

Catalysis of biodiesel production processes using phosphate rock: parametric and optimization study

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Abstract

The diesel fuel shortage and increasing environmental concerns have continued to incentive researchers into biodiesel as a green fuel alternative from renewable feedstocks. In this study, methyl esters were synthesized by alcoholysis of waste fried oil (WFO) using phosphate rock without pre-thermal treatment as a heterogeneous catalyst to minimize the cost and time associated with other catalysts. The optimum operating conditions for transesterification reaction of WFO including methanol-to-oil (M/O) molar ratio, residence time and catalyst loading were depicted by using Response Surface Methodology (RSM) based on Central Composite Design (CCD). The results of RSM analysis recorded that all studied parameters have high significant effect on the response. A maximum conversion yield of 96.37% was obtained at 6/1 M/O molar ratio, 3.08h reaction time and 6.74%wt. PR loading without pre-thermal treatment at temperature of 65°C and agitation speed of 350 rpm. Quality assessment of produced biodiesel using PR at the optimum conditions was achieved and found in agreement with the international ASTM-D 6751 standards.

Keywords: Biodiesel; renewable; alcoholysis; waste fried oil; phosphate rock; response surface methodology; quality assessment; ASTM-D 6751 standards.

1. Introduction

Diesel fuel shortage, hiking of crude oil prices and the greenhouse gases emissions of fossil fuels incentive the Egyptian researchers to search and develop for bio-energy sources ([Borugadda and Goud, 2012](#)). Biodiesel is a renewable, biodegradable, non-toxic and green substitute fuel for petrol-diesel ([Ali, R.M. et al., 2015](#)).

Biodiesel is composed of fatty acids of alkyl esters (FAAE) derived from edible or non-edible vegetal oils via transesterification reaction ([El Shimi, H. et al., 2013](#); [Chisti Y., 2007](#)). Currently, biodiesel is produced by the conventional alkaline catalysts (KOH, NaOH or CH₃ONa) under relatively lower temperatures (50-70°C) and atmospheric pressure ([García-Sancho C. et al., 2011](#)). Processing of waste fried oils (WFOs) is feasible for biofuel synthesis but, contain high FFAs that react with alkaline catalyst forming alkali salt of fatty acids "soap", which decrease the biodiesel conversion yield, and results in serious separation and costly purification steps ([Sathya, T. and Manivannan, A., 2013](#); [Matsushashi H. and Fujita T., 2011](#); [MacLeod CS et al., 2008](#)).

Calcium oxide (CaO) is the common heterogeneous alkaline catalyst experimented in biodiesel production under the same operating conditions employed for homogeneous basic catalysts. CaO has received attention in recent years worldwide as a catalyst for fatty acid methyl esters (FAME) synthesis; due to its availability, low purchased cost, and ease preparation even in nanosize ([Granados ML. et al., 2007a](#); [Zhu H. et al., 2006](#)). However, CaO chemisorbs substantial quantities of H₂O and CO₂ from the atmosphere in few

minutes during its storing (Granados ML. *et al.*, 2009a; Granados ML. *et al.*, 2007b). Furthermore, calcium oxide is combined with the process co-product, glycerol forming calcium glyceroxide which is an air exposure tolerant catalyst, however the process efficiency is reduced; because of its weak basicity than fresh CaO (Kouzu M. *et al.*, 2010; Kouzu M. *et al.*, 2008).

Phosphate rock (PR) is abundant in three major deposits in Egypt, located near the Red Sea in the Valley Nile, and in the Western Desert. Its average price is about US\$ 70 per ton without transportation cost. Egyptian PR is sedimentary with medium grade of 20-28% P₂O₅. It consists mainly of calcium phosphate [Ca₅(PO₄)₂], calcium oxide [CaO], calcium carbonate [CaCO₃], iron oxide [Fe₂O₃], silicon oxide [SiO₂] and traces of magnesium and aluminum oxides, organic and clay matter (Elouear *et al.*, 2008). Sodium phosphate [Na₃PO₄], CaO and MgO had previously utilized as catalysts in biodiesel production (S.T. Jiang *et al.*, 2010), therefore the PR natural components can catalyze the transesterification reaction (El Shimi, H *et al.*, 2015; Olutoye and Hameed, 2011; Dehkordi and Ghasemi, 2012; Borges, and Diaz, 2012).

Optimization of the transesterification process is important and required, but it is commonly performed in classical experiments by changing a single parameter while keeping all the other parameters constant at specified values. This method needs a large number of experiments, and cost and time consuming. Statistical of factorial experimental design can be investigated for optimization of alcoholysis process in order to avoid the limitations of the traditional method and saving money and efforts (El-Gendy, N. *et al.*, 2015). Response surface methodology (RSM) is an effective and brilliant statistical technique for designing such experiments, building models and investigating simple and complex processes for best value determination of yield (Rashid U. *et al.*, 2009).

The current study focused on the prediction of a mathematical model for WFO transesterification using phosphate rock [Ca₅(PO₄)₂F] as a semi-novel catalyst and to describe and evaluate the effects and the relationships between the process variables such as methanol-to-oil molar ratio (M/O), reaction time (h), catalyst loading (%wt./wt. oil), reaction temperature (°C) and agitation speed (rpm); in order to obtain the maximum yield of fatty acid methyl esters (FAMES) or biodiesel. Response surface methodology comprising a central composite design (CCD) was used to evaluate the interactive effect and maintain the best values for the specified process parameters.

2. Materials and methods

2.1. Reagents and materials

The feedstock investigated in this research was waste fried oil (WFO), collected from local restaurants in Giza city, Egypt. The oil is a mixture of soybean and sunflower, and it was used three times at temperature range of 120-180°C. Phosphate rock [Ca₅(PO₄)₂F] as a catalyst for transesterification of WFO to get biodiesel was kindly supplied by El-Nasr Co. for Intermediate Chemicals. Reagents like analytical grade methanol (CH₃OH) (>99%) and concentrated sulfuric acid (H₂SO₄) were kindly supplied by ADWIC, El Nasr Pharmaceutical Product Co.

2.2. Feedstock characterization

The physicochemical properties and fatty acids analysis of WFO feedstock were performed using gas chromatography (GC), and its molecular weight was estimated according to the fatty acids profile, and recorded.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of PR were recorded with X-ray diffractometer (Schimadzu-7000, Japan), using radiation ($\lambda = 1.5418 \text{ \AA}$) and step-scan mode (range: $5-100^\circ 2\theta$, step-time: 0.5 s, step-width: 0.1°) to determine the minerals of PR and to specify if the catalyst samples structure is crystalline or amorphous. Surface morphology, chemical composition and features of the PR samples were characterized at room temperature by Scanning Electron Microscopy (SEM) system equipped with an Energy Dispersive X-ray spectroscopy (EDX) detector to determine the elemental structure of PR (JEOL JSM 6360LA, Japan) with accelerating voltage of 20 kV. The particle size distribution of PR powders was investigated to calculate the catalyst surface area.

2.4. Experimental Design and Statistical Analysis

In the recent study, the effects of three main process variables including; Methanol/Oil M/O ratio (mol/mol; A), reaction time (h; B) and catalyst loading (%wt/wt oil; C), were tested to maximize the FAME “biodiesel” yield throughout the transesterification of the WFO with methanol in the presence of solid catalyst; PR without pre-thermal treatment. The experiments have been carried out by using the CCD with three levels (coded by -1 , 0 and $+1$) and $\pm \alpha$ of ± 1.682 . Design parameters for transesterification process catalyzed by phosphate rock (PR) with all levels ranges are illustrated in Table (1).

Table 1 Design parameters for transesterification process using PR

Process parameter	$-\alpha$	-1	0	$+1$	$+\alpha$
A: Alcohol/feedstock (mol/mol)	1.318	3/1	7.5/1	12/1	13.682
B: Reaction time (hr)	0.5	1	2.5	4	5.682
C: Catalyst loading (%wt)	1.318	3	5	7	8.682

Many trials were undergone to get the appropriate regression model for the obtained experimental data using PR as a catalyst. The suggested regression equation is a cubic polynomial model, in which the response is of power three as shown in “Eq. (1)”.

$$Y^3 = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j \neq i}^3 \beta_{ij} X_i^2 X_j + \sum_{i=1}^3 \beta_{iii} X_i^3 \quad (1)$$

where, Y is the predicted FAME conversion yield (wt.%), β_0 is the intercept term, β_i , β_{ij} , β_{ii} and β_{iii} are the linear, interactive, quadratic and cubic coefficients (i.e. the regression model coefficients), respectively, while, X_i and X_j are the levels of the independent parameters (i.e. the transesterification variables; A, B and C). The Design Expert 7.0.0.Trial statistical software (State-Ease Inc., USA) was examined to design the experimental matrix, suggestion of regression model and achieve the graphical analyses of the practical data, making the statistical analyses of model and evaluate the significance

levels of variables through ANOVA, and additionally this software was used to optimize the recent process.

2.5. Experimental procedure

The collected waste oil feedstock (WFO) is filtered using cascade of filter papers; to remove the suspended burned-food bits, and dried at 110°C for 2h; to evaporate the unwanted moisture content. The acid-methanol solution was prepared freshly by mixing pre-optimized amounts of sulfuric acid (1%wt. oil) and methanol (60%wt. oil) for esterification process of oil FFA. H₂SO₄ was dissolved with continuous stirring on a magnetic stirrer for 5 min. The solution was prepared freshly in order to maintain the catalyst activity. Then, the alcohol amount is recalibrated to certain ratio and mixed with the main heterogeneous catalyst for transesterification process. Esterification of WFO using methanol and sulfuric acid was performed to reduce the feedstock FFA below 0.5%wt. The transesterification of WFO to biodiesel was then performed in a 250 ml round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser. The reactor was initially charged with 50 g of waste fried oil (WFO), and heated to 65 °C at 1 atm. stirred continuously at 350 rpm under control; to avoid splashing in the flask. After the transesterification process, the warm reaction mixture was allowed to cool for 20 min. The reaction mixture was filtrated through a cascade of filter-papers; to recover the catalyst residuals and use again in the next batch. The catalyst residues are washed three times by re-suspension in methanol (45 ml) for 15 min to recover any traces of FAME product left in the residues. The products are then fed to a separating funnel; to get two distinct layers of biodiesel and glycerol; due to the densities difference of 0.86 and 1.22 g/ml, respectively. The biodiesel production processes using PR catalyst are shown in Fig. (1).

The process was demonstrated to be successful by observing the glycerin settling in the bottom soon after stopping mixing of the reactants. The products (biodiesel and glycerin) were obtained in high quality when PR catalyst applied as shown in Fig. (2). Once the glycerol and biodiesel phases have been separated, the excess alcohol in each phase was removed with a flash evaporation process. The recovered alcohol was recycled and reused. The obtained glycerol is pure (>99%), so after 10 min at 100 °C, the bottom layer beaker was removed and the glycerol was left to cool to room temperature. The beaker is reweighed with the glycerol. Treatment of FAMES layer with hot water (60°C) for 2 times is performed; to get rid of any methanol, glycerol and catalyst traces. The gentle water layer is decanted, and then drying of FAMES is achieved; to purify the biodiesel before its analysis.

2.6. Determination of biodiesel conversion yield

After biodiesel purification, its conversion yield was estimated according to "Eq. (2)".

$$\% \psi = \frac{WB * \eta}{WF * \varepsilon} \times 100 \quad (2)$$

Where, ψ is the true biodiesel conversion yield, WB is the biodiesel weight, WF is the feedstock weight, η is FAMES content in the biodiesel layer (purity) and ε is the TG, DG, MG and FFA content in the feedstock, or (100-H₂O%).

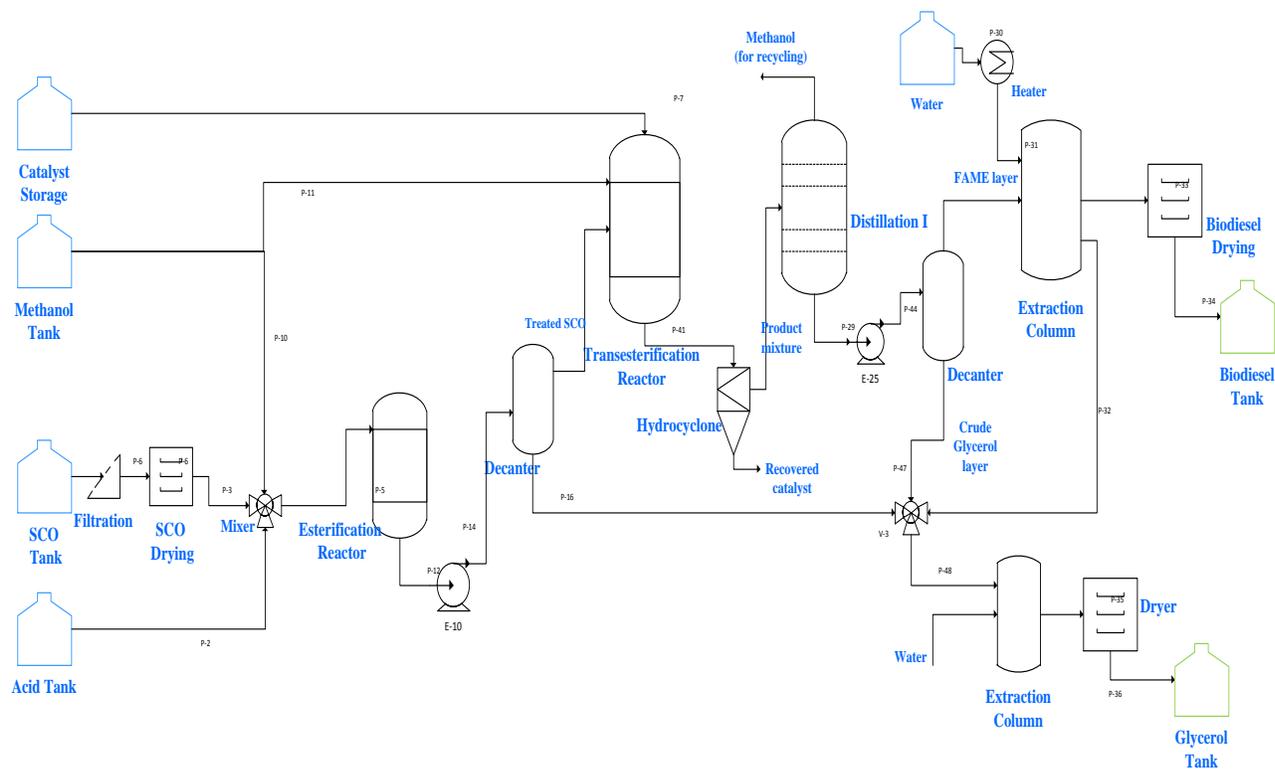


Fig. 1. Biodiesel production process using PR catalyst (El Shimi, H. *et al.*, 2016)

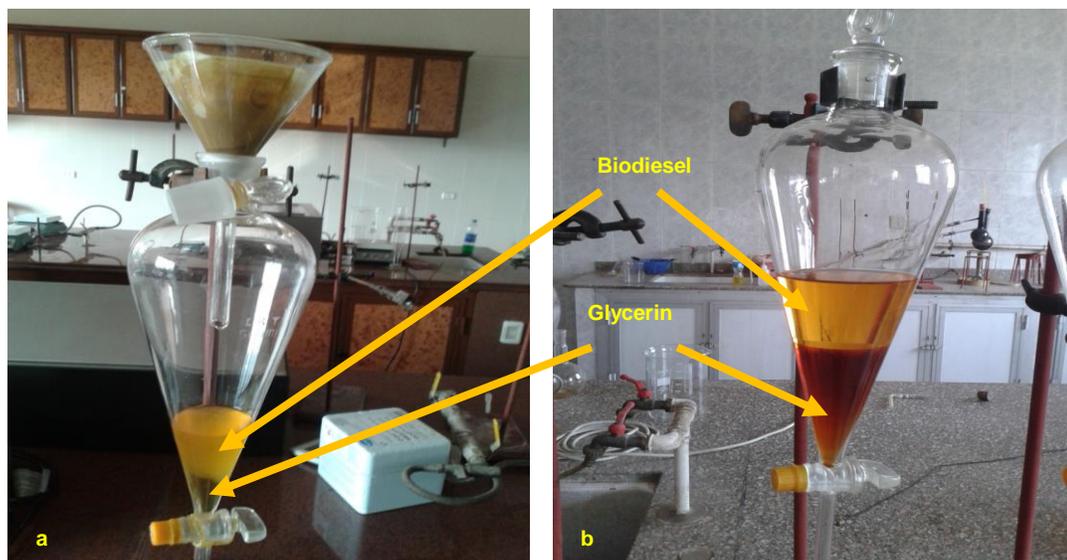


Fig. 2. Separation of biodiesel and glycerin layers; (a) Operating conditions: 9/1 M/O, 2h reaction time, 5.0%wt. PR loading at 65°C and 350 rpm, (b) Operating conditions: 6/1 M/O, 2h reaction time, 1.5%wt. KOH concentration at 65°C and 350 rpm

2.7. Analytical procedure

The oil was converted to fatty acid methyl esters (FAMES) by trans-methylating agent as described by Hammond method (Hammond EW, 1993). FAMES analysis of produced biodiesel was determined using a gas liquid chromatography (GLC). The GLC device was made using Hewlett Packard (HP) Model 6890 Chromatograph. A capillary column 30 m length and 530 μm inner diameter, packed with Apiezon[®] was used. The carrier gas was N₂ with flow 1ml/min. Detector temperature, injection temperature and the column temperature were 280 °C, 300 °C and 100 to 240 °C at 15 °C/min, respectively.

3. Results and discussion

3.1. Characterization of WFO

Fatty acid profile of WFO was determined using GC-MS chromatography as illustrated in Table (2). The predominance of Linoleic acids (59.93%mol.) and Oleic (29.6%mol.) in the stock structure prevail the sustainability of waste fried oil as a good feedstock for fatty acid methyl esters (or biodiesel) production. The calorific value of WFO was estimated to be 10.57 kcal per kg which approved the energetic content of feedstock as a diesel fuel. However, direct use of oils in diesel engine is a problematic; due to its high viscosity (11-17 times diesel fuel), low volatility, they do not burn completely and form deposits in the fuel injector of diesel engine and additionally, acrolein (toxic substance) is formed through thermal decomposition of glycerol (present in TGs).

The acidity of WFO was determined to be 0.8 mg KOH/g oil, hence the FFA content is about 0.4% wt. based on the estimated molecular weight of 280.1 for the constituent fatty acids. Due to the low FFA content (<2% w/w) of the waste fried oil, pretreatment using acid catalyst was not necessary and transesterification catalysis using PR is justified. The average molecular weight of the WFO and the produced biodiesel was calculated to be 878.4 and 294.13 g/mol, respectively.

Table 2 Fatty acid profile and physicochemical properties of WFO

Property	Value
Palmetic acid (C16:0)	7.2%mol
Stearic acid (C18:0)	3.67%mol
Oleic acid (C18:1)	29.6%mol
Linoleic acid (C18:2)	59.93%mol
Flash point	176 °C
Pour point	-6 °C
Cloud point	3 °C
Viscosity at 40°C	5.64 cSt
Calorific value	10.57 kcal/kg
FFA	0.8 mg KOH/g Oil
Moisture content	0.5%wt.

3.2. Characterization of Catalyst

3.2.1. Chemical analysis of used PR

EDAX analysis verified that PR is composed of 33.51% O, 31.42% Ca, 10.75% C, 8.54% P, 7.06% Fe, 6.14% Si, 2.15% S, 0.35% Al and 0.09% Na by weight. This was confirmed that PR is composed of the oxides of these elements because O element is the main constituent and occupies 33.51% by weight and more than 46% by atomic. Of course, the oxides of elements like Ca and Mg will increase the alkalinity strength of the PR and confirm the alkaline performance of PR catalyst in the transesterification reactions besides the phosphate group, PO_4^{3-} .

3.2.2. X-ray diffraction of PR

X-ray diffraction (XRD) pattern was conducted to determine the phosphate minerals of PR and to show if the catalyst structure is crystalline or amorphous. XRD analysis identified the semi crystalline nature of the PR and the major minerals present in phosphate rock. The phosphate mineral was identified as “apatite” $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and “quartz” SiO_2 . Occurrence of apatite implies the presence of CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 which have high strength basic sites beside PO_4^{3-} . XRD analysis of PR catalyst was depicted in Fig. (3).

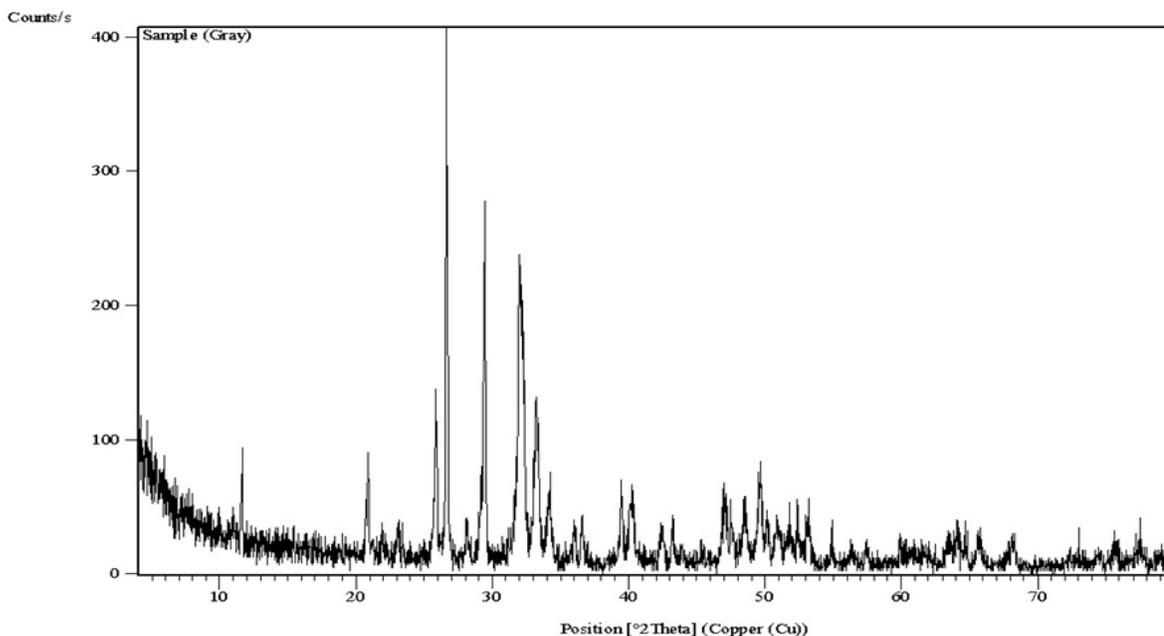


Fig. 3. XRD analysis of PR

3.2.3. Particle size distribution of PR

The mean particle diameter of PR was estimated to be $3\mu\text{m}$ hence, it is expected to have a high specific surface area and catalytic activity.

3.2.4. SEM photography of PR catalyst

The morphology of used PR sample was performed using scanning electron microscopy (SEM) as shown in Fig. (4). SEM shows that the PR is irregular in shape with

well-defined particles. It has rough surfaces, which indicates high surface area. This result confirmed that reported previously by [Elouear et al. \(2008\)](#).

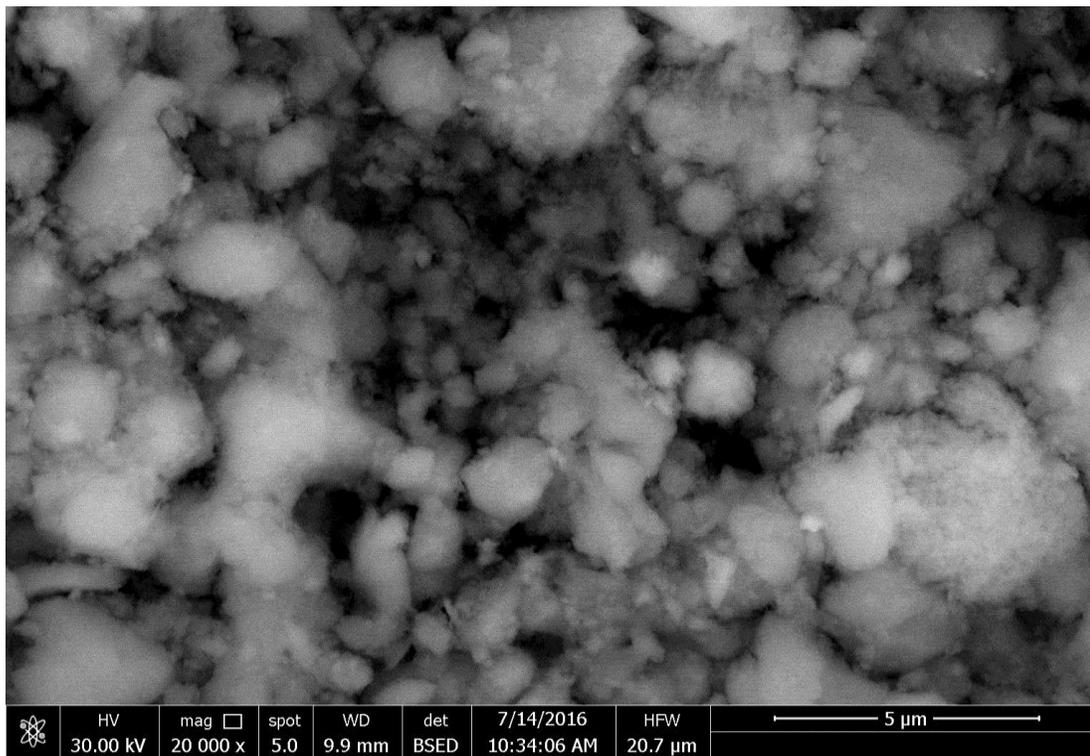


Fig. 4. SEM photographical of PR

3.3. Optimization of biodiesel production process using PR as catalyst

3.3.1. Model fitting and ANOVA

The statistical combinations of reaction factors in coded and actual values along with the theoretical (predicted) and practical (experimental) response are depicted in Table (3). The research experimental plan was able to estimate the reduced cubic model “Eq. (3)”.

$$Y^3 = 10^4 (68.4 - 18.05 X_1 - 63.32 X_2 + 3.34 X_3 + 20.02 X_1 X_2 + 0.39 X_2 X_3 + 0.81 X_1^2 + 8.95 X_2^2 - 0.66 X_1^2 X_2 - 1.97 X_1 X_2^2) \quad (3)$$

The empirical equation model “Eq. (3)” was able to characterize the effect of different variables on the biodiesel conversion yield (Y, wt%). Synergetic parameter effect is indicated by the positive sign terms, while antagonistic effect is appreciated by the negative terms.

The reduction in FAME conversion yield could be performed in case of large methanol (M/O) amount and retention time as reported previously by many researchers. The validity of the fitted regression model was approved and its significance was controlled by F-test using the Design Expert 7.0.0.Trial software. Experimental design matrix and response of FAME is presented in Table (3). The analysis of variance (ANOVA) results are illustrated in Table (4). The suggested regression model is

statistically more significant with F-value of 12.20 and very low probability value (p-value) of 0.0003 at 95% confidence level. As well known, the R^2 and adj R^2 values measure the reliability of the fitted model. The model R^2 and adj R^2 were estimated to be 0.92 and 0.84 respectively, which means that about 92% of the variance in response (FAME yield) was attributed to the process variables, and only 8% of the total variations could not be predicted from “Eq. (3)”. These statistical indicators ensured the well adjustment of the suggested model to the experimental data. Confirmation of model validity and adequacy were reflected by comparing the experimental values of biodiesel yield with the predicted from “Eq. (3)”, as depicted in Table (3) and Fig. (5). Better precision and reliability of experimental results were approved by estimating the values of standard deviation (SD) and coefficient of variation (CV%) that recording 4.1 and 1.677% respectively. The SD and CV% are low enough to consider the suggested model “Eq. (3)” is an effective regression model.

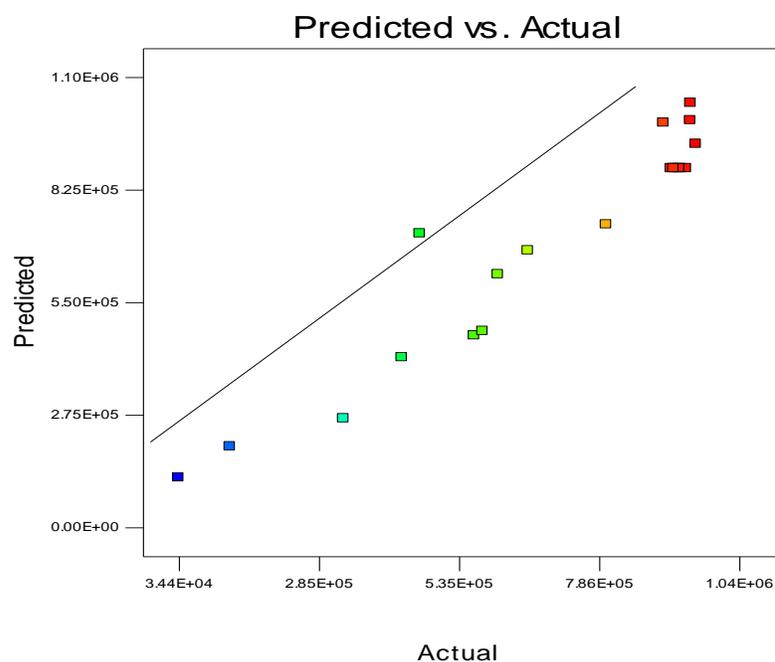


Fig. 5. Comparison between the predicted and actual values of FAME conversion yield

3.3.2. Influences of transesterification variables on FAME yield using PR as catalyst

The contour and RSM plots of the transesterification process parameters with respect to process response were depicted in Fig. (6) and Fig. (7).

Excess alcohol is used to shift the equilibrium towards biodiesel formation and derive the reaction near completion. In catalysis of transesterification process of WFO by PR, the biodiesel yield was decreased when excessive amount of methanol was used; as the biodiesel yield was 97.73% at M/O of 7.5/1 and then decreased to 96.60% at M/O of 13.68/1 at the same operating conditions. Increasing the alcohol loading from 7.5/1 to 12/1 implies 1.6 times the alcohol amount used which causes the methyl esters yield to increase from 97.73% to 98.62%. Basis for a 1 ton waste oil batch, the additional alcohol load is about 0.17 ton, and the methanol purchased cost is US \$1265/ton, hence the additional cost

of methanol to go from 7.5/1 to 12/1 is US\$ 215. Assuming a biodiesel price of US\$1000 per ton, and the additional revenue is US\$9 which is lower than the additional cost of alcohol, US\$215. Therefore, it is economic to use 7.5/1 methanol/oil molar ratio in FAME production.

Loading of PR catalyst was tested in range of 3-7%wt/wt oil while the other operating variables maintained constant. For 1 ton of feedstock, the additional PR mass to go from 3% to 7% is 0.04 ton. As the Egyptian PR cost from El Sebaeya' mine is US\$65/ton, hence the addition cost of PR will be US\$2.6. The additional biodiesel product is approximately 0.0664 ton, and its revenue is US\$66.4, which is much more than the US\$2.6 cost of additional PR amounts. Therefore, the simplified cost analysis verifies that a higher PR/oil weight ratio would be economically choice to enhance the production rate. On the other hand, slight change in the transesterification time led to a significant change in the kinetics rate and therefore in the biodiesel production rate. Reaction time of 1h was not sufficient to complete the process especially if minimum alcohol and catalyst amounts are applied.

In this research, all experiments were carried out at constant temperature and mixing intensity of 65°C and 350 rpm, respectively; to prevent the methanol evaporation and therefore, avoiding the extra cost of alcohol recovery.

The statistical analysis (ANOVA) of the experimental data approved that the significant influence of the investigated variables on FAME conversion yield can be ranked in the increasing order as follows: PR loading (% wt/wt oil) > M/O ratio (mol/mol) >> reaction time (hr). Many researchers reported that the most significant parameter affecting the FAME yield is the initial catalyst load.

Table 3 Experimental design matrix and results using PR catalyst

Run	Methanol/Oil (A)	Reaction time (B)	PR loading (C)	FAME Yield (Y)		Residual
				Experimental	Predicated	
1	3/1 (-1)	1 (-1)	3 (-1)	69.06	64.29	4.77
2	3/1 (-1)	4 (+1)	7 (+1)	87.04	87.77	-0.73
3	12/1 (+1)	1 (-1)	7 (+1)	84.60	85.18	-0.58
4	12/1 (+1)	4 (+1)	3 (-1)	92.80	90.44	2.36
5	3/1 (-1)	1 (-1)	7 (+1)	75.70	74.61	1.09
6	3/1 (-1)	4 (+1)	3 (-1)	83.30	78.25	5.05
7	12/1 (+1)	1 (-1)	3 (-1)	82.58	77.67	4.91
8	12/1 (+1)	4 (+1)	7 (+1)	98.62	97.84	0.78
9	1.318/1(- α)	2.5 (0)	5 (0)	32.53	40.52	-7.99
10	13.682/1(+ α)	2.5 (0)	5 (0)	96.60	99.61	-3.01
11	7.5/1 (0)	0.5(- α)	5 (0)	50.18	58.25	-8.07
12	7.5/1 (0)	5.682(+ α)	5 (0)	98.29	99.81	-1.52
13	7.5/1 (0)	2.5 (0)	1.318(- α)	77.52	89.53	-12.01
14	7.5/1 (0)	2.5 (0)	8.682(+ α)	98.31	96.62	1.69
15	7.5/1 (0)	2.5 (0)	5 (0)	97.60	95.72	1.88
16	7.5/1 (0)	2.5 (0)	5 (0)	97.25	95.72	1.53
17	7.5/1 (0)	2.5 (0)	5 (0)	97.73	95.72	2.01
18	7.5/1 (0)	2.5 (0)	5 (0)	97.36	95.72	1.64
19	7.5/1 (0)	2.5 (0)	5 (0)	98.02	95.72	2.30
20	7.5/1 (0)	2.5 (0)	5 (0)	97.09	95.72	1.37

Table 4 ANOVA results for methanolysis process of WFO catalyzed by PR

Source	Sum of Squares	DF	Mean Square	F value	P value (Prob> F)	
Model	1.495E+012	9	1.661E+011	12.20	0.0003	Significant
A (Alcohol/Oil)	3.758E+011	1	3.758E+011	27.60	0.0004	Significant
B (Time)	4.661E+011	1	4.661E+011	34.22	0.0002	Significant
C (Catalyst)	1.108E+011	1	1.108E+011	8.14	0.0172	Significant
AB	1.666E+009	1	1.666E+009	0.12	0.7338	Non-Significant
BC	1.119E+009	1	1.119E+009	0.082	0.7802	Non-Significant
A ²	2.377E+011	1	2.377E+011	17.46	0.0019	Significant
B ²	2.459E+011	1	2.459E+011	18.05	0.0017	Significant
A ² B	1.111E+011	1	1.111E+011	8.16	0.0171	Significant
AB ²	1.023E+011	1	1.023E+011	7.51	0.0208	Significant
Residual	1.362E+011	10	1.362E+010	----	----	
Lack of Fit	1.357E+011	5	2.714E+010	285.56	0.739	Non-Significant
Pure Error	4.753E+008	5	9.505E+007	----	----	
Cor Total	1.631E+012	19	----	----	----	
CV %= 1.677	R ² = 0.92	Adj R ² = 0.84	Pred R ² = -ve	Std. Dev. = 4.1	Mean =88.62	Adeq Precision = 11.09

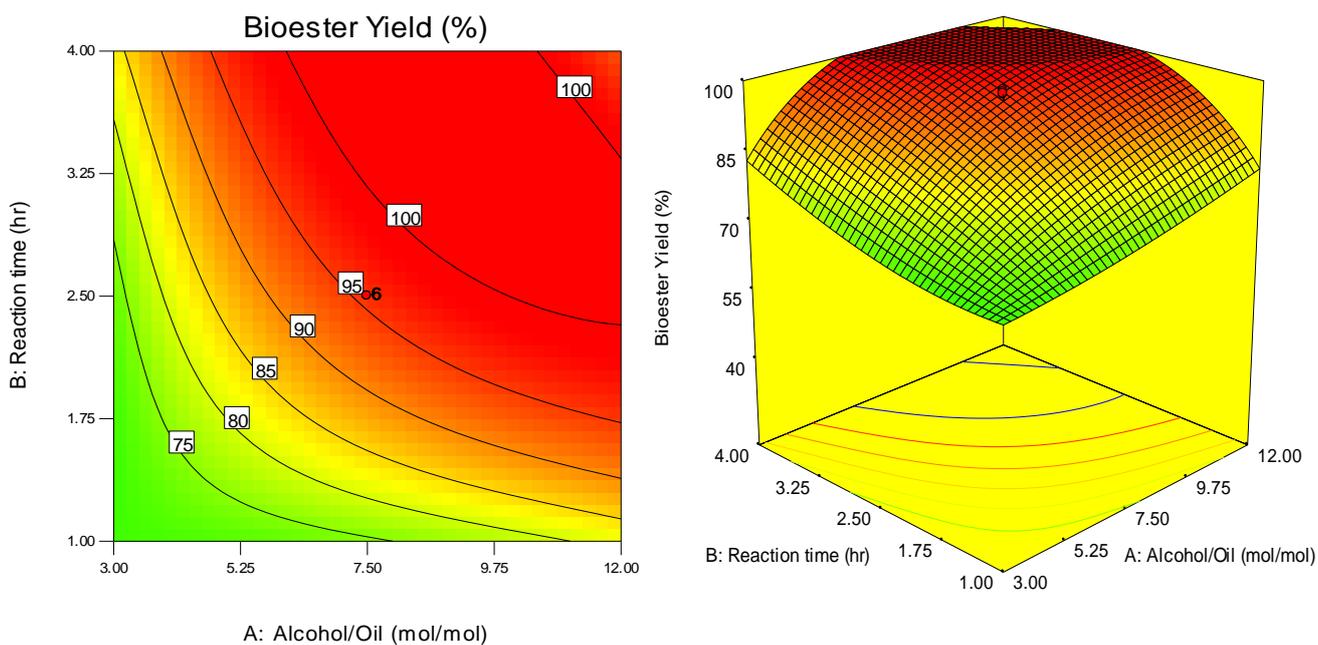


Fig. 6. 2D contour and 3D response surface plots for the interactive effect of alcohol/oil molar ratio and reaction time on bioester yield at PR loading of 5.00% wt

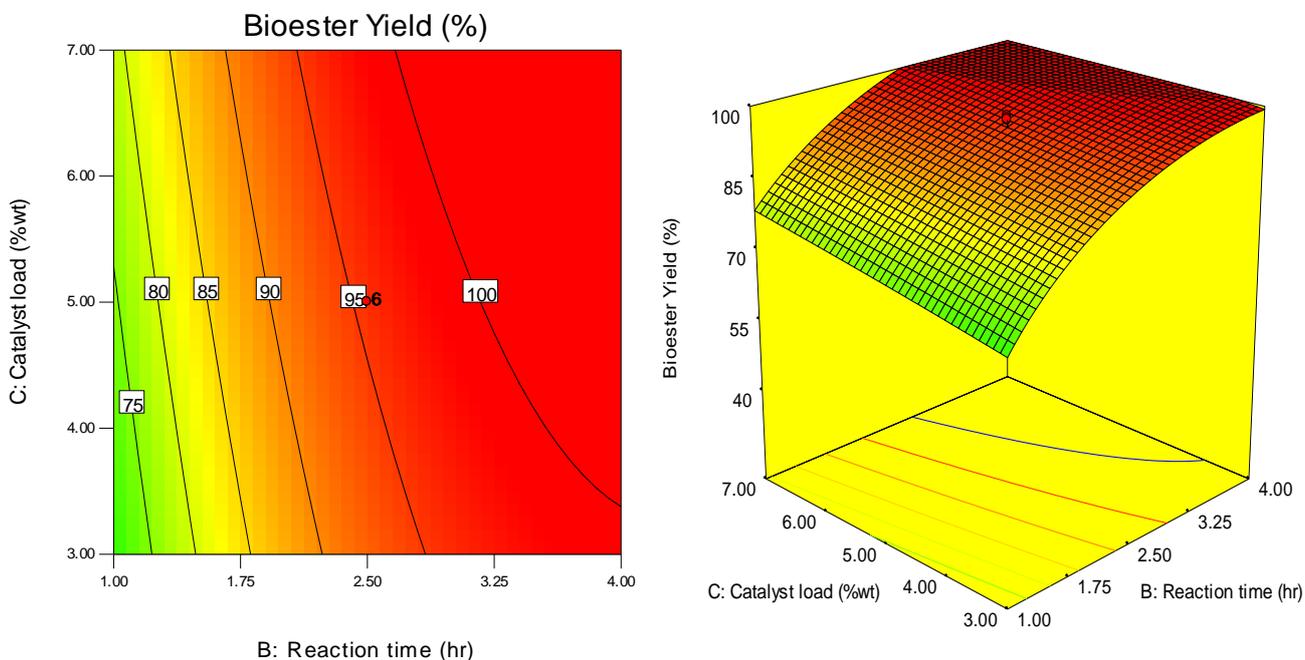


Fig. 7. 2D contour and 3D response surface plots for the interactive effect of reaction time and PR load on bioester yield at methanol/oil molar ratio of 7.50

3.3.3. Process optimization using Design Expert 7.0.0.Trial software

The program combined the individual desirability into a single number and then searched to optimize this function in accordance to the response target. In this research, the selected optimum parameters were; M/O molar ratio of 6.00, reaction time of 3.08 hr and PR initial concentration of 6.74 %wt. obtaining biodiesel yield of 98% at fixed temperature and mixing intensity of 65°C and 350 rpm, respectively. As a result, the biodiesel yield from the experiment is 96.37% as the optimized set of variables, which is nearby the process optimization prediction with an error of 1.69%. The techno-economic appraisal is the key tool to decide the application of these parameters on industrial scale.

3.4. Quality assessment of biodiesel produced by PR catalyst

To confirm the quality specifications of the produced biodiesel “FAMES” under the optimum variables, a certified authority specified the biodiesel fuel for properties of commercial diesel replacement. The specifications of biodiesel obtained from transesterification of WFO using PR as catalyst without calcination is listed in Table (5).

Table 5 Specifications of biodiesel obtained using PR

Property	Unit	PR Biodiesel	Egyptian petro-diesel standards	Biodiesel ASTM-D 6751
Density at 15°C	g/cm ³	0.89	0.85	0.86-0.90
Kinematic viscosity at 40°C	cSt	5.1	1.6-7.0	1.9-6.0
Esters content	%wt.	98	-	>96.5
Flash point	°C	160	>60	>101
Cloud point	°C	13	13	-3 to14
Pour point	°C	9	8	-15 to 6
Diesel index		-	>48	-
Cetane index		47	40-55	48-65
Calorific value	MJ/kg	41.9	>40.8	38-45
Total sulfur	%wt.	0.016	0.57	<0.05
Water content	% vol.	0.05	0.00	<0.1
Ash content	%wt.	0.001	0.02	<0.02
Acid index	mg KOH/g oil	0.25	-	<0.8
Free glycerol	%wt.	0.01	-	<0.02
Total glycerol	%wt.	0.22	-	<0.24

Product quality is important as the modern diesel engines are very sensitive to fuel, so the reaction conversion yield and esters content should exceed 96.5%wt. The higher density value will contribute to a better fuel atomization due to heavier fuel droplets during the fuel injection in the combustion chamber, which will result in better combustion. The high-density value is expected to reduce the produced energy per liter during the performance test. Sulfur content in biodiesel has been detected to be very small, at 0.003%wt., much less than petrodiesel, at 0.57%wt. The low sulfur content in biodiesel leads to reduced SO₂ emission, which contribute to the acid rain phenomenon. Hence, it can be concluded that biodiesel is a very promising biofuel to replace low sulfur diesel in Diesel engines. The calorific value measurement indicates that the biodiesel will release less energy per kg than petrodiesel during the combustion process. The Cetane index of biodiesel is better than petrodiesel, indicating that the readiness of biofuel to self-ignite when exposed to high temperature and pressure in the diesel engine burning chamber is higher than petrodiesel.

4. Conclusions

As extension to this work, the following points are concluded and recommended for the future work;

- Characterization of phosphate rock (PR) as a catalyst for biodiesel production approved its composition as a metal oxides because O element is the main constituent and occupies 33.51% by weight, therefore it can efficiently catalyze the biodiesel production process.
- The process optimization by the Design Expert 7.0.0.Trail software indicated that a 6.00/1 M/O, 3.08h retention time, 6.74%wt. catalyst loading, 65°C process temperature and 350 rpm agitation intensity are sufficient to obtain FAME yield of 96.37% using uncalcined PR. Therefore uncalcined phosphate rock (UCPR) is the appropriate catalyst for biodiesel commercialization.
- Quality assessment of biodiesel fuels produced using PR confirm the international standards.

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