International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

Statistical optimization of bio-diesel production from different types of waste cooking oils using basic heterogeneous catalyst

Nour Sh. El-Gendy* and Samiha F. Deriase

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Abstract

Based on 3- level D- optimal design, a statistical design of experiments (DOE) strategy has been performed to evaluate and investigate the bio-diesel production process, involving as factors: methanol-to-oil molar ratio (M:O), CaO concentration (wt%), reaction time (min) and type of waste cooking oil WCO feedstock. MATLAB software was employed for experimental design and data analysis. The optimum values of the selected predictor variables were obtained according to response surface optimizer. The optimum conditions for the transesterification process were M:O molar ratio of 10.55:1, catalyst concentration of 6.653 wt% and reaction time 100.54 min. The perfect type of oil was waste frying corn oil WFCO. The optimum predicted % yield of bio-diesel was 94.873 %, while the experimental value was ≈ 95%. The quality characteristics of produced bio-diesel and its blends B6-B20 were in good agreement with the international standards specifications. Therefore, it can be acceptable and suitable for diesel fuel.

Key words: Optimization, transesterification, waste cooking oil, CaO

Full length article Received: 14-07-2013 Accepted: 30-07-2013 Available online: 31-07-2013
**Corresponding Author*, e-mail: nourepri@yahoo.com Tel: (+20) 100 1443208 Fax: 202 2 274 7433

1. Introduction

The conventional process of bio-diesel production from waste cooking oil WCO proceeds in transesterification of oils using homogeneous catalysts. However, the homogeneous catalytic process suffers some drawbacks, namely; equipment corrosion; unfeasibility of the catalyst; side saponification reaction which leads to soap formation, and hence emulsification of bio-diesel and glycerol, making it difficult to separate and to purify the biofuel and also give rise to increased purification costs, lower yield and an inevitable production of wastewater from washing process of unreacted catalyst and glycerides. This process is expensive and requires several refining processes, which consequently, increase bio-diesel cost [1, 2]. The heterogeneous catalytic process overcomes these problems, since the solid catalysts can be easily recovered and therefore potentially be reusable. Besides, a neutralization step with large amount of wastewater production would be eliminated. This would convert up to more than 95% of used WCO to pure bio-diesel and the rest would be pure glycerol [3]. Solid-base catalysts, reported to have great potential for bio-diesel production with reasonable reaction rates under mild conditions. Alumina-supported alkali elements/ hydroxides, MgO, CaO, ZrO_2, calcinated MgAl hydrotalcites, anion-exchange resin and alkali-exchanged zeolite are used to study bio-diesel synthesis [4-6]. In brief, heterogeneous catalysts e.g. calcium oxide CaO, have attracted attention due to the elimination of neutralization, lack of toxicity, ability to withstand high temperatures, ease of recycling, low cost, abundantly available in nature as limestone and its performance for bio-diesel production is comparable to several homogenous catalysts [7] .

The aim of this research is to study the feasibility of utilization of CaO as a heterogeneous basic catalyst for production of bio-diesel from different types of waste cooking oils WCO. A statistical design of experiments DOE strategy would be performed to evaluate and investigate the bio-diesel production process. The optimum values of the selected predictor variables would be predicted according to response surface optimizer. Furthermore, this study aims also to study the physico-chemical characteristics of the produced bio-diesel and its blends with petro-diesel.

2. Materials and Methods

2.1. Materials

Pure calcium oxide as heterogeneous basic catalyst and methanol (AR Grade) were purchased from Fluka Chemical Corp. UK. Commercial Egyptian petro-diesel was obtained from a local fueling station.

2.2. Collection and pretreatment of waste cooking oil

Different types of waste cooking oils WCO were used in this study. Waste frying oils WFO, were collected from local restaurants, while waste frying sun flower oil WFSFO and waste frying corn oil WFCO were collected from domestic wastes. The collected WCO were centrifuged and filtered to remove any suspended matters and burned food bits, etc. Then it was heated at 105^{o}C for 2 h to remove any unwanted water present by evaporation. Some physico-chemical characteristics of the collected WCO were studied (Table.1.).

2.3. Pretreatment of calcium oxide

The CaO catalyst was activated by calcination at 800^{o}C for 2 h under N_2 atmosphere before use, since CaO is poisoned very fast by atmospheric water vapor and CO_2.

2.4. Transesterification process

The transesterification reactions were conducted in a laboratory-scale setup; two-necked 500 mL flask equipped with a reflux condenser and a thermometer on a magnetic heat stirrer set at 60^{o}C and 300 rpm. After the prescribed time of reaction, the mixture was allowed to separate overnight. The lower layer is glycerol and solid catalyst, was centrifuged to obtain pure glycerol and catalyst which can be re-used again. The upper layer is bio-diesel and un-reacted methanol, was drained out and transferred into a sample flask of a rotary evaporator to recycle methanol at 65^{o}C and 20 kPa. The obtained purified bio-diesel was then bottled and kept for blending with commercial Egyptian petro-diesel and characterization studies. The yield of bio-diesel was calculated according to Boro et al. [8] by using the following equation:

$$\%Yield = \frac{Weight\ of\ produced\ bio-diesel}{Weight\ of\ used\ WCO} \times 100 \qquad (1)$$

2.5. Experimental design and statistical analysis

The main goal of the present study is to model and optimize the transesterification process using CaO, by performing a series of controlled laboratory designed experiments and predict a regression model defining the distribution of the response variable (bio-diesel yield) in terms of four explanatory variables (factors). These factors were; X_1 methanol : oil M:O molar ratio, X_2 CaO concentration wt%, X_3 reaction time min and finally the type of waste cooking oil X_4. These variables were elucidated and investigated through DOE at three different levels. The total number of experimental runs was 15. Table.2. describes the settings of the factors with their corresponding actual values and the experimental design with actual and predicted response.

The model that is found to estimate the response was the second-order quadratic model, represented by the following equation:

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2 \qquad (2)$$

Where, Y is the yield of the reaction (% production of bio-diesel), n is the number of factors, β_o is the intercept term, β_i, β_{ij} and β_{ii} are the linear, interactive and quadratic coefficients, respectively. x_i's are the independent variables (factors) under study.

The optimum values of the selected explanatory variables (x_i's) were evaluated by response surface optimizer.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). MATLAB 7.0.0 software was used for experimental design and data analysis.

2.6. Gas chromatography (GC) analysis

The fatty acid methyl esters FAME composition of the produced bio-diesel was analyzed using GC. The analysis was carried out by using Agilent 6890 plus, equipped with a HP-50 capillary column (0.53 mm x 30 m, 0.5 µm film) and a flame ionization detector (FID). Pure nitrogen was used as a carrier gas (4 mL/min). 250^{o}C injector temperature, 280^{o}C detector temperature, split ratio (1:50), sample size 1 µL, and the temperature program used was 80–240^{o}C at a fixed rate of 5^{o}C/min. The identification of the FAME was established by chromatographic reference mixture of FAME of known composition.

2.7. Physico-chemical characterization of the produced bio-diesel and its blends with petro-diesel

The purified product obtained from oil esterification was tested for estimating and evaluating its fuel properties using the standard methods of analysis for petroleum products, American Society for Testing and Materials ASTM standards methods. The results were compared with the Egyptian standards for petro-diesel and European and American standards of bio-diesel (EN14214 and D-6751, respectively). Three bio-petro-diesel blends were prepared by blending bio-diesel at proportions of 6%, 10% and 20% by volume with petro-diesel and their physico-chemical characteristics were also studied. The results were compared with an Egyptian petro-diesel sample and American standards of bio-petro-diesel blends (D-7467, respectively).

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 physico-chemical characterization of the collected WCO

It is important to study some physico-chemical characteristics for the collected WCO as the produced bio-diesel would depend on the type of the WCO feedstock. The data listed in Table.1. illustrate the characteristics of the collected WCO. The density at 15.56^{o}C, kinematic viscosity at 40^{o}C, total acid number, saponification value, iodine value and molecular weight for WFO are; 0.9327 g/cm^3, 64 cSt, 2.15 mg KOH/g oil, 201 mg KOH/g oil, 111 mg I_2/100 g oil and 846.37, respectively. While those for WFSFO and WFCO are nearly the same, recording; 0.9219 and 0.9206 g/cm^3, 36.6 and 33.3 cSt, 1.85 and 1.34 mg KOH/g oil, 191 and 189 mg KOH/g oil, 127 and 121 mg I_2/100 g oil and 889.77 and 896.83, respectively.

3.2. Validation of the elucidated regression model

The objective of the data analysis were to fit the regression model equation, specify regression coefficients and recognizing significant model terms, and finally

determine the factors optimum levels which would lead to a maximum response. Since the response was the % yield of bio-diesel, an empirical regression model was employed for a better understanding of the correlations between the explanatory factors and response applying a second degree polynomial equation. Based on D-optimal design and experimental data listed in Table.2, the second-order quadratic model can be given as follows:

$$Y = 35.92 - 5.3327\,X_1 + 7.4808\,X_2 + 3.9312\,X_3 - 1.9945\,X_4 - 5.433\,X_1X_2 + 0.357\,X_1X_3 - 3.0198\,X_1X_4 + 0.1748\,X_2X_3 + 15.119X_2X_4 - 0.3617\,X_3X_4 + 3.67\,X_1^2 - 5.864\,X_2^2 + 0.0028X_3^2 + 4.827\,X_4^2 \quad (3)$$

As for a good fit model, it is recommended that, coefficient of determination R^2 should be close to unity. Thus, the variation of the response was evaluated by measurement of coefficient of determination. The value of R^2 at the fitted model was found to be 0.9379 substantiated that, 93.79% of the total variation in response could be attributed to the experimental factors. This ensures the goodness of fit and confirming the adequacy of the regression model. Also the F ratio and P value of the quadratic model were calculated to be 815.918 and <0.0001, respectively indicating the significance of the model specified previously at 95% confidence level. That was also reflected by the good agreement between experimental and predicted values of response variable, as shown in Table 2.

The predicted values versus experimental ones for % yield of bio-diesel with R^2 value of 0.9624 are presented in Figure.1.a. The predicted and experimental values were in reasonable agreement (R^2 value closed to unity). This indicates that, the data fit well with the model and convincingly the model gave a good estimate of response for the system within the studied range. In addition, investigation on residuals to validate the adequacy of the model was performed. Residual is the difference between the observed and predicted response. This analysis was examined using the plot of residuals versus predicted response (Figure.1.b.). The quality of the fit is good because the residual distribution does not follow a trend with respect to the predicted values of response variable, which indicate that the quadratic model adequately represent the bio-diesel % yield over the studied experimental range.

Analysis of variance (ANOVA) was applied to establish the statistical significance of the model parameters at 95% confidence level. The significance of each parameter (coefficient) was determined by t- and p-values (Table.3.). The larger the magnitude of the t-values and smaller the P-values, the more significant is the corresponding coefficient. Data listed in Table.3. imply that, the variables with the largest effects i.e. highly significant, were the linear effects of both M:O molar ratio and catalyst concentration and the interactive effect of catalyst loading and type of WCO feedstock. While the linear effects of both the reaction time and type of feedstock, the interactive effects of M:O and catalyst loading, and that of M:O and type of feedstock and the quadratic effects of both catalyst loading and type of WCO, expressed a significant effect on the % yield of bio-diesel. The interactive effect of M:O and reaction time showed a slight significant effect on the transesterification reaction. But, the interactive effects of catalyst loading and reaction time and that of type of WCO feedstock and reaction time have no significant effects on the transesterification process.

3.3. Effect of using different types of WCO on the activity of CaO

Analysis of variance (ANOVA) has been performed to investigate the effect of using different types of WCO feedstock on the % yield of bio-diesel produced in the transesterification process. The standard ANOVA Table.4., illustrates, the sums of squares (SS), degrees of freedom (df), mean squares (MS), F statistic and p-value. As shown from data listed in Table 4. The small p-value of 0.0012, indicates that the three types of oil used (WFSFO, WFCO, and WFO) are significantly different in their effect on the bio-diesel yield. The box plots presented in Figure.2., confirms this graphically, and show that using the WFCO produced the highest % bio-diesel yield then, came the other two types of WCO feed stocks; WFSFO and WFO, in a decreasing order. The statistical analysis using ANOVA also confirms the data listed in Tables.2 and 3.

3.4. Optimization of transesterification process

In this work, the numerical optimization was conducted through response optimizer available in MATLAB software (version 7.0.0), to get the the optimum levels (values) of the selected variables which would result in the desired maximum response (% yield of bio-diesel) from WFCO as the recommendable type of WCO feedstock within studied experimental range.

***3.4.1. Effect of M:O molar ratio**:* According to the response surface optimizer presented in Figure.3., although the excess methanol than M:O 10.55:1, resulted in a slight increase in the response, but this predicted results were not too much higher than that of 94.873%. Therefore, it would be reasonable to consider the optimal level M:O 10.55:1 in order to decrease extra costs of the process. Since, higher molar ratio of M:O is not favourable for the purification of product in the following separation process. Also, recovery of the excessive methanol will consume large amounts of energy.

3.4.2. Effect of CaO concentration: It could be seen from Table.3. and Figure.3., that the linear term of catalyst loading was highly significantly affecting the % yield ($p = 0.00001$). In this regards, the corresponding estimated coefficient revealed a positive correlation between the linear term of catalyst concentration and the response. Accordingly, the highest %yield of bio-diesel was achieved when the catalyst concentration was 6.65 wt%. Since, the optimal amount of the catalyst displayed to be sufficient, increasing the catalyst amount not only will decrease the response but, also would add extra costs to transesterification process.

3.4.3. Effect of reaction time: The recorded results in Table 3, showed that the response was profoundly influenced by the reaction time (P=0.0393). The linear term of the reaction time, with the low p-value, was shown to be a significant term. This means that when the reaction time increased, a greater amount of % yield of bio-diesel would be produced. From Fig. 3 the reaction time of 100.56 min was shown to be enough for getting the maximum % yield.

According to the response optimizer graph Fig. 3, the maximum value of % yield of bio-diesel was predicted to be ≈ 94.873% at M:O molar ratio of 10.55:1, catalyst

concentration of 6.65 wt%, and a reaction time of 100.54 min using WFCO as WCO feedstock.

The methanol/oil molar ratio is one of the most important factors affecting the yield of bio-diesel. Although, stoichiometric ratio requires three moles of methanol for each mole of oil, the transesterification reaction is commonly carried out with an extra amount of methanol in order to shift equilibrium towards the direction of methyl ester formation. In fact, the higher amount of methanol up to 10.55:1 shifted the reaction equilibrium to the forward direction by promoting the formation of methoxide species on CaO surface. However further increase in M:O molar ratio up to 12:1 did not promote the reaction. Since, the glycerol might have dissolved in excessive methanol, which consequently might have inhibited the reaction of methanol with oil and catalyst. With the increase of CaO concentration up to 6.65%, bio-diesel yield (wt %) increased, due to the increase in the total number of available catalytic active sites for the reaction. According to Liu et al. [9], the decrease in FAME (bio-diesel) yield at higher levels of methanol content might be due to the dilution effect on catalyst and reactants. According to Kouzu et al. [10], with the increase in reaction time, the biodiesel yield increases to a certain limit producing what is called S-shape curves. This might be attributed to the variation of the reaction order as transesterification progressed. Transesterification obviously occurred at the boundary between oil and methanol in the early stage, where the reaction rate might be zero-order kinetic with respect to oil concentration. The reaction rate is then changed from zero-order to first order kinetics, due to the good miscibility in the reaction mixture. According to Liu et al. [9] and Yan et al. [11], the transesterification of oil with methanol in the presence of heterogeneous catalysts is a three-phase reaction system. Accordingly, the reaction rate might be reduced due to the mass transfer resistance on the boundary between the oil and methanol phases. So in this study, the mixing rate was set at 300 rpm to facilitate proper contact between reactants (oil, methanol and CaO catalyst) which consequently, increased the bio-diesel yield without turbulence in the mixture. Liu et al. [9] and Yan et al. [11] also reported that, the FAME yield is also affected by mass transfer between the reactants and catalyst. Accordingly, high catalyst concentration causes the reactants mixture to be more viscous, which causes a decrease in the reaction rate and consequently decreases in FAME yield, due to mass transfer resistance. Liu et al. [9] reported that the optimum molar ratio for the transesterification of soybean oil at 65^{o}C is 12:1. Kouzu et al. [10], used 12:1 M:O for transesterification of WCO.

3.5. FAME composition of the bio-diesels produced from the WCO feedstock

The FAME composition of the produced bio-diesels is shown in Table.5. Bio-diesel, produced from WFO is characterized by higher saturated FAME than that produced from WFSFO and WFCO, recording; ≈ 71% and 29% of saturated and unsaturated FAMEs, respectively. While WFSFO and WFCO have nearly the same composition, recording an average of ≈ 12.8% and 87.2% saturated and unsaturated FAMEs, respectively.

3.6. Physico-chemical characterization of produced bio-diesel from WFCO after optimization of transesterification process

By applying the aforementioned optimum conditions, the obtained % bio-diesel yield was ≈ 95%. The produced bio-diesel was evaluated on the basis of its fuel properties compared to Egyptian petro-diesel and international bio-diesel standards as shown in Table.6. All the properties of the produced bio-diesel are completely acceptable and meet most of the specifications. So it can be ranked as a realistic fuel and as an alternative to petro-diesel. The iodine value which is a measure of unsaturation degree was measured for the WFCO and produced bio-diesel recording; 121 and 102 mg I_2/100 g oil, respectively. The degree of unsaturation greatly influences fuel oxidation tendency. According to EN 14214, methyl esters used as diesel fuel must have an iodine value less than 120 g I_2/100 g sample. Van Gerpen [12] reported that the base catalyzed reaction is very sensitive to the content of free fatty acids, which should not exceed a certain limit recommended to avoid deactivation of catalyst, formation of soaps and emulsion. The acid value measures the content of free acids in the sample, which has influence on fuel aging. The acid value of produced bio-diesel was 0.5 mg KOH/g while that of WFCO 1.34 mg KOH/g with average lowering of ≈ 63%, indicating good transesterification process. The produced bio-diesel TAN is relatively high but within the ASTM D6751 bio-diesel standards. Candeia et al., [13] reported that, the bio-diesel with high TAN causes operational problems, such as corrosion and pump plugging, caused by corrosion and deposit formation. The saponification value represents milligrams of potassium hydroxide required to saponify one gram of oil. The obtained bio-diesel has higher saponification value than that of the WFCO recording ≈ 189 and 201 mg KOH/g oil, respectively. The average percentage of the increase in saponification value was ≈ 5.97%. It is known that a triglyceride has 3 fatty acid chains associated and each triglyceride will give 3 methyl esters, stoichiometricaly it may be expected that the same amount of fatty acid carbon chain in neat feedstock oil and bio-diesel will react with the same amount of KOH giving the soaps, i.e., their saponification values will be the same. But this assumption could be varied in case of using WCO as a feedstock, as its properties differ significantly from neat oils as a consequence of cyclization, polymerization and degradation of triglycerides that occur during the frying process. The recorded decrease in density, viscosity and TAN after transesterification indicated good transesterification process under the obtained optimum conditions. The flow properties of the produced bio-diesel are as follows; density at 15.56^{o}C, 0.8902 g/cm^{3}; viscosity at 40^{o}C, 5.68 cSt; cloud point, 0^{o}C and pour point, -3^{o}C. Felizardo et al. [14] reported that density at 15^{o}C and kinematic viscosity at 40^{o}C are important properties, mainly in airless combustion systems because they influence the efficiency of atomization of the fuel, flow and distribution.

The cold flow properties, including CP and PP, have much lower values in the produced biodiesel (0 and -3, respectively) than those of the Egyptian petro-diesel sample (9 and 6, respectively). This indicates better cold flow properties and increases the advantages of the produced bio-diesel, as it is more suitable in cold conditions.

Table 1: Physico-chemical properties of collected WCO

Parameter \ Type of oil	WFO	WFSFO	WFCO
Density @ 15.56°C, g/cm^3	0.9327	0.9219	0.9206
Viscosity @ 40 °C, cSt	64	36.6	33.3
Total acid number, mg KOH/g	2.15	1. 85	1.34
Iodine number mg I_2/100g	111	127	121
Saponification value mg KOH/g oil	201	191	189
Molecular weight	846.37	889.77	896.83

Table 2: Experimental design matrix with Experimental and predicted values of bio-diesel yield

	Factors/Levels									
	M:O (Molar ratio) X_1		CaO (wt%) X_2		Time (min) X_3		Type of WCO X_4		Bio-diesel yield (wt %)	
Run number	**Coded value**	**Actual value**	**Coded value**	**Actual value**	**Coded value**	**Actual value**	**Coded value**	**Actual value**	**Experimental**	**Predicted**
1	3	12:1	3	9	3	120	2	WFSFO	79	77.9
2	1	6:1	3	9	3	120	1	WFCO	88.5	90
3	2	9:1	3	9	2	60	3	WFO	75	76.7
4	1	6:1	3	9	1	30	2	WFSFO	82.9	83.2
5	1	6:1	2	6	3	120	3	WFO	76	76.09
6	2	9:1	3	9	1	30	3	WFO	74.3	75.9
7	2	9:1	2	6	1	30	2	WFSFO	83.5	83.7
8	3	12:1	1	3	1	30	1	WFCO	85.4	87
9	1	6:1	1	3	1	30	1	WFCO	91	90.3
10	1	6:1	1	3	2	60	2	WFSFO	88.4	89.1
11	2	9:1	2	6	3	120	1	WFCO	84	82.9
12	2	9:1	1	3	3	120	2	WFSFO	91	93
13	3	12:1	1	3	3	120	3	WFO	78	77.5
14	3	12:1	2	6	1	30	3	WFO	81	79.9
15	3	12:1	2	6	2	60	1	WFCO	90.3	88.95

Table 3: Significance of regression parameters (coefficients)

Model term	Parameter estimate	t- value	p-value	Degree of significance
X_1	-5.3327	-22.78	0.001	Highly significant
X_2	7.4808	35.05	0.00001	Highly significant
X_3	3.9312	-12.89	0.0393	Significant
X_4	-1.9945	-10.64	0.0126	Significant
X_1*X_2	- 5.433	19.79	0.0210	Significant
X_1*X_3	0.357	0.06	0.0645	Slightly significant
X_1*X_4	-3.0198	-12.03	0.03074	Significant
X_2*X_3	0.1748	0.02	0.0817	Not significant
X_2*X_4	15.119	54.07	<0.0001	Highly significant
X_3*X_4	-0.3617	-0.004	0.872	Not significant
X_1^2	3.67	2.17	0. 198	Not significant
X_2^2	-5.864	-18.80	0.0231	Significant
X_3^2	0.0028	0.01	0.674	Not significant
X_4^2	4.827	13.001	0.0331	Significant

Table 4: ANOVA table for investigating the effect of using different feedstock of WCO on the activity of CaO

Source	SS	Df	MS	F	Prob>F
Groups	324.108	2	162.054	12.42	0.0012
Error	156.576	12	13.048		
Total	480.684	14			

Table 5: A summary of the identified fatty acid methyl esters (FAME)

Type of oil / FAME	WFO	WFSFO	WFCO
	wt.%	wt.%	wt.%
Palmitic acid methyl ester (C16:0)	24.36	8.9	9.74
Stearic acid methyl ester (C18:0)	46.35	4.3	2.7
Oleic acid methyl ester (C18:1)	24.68	19	19.7
Linoleic acid methyl ester (C18:2)	4.61	67.8	67.9
Saturated FAME	70.71	13.20	12.4
Unsaturated FAME	29.29	86.8	87.6

Table 6: Physicochemical properties of bio-diesel produced from WFCO using CaO compared to international standards of bio-diesel and Egyptian petro-diesel standard specifications

Test	Unit	Produced bio-diesel	Egyptian perto-diesel standards	Bio-diesel (EN14214)	Bio-diesel D-6751
Density @ 15.56 ^{o}C	**g/cm^{3}**	0.8902	0.82-0.87	0.86-0.9	----
Kinematic viscosity @ 40 ^{o}C	**cSt**	5.68	1.6-7	3.5-5	1.9-6
Pour point	**^{o}C**	-3	4.5	----	----
Cloud point	**^{o}C**	0	----	----	----
Total acid number	**mg KOH/g**	0.5	Nil	< 0.5	< 0.8
Total S	**wt%**	Nil	< 1	< 0.01	< 0.05
Water content	**ppm**	151	1500		
Flash point	**^{o}C**	155	> 55	> 101	> 130
Calorific value	**MJ/Kg**	39.51	> 44.3	32.9	----
Cetane number	**-**	44	> 55	> 51	> 47
Iodine number	**mg I_2/100g**	102	----	< 120	----

Table 7: Physico-chemical properties for prepared blends compared to standards specifications of bio-diesel blends B6-B20 and Egyptian petro-diesel sample

Test	Unit	Egyptian Perto-diesel sample	B6	B10	B20	Bio-diesel blends ASTM D-7467
Density @ 15.56 ^{o}C	**g/cm^{3}**	0.839	0.843	0.854	0.870	- - -
Kinematic viscosity @ 40 ^{o}C	**cSt**	3.59	4.40	4.44	4.51	1.9-4.1
Pour point	**^{o}C**	6	3	3	0	- - -
Cloud point	**^{o}C**	9	6	3	3	- - -
Total acid number	**mg KOH/g**	0.41	0.45	0.47	0.5	< 0.3
Total S	**wt%**	0.82	0.72	0.65	0.4	< 0.05
Water content	**ppm**	88.81	95	105	120	- - -
Flash point	**^{o}C**	88	78	86	96	> 52
Calorific value	**MJ/Kg**	45.31	44.88	43.31	42.00	- - -
Cetane number		61.79	59.80	57.03	49.42	> 40

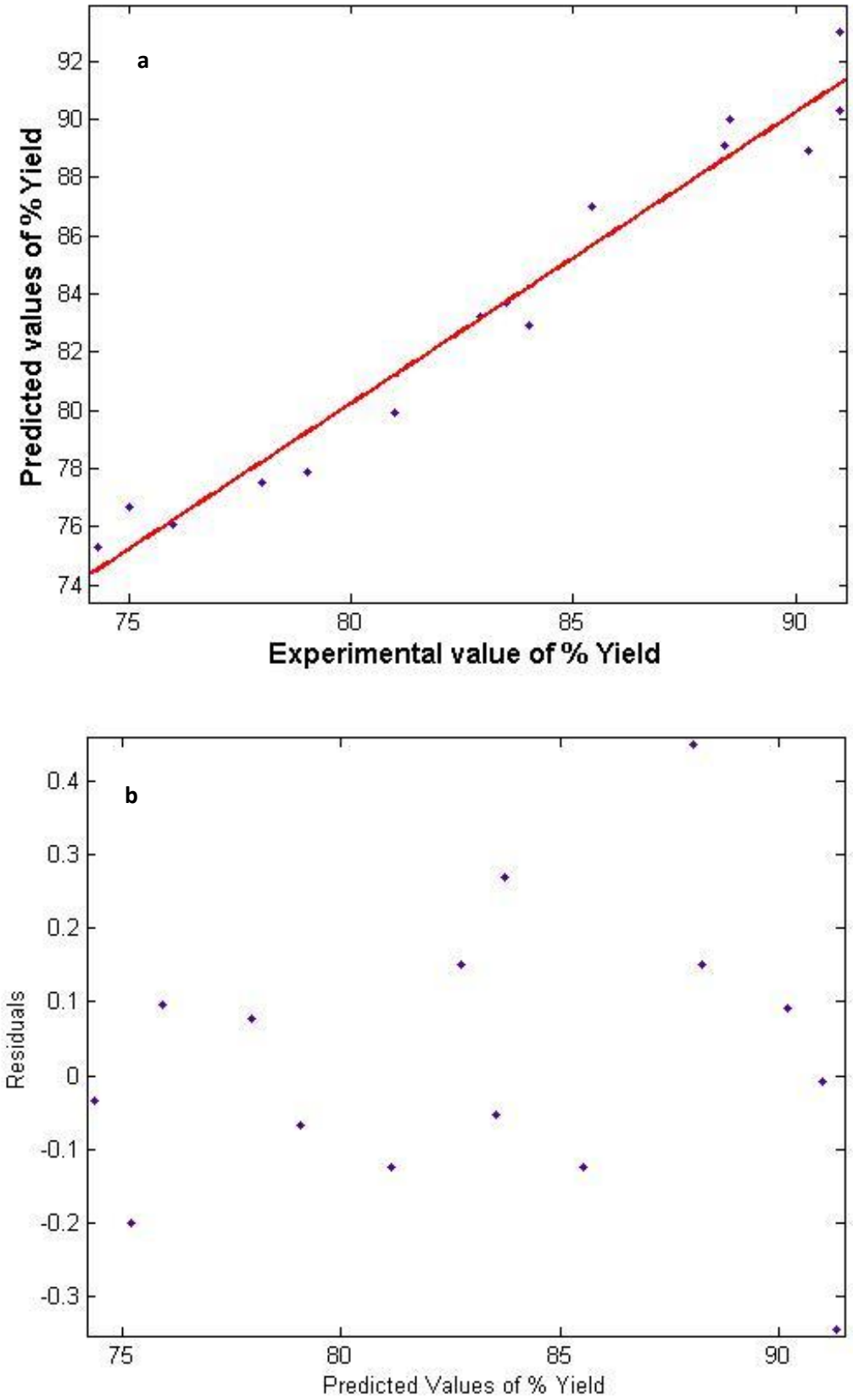

Fig. 1. (a) Model fit profile **(b)** Residual plot of bio-diesel yield for the model

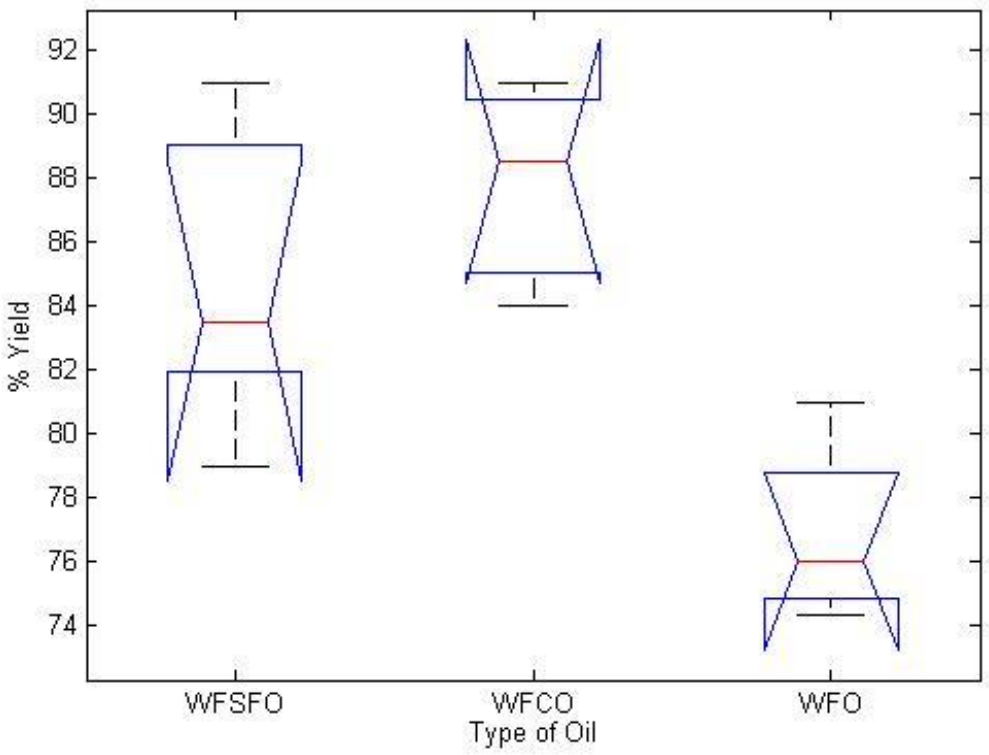

Fig. 2. Box plot graph showing the effect of using different types of WCO feedstock on the transesterification process

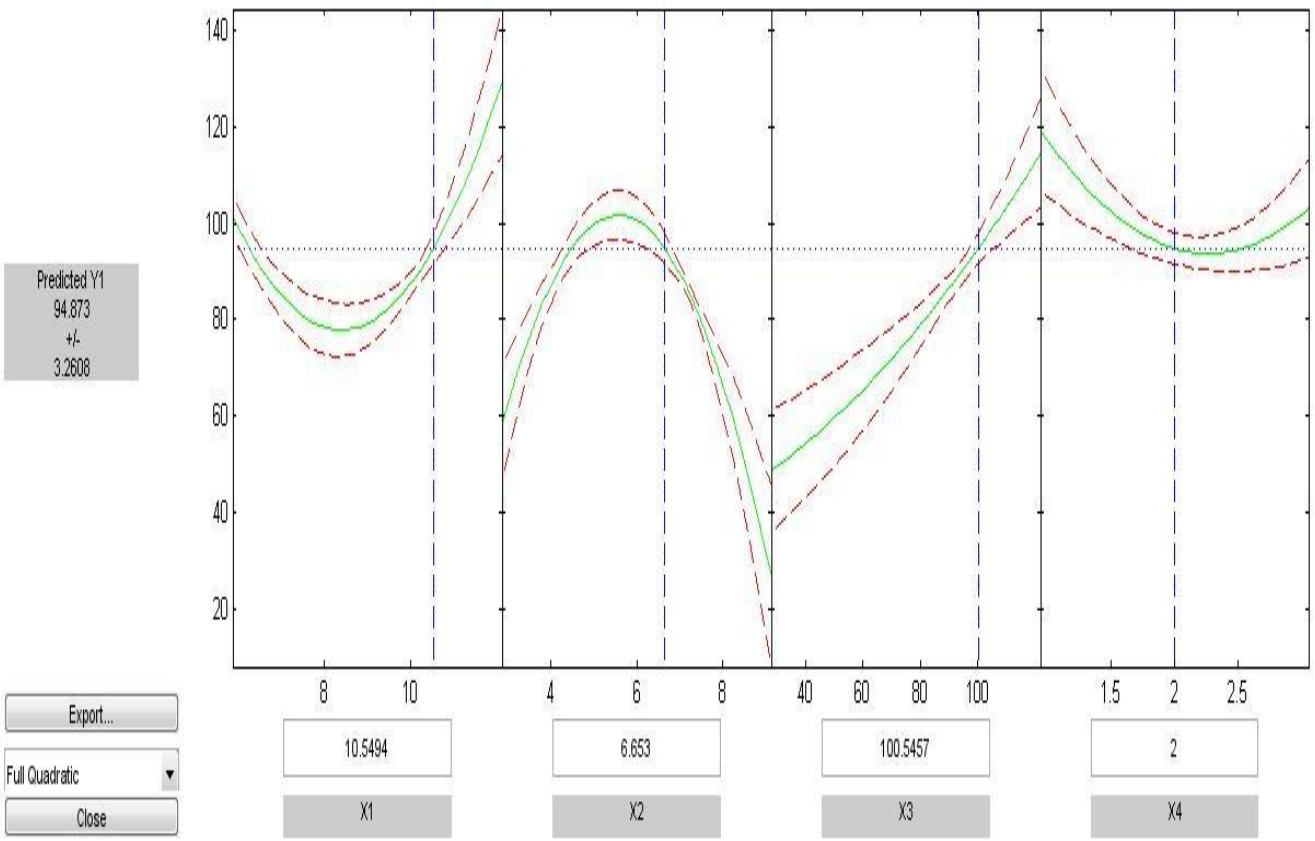

Fig. 3. Response optimizer graph

The produced bio-diesel has lower CV (39.51 MJ/kg) than that of the Egyptian petro-diesel sample (45.31 MJ/kg).The water content of the produced bio-diesel is higher than that of the Egyptian petro-diesel sample recording 151 and 88.81 ppm, respectively. But it is within the recommendable bio-diesel standards, < 500 ppm.

The produced bio-diesel has three major advantages; it is free of sulfur, while petro-diesel has 0.82% sulfur. So it meets the aim of petroleum industry for free sulfur diesel fuel and the bio-diesel combustion will not produce sulfur oxides which lead to corrosion of the engine parts and environmental pollution. The produced bio-diesel has a higher FP 155^{o}C, compared to 88^{o}C for petro-diesel. So bio-diesel is much less flammable fuel than petro-diesel and, hence it is much safer in handling, storage and transport. In addition, the viscosity of the produced bio-diesel 5.68 cSt, is competitive to regular Egyptian standards for petro-diesel 1.6-7 cSt. Hence, no hardware modifications are required for handling the produced bio-diesel in the existing engine. However, the cetane number CN of produce bio-diesel 44 was lower than that of Egyptian petro-diesel sample 61.79. This value of CN is reasonable due to FAMEs composition (Table.5.), which is mainly consisted of ≈ 8.9% palmitic-, 4.3% stearic, 19% oleic- and 67.8% linoleic- acid methyl esters. The CN of these methyl esters is ≈ 74.4, 81.3, 56.77 and 31.8, respectively [15]. The CN increases with increase in chain length and decrease with increase in unsaturation.

3.7. Physico-chemical properties of the blends

Blends of the produced bio-diesel and petro-diesel were prepared, and the results of their analysis compared to the Egyptian petro-diesel sample and ASTM standard specifications of B_6-B_{20} (ASTM D-7476) are listed in Table 7. The data indicate that the density and viscosity increased with the increase of volume percentage of bio-diesel. Their values also agree with the Egyptian petro-diesel standards and may lead to better lubricity. Although the TAN of B_{100} decreased with blending, its values in the prepared blends are higher than that of Egyptian petro-diesel sample and Egyptian ptero-diesel standards, and slightly higher than the recommended bio-petro-diesel blends standards (ASTM D-7476). The cold flow properties of the diesel fuel, CP and PP were improved by blending. The total sulfur content decreased with increasing bio-diesel percentage which consequently would decrease the SOx emission and decrease environmental pollution. The water content the blends increased with the increase of volume percentage of bio-diesel, but within the permissible limits. The FP of the prepared blends increased with increasing bio-diesel percentage in the blends. But the CV and CN of the prepared blends decreased with increasing bio-diesel percentage in the blends. All the measured properties of the prepared blends agree with the Egyptian petro-diesel and ASTM blends standards.

4. Conclusions

The preference of WFCO and WFSFO as WCO feedstock than that of WFO might be attributed to their chemical constituents and physico-chemical characteristics. More research is recommended to investigate the effect of chemical composition of the feedstock on the transesterification process.

References

[1] N. Shibasaki-Kitakawa, H. Honda, H. Kuribayashi, T. Toda, T. Fukumura, T. Yonemoto, (2007). Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. Bioresource Technology, 98: 416-421.

[2] P.L. Boey, G.P. Maniam, Sh. Abd Hamid, (2011). Performance of calcium oxide as a hetergoenous catalyst in biodiesel production: a review. Chemical Engineering Journal, 168: 15-22.

[3] M. Zabeti, W.M.A. Wan Daud, M.K. Aroua, (2009). Activity of solid catalysts for biodiesel production: a review. Fuel Processing Technology, 90: 770–777.

[4] F.R. Ma, M.A. Hanna, (1999). Biodiesel production: a review. Bioresource Technology, 70: 1-15.

[5] L. Gao, G. Teng, J. Lv, G. Xiao, (2010). Biodiesel synthesis catalyzed by the KF/Ca-Mg-Al hydrotalcite base catalyst. Energy Fuel, 24: 646-651.

[6] W. Suryaputra, I. Winata, N. Indraswati, S. Ismadji, (2013). Wast capiz (*Amusium cristatum*) shell as a new heterogenous catalyst for biodiesel production. Renewal Energy, 50: 795-799.

[7] M. Kouzu, J. Hidaka, (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: a review. Fuel, 93: 1-12.

[8] J. Boro, A.J. Thakur, D. Deka, (2011). Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. Fuel Processing Technology, 92: 2061-2067.

[9] X. Liu, X. Piao, Y. Wang, S. Zhu, H. He, (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst fuel. Fuel, 87: 216-221.

[10] M. Kouzu, T. Kasuno, M. Tajika, S. Sugimoto, S. Yamanaka, J. Hidaka, (2008). Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production fuel. Fuel, 87: 2798-2806.

[11] S. Yan, H. Lu, B. Liang, (2008). Supported CaO catalysts used in the transesterification a rapeseed oil for the purpose of biodiesel production. Energy Fuels, 22: 646-651.

[12] J. Van Gerpen, (2005). Bio-diesel processing and production. Fuel Processing Technology, 86: 1097-1107.

[13] R.A. Candeia, M.C.D. Silva, J.R. Carvalho Filho, M.G.A. Brasilino, T.C. Bicudo, I.M.G. Santos, (2009). Influence of soybean biodiesel content on basic properties of biodiesel-diesel blends. Fuel, 88: 738-743.

[14] P. Felizardo, J.N. Correia, I. Raposo, J.F. Mende, R. Berkemier, J.M. Bordado, (2006). Production of biodiesel from waste frying oils. Waste Management, 26: 489-494.

[15] A.I. Bamgboy, A.C. Hansen, (2008). Prediction of cetane number of bio-diesel fuel from the fatty acid methyl ester (FAME) composition. International Agrophysics, 22: 21-29.