



The Effect of Mixing on CaO Catalyzed Biodiesel Production Process

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Abstract--Stainless steel lab scale batch mechanical stirred reactor of 1 liter volume was used for biodiesel production from sunflower vegetable oil and methanol in the presence of calcium oxide catalyst. Three operating variables were studied; impeller speed, catalyst amount, and reaction time. The temperature and methanol-to-oil molar ratio were held constants at 60 °C and 9 respectively. Response surface methodology (RSM) was applied with central composite design (CCD) of experiments. The practical optimum biodiesel yield was about 96% at impeller speed of 800 RPM, catalyst amount of 2 %, and reaction time of 2 h. First order reaction gave a good fit with respect to the concentrations of triglyceride at conditions near the optimum. The apparent reaction rate constants were 1.31, 1.71, and 2.2 h⁻¹ for impeller speeds of 600, 800, and 1000 RPM respectively. The reaction time decreased to about 1.5 h at power per unit volume above 4 kW/m³.

Keywords: CaO, Heterogeneous catalyst, Mixing, RSM

I. Introduction

Biodiesel is the alternative biofuel that can be used on its own or mixed with petroleum diesel fuel in ratios for conventional engine without any further modification. The direct utilization of vegetable oil in diesel engines was problematic due to their inappropriate physical properties such as high viscosity, lower pour point, high flash point, high molecular weight of triacylglycerol resulted in incomplete combustion due to low volatility, polymerization of unsaturated fatty acids and formation of carbon deposits [1].

Transesterification, also called alcoholysis, is the reaction of an oil or fat (triglyceride) with an alcohol (usually methanol) in presence of catalyst to form fatty acid methyl esters (FAME or biodiesel) and glycerol (Gly), the basic reaction given in Eq. (1).

 $TG + 3MeOH \rightarrow 3 FAME + Gly$ (1)

According to American society for Testing and Materials (ASTM), biodiesel is defined as a monoalkyl esters derived from lipid feedstock. Wide ranges of feedstock have been assessed for biodiesel production and could be divided into different classes, such as edible oils, non-edible oils, waste oils, animal fats and algal lipids. Different forms of plant oils, animal fats and other sources are used for producing biodiesel. B100 (100% biodiesel and 0% petroleum –diesel) is a clean burning fuel (for its oxygen content) with low exhaust emissions, nontoxic, biodegradable fuel, and free from sulfur, aromatic hydrocarbons, metal and crude oil residues, therefore it is used in any diesel engine with little or no engine modification [2-4].

Homogeneous base-catalyzed transesterification is much faster than acid-catalyzed transesterification, but the homogeneous base-catalyzed method has some disadvantages; soap is produced from the reaction of the free fatty acids (FFA) with the base catalyst. The formation of soap not only consumes the catalyst but also causes the emulsification of the biodiesel produced and the glycerol (a byproduct), which would make the separation process very difficult. A large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction. Therefore, it is considerably more costly to separate the catalyst from the produced solution. By using a heterogeneous catalyst, the cost of processing is lowered due to the following features: (1) the catalyst can be recycled (reused), (2) there is no or very less amount of waste water produced during the process, (3) separation of biodiesel from glycerol is much easier, (4) non corrosive and (5) environmentally benign and present Disadvantage fewer disposal problems. of heterogeneous catalyst is the longtime of reaction due to poor mass transfer between immiscible reactants and poor mixing. Mixing efficiency is one of the





most important factors to improve the biodiesel yield due to the improve efficiency of the mass transfer between the reactants. The reaction is very slow when poor mixing and poor dispersion of alcohol into the oil feedstock. Mechanical agitation is normally applied in production of biodiesel in order to increase contact between the vegetable oil, alcohol, and catalyst [1].

Abdel-Rahman et al [5] found some variations or contradictions in the literature on the use of CaO catalyst. Limited research works were done on the effect of mixing especially for heterogeneous catalyzed process [6-8].

The objectives of the present study are; to design experiments to identify the effect of three operating variables, namely: agitation speed (N), CaO catalyst content (Ccat) and reaction time (t) on the biodiesel yield from sunflower vegetable oil and methanol in batch mechanical stirrer reactor using response surface methodology (RSM) with central composite design (CCD) of experiments, to obtain the optimum operating conditions for maximum biodiesel yield, and to study the reaction kinetics and the effect of mixing as power per unit volume required for mechanically agitation at conditions near the optimum.

II. Experimental Work

Refined edible sunflower oil (Turkey) was used in the present study for the transesterification process. The oil was with high triglycerides and low free fatty acid content. Table 1 shows the physical properties of vegetable oil used in this study. Methanol (CH₃OH) of 99.8 % purity and calcium oxide (CaO) of 99.9 % purity, manufactured by Altakana scientific Inc./UK, were used.

Table 1: Physical properties of the sunflower Oil.

Property	Values
density(g/cm ³) @ 15 °C	0.912
viscosity (mm ² /sec)@ 40 °C	35
Acid value (mg KOH)	0.24
FFA %	0.085
molecular weight (g/gmol)	883

Fig. 1 shows the methodology diagram for the transesterification process. The process involved of cylindrical stainless steel batch reactor with baffles located in water bath (1400Watts capacity) with digital temperature control. Baffles are normally used, to improve the mixing and reduce problems from vortex formation. The reactor was of a 1-liter

volume, diameter (D) of 110 mm, height (L) of 145 mm. The impeller was hub mounted flat blade agitator of 45 mm diameter.. The agitator was located at 5 cm from the bottom of the vessel. A digital mixer was used with variable agitation speed. Fig. 2 shows the experimental set-up.

The operating conditions range used in the present study are; impeller speed (200-1000 RPM), CaO catalyst amount (1-5 %), and reaction time (0.5-2.5 h). Reaction temperature and methanol-to-oil molar ratio were held constants at 60 °C and 9 respectively. The ranges of the operating variables were selected based on the results of some preliminary tests and the most suitable vales reported in literature [5].



Figure (1): The methodology diagram for the transesterification process.



Fig. 2: Experimental set-up

Calcium oxide (CaO) was calcinated at 700 °C for 2 h under atmospheric pressure to obtain the catalytic active form, then cooled and stored in a desiccator containing silica gel. The reactor (Digital adjusted mixer speed) was charged with 500 ml of sunflower oil and located in a water bath until it achieved the desired reaction temperature. The methanol and





catalyst mixture were added to the reactor. The reaction mixture was separated into two layers. The upper layer (biodiesel cut) was then centrifuged (4500 rpm, 10 min) and dried in oven ($150 \circ C$ for 3 h) to remove the catalyst and methanol. The lower layer (Glycerol cut) was also centrifuged and dried to remove the catalyst and methanol. The weight of glycerin produced was used for the calculation of fatty acid methyl ester (FAME) produced and biodiesel yield using the following stoichiometric equations:

$$W_{FAME} = 3W_{Gly} * (M_{WFAME} / M_{WGly})$$
(2)

$$Y = W_{FAME} / W_{TG}$$
(3)

The design of experiments for the transesterification process were developed and optimized using response surface methodology (RSM) with central composite design (CCD) of experiments provided by Design-Expert software (6.0.6). The experiments design selected assists in obtaining a quadratic empirical polynomial equation of the biodiesel yield (response or dependent variable) as a function of the three process variables (independent variables). Six zero levels (center levels) were selected and applied in a central composite design (CCD) so as to establish the experimental design matrix. Table 2 shows the coded and actual reaction variables used in the experimental design. Agitation speed (X_1) , catalyst amount (X_2) , and reaction time (X_3) were chosen with center values of 600 RPM, 3 %, and 1.5 h respectively.

 Table 2: Coded and actual Variables of the experiments design

Real	Coded		Var	iables I	.evels	
variables	variables	-2	-1	0	+1	+2
N	X ₁	200	400	600	800	1000
C _{cat}	\mathbf{X}_2	1	2	3	4	5
t	X ₃	0.5	1	1.5	2	2.5

The CCD 3-factors consisted of 20 experiments $(2^{J}+2J+m)$, where J is the number of factors and m the number of replicated center points), eight factorial points (2^{J}) , six axial points $(2 \times J)$, and six replicated center points (m= 6). The independent variables are coded to two levels namely: low (-1)and high (+1), whereas the axial points are coded as $-\alpha$ and $+\alpha$. In this study, modified $\alpha=2$ value was used which is the distance of the axial point from center and makes the design rotatable. The center points are usually repeated six times to determine the experimental error (pure error) and the reproducibility of the data [9].

The complete design matrix corresponding to the CCD design in terms of real and coded independent variable is presented in Table 3 with experimental results. The experiments were run at random in order to minimize errors from the systematic.

Table 3: Experiments	design	by	central	composite
rotatable	design	(C	CRD)	

Exp.	Real variables			Coded			Y
No.				variables			%
	Ν	Ccat	t h	X1	X2	X3	
	RPM	%					
1	400	2	1	-1	-1	-1	71
2	800	2	1	1	-1	-1	80
3	400	4	1	-1	1	-1	61
4	800	4	1	1	1	-1	72
5	400	2	2	-1	-1	1	87
6	800	2	2	1	-1	1	96
7	400	4	2	-1	1	1	71
8	800	4	2	1	1	1	80
9	200	3	1.5	-2	0	0	64
10	1000	3	1.5	2	0	0	93
11	600	1	1.5	0	-2	0	79
12	600	5	1.5	0	2	0	63
13	600	3	0.5	0	0	-2	65
14	600	3	2.5	0	0	2	98
15	600	3	1.5	0	0	0	79
16	600	3	1.5	0	0	0	80
17	600	3	1.5	0	0	0	78
18	600	3	1.5	0	0	0	81
19	600	3	1.5	0	0	0	82
20	600	3	1.5	0	0	0	79

III. Results and Discussion

3.1 General Analysis

Design-Expert software (6.0.6) with response surface methodology (RSM) and a central composite design (CCD) technique experiments design was used for statistical analyzing of the experimental data. A modified empirical second-order polynomial model (Eq.4) was obtained to predict biodiesel yield as a function of the selected three variables by applying the multiple regression analysis method of the experimental data. The coefficients of terms; N^2 , t^2 , Nt, NCcat, and tCcat were canceled because they were statistically insignificant.

$$Y = 35.13 + 0.03N + 8.375Ccat + 14.5t - 2.25Ccat^{2}$$
(4)

The analysis of variance (ANOVA) for biodiesel yield indicated that the correlation coefficient of the equation is 0.9482 with 2.86 % standard deviation. The high value of the correlation coefficient indicates a good correlation. Fig. 3 shows the yield predicted values versus the experimental values (actual) also indicating a good estimate of response for the system in the range studied.







Fig.3: Predicted vs. Actual biodiesel yield of Eq. 4

Fig. 4 shows the perturbation effect of agitation speed, catalyst concentration and reaction time on biodiesel yield. The yield increased linearly with increasing both agitation speed and reaction time. The effect of the two variables was almost identical. Negative effect of the catalyst amount was found above 2%. The perturbation was considered at center values for the three variables.



Fig. 4: Effect perturbation parameters on biodiesel yield

3.2 Effect of Catalyst Content

Figs. 5 and 6 show the effect of catalyst concentration on the yield biodiesel at different impeller speed and reaction time. Negative effect of the catalyst amount above 2% on the biodiesel yield on was noticed. This result is in agreement with that found by literature [7, 10]. This may be attributed to the formation of soap at an excessive amount of CaO catalyst leading the formation of an emulsion through increasing viscosity and complicates the recovery of the biodiesel [11].



Fig. 5: The effect of catalyst concentration at different agitation speeds, and at constant reaction time of 2 h.



Fig. 6: The effect of catalyst concentration at different reaction time and constant agitation speed of 800 RPM.

3.3 Effect of Impeller Speed

Fig. 7 shows the effect of impeller speed on the yield biodiesel at different reaction time and at constant 2% catalyst content. The yield linearly increased with increasing agitation speed in agreement with [6], and disagreement with [7]. At impeller speed of 400 rpm the yield of biodiesel reach 90% only at high reaction time (t>2.5 h). Whereas at impeller speed of 1000 rpm the yield of biodiesel reach 90% at reaction time t=1.5 h.

3.4 Effect of Reaction Time

Fig. 8 shows the positive relationship between reaction time and biodiesel yield. The yield linearly increased with increasing reaction time in agreement with that found by literature [10,12-13]. The effect of the two variables; impeller speed and reaction time was almost identical.







Fig. 7: The effect of agitation speed and reaction time at constant catalyst concentration of 2%.



Fig. 8: The effect of reaction time and agitation speed at constant catalyst concentration of 2%.

3.5 Process Optimization

The practical optimum yield of the biodiesel was about 96% at operating condition of impeller speed 800 RPM, catalyst amount 2 %, and reaction time 2 h, as shown in Figs. 9 and 10 for contour and 3D forms respectively. The yield above the practical optimum was of the empirical equation prediction and not really occurred. The catalyst amount was fixed at 2% to avoid the side reaction (saponification). Increasing both the impeller speed and reaction time, to their higher levels also increases the side reaction.



Fig. 9: The contour diagrams for the effect of both impeller speed and reaction time on biodiesel yield, at constant 2% catalyst content.





3.6 Reaction Kinetics

Assuming irreversible chemical reaction, the rate equation can be represented as follows [13]:

$$r = k C_{TG}^{\alpha} C_{MeOH}^{\beta}$$
(5)

For excess methanol, the equation becomes;

$$-r = k_{app} C_{TG}^{\alpha}$$
 (6)

The reaction order at optimum operating conditions; agitation speed (N=800rpm) and catalyst concentration (Ccat=2 %), was found to be first order reaction. Figs. 11 and 12 show the effect of agitation speed on the reaction rate constant of first order reaction. First order reaction was found to give good fit with respect to the concentrations of triglyceride at conditions near the optimum. The apparent reaction rate constants (k_{app}) were 1.31, 1.71, and 2.2 h⁻¹ for different impeller speeds of 600, 800, and 1000 RPM respectively. This result is in agreement with that found by literature [12-14].







Fig. 11: The reaction rate constant of first order reaction at different impeller speeds and at constant catalyst content =2%



Fig. 12: The effect of impeller speed on reaction rate constant

3.7 Power per Unit Volume (P/V)

The power per unit volume (P/V) required for the mechanical agitator of the reactor at conditions near the optimum was studied. For system in turbulent mode, the required power per unit volume for the mechanical agitator is calculated by the following equation [15]:

$$(P/V) = K \rho N^3 d^5 / V_R$$
 (4)

Where K is a constant, dependent on the impeller type (K=6 for radial impeller used), ρ is the density of biodiesel product (ρ =850kg/m³), d is the diameter of impeller (d=45mm) and V is the volume of reactor (V_R=1 liter).

Fig. 13 shows the effect of power per unit volume on the biodiesel yield at different reaction time (1.5, 2. and 2.5 h). The reaction time could be decreased to about 1.5 h at power per unit volume above 4 kW/m^3 .

Figure (14) shows the effect of power per unit volume of mechanical agitation on the reaction rate constant of first order reaction, which is more representative parameter than impeller speed.



Figure (13): The effect of power per unit volume and reaction time on the biodiesel yield



Figure (14): The effect of power per unit volume of mechanical agitation on reaction rate constant.

IV. Conclusions

- 1. The yield of biodiesel increased linearly with increasing both impeller speed and reaction time in the range studied. The effect of the two variables was almost identical.
- 2. Negative effect of the catalyst amount above 2% on the biodiesel yield was found.
- 3. The practical optimum yield of the biodiesel was about 96% at operating condition of impeller speed 800 RPM, catalyst amount 2 %, and reaction time 2 h.
- 4. First order reaction with respect to the concentrations of triglyceride was found at conditions near the optimum. The reaction rate constants were 1.31, 1.71, and 2.2 h⁻¹ for different impeller speeds of 600, 800, and 1000 RPM respectively; corresponding to the power per unit





A _V	Acid value	mg KOH/g		
Ccat	Catalyst content	%		
C _{MeOH}	Methanol concentration	mol/ m ³		
C _{TG}	Triglyceride Concentration	mol/m ³		
D	Vessel diameter	mm		
d	Diameter of impeller	mm		
FFA	Free fatty acid	%		
Κ	Impeller type constant	-		
k	Reaction rate constant	hr⁻¹		
k _{app}	Apparent reaction rate constant	hr ⁻¹		
Mw _{FAME}	Molecular weight of FAME	g/mole		
Mw _{gly}	Molecular weight of glycerol	g/mole		
Mw _{TG}	Molecular weight of triglyceride	g/mole		
Ν	Agitation speed	RPM		
Р	The consumed power	kw		
\mathbb{R}^2	Regression coefficient	-		
R _{AO}	Molar alcohol-to-oil ratio	-		
r	Rate of reaction	mole/m ³ h		
Т	Temperature	°C		
t	Reaction time	hr		
V	Volume of Mixture	m ³		
V _R	Volume of reactor	m ³		
WFAME	Weight FAME	g		
Wgly	Weight glycerol	g		
W _{TG}	Weight oil	g		
\mathbf{X}_1	Agitation speed coded variable	-		
X_2	catalyst content coded variable	-		
X_3	Reaction time coded variable	-		
Y	yield of biodiesel	-		
volum	(\mathbf{D}/\mathbf{V}) of 0.04 2.22 and	$1.26 \ 1 M/m$		

volume (P/V) of 0.94, 2.23, and 4.36 kW/m^3 respectively.

5. The power per unit volume (P/V) required for the mechanical agitator of the reactor at conditions near the optimum was studied. The reaction time decreased to about 1.5 h at power per unit volume above 4 kW/m^3 .

Nomenclature

Greek symbol

α	Order of triglyceride Conc.	-
β	Order of Methanol Conc.	-

Abbreviations

ANOVA	Analysis of variance
ASTM	American Society for Testing Materials
B ₁₀₀	pure biodiesel
CCD	Central Composite Design
DOE	Design of experiments
FAME	Fatty acid methyl esters
MeOH	Methanol
RSM	Response Surface Methdology
TG	Triglyceride
Av	Acid value
FFA	Free fatty acid

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