

## Response Surface Optimization of an Alkaline Transesterification of Waste Cooking Oil

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**Abstract:** Rotatable central composite design of experiments was employed to investigate the significance and interactive effects of methanol:oil molar ratio, catalyst concentration, operating temperature, reaction time and mixing rate on a base catalyzed transesterification reaction of waste cooking oil to maximize the biodiesel yield. Based on a multiple regression analysis, a second order polynomial equation for biodiesel yield was obtained and its validity was confirmed. The optimum conditions for maximum biodiesel conversion of  $\approx 99\%$  was depicted to be 7.54:1 M:O, 0.875 KOH wt%, 52.7°C, 1.17 h and 266 rpm. The overall physico-chemical properties of the produced biodiesel were acceptable.

**Keywords:** Response surface methodology, transesterification, waste cooking oil, biodiesel, fuel properties.

### 1. Introduction

Due to the exponential growth of world population and the worldwide increase of the energy demand with the decrease of the petroleum resources, the research of alternative and renewable energy sources is mandatory. Biodiesel as a non-petroleum renewable-based fuel is regarded as a petro-diesel substitute with the advantage of being biodegradable, non-toxic and reducing the greenhouse emissions.<sup>1,2</sup> The major challenge for commercialization of biodiesel is its production cost, where approximately 70-95% of the total cost is related to the oil feedstock.<sup>3</sup> Moreover, with the increment of the worldwide population, more land is needed for cultivation of human food crops rather than to produce oilseeds for biodiesel production and more amount of waste cooking oil (WCO) is produced from household, restaurants and food industries, which would cause environmental problems and add to the governmental burden for waste management.<sup>2</sup> The recycling of WCO to biodiesel would solve the aforementioned problems and lower the overall cost of biodiesel.<sup>4</sup>

There are four routes for the biodiesel production from WCO; base, acid and enzyme catalyzed transesterification and non-catalytic transesterification ones.<sup>5</sup> Methanol, the short chain alcohol, is the most recommendable alcohol for the transesterification reaction for its availability, polarity and low cost.<sup>6</sup> The base-catalyzed transesterification reaction is the most common in the industrial scale, for its high rate, moderated reaction conditions, low cost and easy installation.<sup>2</sup> But its main drawback is the soap formation side reaction, which would consume the catalyst, complicate the separation and purification steps and consequently decrease the biodiesel yield.<sup>7</sup>

The aim of this work was to maximize the biodiesel conversion by modeling and optimizing the transesterification process of WCO using KOH as a basic homogenous catalyst, throughout the application of rotatable central composite design (RCCD) of experiments. Response surface methodology (RSM) was aimed to be used to understand the interactive relationships between five operating variables; methanol:oil molar ratio, catalyst loading, process temperature, reaction time and the mixing rate and their impacts on the bio-diesel yield.

## 2. Materials and methods

### 2.1 Materials

The WCO was collected from a local restaurant in Giza, Egypt. Pure potassium hydroxide as alkaline catalyst, anhydrous sodium sulfate and methanol (AR Grade) were purchased from Fluka Chemical Corp.

### 2.2 The pretreatment of the WCO

The collected WCO was centrifuged and filtered to remove any suspended matter and burned food bits, etc. Then it was heated at 105°C for 2 h to remove any traces of unwanted water by evaporation.

### 2.3 The transesterification process

The transesterification reactions were conducted in a 250 mL glass three-necked batch reactor, containing a known quantity of the WCO and equipped with a reflux condenser and a thermometer, placed on a magnetic heat stirrer set at different temperature and mixing rate, according to the required experimental conditions. The magnetic stirrer was supplemented with a thermostat to keep the reactor temperature constant, during the reaction. The transesterification was carried out in a basic medium, where KOH was used as a catalyst. The required concentration of the catalyst was dissolved in a required amount of methanol. Once the WCO in the reactor reached the required temperature, alcohol solution containing the dissolved catalyst was added. The reaction time was calculated after the mixture reached the required temperature. After the prescribed time of the reaction, the mixture was carefully poured into a separating funnel and allowed to separate overnight. Two phases with different density were formed; the lower layer (glycerol and un-reacted methanol, catalyst and traces of unreacted WCO) was drained out and transferred into a sample flask of a rotary evaporator to recycle methanol at 65°C and 20 kPa. The upper layer (crude biodiesel i.e. crude FAME) was washed with warm distilled water (50°C) for purification from any saponification by-products, catalyst and glycerol residuals. The washing process was repeated until neutral pH. After that, the purified biodiesel (i.e. purified FAME) was heated at 105°C for 2 h and then dried over anhydrous sodium sulfate to get rid of any unwanted water or traces of alcohol. The obtained purified biodiesel was then bottled and kept for characterization studies. The yield of the biodiesel was calculated according to Rashed and Anwar.<sup>8</sup>

$$\% \text{ yield} = \frac{\text{weight of the purified produced FAME (g)}}{\text{weight of WCO feedstock (g)}} \times 100 \quad (1)$$

### 2.4 The experimental design and statistical analysis

In this study, the effects of five operating parameters including; Methanol:Oil M:O molar ratio (A), catalyst concentration wt% (w:w, B), operating temperature °C (C), reaction time h (D) and mixing rate rpm (E), were investigated to maximize the biodiesel yield throughout the transesterification of the WCO with methanol in the presence of the basic homogenous catalyst; KOH. The experiments have been carried out by using the RCCD with three levels (coded by - 1, 0 and + 1) and  $\pm \alpha$  of  $\pm 1.82116$ . The total number of experiments was 26 runs. That included; 11 factorial points and 10 axial points which would allow the estimation of all the main effects and the determination of all the quadratic terms, respectively, in addition to the 5 replicates at the center points which would provide a check of the adequacy of the model prediction and assess the pure error. The selection of the levels was based on the results obtained in preliminary studies.<sup>2</sup>

The experimental runs with both coded and un-coded values are presented in Table.1, and the RSM was used for the statistical analysis of the obtained experimental data.

The model used in this study to estimate the response surface was the quadratic polynomial, which can be represented by the following equation:

$$Y = \beta_0 + \sum_{i=1}^5 \beta_i x_i + \sum_{i=1}^4 \sum_{j=i+1}^5 \beta_{ij} x_i x_j + \sum_{i=1}^5 \beta_{ii} x_i^2 \quad (2)$$

where, Y is the predicted biodiesel yield wt.%,  $\beta_0$  is the intercept term,  $\beta_i$ ,  $\beta_{ij}$  and  $\beta_{ii}$  are the linear, interactive and quadratic coefficients (i.e. the model coefficients), respectively, while,  $x_i$ 's are the levels of the independent variables (i.e. the factors under study).

The statistical software Design Expert 6.0.7 (Stat-Ease Inc., Minneapolis, USA) was used for design of experiments, regression and graphical analyses of the data obtained, doing the statistical analyses of the model and determine the significance levels of different parameters by evaluation of the analysis of variance (ANOVA), and it was also used for the optimization of the transesterification process.

## 2.5 The physico-chemical characterization of the produced biodiesel

The purified product obtained from the transesterification of WCO using the selected optimum conditions was tested for estimating and evaluating its fuel properties, using the standard methods of analysis for petroleum products.<sup>9</sup>The results were compared with the Egyptian standards for petro-diesel and the European<sup>10</sup> and the American<sup>11</sup> biodiesel standards.

The FAME composition of the produced biodiesel was analyzed using gas chromatography equipped with a flame ionization detector GC/FID (Agilent model 6890 plus, USA) and a HP-50 capillary column (0.53 mm x 30 m, 0.5  $\mu$ m film). Pure nitrogen was used as a carrier gas (4 mL/min). Further, 250°C injector temperature, 280°C detector temperature, split ratio (1:50), sample size 1  $\mu$ L, and the temperature program used was 80–240°C at a fixed rate of 5°C/min. The identification of the FAME was established by chromatographic reference mixture of FAME of a known composition.

All the properties were analyzed in two replicates and the final results given below were obtained as the average values.

## 3. Results and Discussion

### 3.1 The free fatty acid content of the WCO feedstock

The free fatty acid FFA content of the WCO was reported to have a negative influence on the purity of the produced FAME and the consumption of the catalyst during the transesterification reaction.<sup>12</sup>The high FFA content would consume large amount of KOH for neutralization side reaction, which would consequently lead to incomplete methanolysis. That in turn would lead to a rise in the glyceride levels in the methyl ester phase, which would consequently lead to a lower FAME content i.e biodiesel yield. In this study, the FFA content of the used WCO feedstock recorded 0.522%, with a total acid number TAN of 1.04 mg KOH/g WCO. Sharma et al.<sup>13</sup> reported that for a good alkaline transesterification reaction, the TAN of the oil feedstock should be less than 2 mg KOH/g.

### 3.2 The statistical analysis and the validation of the predicted model

The RCCD has the advantage that it permits the use of relatively few combinations of variables which would cover a wide range of variables, determine and optimize a complex response function. The necessary number of test runs in this study, was 26, which represented a big advantage since the number of tests was reduced in relation to the normal central composite design of experiments, which would normally give 50 runs of experiments. The statistical combinations of variables in coded and actual values along with the predicted and experimental response are presented in Table.1.

That experimental plan was able to depict the following second order quadratic model equation by applying the multiple regression analysis:

$$Y = 85.2 + 6.79A + 9.08B + 1.87C - 1.95D - 6.86E - 2.79A^2 - 2.76B^2 - 3.35C^2 - 0.740D^2 - 0.423E^2 - 8.65AB + 0.594AC + 1.96AD + 6.95AE - 6.98BC - 5.53BD + 0.129BE + 1.38CD + 6.872CE + 9.11DE \quad (3)$$

The regression model Eq.3 was able to characterize the influence of the different considered variables on the process biodiesel yield (Y, wt%). The positive sign in front of the terms indicated synergetic effect, whereas the negative sign indicated antagonistic effect. It was clearly obvious from Eq. 3, that the linear terms of M:O molar ratio, catalyst loading wt% and temperature °C had positive coefficients, but their quadratic terms had negative coefficients. This would indicate that an increase in M:O, catalyst loading and temperature to a certain extent, could increase the biodiesel yield. However, a reduction in the biodiesel yield could be occurred when applying too high M:O, catalyst concentration and temperature. Similar observation was reported by Charoenchaitrakool and Thienmethangkoon.<sup>14</sup>

The validity of the fitted model was evaluated and its statistical significance was controlled by F-test. The analysis of variance (ANOVA) for the response surface full quadratic model Eq.3 was given in Table 2. It can be indicated that the model Eq.3 was very highly statistically significant at 95% confidence level, with F-value of 25.9 and low probability p-value of 0.000954. The values of the determination coefficient  $R^2$  and the adjusted coefficient  $R_{adj}^2$ , which measure the model fitting reliability, were calculated and found to be 0.990 and 0.952, respectively. This suggested that, approximately 99% of the variance was attributed to the variables, which indicated the high significance of the model, where, only 1 % of the total variations could not be explained by the model Eq.3, which ensured the good adjustment of the above predicted model to the experimental data. Confirmation of the adequacy of the regression model was reflected also by the good agreement between the experimental and the predicted values of the response variables as shown in Table.1. Where, the experimental biodiesel yield ranged from 58.5 to 95.5% and their corresponding predicted values were 59.6 and 96.6%, respectively. The "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 20.8 for model Eq. 3 indicated the adequate signal. This model was reliable and could be used to navigate the design space. The standard deviation SD and the coefficient of variance were low, recording; 1.98 and 2.53 for model Eq.3, respectively. That indicated a better precision and reliability of the carried out experiments.

Analysis of variance was also used to determine exactly which of the factors (independent variables) significantly affected the response variable (i.e. biodiesel yield). According to the results listed in Table 2, the M:O molar ratio and catalyst loading wt% had a very highly positive statistical significant effect on the biodiesel yield while the process temperature had a positive statistical significant effect, with p-values of 0.000311, < 0.0001 and 0.0594, respectively. But the process time had a non-statistical significant negative effect on the biodiesel yield and the mixing rate had a very highly negative statistical significant effect, with p-values of 0.487 and 0.000293, respectively. The analysis of variance and the multiple regression analysis indicated that, the quadratic effects of M:O molar ratio and catalyst loading had a highly negative statistical significant effect on the biodiesel yield, with p-values of 0.00188 and 0.00189, respectively, while that of the process temperature had a very highly negative statistical significant effect (p = 0.000777). The quadratic effect of the reaction time had a negative statistical significant effect, but the doubling of the mixing rate had a non-statistical significant negative effect on the biodiesel yield, with p-values of 0.0304 and 0.619, respectively. The interaction between the M:O molar ratio and the catalyst loading (AB) expressed a very highly negative statistical significant effect on the biodiesel yield, while that of catalyst loading and process temperature (BC) and catalyst loading and reaction time (BD) had highly negative statistical significant effects with p-values of 0.000891, 0.00257 and 0.0027, respectively. This negative influence might be due to the formation of by-products (soaps). But the interaction between M:O and mixing rate (AE) and that of process temperature and mixing rate (CE) had a highly positive statistical significant effects (p = 0.00109 and 0.00115, respectively). The interactive effect of reaction time and mixing rate (DE) expressed a very highly positive statistical significant effect on the yield (p= 0.000694). Since the process temperature, the M:O molar ratio and the initial catalyst concentration were highly significant in their quadratic level, they could act as limiting conditions and little variation in their value would alter the conversion.

In conclusion since the reaction time (D, h), the doubling of mixing rate ( $E^2$ ), the interaction of M:O ratio with process temperature (AC, p = 0.313), M:O with reaction time (AD, p = 0.315), catalyst loading with

mixing rate (BE,  $p = 0.509$ ) and process temperature with reaction time (CD,  $p = 0.573$ ) did not significantly affect the biodiesel yield, so they could be excluded from the mathematical model Eq.3 to be:

$$Y = 85.2 + 6.79A + 9.08B + 1.87C - 6.86E - 2.79A^2 - 2.76B^2 - 3.35C^2 - 0.740D^2 - 8.65AB + 6.95AE - 6.98BC - 5.53BD + 6.872CE + 9.11DE \quad (4)$$

### 3.3 The response surface plots and the interactive effects of different process variables on the biodiesel yield

To assess the interactive relationships between the studied independent variables and the response of the predicted model Eq.4, the 3D surface response plots were obtained using Design Expert 6.0.7 software (Figures 1.a. – 1.f.).

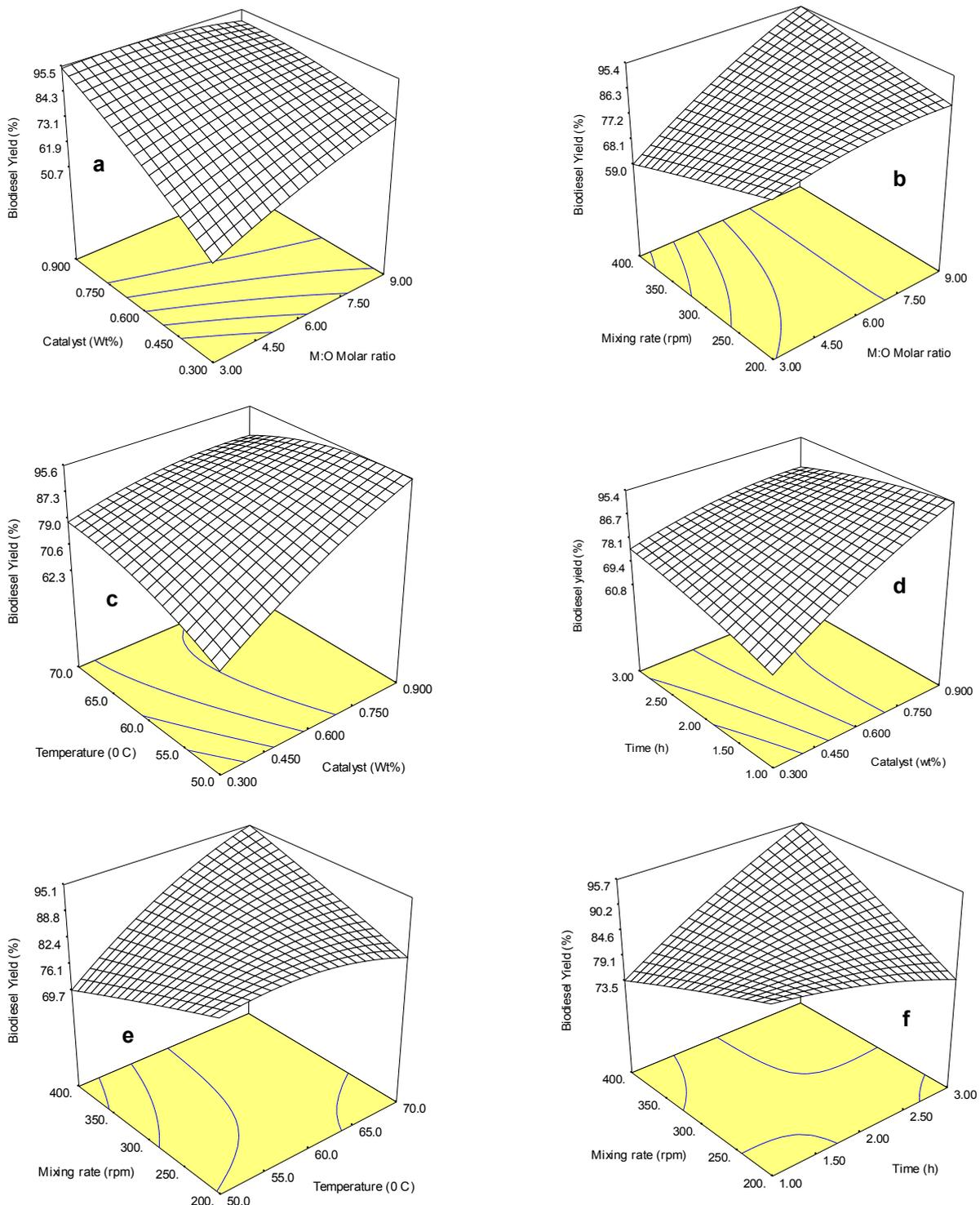


Figure.1. The RSM plots

The plot Figure 1. a. represented the negative interactive effect of M:O and catalyst loading, at constant reaction temperature, time and mixing rate of 60°C, 2 h and 117.88 rpm, respectively. At low molar ratio values (< 6:1), the biodiesel yield increased with catalyst concentration. The catalyst concentration in the methanol phase would be relatively high within low M:O ratios, which would consequently result in a higher diffusion rate of catalyst in the WCO phase, thus a high conversion rate occurred. It was obvious that the high biodiesel conversions were obtained at high M:O molar ratio and catalyst loading, but to a certain limits, recording maximum biodiesel yield of  $\approx 95.5\%$  at M:O and initial KOH concentration of 6:1 and 0.6 wt.%. This might be attributed to the stoichiometry of the transesterification, as 3 moles of methanol is required for 1 mole of triglyceride, since the transesterification reaction involves the conversion of one ester and an alcohol towards another ester and another alcohol, producing 3 moles of fatty acid ester and 1 mole of glycerol. So an excess of alcohol is required to derive the reaction near completion. On the other hand, an excessive amount of methanol and KOH decreased the biodiesel yield, as excessive methanol would make the recovery of glycerol difficult, as it tends to prevent the gravity separation of the glycerol. When glycerol remains in the biodiesel phase, it helps in driving the equilibrium back to the left, thereby lowering the FAME yield.<sup>15</sup> The positive interactive effect of M:O and mixing rate was very obvious in the RSM plot Figure 1. b., where there was an overall increase in the biodiesel yield with the increment of M:O molar ratio and the mixing rate. Figure 1. c. showed the response for the interactive factor of process temperature and initial catalyst concentration at constant M:O, process time and mixing rate of, 6:1 molar ratio, 2 h and 117.88 rpm, respectively. A low conversion occurred at low temperature and catalyst concentration. The 3D response surface plot indicated that the biodiesel yield generally increased with the increase of temperature and catalyst loading, but to a certain limits, recording maximum biodiesel yield of  $\approx 95.5\%$  at initial KOH concentration of 0.6 wt% and 60°C. The biodiesel yield was progressively decreased at high level of temperature and low level of catalyst concentration and also at higher level of KOH and temperature (i.e higher than  $\approx 0.85\%$  and 65.5°C, respectively). This might be attributed to the formation of potassium soaps as a side reaction which is favored at higher temperatures and KOH concentration. The negative interactive effect of the initial catalyst concentration and reaction time was very obvious, as illustrated in Figure 1. d. the biodiesel yield was low at low catalyst and reaction time. However, a linear relationship existed between the catalyst concentration and the kinetic rates, where, at lower catalyst concentrations, the biodiesel conversion at a given time increased sharply with increasing of catalyst concentration; thus a slight change of the catalyst concentration led to a significant increase in the rate of biodiesel production. However, that effect decreased as the catalyst concentration increased. It was also obvious from Figure 1. d., that at lower reaction time increment of catalyst concentration increased the biodiesel yield. But according to Demirbas,<sup>5</sup> the advantage of using less time and more catalyst is the possibility of obtaining lower production cost. But, that would consequently add more cost for alcohol and glycerol recovery. The RSM plot Figure 1. e. represented the positive interactive effect of mixing rate and process temperature at constant M:O 6:1, catalyst concentration 0.6% and reaction time 2 h. The biodiesel yield was low at low temperature and mixing rate, but increased with the increment of both factors. The biodiesel was produced more rapidly with increasing temperature, which might be attributed to the increase in the reaction rates, the intensification of the mass transfer coefficients and the increment of the solubility of the components, where the reactants would be more evenly distributed between phases with the increase of the temperature. It was obvious from Figure 1. e., that as temperature increased, a less mixing speed was needed to achieve a certain amount of the biodiesel conversion at a given time, so applying an optimal dynamic distribution of the mixing speed and temperature would reduce the energy consumption while maximizing the biodiesel production. This consequently would minimize the energy costs, including the mixture heating cost and the mixing cost. However, detailed price information relating to energy, WCO, methanol, glycerol, catalyst, process time, reaction temperature and biodiesel is required to find the optimal conditions. Therefore, a further study with more focus on the economics of the biodiesel is recommended. Figure 1. f. showed the positive interactive effect of mixing rate and time on the biodiesel yield. In the transesterification reaction, initially there is two immiscible phases, where the reaction is diffusion-controlled and consequently, poor diffusion between the phases would result in a slow rate of conversion. So the low mixing rate and short process time would produce low biodiesel yield. But as FAME are formed they would act as a mutual solvent for the reactants and consequently, a single phase would be formed and mixing become insignificant.

The statistical analysis of the experimental range studied identified that the significant effect of the studied variables on the biodiesel yield can be ranked in the following decreasing order catalyst loading wt% > mixing rate rpm  $\geq$  M:O molar ratio >> process temperature °C >>> reaction time h. In this study, the conversion was high within KOH concentration of 0.35 – 0.85%. Bautista *et al.*<sup>12</sup> reported that the initial catalyst concentration is the most important factor affecting the biodiesel yield, and mentioned that excess KOH would

increase the saponification reaction, and the potassium soaps would be dissolved in the glycerol layer due to the polarity, which would in turn decrease the FAME yield. According to Vicente *et al.*<sup>16</sup> the excessive amount of catalyst increases emulsion formation. Ghadge and Raheman<sup>17</sup> reported that low catalyst concentration increases biodiesel yield with methanol-to-oil ratio. El Sabagh *et al.*<sup>18</sup> reported that the concentration of alkali catalyst is strongly dependent on the type of the oil used. The WCO and methanol are immiscible, so the mixing rate is a very important factor to increase the contact surface area of the reactants and to avoid the external mass transfer limitation.<sup>7</sup> Within the studied experimental range, the maximum conversion occurred when applying mixing rate 200 – 395 rpm. The molar ratio of 6:1 is generally considered the most appropriate for methanol.<sup>19</sup> In this work the maximum conversion was obtained within a range of 6.5:1 – 8.5:1 M:O molar ratio. Silva *et al.*<sup>20</sup> reported that the alcohol concentration results in a greater biodiesel conversion within shorter time. It is well known from chemical kinetics that the rate of reaction increases with the increase of temperature as the viscosity of WCO decreases and the miscibility of methanol in the WCO increases with temperature.<sup>5</sup> In this study, the maximum conversion occurred within 53 - 65.5°C. The boiling point of methanol is 65°C,<sup>12</sup> therefore, M:O molar ratio would be safely used in a relatively high ratio within this temperature range. The reaction time is an important factor affecting the transesterification reaction. In this study, the biodiesel yield increased with time. But the positive significant effect of time on conversion rate decreased after a certain limit (1 h), where the biodiesel yield remained nearly sustained within time range 1 – 3 h, and further increase in the reaction time, decreased the biodiesel yield. Leung and Guo<sup>3</sup> reported that excess reaction time does not promote the conversion but favored the reverse reaction of transesterification, decreasing the biodiesel yield. The rate of reaction is directly proportional to the concentration of the WCO in the reaction mixture, and as the reaction proceeds the concentration of WCO decreases and hence the rate of the reaction.

### 3.4 The optimization of the transesterification process

The optimization process was carried out to determine the optimum values of the studied five parameters affecting the transesterification process of WCO with methanol in the presence of KOH as a homogenous basic catalyst, in order to maximize the conversion i.e. the biodiesel yield%. This was done using Design Expert 6.0.7 software (State-Ease Inc., Minneapolis, USA). According to the software optimization step, the desired goal for each of the chosen transesterification parameter (A initial M:O molar ratio, B initial catalyst concentration wt%, C process temperature °C, D reaction time h and E mixing rate rpm) was defined within the studied levels range to achieve the highest performance. The program combined the individual desirability into a single number and then searched to optimize this function based on the response goal. Accordingly, the optimum conditions giving the maximum calculated biodiesel yield were illustrated in Table 3., with desirability function value of 1. The experimental biodiesel yields of these conditions were found to be matched well with the predicted ones with average percentage error and standard deviation of 1.48% and 1.03, respectively. That indicated; the process optimization based on RCCD of experiments was capable and reliable to optimize the transesterification process. Based on the obtained lowest FFA content, which indicated the best conversion with the highest biodiesel yield, the selected optimum conditions were; M:O molar ratio of 7.54:1, KOH initial concentration of 0.875% (wt%), process temperature of 52.7°C, reaction time of 1.17 h and mixing rate of 266 rpm.

El-Gendy *et al.*<sup>2</sup> reported that the maximum conversion of WCO occurred at 9:1 M:O molar ratio, using 0.6 wt% KOH in a 1 h transesterification reaction at 60°C and mixing rate of 300 rpm.

### 3.5 The physico-chemical characterization of the obtained purified biodiesel

The percentage of FAME in the purified final product prepared under the selected optimum conditions was determined by GC/FID and listed in Table.4. The produced biodiesel was characterized by high concentration of unsaturated and polyunsaturated FAME which would greatly influence the fuel oxidation tendency.<sup>2</sup>

All of the studied biodiesel properties were acceptable and met most of the standard specifications. So it could be ranked as a realistic fuel to be alternative or complementary for the conventional petro-diesel.

The density of the produced biodiesel (0.895 g/cm<sup>3</sup>) was higher than that of the petro-diesel sample (0.852 g/cm<sup>3</sup>). The higher the density and viscosity of the fuel the poorer will be the efficiency of the atomization of the fuel, thus an incomplete combustion and carbon deposition on the injectors would occur.<sup>1</sup> Fuel with high paraffinicity has high specific gravity and a low API. The specific gravity of the produced

biodiesel (0.896) was higher than that of the petro-diesel (0.853). But the API value of the biodiesel (26.39) was lower than that of petro-diesel (34.39). Thus, volumetrically, biodiesel would deliver a slightly greater amount of fuel.<sup>21</sup>The produced biodiesel recorded higher viscosity (4.4 cSt) than that of petro-diesel sample (3.3 cSt). But it was within the recommendable range of the standard specifications (Table.5). So it would offer better lubrication and protection for moving parts of an engine.

The cold flow properties of the produced biodiesel were good, recording cloud and pour points of -3 and -7°C, respectively.

The TAN of the produced biodiesel (0.028 mg KOH/g biodiesel) was lower than that of the petro-diesel sample (0.41 mg KOH/g diesel). Thus lower corrosion and pump plugging, caused by corrosion and deposit formation would occur. It also confirmed the high efficiency of the transesterification process were  $\approx 97.31\%$  decrease in TAN of the WCO feedstock was achieved.

The produced biodiesel had major advantages over petro-diesel, as it was free of sulfur, while petro-diesel had 0.82% sulfur. So it met the aim of petroleum industry for free sulfur diesel fuel and the biodiesel combustion will not produce sulfur oxides which would lead to corrosion of the engine parts and environmental pollution.

The flash point FP of the produced biodiesel was approximately twice that of the petro-diesel sample, recording; 127 and 63°C, respectively. Thus it would be safer than the petro-diesel from the stand point of fire-hazards. The calorific value of the produced biodiesel was 39.6 MJ/kg and its heat content was nearly 87% that of the petro-diesel sample. Although the diesel index DI of the produced biodiesel (53.57) was lower than that of petro-diesel sample (59.79), but it was within the recommendable range of the Egyptian standards for diesel fuel ( $> 48$ ). The cetane number CN of a fuel reflects its ignition delay. The higher the CN of biodiesel is, the shorter the ignition delay and the lower the nitrogen oxides emissions. Thus, high CN is desirable for engine fuel, where it would facilitate easy start of compression ignition engines and lessen the engine roughness. The CN of the produced biodiesel was 48.57, which was approximately 78.60% of that of the petro-diesel sample. The cetane number increases with the chain length and decreases with the increase of double bonds.<sup>18</sup>

#### 4. The economics of biodiesel

Estimation for the cost of the biodiesel produced from waste cooking oil using the selected optimum conditions for the transesterification process has been done and depicted in Table.6. Based on the current price of the biodiesel, announced by the US Department of Energy (<http://www.afdc.energy.gov/fuels/prices.html>), this would give an income of approximately \$1.821/gallon biodiesel. Hence, biodiesel production from WCO could be a good substituent to petro-diesel, leading to savings in foreign exchange for importing and generating employment.

Table 1. Experimental design matrix with experimental and predicted biodiesel yield

Run number	M:O (A)	KOH concentration (B)	Process temperature (C)	Process period (D)	Mixing rate (E)	Biodiesel yield		Residual
						Experimental	Predicted	
1	6 (0)	0.6 (0)	60 (0)	2 (0)	300 (0)	85.6	84.9	0.748
2	6 (0)	1.15 (+ $\alpha$ )	60 (0)	2 (0)	300 (0)	91.8	92.9	-1.07
3	3 (-1)	0.3 (-1)	70 (+1)	3 (+1)	400 (+1)	64.4	63.8	0.602
4	9 (+1)	0.3 (-1)	70 (+1)	1 (-1)	400 (+1)	82.2	81.6	0.602
5	6 (0)	0.6 (0)	60 (0)	2 (0)	482.12 (+ $\alpha$ )	70.5	71.6	-1.09
6	6 (0)	0.6 (0)	78.21 (+ $\alpha$ )	2 (0)	300(0)	76.7	77.8	-1.09
7	6 (0)	0.6 (0)	60 (0)	0.18 (- $\alpha$ )	300 (0)	80.5	81.6	-1.09
8	6 (0)	0.6 (0)	60 (0)	2 (0)	117.88 (- $\alpha$ )	95.5	96.6	-1.09
9	6 (0)	0.6 (0)	60 (0)	2 (0)	300 (0)	85.5	84.9	0.648
10	3 (-1)	0.9 (+1)	70 (+1)	1 (-1)	400 (+1)	73.0	72.4	0.602
11	3 (-1)	0.9 (+1)	70 (+1)	3 (+1)	200 (-1)	70.5	69.9	0.602
12	3 (-1)	0.9 (+1)	50 (-1)	3 (+1)	400 (+1)	70.0	69.4	0.602
13	9 (+1)	0.9 (+1)	50 (-1)	3 (+1)	200 (-1)	78.0	77.4	0.602
14	9 (+1)	0.3 (-1)	70 (+1)	3 (+1)	200 (-1)	82.4	81.8	0.602
15	9 (+1)	0.3 (-1)	50 (-1)	3 (+1)	400 (+1)	78.9	78.3	0.602
16	9 (+1)	0.9 (+1)	70 (+1)	1 (-1)	200 (-1)	84.5	83.9	0.602
17	6 (0)	0.6 (0)	60 (0)	2 (0)	300 (01)	85.5	84.9	0.648
18	9 (+1)	0.9 (+1)	50 (-1)	1 (-1)	400 (+1)	78.5	77.9	0.602
19	6 (0)	0.6 (0)	60 (0)	3.82 (+ $\alpha$ )	300 (0)	78.4	79.5	-1.09
20	6 (0)	0.6 (0)	41.79 (- $\alpha$ )	2 (0)	300 (0)	69.9	71.0	-1.09
21	6 (0)	0.6 (0)	60 (0)	2 (0)	300 (0)	85.5	84.9	0.648
22	11.46 (+ $\alpha$ )	0.6 (0)	60 (0)	2 (0)	300 (0)	87.5	88.6	-1.09
23	0.54 (- $\alpha$ )	0.6 (0)	60 (0)	2 (0)	300 (0)	62.8	63.9	-1.09
24	6 (0)	0.6 (0)	60 (0)	2 (0)	300 (0)	85.8	84.9	0.948
25	6 (0)	0.05 (- $\alpha$ )	60 (0)	2 (0)	300 (0)	58.5	59.6	-1.07
26	3 (-1)	0.30 (-1)	50 (-1)	1 (-1)	200 (-1)	73.0	71.8	1.20

Table.2. Analysis of variance of the fitted quadratic regression model Eq.3:

Source	SS*	df*	MS*	F-value	p-value	Remarks
<b>Model</b>	2.03E+003	20	101	25.9	0.000954	Very highly significant
<b>A</b>	305	1	305	77.9	0.000311	Very highly significant
<b>B</b>	554	1	554	142	< 0.0001	Very highly Significant
<b>C</b>	23.1	1	23.1	5.90	0.0594	Significant
<b>D</b>	2.20	1	2.2	0.563	0.487	Non-significant
<b>E</b>	313	1	313	79.8	0.000293	Very highly significant
<b>A<sup>2</sup></b>	140	1	140	35.7	0.00188	Highly significant
<b>B<sup>2</sup></b>	140	1	140	35.6	0.00189	Highly significant
<b>C<sup>2</sup></b>	206	1	206	52.6	0.000777	Very highly significant
<b>D<sup>2</sup></b>	35	1	35	8.94	0.0304	Significant
<b>E<sup>2</sup></b>	1.10	1	1.10	0.280	0.619	Non- significant
<b>AB</b>	194	1	194	49.6	0.000891	Very highly significant
<b>AC</b>	4.93	1	4.93	1.26	0.313	Non- significant
<b>AD</b>	4.88	1	4.88	1.25	0.315	Non-significant
<b>AE</b>	178	1	178	45.4	0.00109	Highly significant
<b>BC</b>	122	1	122	31.0	0.00257	Highly significant
<b>BD</b>	119	1	119	30.3	0.00270	Highly significant
<b>BE</b>	1.98	1	1.98	0.504	0.509	Non-significant
<b>CD</b>	1.42	1	1.42	0.363	0.573	Non-significant
<b>CE</b>	174	1	174	44.4	0.00115	Highly significant
<b>DE</b>	217	1	217	55.3	0.000694	Very highly significant
<b>Residual</b>	19.6	5	3.92			
<b>Pure Error</b>	0.0680	4	0.017			
<b>Corrected total</b>	2.05E+003	25				

\*SS: sum of squares      df: degree of freedom      MS: mean square

**Table.3. Optimum condition solutions for the transesterification process**

\*StD: the standard deviation.

Run number	M:O	Catalyst	Temperature	Time	Mixing rate	Biodiesel yield		Desirability	Percentage error	StD*	Percentage decrease in FFA
						Predicted	Experimental				
1	8.42:1	0.832	54.9	1.25	240	99.9	97.8	1	2.15%	1.48	82.10%
2	8.82:1	0.406	63.3	2.87	352	97.1	98.8	1	1.72%	1.20	70.50%
3	6.28:1	0.809	59.7	1.70	218	99.1	98.9	1	0.2%	0.14	70.50%
4	8.52:1	0.673	64.8	2.88	395	96.7	95.7	1	1.04%	0.71	57.09%
5	8.76:1	0.362	65.7	2.51	384	98.8	98.5	1	0.3%	0.21	83.91%
6	8.56:1	0.654	62.4	2.90	391	95.7	96.5	1	0.83%	0.57	83.91%
7	7.54:1	0.875	52.7	1.17	266	102	99.2	1	2.82%	1.98	97.32%
8	6.45:1	0.846	55.5	1.90	204	101	98.3	1	2.75%	1.91	70.50%

**Table.4. A summary of the identified fatty acid methyl esters (FAME)**

FAME	wt%
Myristic acid methyl ester (C14:0)	0.14
Palmitic acid methyl ester (C16:0)	10.02
Stearic acid methyl ester (C18:0)	1.54
Oleic acid methyl ester (C18:1)	77.68
Linoleic acid methyl ester (C18:2)	3.64
Linolenic acid methyl ester (C18:3)	6.62
Arachidic acid methyl ester (C20:0)	0.36
Saturated FAME	12.06
Unsaturated FAME	77.68
Polyunsaturated FAME (PUFA)	10.26

**Table.5.** The physico-chemical characteristics of the produced biodiesel compared to the Egyptian petro-diesel standard specifications, the international standards of biodiesel and an Egyptian Petro-diesel sample

Test	Unit	Produced biodiesel	Egyptian petro-diesel sample	Egyptian petro-diesel standard specifications	Biodiesel EN14214	Biodiesel ASTM D6751
Density at 15.56°C	g/cm <sup>3</sup>	0.895	0.852	0.82 – 0.87	0.86 – 0.9	---
Specific gravity		0.896	0.853	---	---	---
API		26.39	34.39	---	---	---
Kinematic viscosity at 40°C	cSt	4.4	3.3	1.6 - 7	3.5 - 5	1.9 - 6
Cloud point	°C	-3	0	---	---	---
Pour point	°C	-7	-5	4.5	---	---
Total acid number	mg KOH/g oil	0.028	0.41	Nil	< 0.5	< 0.8
Total sulfur	wt%	Nil	0.82	< 1	< 0.01	< 0.05
Flash point	°C	127	63	>55	> 101	> 130
Calorific value	MJ/kg	39.6	45.49	>44.3	32.9	---
Diesel index		53.57	59.79	> 48	---	---
Cetane number		48.57	61.79	>55	> 51	> 47

**Table.6.** An estimation for the cost of biodiesel

Item	Price
Methanol cost (\$/liter biodiesel)	0.072
KOH cost (\$/liter biodiesel)	0.02
Waste cooking oil cost (\$/liter biodiesel)	0.333
Utilities cost (\$/liter biodiesel)	0.036
Other chemicals costs (\$/liter biodiesel)	0.027
Fixed cost (maintenance, salaries and insurance) (\$/literbiodiesel)	0.027
Biodiesel production cost (\$/liter)	0.515
Biodiesel production cost (\$/gallon)	1.949
*Current market price biodiesel (\$/gallon)	3.77

\*Rates as on April, 2015, according to the US Department of Energy  
<http://www.afdc.energy.gov/fuels/prices.html>

## 5. Conclusions

Response surface methodology based on the rotatable central composite design of experiments was successful in identifying the determining variables in an alkaline transesterification reaction for achieving approximately total conversion of triglycerides in the waste cooking oil to fatty acid methyl esters i.e.  $\approx 99\%$  purified biodiesel yield. The produced biodiesel was characterized by zero sulfur, lower total acid number, better cloud and pour points and higher flash point which added to the advantages of the produced biodiesel and all its physico-chemical characteristics were also acceptable. That encourages for its application as an alternative or complementary eco-friendly and renewable fuel to the conventional petro-diesel. A detailed techno-economic study is undertaken now in EPRI biotechnology lab, to minimize the energy and capitals cost and maximize the production of high quality biodiesel yield.

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