Abstract:** Waste oils are becoming increasingly more important as feedstock for the production of fuels and glycerol as byproduct. Optimization of homogeneous transesterification of waste frying oil (WFO) to biodiesel over hydroxide potassium (KOH) catalyst have been investigated. In this respect, response surface methodology (RSM) was applied to determine the relationships between methanol and WFO molar ratio (3:1–12:1), KOH concentration (0.5%–2%) and temperature (25–65 °C) on the conversion yield. Transesterification of WFO produced 96.33% maximum methyl ester yield at the optimum methanol/WFO molar ratio 7.3:1, KOH loading 0.5 wt. % and the reaction temperature was 58.30 °C. The physicochemical properties of optimized biodiesel met the requirements of the European Norm 14214, such as kinematic viscosity at 40 °C 4.57 mm<sup>2</sup>/s, the sulfur content 0.005 wt. %, and the density at 15 °C 889.3 kg/m<sup>3</sup>. This study also examined the accelerated oxidation of biodiesel and biodiesel/diesel blends under combined temperature and air effect at different periods of time while measuring their acidity. Results have shown that total acid number increased proportionally to the biodiesel content of the biodiesel/diesel blends from 0.5 mgKOH/g for B7 (7% (v/v) biodiesel and 93% (v/v) diesel) up to 2.8 mg KOH/g for B100 (100% biodiesel). The synthesized trans-esterified oil can be a potential alternative to petrodiesel, hence its application at an industrial scale. This work also reports some properties of crude glycerol (CG) derived from biodiesel from WFO. The glycerol yield (%), pH, water content (wt. %), density at 15 °C (g/cm<sup>3</sup>), and kinematic viscosity at 40 °C (mm<sup>2</sup>/s) was analyzed according to standard test methods.

**Keywords:** waste frying oil; transesterification; biodiesel; optimization; crude glycerol; oxidative stability

## 1. Introduction

By 2030, the consumption of biofuels in transportation needs to triple to meet the projected fuel demand and the requirement for 10% of biofuels to be used in transportation—up from 3% in 2017—according to the SDS (Sustainable Development Scenario). However, in the next five years, a growth of only 2.5% is expected.

As shown in Figure 1, China, India, and Latin America are experiencing a greater acceleration in demand for biofuels in the SDS. Hence, biofuel production in these countries should increase over the next five years. The transport biofuel industries are at a premature step in Mexico and South Africa. To stay in sync with the SDS, market development and technological progress are also needed [1].



**Figure 1.** Biofuels consumption in 2017 vs. Sustainable Development Scenario (SDS) targets [1].

Amongst biofuels, biodiesel is considered the best choice in the face of environmental pollution, the decreases in crude oil reserves followed by exponential price growth. So biodiesel production is an alternative to producing clean, biodegradable, non-toxic and renewable fuels [2–8]. At the same time, biofuel can be used as an additive to, or substitute fuel for, conventional diesel [9]. Recently, the production of biodiesel has attracted considerable attention as a biofuel that can contribute to decreasing our dependence to fossils fuels [10,11].

These days, the cost of biodiesel is high compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oil [12–17]. However, the use of WFO and animal fat in biodiesel production reduces their price [18,19]. Using WFO over other vegetable oils in producing biodiesel is of great benefit, as it prevents the toxic discharge of such oils in nature, and it does not require any additional plant culture. In fact, WFO is advantageous not only from an environmental stance, but also from an economic point of view, since this source of raw material is less expensive. Moreover, it reduces problems of contamination; reusing waste grease can reduce the governmental burden of disposing the waste, maintaining public sewers, and treating the oil wastewater [20–22]. However, these oils are known for their high viscosity and low volatility. Hence, direct use of these oils is problematic for injectors and piston engines as it results in deposits in the combustion chamber, difficulty for cold start, and blocking in injection systems [8]. It is, therefore, imperative to reduce these channels transesterifying oil methyl ester. As a matter of fact, the quality of the biodiesel depends on the feedstock and the process of production. Therefore, it is inevitable to face the challenges in biodiesel production, such as improving its physicochemical characteristics and reducing its viscosity [22]. Biodiesel can be obtained through different processes, but transesterification is the most widely used method thanks to its technical simplicity and efficiency [23–28].

The oils of the transesterification reaction are carried out in the usual way with methanol in the presence of basic homogeneous catalysts, such as NaOH or KOH. It is worth noting that unlike basic homogenous catalysts, the acid catalysts are used less frequently employed in this type of transformation, as they require larger excesses of alcohol and higher temperatures for longer periods. Moreover, they are less sensitive to moisture and, in particular, are not affected by the acidity of the oil [29,30]. In the transesterification reaction, triglycerides are converted, stepwise, to diglyceride, monoglyceride, and finally glycerol, which sinks to the bottom [31]. In addition, biodiesel that floats on top of the glycerol is an important byproduct and can be burned for heat or used as a feedstock in the cosmetic industry [32–34].

Furthermore, the booming of biodiesel production creates a surplus of glycerol production, considering that its global production in 2015 was more than 300,000 m<sup>3</sup>. Glycerol is a versatile renewable raw material that is purified or distilled, and is mainly used in the chemical industry, but also as a humectant and solvent in foods and beverages [35]. The variety of glycerol's industrial applications has led to research interests focusing on new areas for using crude glycerol (CG), taking into account that its purification is an expensive process [36]. These areas include the production of polymers, fuel additives, hydrogen, ethanol, etc., in an attempt to provide high-value-added products with lower environmental impacts and thus not impeding biodiesel production [35,37].

The biodiesel yield is influenced by several operating parameters, such as the effect of temperature, alcohol-to-oil molar ratio, and the concentration of catalyst. In this study, biodiesel was prepared from WFO. To achieve high biodiesel yield production, transesterification reaction conditions, like homogeneous catalyst concentration (KOH), methanol/WFO molar ratio, and reaction temperature were optimized statistically by response surface methodology (RSM), based on three-level three-factor Box–Behnken design (BBD).

RSM is an efficient numerical technique used to optimize multifactorial experiments and evaluate the effects of many factors for the required responses. Among the steps of optimizing RSM is the prediction equation model that defines the effects of independent variables. The response to different levels of reaction variables can be evaluated by the model equation. The experimental data were tailored to the full quadratic equation, the design matrix and the adequacy of each term were examined using ANOVA [38].

RSM could solve the problem of knowing where the experimental limits should be, what the range should be, and help to define the optimal range where maximum efficiency can be achieved. Other benefits are cost reduction and a reduction in the number of experiments to be done, saving money, time, and effort. The experimental plan for biodiesel synthesis is capable of stimulating transesterification conditions with good error estimates [39].

The optimized biodiesel physicochemical properties, like kinematic viscosity, flash point, and density, were measured. The aging of biodiesel and its blends (B7 and B20) with market diesel was also studied, evaluating the effect of fatty acid methyl ester (FAME) content, temperature, and air in the aging process by monitoring the total acid number (TAN). The produced CG was also analyzed.

## 2. Materials and Methods

### 2.1. Material

The study made use of HPLC grade methanol (CH<sub>3</sub>OH, purity 99.8%), hydroxide potassium pellets (KOH, purity 85%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, purity >98.9%), phenolphthalein, potassium iodide (KI), anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, purity >99%), reagent Wj's, glacial acetic acid (CH<sub>3</sub>COOH), chloroform (CHCl<sub>3</sub>, purity 99%), absolute ethanol (EtOH), diethyl ether (C<sub>4</sub>H<sub>10</sub>O), carbon tetrachloride (CCl<sub>4</sub>), hexane (C<sub>6</sub>H<sub>14</sub>, purity 85%), and hydroxide sodium (NaOH, purity 98%). All chemicals were analytical grade and purchased from Digital System (Tunisia). The chemicals for the titrimetric analysis of TAN were ethanol (denatured with 0.5–1.5 vol % 2-butanone and approximately 0.001% Bitrex, ≥98%), diethyl ether (≥98%), and phenolphthalein purchased from Sigma-Aldrich Co. Potassium hydroxide, 0.1mol/L in ethanol, was purchased from Chem Lab.

### 2.2. Measurement of WFO, Optimized Biodiesel and Crude Glycerol Properties

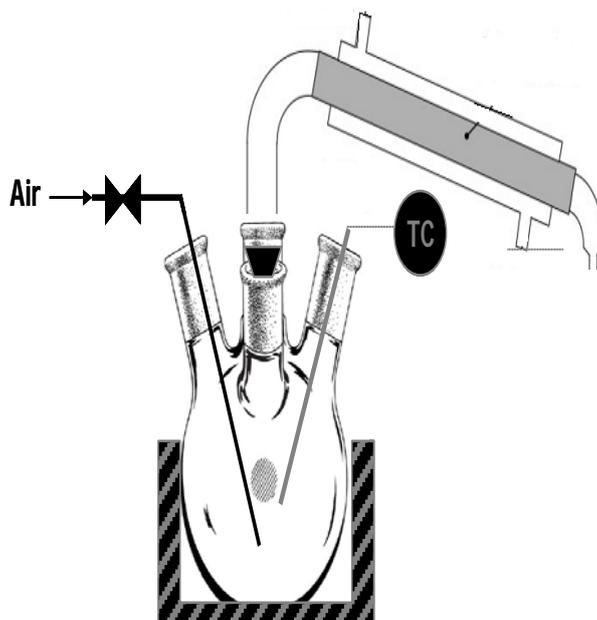
The waste frying oil (WFO) was obtained from Sfax university restaurant, Tunisia, and then its physicochemical properties were measured (Table 1).

**Table 1.** Physical and chemical properties of treated oil samples were determined.

Property	Units	Value
Acid value	mg KOH/g	0.63
Peroxide value	meqO <sub>2</sub> /kg	6.75
Iodine value	mg I <sub>2</sub> /100 g	109.98
Density at 15 °C	kg/cm <sup>3</sup>	926
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	37.31
Fatty acid composition, wt. %	C12:0	0.00
	C14:0	0.01
	C16:0	11.54
	C16:1	0.13
	C17:0	0.11
	C17:1	0.06
	C18:0	4.49
	C18:1	23.52
	C18:2	52.81
	C18:3	6.76
	C20:0	0.34
	C20:1	0.23

The methyl ester (ME) composition was obtained by an Auto System gas chromatograph (GC) equipped with a flame ionization detector (FID) (HP 6890N, Agilent (Palo Alto, CA, USA)). The column utilized was a capillary Agilent CP-Sil88 (length = 50 m, i.d. = 0.25 mm, and film thickness = 0.20 µm), and the analysis conditions were as follows: the initial column temperature was settled at 165 °C for 25 min, then raised at a gradient of 5 °C/min to 195 °C; the temperature of the injector and detector was set at 250 °C; helium was employed as the carrier gas at a flow rate of 1 mL/min and 1:100 split ratio; the injection volume was 1 µL [40].

Biodiesel and the CG were analyzed using EN 14214 and other standard test methods. Density at 15 °C and kinematic viscosity at 40 °C measurements were made under EN ISO 3675:1998 and EN ISO 3104:1994 respectively [41,42]. The iodine value and acid value were realized by simple titration under EN 14104:2003 and EN 14111:2003 respectively [43,44]. In addition, the content of water was measured by the Karl Fischer method ISO 12937:2000 [45]. Concerning the flash point, it was determined by the Pensky–Martens closed-cup method ISO 2719:2002 [46], and the sulfur content was quantified under EN ISO 13032:2012 [47]. For oxidative stability (OS), fuels were prepared through the blending of biodiesel and diesel fuel B7 and B20. The biofuels were oxidized at 120 °C for 2, 4, and 6 h with an air flow rate of 100 mL/min in the fuel thermal-aging apparatus of the chemical process and energy resources institute and the center for research and technology Hellas (CPERI/CERTH), as illustrated in Figure 2.



**Figure 2.** Schematic diagram of the CPERI/CERTH fuel thermal-aging apparatus.

Three hundred milliliters of each biofuel were oxidized in a four-necked flask placed in a heating mantle. Temperature was controlled automatically via a thermocouple immersed in the vessel while air was bubbled via a ground-glass nozzle. Oxidized samples were collected after the end of the experiment for determining TAN and were analyzed according to EN 14104. The peroxide value was determined by simple titration [48].

### 2.3. Biodiesel Preparation

The collected waste frying oil (WFO) was firstly filtered to remove food residues and any suspended matter. WFO was then heated at 105–110 °C to remove all moisture. The batch transesterification reactions were conducted in a laboratory-scale setup using a three-necked 250 mL flask equipped with a reflux condenser. Next, a specific amount of KOH pellets was weighted (0.5–2 wt. %) and dissolved in the required amount of methanol (3:1–12:1). The potassium methoxide solution was then added to the preheated oil. Following this, all of the components were heated up to the desired temperature (25–65 °C) with a stirring speed of 600 rpm using a paraffin oil bath and a magnetic hot plate stirrer with a temperature controller. After the transesterification process, the mixture is transferred into a separating funnel. Two layers are formed: the upper layer is the desired product, i.e., biodiesel, and the lower layer is CG. Glycerol was recovered for further characterization. The biodiesel was washed by hot water (70–80 °C) several times until the rinses were clear until the wash water became clear and neat. Then, the washed methyl ester was dried at 105 °C. The biodiesel yield can be calculated following this equation:

$$\text{Conversion yield (\%)} = \frac{\text{Pure biodiesel (g)}}{\text{Oil used (g)}} \times 100 \quad (1)$$

### 2.4. Box–Behnken Design (BBD):

A three-level BBD was carried out to investigate the effect of the transesterification operation conditions, and to obtain the best biodiesel in terms of yield. In this respect, reaction temperature (A), methanol/oil molar ratio (B), and catalyst concentration (C) were selected. Each factor was codified

by  $-1$ ,  $0$ , and  $+1$ , respectively corresponding to low, center, and high levels. The coded values of the process variables were determined by the following equation:

$$X_i = \frac{x_0 - x_1}{\Delta_x} \quad (2)$$

Noting that  $x_i$  is the coded value of the first variable,  $X_i$  represents the uncoded value of the first test variable,  $\Delta_x$  is the difference between the proceeding values, and  $x_0$  is the uncoded value of the first test variable at the center point. The factor levels with the corresponding real values and the design matrix are shown in Table 2.

**Table 2.** Experimental range and levels of the independent variables. WFO is the waste frying oil.

Factors	Units	Code	Levels		
			$-1$	$0$	$1$
Temperature	$^{\circ}\text{C}$	A	25	45	65
Methanol/WFO ratio	mol/mol	B	3:1	7.5:1	12:1
Catalyst concentration	%	C	0.5	1.25	2

Fifteen experiments, including 12 factorial and 3 central runs, were performed in random order to avoid systematic error. The regression analysis was performed to estimate the response function as a second-order polynomial equation, as explained in Equation (3):

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (3)$$

Given that  $Y$  is the predicted response, i.e., the conversion to biodiesel, ( $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ ), ( $\beta_{12}$ ,  $\beta_{13}$  and  $\beta_{23}$ ), and ( $\beta_{11}$ ,  $\beta_{22}$  and  $\beta_{33}$ ) are respectively the linear, interactions, and quadratic coefficients of the independent variables of the response. The data were analyzed using Design-Expert Software (version 7.0.0, Stat-Ease, Inc., Minneapolis, MN, USA) and the coefficients were interpreted using F-test. Model validation and significance of factors were evaluated by the analysis of variance (ANOVA).

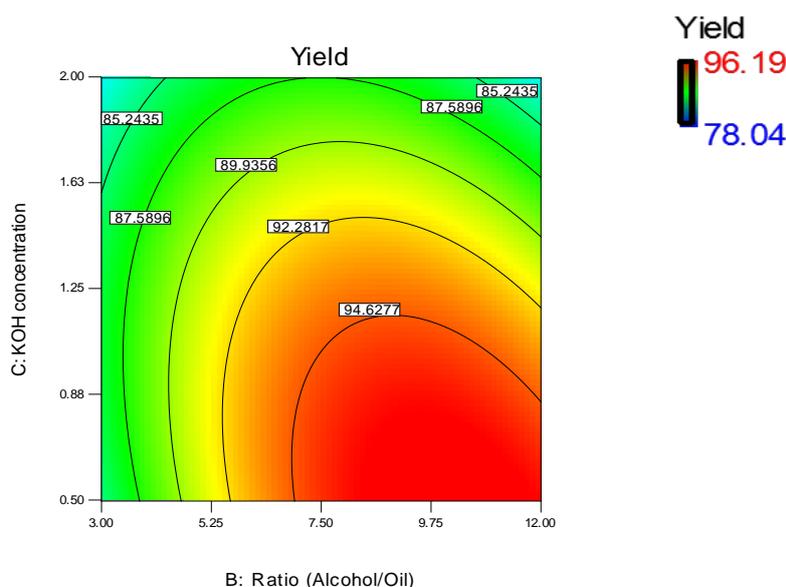
### 3. Results and Discussion

#### 3.1. Effects of Transesterification Reaction Parameters and Regression Model Validation

##### 3.1.1. Effect of Methanol/WFO Molar Ratio

Methanol-to-oil ratio (A) is one of the most important factors affecting the percent of ME. The transesterification process necessarily required a minimum of 3:1 methanol-to-oil ratio to yield 3 mol of ester and 1 mol of glycerol [49]. In this study, the range of methanol-to-oil ratio is taken from 3:1 to 12:1. A significant effect was shown on the response with a p-value of 0.0037.

Figure 3 shows the three-dimensional surface plot of the combined effects of the methanol-to-oil molar ratio and catalyst concentration (BC) on the biodiesel yield at  $45^{\circ}\text{C}$ , in which the yield of esters increases with the increase of the ratio molar at 0.5% to 1.25% of catalyst concentration. However, at high catalyst concentration, the yield decreases from 87.61% to 82.81% with an increase of the molar ratio. However, the higher molar ratio (12:1) of alcohol to oil interferes with the separation of glycerol because there is an increase in solubility. The excess of alcohol seems to favor conversion of di- to monoglycerides, but there is also a slight recombination of esters and glycerol to monoglycerides because their concentration keeps increasing during the reaction, in contrast to reactions conducted with low molar ratios [50].



**Figure 3.** The three-dimensional surface plot of the combined effects of the methanol-to-oil molar ratio and catalyst concentration (BC) on the biodiesel yield at 45 °C.

### 3.1.2. Effect of Catalyst Concentration

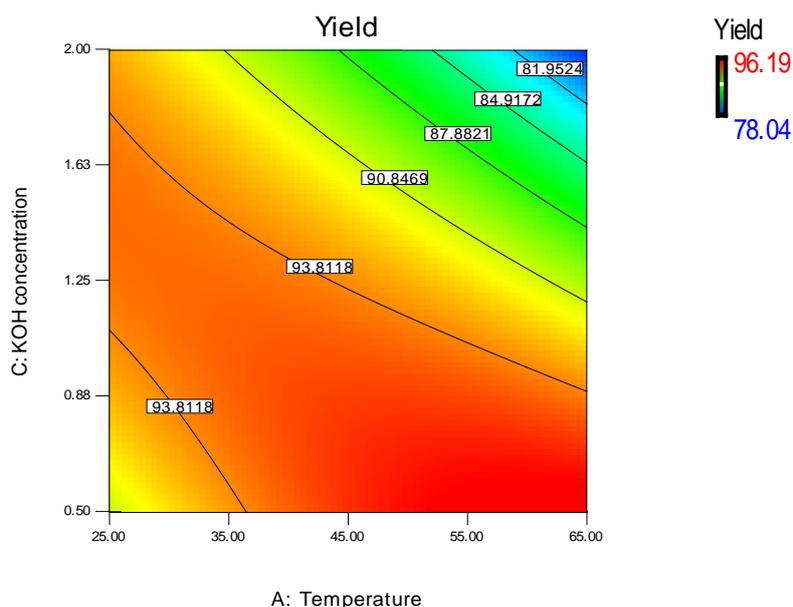
ANOVA analysis shows that KOH concentration is the most influential factor since the  $p$ -value is less than 0.05 (Table 3).

**Table 3.** Response surface quadratic model.

Source	Sum of Squares	df	Mean of Square	F value	$p$ -Value Prob > F
<b>Model</b>	456.80	9	50.76	22.03	0.0017 <i>significant</i>
<b>A: Temperature</b>	33.21	1	33.21	14.42	0.0127
<b>B: Ratio (Alcohol/Oil)</b>	60.61	1	60.61	26.31	0.0037
<b>C: KOH concentration</b>	120.13	1	120.13	52.15	0.0008
<b>AB</b>	13.00	1	13.00	5.64	0.0635
<b>AC</b>	100.70	1	100.70	43.72	0.0012
<b>BC</b>	30.42	1	30.42	13.20	0.0150
<b>A<sup>2</sup></b>	9.11	1	9.11	3.95	0.1035
<b>B<sup>2</sup></b>	81.93	1	81.93	35.56	0.0019
<b>C<sup>2</sup></b>	17.80	1	17.80	7.73	0.0389
<b>Residual</b>	11.52	5	2.30		
<b>Lack of Fit</b>	9.15	3	3.05	2.57	0.2922 <i>not significant</i>
<b>Pure Error</b>	2.37	2	1.19		
<b>Cor Total</b>	468.31	14			

$R^2 = 0.972$

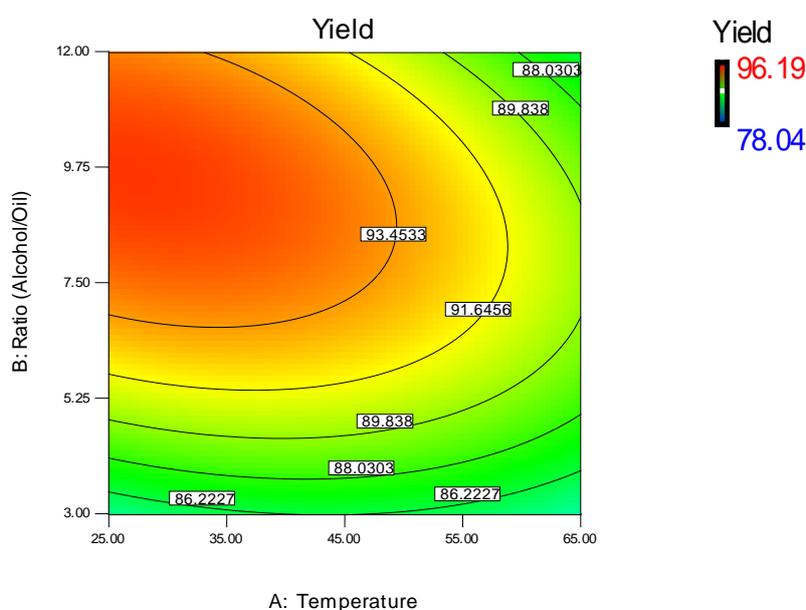
The three-dimensional surface plot (Figure 4) shows that biodiesel yield increases gradually at a transesterification temperature lower than 35 °C, whereas at high temperatures ( $\geq 35$  °C) and at a catalyst concentration above 1.25%, the yield decreases from 90.07% to 78.98%. Actually, this demonstrates that the excess of KOH results in the formation of soaps through a saponification reaction. Therefore, ester and glycerol emulsification take place, which makes it hard to separate the biodiesel, leading to ester losses and a decrease in the biodiesel yield [24]. However, an insufficient amount of catalyst resulted in the incomplete conversion of triglycerides into the esters.



**Figure 4.** The three-dimensional surface plot of the combined effects of the catalyst concentration and the temperature (AC) on the biodiesel yield at the methanol-to-oil molar ratio 7.5:1.

### 3.1.3. Effect of Transesterification Temperature

The temperature has a moderately significant effect on the yield with a *p*-value of 0.0127. The combined effect of the temperature and ratio molar methanol/WFO are illustrated in Figure 5, which shows that at the high molar ratio, the yield increases slowly from 93.93% to 94.15% at low temperature; however, it decreases to 84.41% at the low molar ratio and a high temperature. This can be justified as follows: beyond a certain temperature, alcohol starts to evaporate and slows down the reaction. In addition, during the use of a basic catalyst, the saponification reaction that occurs concurrently with transesterification will be favored beyond certain thresholds of temperature.



**Figure 5.** The three-dimensional surface plot of the combined effects of the methanol-to-oil molar ratio and the temperature (AB) on the biodiesel yield at the catalyst concentration 1.25%.

### 3.1.4. Regression Model Validation

A regression analysis was carried out to fit the response function and predict the outcome of ME yield using a model. The latter is given by Equation (4) with coded values.

$$Y(\%) = +93.68 - 2.04 \times A + 2.75 \times B - 1.80 \times C - 3.88 \times A \times B - 5.02 \times A \times C - 2.76 \times B \times C - 1.57 \times A^2 - 4.71 \times B^2 - 2.20 \times C^2 \quad (4)$$

Knowing what A, B and C are, the reaction conditions as shown in Table 2.

The results of the analysis of variance (ANOVA) are summarized in Table 3. In these cases, the *p*-value, which is less than 0.05, indicated that the particular term was statistically significant. The analysis demonstrated that the significant terms are A, B, C, BC, B<sup>2</sup>, and C<sup>2</sup> for biodiesel yield. The coefficient of correlation, R<sup>2</sup> for the model was 0.975. This indicates that only 2.46% of the total variability was not explained by the model terms. The high R<sup>2</sup> value confirms that the obtained model can give a convincingly good estimation of the response of the transesterification process in the studied range. The non-significant lack of fit test (*p*-value = 2.57) for the developed model shows that the model perfectly fits the data.

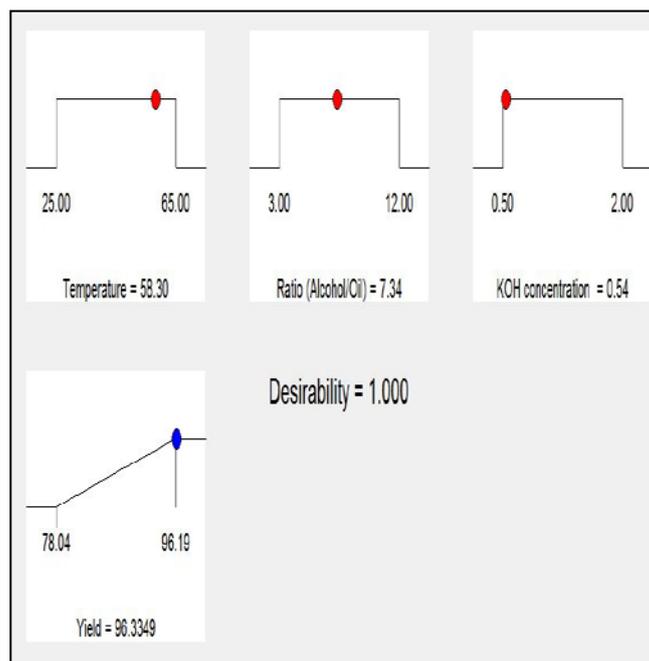
Comparing the observed values and the predicted ones for ME yield, presented in Table 4, it is noted that the predicted values were not far away from the experimental ones, indicating that the developed model was successful in estimating the correlation between the transesterification condition variables and biodiesel ester yield.

**Table 4.** Experimental design matrix and experimental results of the conversion yield.

Run No.	Temperature (A, °C)	Methanol/WFO Ratio Molar (B, mol/mol)	Catalyst Concentration (C, wt. %)	Observed Yield (Y <sub>1</sub> , %)	Predicted Yield (Y <sub>1</sub> , %)
1	25	7.5	2	94.27	93.10
2	45	3	2	82.88	82.91
3	45	7.50	1.25	94.94	93.68
4	65	7.5	2	78.04	78.99
5	25	3	1.25	83.74	84.88
6	65	12	1.25	87.46	86.31
7	25	12	1.25	93.02	93.99
8	45	7.5	1.25	93.08	93.68
9	65	3	1.25	85.39	84.41
10	45	12	0.5	96.19	96.16
11	45	12	2	82.70	82.90
12	45	3	0.5	85.34	85.14
13	65	7.5	0.5	95.6	96.77
14	25	7.5	0.5	91.76	90.81
15	45	7.5	1.25	93.03	93.68

### 3.2. Parameters Optimization of the Transesterification Process

Based on the obtained model (Y) and the input criteria, the BBD is able to optimally design the desired response to the transesterification process. The optimum biodiesel yield was performed based on the three variables set in the range of experimental runs. The Design-Expert software predicted that the optimized conditions for ME yield will be obtained when the KOH amount, methanol/WFO molar ratio, and temperature were 0.5 wt. % of catalyst, 7.3 molar ratio, and 59.81 °C, respectively, with a predicted methyl ester yield of 96.33 wt. % (Figure 6).



**Figure 6.** Optimum conditions obtained by response surface methodology (RSM).

The experimental ME yield was 95.00 wt. %. This shows that the obtained experimental value was in perfect agreement with the calculated value from the model (Equation (4)). The obtained optimum conditions have been compared to some similar studies, as shown in Table 5. The presented results show that the maximum yield has been obtained at the suggested conditions of this study.

**Table 5.** Comparison between the present work and other results.

Optimum Conditions	Yield %	References
KOH 0.5 wt. %, 7.3:1, 58.30 °C, 600 rpm, 60 min	96.33	This work
KOH 1.5 wt. %, 20:1, 60 °C, 300 rpm, 60 min	93.00	[51]
KOH 1.2 wt. %, 6:1, 60 °C	80.80	[52]
KOH 1.2 wt. %, 4.5:1, 62 °C, 600 rpm, 75 min	93.00	[53]
KOH 1.4 wt. %, 7.5:1, 65 °C, 500 rpm, 60 min	99.39	[54]
KOH 1.2 wt. %, 9:1, 60°C, 0.43 min	89.00	[55]
NaOH 0.72 wt. %, 9:1, 65 °C, 45 min	92.05	[24]

### 3.3. Properties of the Optimized Biodiesel

Table 6 tabulated the physicochemical properties of optimized biodiesel. The properties of produced biodiesel had a reasonable agreement with previous studies [56,57] in addition to EN 14214 biodiesel standard. Kinematic viscosity is an important property for fuel atomization and distribution, which was inside the range of standards with a value of 4.57 mm<sup>2</sup>/s. The flash point was 156 °C, which is an elevated value that has the advantage of higher safety than the petrodiesel for transport purposes. This value actually meets the requirements of the EN 14214 biodiesel standard.

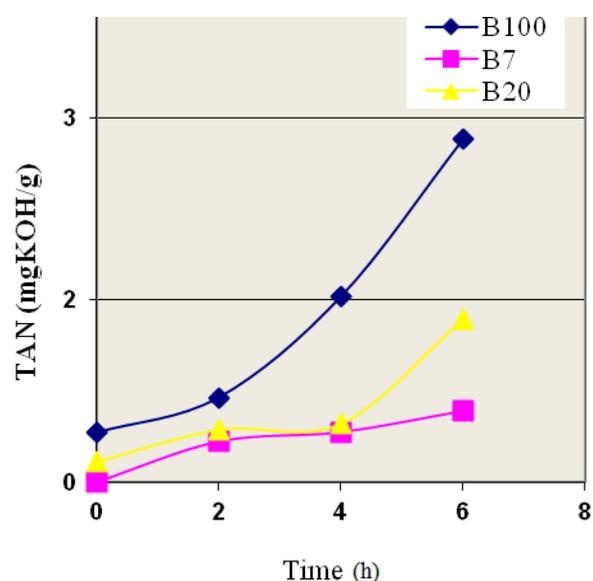
**Table 6.** Physical and chemical properties of optimum biodiesel from WFO.

Property	Units	Biodiesel	Diesel	[56]	[57]	EN14214
Methyl ester	% (w/w)	100	-	-	-	Min 96
Density at 15 °C	kg/m <sup>3</sup>	889.3	834.5	884.0	881.7	860–900
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	4.57	2.70	4.63	6.81	3.5–5.00
Flash point	°C	156	58	161	173	Min 120
Sulfur content	% (w/w)	0.0058	0.1571	-	-	0.05
Water content	ppm	100	-	468	530	Max 500
Iodine value	mg I <sub>2</sub> /100 g	105.96	-	108	125.28	Min 120
TAN	mg KOH/g	0.41	-	0.6	0.22	Max 0.5
Peroxide value	meqO <sub>2</sub> /kg	78.16	-	-	26.01	-

### 3.4. The Accelerated Oxidation of the Biodiesel and Its Blends

Oxidative stability (OS) is an indication of the resistance to degradation of the fuel due to oxidation during long-term storage, and is of great importance in the context of possible problems with engine parts. Upon oxidation, biodiesel forms products that can lead to many operating issues, such as the formation of deposits, eventually leading to complete failure of the fuel injection equipment (FIE) [58]. The factors that influence the oxidation susceptibility of biodiesel are the fatty acid structure; temperature; presence of certain metals or light, as well as the exposed surface area between biodiesel and air [59–61]. Biodiesel produced from WFO via transesterification and its blends with diesel (B7, B20) were oxidized under the conditions previously described, and their degradation was monitored via TAN analysis.

Results are presented in Figure 7. It can be observed that the investigated oxidation conditions significantly influence the acidity of the biofuels. More specifically, the highest acidity was observed for B100 after 6 h of accelerated oxidation, while increasing the biodiesel ratio in the blends.

**Figure 7.** Total acid number (TAN) of oxidized samples at 120 °C vs. oxidation time (h).

Also, the oxidation time for TAN increased, leading to full degradation. Furthermore, it can be assumed that the combined exposure to air and high temperature contributes to the biofuel's degradation, whereas TAN values increased as the oxidation time increased.

## 4. Properties of Crude Glycerol as a Byproduct of Optimized Biodiesel

In this study, CG made from the transesterification of WFO has low glycerol content because of impurities. Hence, before CG can be used for possible value-added applications, its physical and

chemical characterization is required. The properties of crude glycerol byproduct are illustrated in Table 7.

**Table 7.** Physical and chemical properties of CG derived from optimized biodiesel.

Crude Glycerol	Results	Kongjao et al. [62]	Quality Specifications [63]
Color	Dark Brown	Dark Brown	
Glycerol yield (wt. %)	30.40	28.56	40%–88%
pH	9.5	10–11	4–9
Density at 15 °C (g/cm <sup>3</sup> )	1.01	1.01	NA
Viscosity at 40 °C (mm <sup>2</sup> /s)	26.35	42.41	NA
Water content (wt. %)	7.2	6.7	12%

In comparison with the work of Kongjao et al. [62], our process gave the best yield of CG of approximately 30%. A high glycerol content with a dark brown color was obtained in both cases, and a similar density for both studies. The pH is close to 10 due to the existence of residual alkalis, such as KOH, resulting from the transesterification process. The high viscosity of the CG obtained by Kongjao et al. [59] suggests the presence of soaps and other dissolved materials, including glycerides, esters, and viscosity of the raw material. The water content is approximately 7 wt. %, which can be attributed to the moisture absorption from the washing stage during the production process.

## 5. Conclusions

A second-order model was found using RSM optimization to predict biodiesel yield based on transesterification parameters. This work postulates that the coefficient of determination ( $R^2$ ) has a value of 0.975, confirming the validation of the model. The ANOVA analysis demonstrated that the concentration of KOH, methanol/WFO ratio, and temperature had a significant effect on the biodiesel yield.

The maximum yield of biodiesel of 96.33% was obtained with KOH as catalyst at 0.5%, a methanol/WFO ratio of 7.33 mol/mol, and a temperature of 59.81 °C. The optimal properties of biodiesel, such as the kinematic viscosity at 40 °C, the density at 15 °C, the acid value, the flash point, the sulfur content and the water content. They give us respectively 4.57 mm<sup>2</sup>/s, 889.3 kg/m<sup>3</sup>, 0.4 mg KOH/g, 156 °C, 0.0058 wt.% and 100 ppm that they respect the European Norm EN 14214.

The degradation of biodiesel and its blends with diesel were examined via accelerated oxidation conditions, and the results showed that the combined effects studied of temperature and air have important effects on their acidity.

CG has proven to be a valuable co-product of biodiesel production. The characterization of some GC properties was also studied. Included among them is the yield of glycerol, which was 30.40% by weight.

The application of glycerol in its raw form should be explored further in future studies, and biodiesel production has been proven to be a good alternative to petroleum-based fuel and can be developed on an industrial scale because of its cost effectiveness.

**Author Contributions:** All authors contributed extensively to the work presented in this paper. M.H. and S.N.B. designed the structure of the entire manuscript and contributed to its preparation and writing. F.M. completed the part of the optimization, analyzed the results and designed the graphic material. L.P.C. conducted the accelerated oxidation experiments of biodiesel and their mixtures and analyzed the results. S.B. and M.B. revised the paper.

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