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Study of Parametric Effects and Kinetic Modeling of Trans-esterification Reaction for Biodiesel Synthesis

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Abstract

A kinetic study of KOH-catalyzed trans-esterification of sunflower oil with methanol is carried out. Overall trans-esterification reaction consists of three consecutive second-order reversible reaction steps. Effects of methanol-to-oil molar ratio (MR), reaction temperature and catalyst loading on fatty acid methyl esters (FAME), triglycerides (TG), diglycerides (DG) and monoglycerides (MG) are evaluated by using statistical approach of Taguchi method with L9 orthogonal array and analysis of variance (ANOVA). Orders of parametric effects on FAME, TG, DG and MG based on the relative contribution of the three parameters are presented. Catalyst loading is found to be a significant control parameter for FAME, TG and DG wherein insignificant parameter for MG. The temperature is insignificant for TG and DG reduction wherein it has an important influence on the minimization of MG. The combination of parameters which yielded ~95% of FAME with reasonable purity is 0.5 wt% catalyst loading, 50°C temperature and 7 MR.

Keywords: Kinetic modeling, taguchi method, trans-esterification, biodiesel.

Introduction

Biodiesel is considered as a possible alternative and future fuel for diesel engine due to the predicted shortage of fossil fuels and increase in the price of the petroleum. It is biodegradable, non-toxic, and environmentally benign with low emission profiles[1]. Biodiesel, a mixture of alkyl esters of fatty acids, is usually synthesized by the base-catalyzed trans-esterification of oils or fats with short chain alcohols. Different types of catalysts such as base, acid or lipase are used in trans-esterification for biodiesel synthesis but the base-catalyzed reaction is the most common in the industry due to easier, faster and cheaper processing[2].

The effect of various process parameters on trans-esterification reaction for biodiesel production is important to understand to produce cost-effective biodiesel. A statistical Taguchi approach has been used by several researchers to analyze the parametric effects on the trans-esterification process[3-6]. Taguchi method is a statistical analysis of a system and utilizes various orthogonal arrays for the design of experiments[7-8]. Taguchi orthogonal array, where only a fraction of the total combination of parameters is considered, minimizes the number of experiments while covering a wide range of operating conditions and keeping all the information/data intact.

Yusup and Khan (2010)[3] used Taguchi design of experiments and studied the effects of catalyst amount, temperature and alcohol-to-oil ratio on fatty acid methyl esters (FAME or biodiesel) yield. They reported that the yield of FAME exceeded 98% after 5 h of reaction at the optimum reaction condition: 55°C temperature, 8:1 methanol-to-oil molar ratio and 2 wt% of potassium hydroxide (KOH). Ramezani et al. (2010)[4] investigated the effects of parameters on castor oil trans-esterification reaction using Taguchi method consisting four parameters and three levels. Reaction temperature (25, 65 and 80°C), mixing intensity (250, 400 and 600 rpm), alcohol/oil ratio (4:1, 6:1 and 8:1) and catalyst amount (0.25, 0.35 and 0.5%) were selected as experimental parameters. It has been concluded that the reaction temperature and mixing intensity can be optimized only. Optimization of temperature, reactants proportion and methods of purification for trans-esterification of sunflower oil was carried out by Antolin et al. (2002)[5] using Taguchi methodology. The best combination of variables with prescribed washing method is reported as 0.28 wt% KOH, 3 alcohol-to-oil ratio and 70°C at which the biodiesel yield >96% was reached. The standard L16 (4^5) orthogonal array of experiments with four main process conditions (i.e. methanol quantity, reaction time, reaction temperature and catalyst amount) in the trans-esterification of camelina oil for obtaining the maximum biodiesel yield were investigated by Wu and Leung[6]. The optimal experimental condition, based on the results of range analysis and analysis of variance (ANOVA), was reported to be 8 methanol-to-oil ratio, 50°C temperature, 1 wt% KOH and a reaction time of 70 min. 98.4% FAME yield was obtained at optimal condition and based on F-value (the significance factor), the order of process parameters for FAME yield was given as catalyst amount > reaction time > molar ratio > temperature.

Other such studies for process optimization using Taguchi method are mainly based on FAME yield. There are no reports in the open literature that quantify the contribution of individual

parameters or relative significance of individual parameters toward overall reaction kinetics where overall reaction entails the presence of FAME, triglycerides (TG), diglycerides (DG) and monoglycerides (MG) in the reaction mass. The relative contributions of ultrasonic power, ultrasonic frequency, methanol-to-oil molar ratio and catalyst loading were evaluated for trans-esterification of soybean oil using Taguchi optimization methodology with standard L9 orthogonal array[9]. However, these contributions or significance of parameters were only for FAME yield. Therefore, a study is required to understand how the overall trans-esterification kinetics (FAME, TG, DG and MG) is affected by the various parameters such as alcohol-to-oil molar ratio, reaction temperature, duration of reaction and catalyst concentration to maximize the yield and purity of alkyl esters. With this study in view a statistical Taguchi design of experiments is used here. KOH-catalyzed trans-esterification of sunflower oil with methanol is carried out and kinetic modeling of biodiesel synthesis is also presented.

Material and Methods

Reagents: Methanol (GR grade, moisture < 0.02%), water (HPLC grade), *n*-hexane (HPLC grade), acetonitrile (chromatography LiChrosolv), hydrochloric-acid (35 wt%) and glacial acetic acid are supplied by Merck India Ltd. Refined sunflower oil (max. 0.1 wt% FFA) is purchased from Liberty Oil Mills Ltd., Mumbai, India. Potassium hydroxide (extra pure AR) is supplied by Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Standard diglycerides (dipalmitin, distearin, diolein and dilinolein glycerides) and standard monoglycerides (monopalmitin, monostearin, monoolein and monolinolein glycerides) are purchased from Nu-Chek Prep, Inc., USA. Standard sunflower-FAME is prepared in the laboratory and refined sunflower oil is treated as standard triglycerides. These standard glycerides and esters are used as references for calibration of FAME, TG, DG and MG using High Performance Liquid Chromatography (HPLC) analytical method to monitor trans-esterification reaction as discussed later.

Table-1
L9 orthogonal array (Taguchi design of experiments) for trans-esterification of sunflower oil

Exp. No.	Catalyst Loading (wt%)	Temperature (°C)	Molar Ratio (MR)	Empty (e)[a]
1	0.1	40	3	1
2	0.1	50	5	2
3	0.1	60	7	3
4	0.3	40	5	3
5	0.3	50	7	1
6	0.3	60	3	2
7	0.5	40	7	2
8	0.5	50	3	3
9	0.5	60	5	1

[a] Empty means not filled by any parameter and 1, 2, 3 are coded units.

Taguchi design of experiments: In this study, standard L9 (3^4) orthogonal array of experiments are conducted for KOH-catalyzed trans-esterification of sunflower oil with methanol. The design matrix of experiments is shown in table 1. First three columns are filled with reaction parameters; the last one is left empty, which carries two degree of freedom for residual error and is used for calculation of F-value in ANOVA. Reaction parameters are varied at three levels each: catalyst loading, 0.1-0.3-0.5 wt%; temperature, 40-50-60°C; and molar ratio (MR), 3-5-7. MR is defined as ratio of moles of methanol to moles of sunflower oil. Catalyst loading (wt%) is determined based on amount of oil.

Experimental Procedure: 200 g of refined sunflower oil is taken in a 1-liter, 4-neck round bottom flask. The flask is placed in an oil bath and heated up to the set reaction temperature. Calculated amount of KOH-methanol solution is heated up to the set reaction temperature in a separate round bottom flask fitted with a condenser. Pre-heated KOH-methanol solution is then added to the sunflower oil flask. Point of addition of KOH-methanol solution is considered as the starting time of the reaction. Through out the reaction, the mixture is stirred at 600-700 RPM. 5 ml *n*-hexane is taken in 25 ml vials, which are kept in the salt–ice bath. Samples (2-3 ml each) are drawn from the reactor for analysis at different intervals. Samples are then transferred to 25 ml vials and well mixed with cold *n*-hexane to stop the reaction. To neutralize KOH catalyst present in the sample, 5 ml of aqueous HCl-solution is added gradually using burette and followed by centrifuging for 15 minutes (4000 RPM) to separate the aqueous and organic layers. Aqueous layer is removed by a pipette and discarded. Then, the organic layer is washed with 4-5 ml of water and the mixture is centrifuged to remove excess HCl from the organic layer. The washing step is repeated two more times to ensure complete removal of HCl. The washed organic layer is transferred to a 10 ml vial which is kept in a vacuum oven at 70°C to remove water, methanol, and *n*-hexane.

Experimental Analysis and Data Interpretation: HPLC with Eclipse XDB-C18 column has been used for analysis of FAME, TG, DG and MG. Acetonitrile is used as mobile phase at a flow rate of 1.0 ml/min, detector wavelength is fixed at 205nm and composition is analyzed by ChemStation software. Approximately 0.025 g of sample is dissolved in 5 ml of iso-propanol and *n*-hexane mixed solvent (ratio IPA:hexane is 5:4 v/v). The HPLC column is very sensitive to pH of the solution. Therefore, care has been taken to remove all the acids and alkali from the sample to keep sample pH at 7. Each chromatographic run is performed using Gradient method with the following solvent systems: liquid B = water with 0.1 % acetic acid; liquid C (5:4 v/v) = IPA:Hexane; and liquid D = ACN with 0.1 % acetic acid. Taguchi analysis with signal-to-noise ratio (SN ratio) and analysis of variance (ANOVA) are done with MINITAB 15 software and available spreadsheet templates on the website www.ee.iitb.ac.in/~apte/CV_PRA_TAGUCHI.htm. Kinetics modeling is carried out with non-linear regression

fitting of kinetic data to reaction rate models using a MATLAB code. The strategy of the ANOVA calculations is to statistically analyze the variation that each parameter causes relative to the total variation observed in the results.

Results and Discussion

Kinetic Modeling: The overall trans-esterification process for biodiesel synthesis is a sequence of three consecutive reversible reactions as shown in reaction scheme 1[10]. In the first reaction, diglyceride (*DG*) is obtained from triglycerides (*TG*); in the second, monoglyceride (*MG*) is produced from diglyceride; in the third reaction, glycerol (*Gly*) is obtained from monoglycerides. In all the reactions biodiesel (*FAME*) is produced.

$$Triglyceri\ des\ (TG) + Methanol\ (A) \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} Diglycerid\ es\ (DG) + Biodiesel\ (FAME)$$

$$Diglycerid\ es\ (DG) + Methanol\ (A) \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} Monoglycer\ ides\ (MG) + Biodiesel\ (FAME)$$

$$Monoglycer\ ides\ (MG) + Methanol\ (A) \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} Glycerol\ (Gly) + Biodiesel\ (FAME)$$

Reaction Scheme 1. Overall trans-esterification reaction of sunflower oil with methanol. Concentrations of TG, DG, MG and FAME are measured at different intervals of time (0.5, 1, 3, 6, 10, 15, 25, 40 and 60 minutes). Figure 1 shows these concentrations for the experiment L9/3 and L9/8. Rapid decrease in TG and increase in FAME with time is observed. Variation in DG and MG is non-monotonous as both of them increase in the first few minutes of the reaction reaching to maxima (peak) after which they both decrease and attain equilibrium. Similar behavior is observed for all L9 experiments. Maximum yield of FAME is found to be 89.79% is obtained from the experiment L9/9 (i.e. 0.5 wt% catalyst loading, 60 °C temperature and 5 MR).

Mixing of methanol with oil forms two immiscible phases as methanol is insoluble in oil. However, as soon as the methyl esters appear in the reaction system, esters act as a co-solvent for the system because esters are soluble in the vegetable oil and also in the methanol. As a result, the reaction shows an induction period because mass transfer controls the kinetics in the beginning of the reaction[11]. It is observed that the conversion of oil is a strong function of stirring speed until 600 RPM; above this speed the reactions are not limited by mass transfer. Therefore, the stirring speed is maintained at 600-700 RPM during the experiments. The pseudo-homogeneous models for reversible second-order kinetics considered are as follows:

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_{-1}[DG][FAME] \quad (1)$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_{-1}[DG][FAME] - k_2[DG][A] + k_{-2}[MG][FAME] \quad (2)$$

$$\frac{d[MG]}{dt} = k_2[DG][A] - k_{-2}[MG][FAME] - k_3[MG][A] + k_{-3}[Gly][FAME] \quad (3)$$

$$\frac{d[FAME]}{dt} = k_1[TG][A] - k_{-1}[DG][FAME] + k_2[DG][A] - k_{-2}[MG][FAME] + k_3[MG][A] - k_{-3}[Gly][FAME] \quad (4)$$

Consumption of methanol and formation of glycerol are estimated by mass balance:

$$[A] = MR * [TG]_0 - [FAME] \quad (5)$$

$$[Gly] = [TG]_0 - ([TG] + [DG] + [MG]) \quad (6)$$

The differential equations 1-4, coupled with mass balance equations 5-6, are solved using a MATLAB code to determine the rate constants $(k_1, k_{-1}, ..., k_{-3})$. The predicted results are compared with experimentally measured concentrations at different intervals of time. The difference between the experimental and predicted concentrations are squared and summed up:

$$F = \Sigma (Experimental\ Conc. - Predicted\ Conc.)^2 \quad (7)$$

The rate constants are obtained by minimizing F in equation 7 by *fmincon* (built-in optimization routine) of MATLAB. The final optimal values of the rate constants are used to predict the concentrations of different species shown in figure 1. Good agreement between reaction kinetic models and experiment is found. Three consecutive reversible reaction steps with second-order pseudo-homogenous rate models are also reported by Karmee et al. (2006)[12] for trans-esterification of pongamia oil and Cao et al. (2009)[13] for trans-esterification of canola oil. F is minimized for each of the L9 experiments and the optimum rate constant values for all the experiments are shown in table 2.

From table 2, the trends in equilibrium constants (rate constant quotient) found is $K_3 > K_1 > K_2$ which is similar to those reported by Karmee et al.[12]. The trends observed for the backward rate constants of the three steps is $k_{-2} > k_{-1} > k_{-3}$, which means that the reversibility rate of the third step is small. The exact similar trend among the backward rate constants is also found by others[10,11,14]. Such trends, however, are not found for the forward rate constants. Among the forward rate constants, the following trends are observed: $k_2 > k_1$; $k_2 > k_3$ except in L9/1 and L9/8 experiments; and there is no relationship between k_1 and k_3. According to the Karmee et al.[12], k_1 was the highest and k_2 was the smallest i.e. $k_1 > k_3 > k_2$. Noureddini and Zhu[11] reported that $k_3 > k_2 > k_1$ for trans-esterification of soybean oil with methanol at 50°C using NaOH as catalyst. For trans-esterification of soybean oil with butanol using NaOBu as catalyst, Freedman et al.[14] observed that $k_1 > k_2 > k_3$ just opposite to Noureddini and Zhu[11]. Therefore, more detailed work is required to understand the relationships between the forward rate constants. Such work is beyond the scope of this paper.

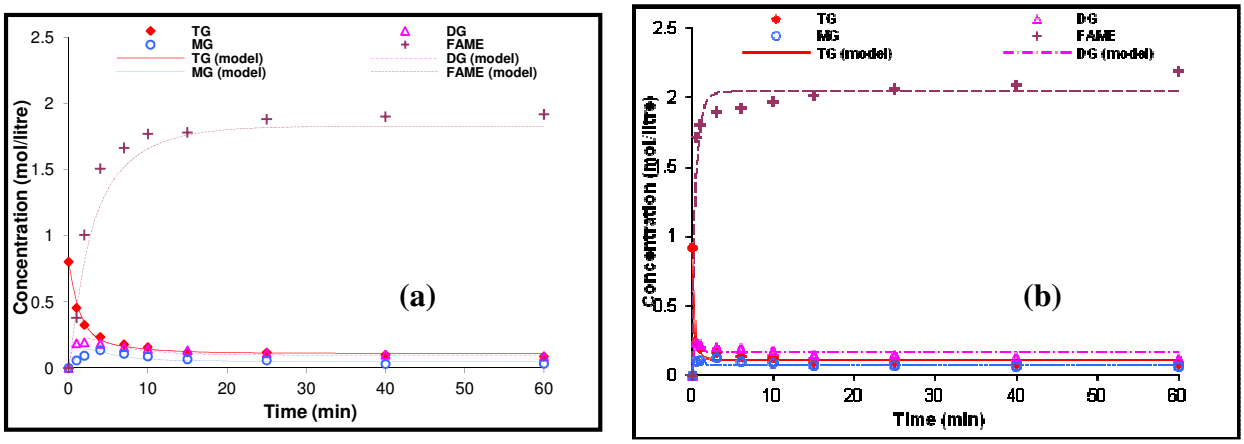


Figure-1
Kinetic model fit vs experiment for (a) Experiment L9/3: 0.1 wt% KOH, 60 °C and 7 MR (b) Experiment L9/8: 0.5 wt% KOH, 50 °C and 3 MR. Circle, diamond, triangle and + are experimental values and lines are predicted values from kinetic rate models

Table-2
Optimal values of rate constants and rate constants quotient for L9 experiments.

Rate Constant[a]	L9 Experiments								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
k_1	0.07907	0.131461	0.090845	0.207593	0.203569	1.00201	0.200918	1.415123	0.942145
k_{-1}	0.083783	0.244563	0.213753	0.348015	0.545541	0.341728	0.418977	0.350218	0.563147
k_2	0.103258	0.210114	0.171481	0.358226	0.316015	1.45974	0.290328	2.776	1.778532
k_{-2}	0.137154	0.424852	0.685387	0.689943	0.966319	0.777782	0.532398	2.191179	1.944903
k_3	0.209015	0.114279	0.13413	0.138503	0.090445	1.221494	0.143884	3.2363	1.644001
k_{-3}	0.04881	0.023043	0.02612	0.037037	0.011021	0.156015	0.039814	0.143025	0.144713
$K_1 = k_1/k_{-1}$	0.943747	0.537534	0.424999	0.596505	0.373151	2.932186	0.479544	4.040695	1.673
$K_2 = k_2/k_{-2}$	0.752857	0.494558	0.250196	0.519211	0.327029	1.876797	0.545323	1.266898	0.914458
$K_3 = k_3/k_{-3}$	4.282206	4.9594	5.135103	3.739593	8.206762	7.829335	3.613934	22.62748	11.36041

[a] Units of rate constants is liter.mol^{-1}.min^{-1} and K_1, K_2 and K_3 are rate constants quotient

Effects of Reaction Parameters on Kinetics of FAME, TG, DG and MG: Selection of proper response factor is important in Taguchi method to avoid misleading and ambiguity in results from SN ratio analysis and ANOVA[7]. Moles of TG, DG, MG and FAME after 60 minutes of reaction, instead of concentration in mol/liter, are treated as response factors for Taguchi analysis. Moles of FAME, DG and MG formed and moles of TG left in the reaction mixture are calculated based on initial 0.228311 moles (200 g) of sunflower oil for all the experiments. Target is to get maximum yield of biodiesel, however, DG and MG are formed as byproducts in overall trans-esterification reaction. It is discussed earlier (figure 1) that DG and MG increases in the initial period of the reaction but later on both of them decrease and attain equilibrium. Therefore, maximum yield of biodiesel can be achieved when the residual TG, DG and MG are lowest in the reaction mixture. Hence, to get the best combination of parameters for maximum yield of FAME, Taguchi analysis is carried out by applying 'larger-is-better' SN ratio for FAME as presented in equation 8 and 'smaller-is-better' SN ratio for TG, DG and MG as shown in equation 9. Maximization of 'larger-is-better' SN ratio results in maximization of FAME yield and maximization of 'smaller-is-better' SN ratio results in minimization of TG, DG and MG.

$$'Larger\text{-}is\text{-}better'\ \ SN\ ratio = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (8)$$

$$'Smaller\ \ -is\text{-}better'\ \ SN\ ratio = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}y_i^2\right) \quad (9)$$

where y is response factor and n is number of observations.

Figure 2 shows parity plot between predicted-SN ratio from Taguchi additivity model (linear model analysis of SN ratios) and observed-SN ratio from experimental values of FAME, TG, DG and MG. It can be seen that the predicted values match the observed values reasonably well within the range of experimental conditions, with R^2 >96%. The plot suggests the applicability and reliability of the Taguchi analysis over a range of experimental conditions with sufficient degree of accuracy.

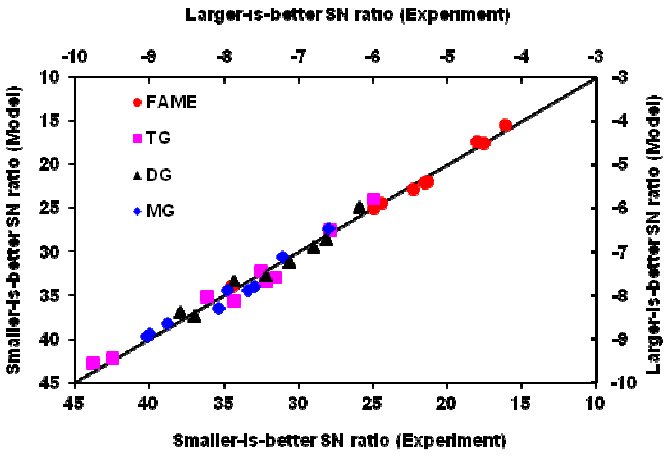


Figure-2
Parity plot for SN ratio of FAME, TG, DG and MG

ANOVA table for SN ratio analysis of FAME, TG, DG and MG are given in tables 3, 4, 5 and 6, respectively. Calculation of sum of square (*SS*), variance (*V*), F-values and percentage relative contribution (*RC*) are expressed in equations 10-13, respectively.

$$SS_P = \frac{SN_1^2}{N_1} + \frac{SN_2^2}{N_2} + \frac{SN_3^2}{N_3} \quad (10)$$

$$Vp = \frac{SS_P}{DF_P} \quad (11)$$

$$F\text{-}value = \frac{SS_P}{V_e} \quad (12)$$

$$RC = SS_P * 100 / SS_T \quad (13)$$

where SS_T is the total sum of squares; SS_P is the sum of square due to parameter P; SN_1 is the sum of SN ratio of experiments involving parameter P at level 1; N_1 is the number of experiments containing parameter P at level 1; V_P is the variance due to parameter P; V_e is the error variance; DF_P is the degree of freedom of parameter.

The F-value is used as a criterion to distinguish the important and less significant parameters. In this study, every reaction parameter and error variance has two degrees of freedom. Hence, a parameter has an important influence on the response if the F-value is ≥ 9 (confidence level of 90%), significant influence if the F- value is ≥19 (confidence level of 95%) and very significant influence if the F- value ≥ 99 (confidence level of 99%). It should be noted that the validity of interpretation of ANOVA table is only within the range of the levels considered for the parameters. It does not imply that if the F-value for a parameter is < 9 then the parameter has no effect on the response absolutely. Instead, it simply means that the variation in the response due to changes in the levels of parameter is insignificant compared to the errors in the range of the selected levels.

Effects on Biodiesel (FAME): The main effects plot in Figure 3a shows those 'larger-is-better' SN ratio increases with the increase in catalyst loading, temperature and MR which implies that the yield of FAME increases with the increase in these parameters. According to the design array in table 1, fourth column is not filled by any parameter and kept empty. Therefore, no effect should be appearing in the main effect plot and a straight line along the Mean-line is expected. However, in practice, some effects often appear as residual error which infers one or more of the following: the presence of interaction between the parameters, missing of any major process parameter(s), presence of noise (uncontrollable factors) and experimental error in measured response factor, etc. Some little effect due to empty column can be seen in Figure 3a. However, it is found from percentage contribution calculation that the residual error is 0.84% only as shown in figure 3b. Residual error less than 5% can be ignored without losing any significant information from the observed results[8]. Catalyst loading contributes 46.44% to FAME yield which is followed by 40.71% contribution of MR as shown in figure 3b. Catalyst loading and MR have significant effect on FAME yield with 95% confidence level as F-value > 19 (table 3). However, temperature has an important influence with 90% confidence level (19 > F-value > 9) even though the relative contribution of temperature is 12.02% (figure 3b) which is much smaller in comparison to the catalyst loading and MR contributions.

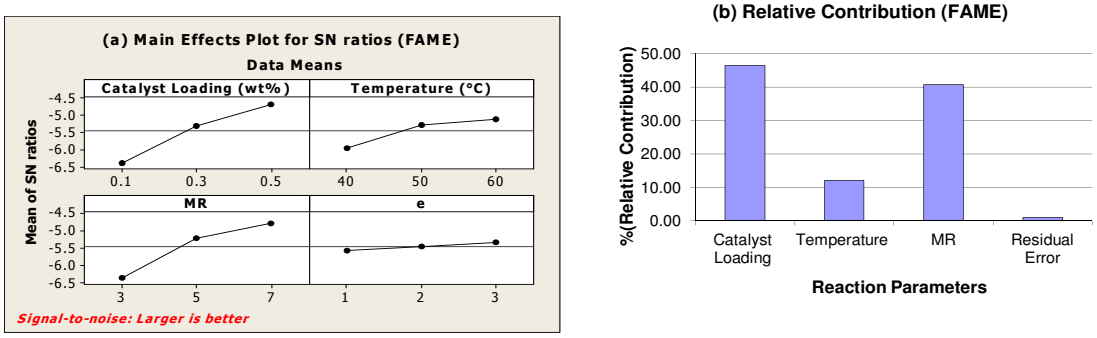


Figure-3
Effect of reaction parameters on biodiesel (FAME) after 60 minutes of reaction (a) Main effect plot for 'larger-is-better' SN ratio analysis (b) Relative contribution of parameters within the range studied.

Table-3
ANOVA table for 'larger-is-better' SN ratio of FAME

Parameters	Degree of Freedom (*DF*)	Sum of Square (*SS*)	Variance (*V*)	F-value	
Catalyst loading	2	4.47997	2.239985	55.418	Significant[a]
Temperature	2	1.1595	0.579750	14.343	Significant[b]
MR	2	3.92718	1.963590	48.580	Significant[a]
Residual error	2	0.08084	0.040420		
Total	8	9.64749			

[a] Significant at 95% confidence: F(0.05,2,2) = 19 (Bagachi)[8], [b] Significant at 90% confidence: F(0.05,2,2) = 9 (Bagachi, 1993)[8]

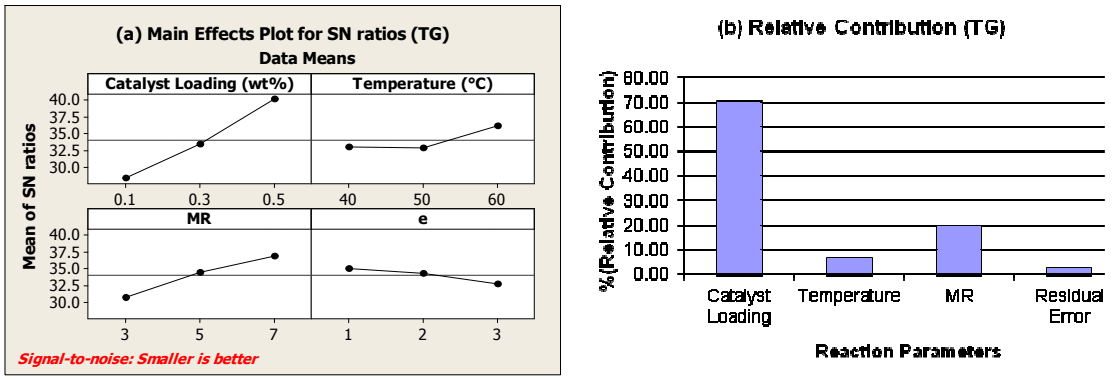


Figure-4
Effect of reaction parameters on TG after 60 minutes of reaction (a) Main effect plot for 'smaller-is-better' SN ratio analysis (b) Relative contribution of parameters within the range studied

Table 4
ANOVA table for 'smaller-is-better' SN ratio analysis of TG

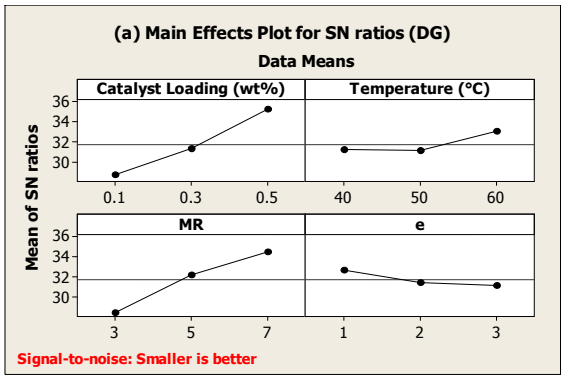
Parameters	Degree of Freedom (*DF*)	Sum of Square (*SS*)	Variance (*V*)	F-value	
Catalyst loading	2	213.148	106.574000	26.409	Significant[a]
Temperature	2	20.96	10.480000	2.597	
MR	2	60.675	30.337500	7.518	
Residual error	2	8.071	4.035500		
Total	8	302.854			

[a] Significant at 95% confidence: F(0.05,2,2) = 19 (Bagachi)[8], [b] Significant at 90% confidence: F(0.05,2,2) = 9 (Bagachi)[8]

Effects on Triglycerides (TG): The main effects plot in figure 4a shows that the 'smaller-is-better' SN ratio increases with the increase in catalyst loading, temperature and MR which implies that TG decreases in reaction mixture with the increase in these parameters. Figure 4b shows that in the reduction of TG, the catalyst loading has the major contribution of 70.38% followed by MR contribution of 20.03%. Contribution of temperature is found to be less than 10%, (6.92% only). According to the F-value criterion, only catalyst loading has significant effect on TG reduction with 95% confidence level as F-value > 19 (table 4). F-values for MR and temperature are less than 9 and thus, both parameters are insignificant which means reduction in TG due to changes in the levels of MR and temperature are insignificant compared to the errors in the range of the parameters studied. Residual error is found to be 2.66% the calculation of percentage relative contribution (figure 4b).

Effects on Diglycerides (DG): The main effects plot in Figure 5a shows that the 'smaller-is-better' SN ratio increases with the increase in catalyst loading, temperature and MR which directly implies that DG decreases in reaction mixture with the increase in these parameters. Figure 5b shows that in the minimization of DG, the catalyst loading has 48.88% contribution which is followed by MR contribution as 42.14%. Contribution of temperature is found to be 5.70% only (less than 10%). Catalyst loading and MR have the important influence on DG minimization with 90% confidence level as F-value is > 9 and < 19 (table 5). F-value for temperature is far less than 9 and thus, defined insignificant which means reduction in DG due to changes in the levels of temperature is insignificant compared to the errors in the range of the parameters studied. Residual error is found to be 3.28% from the calculation of percentage relative contribution (figure 5b).

Effects on Monoglycerides (MG): The main effects plot in Figure 6a shows that the 'smaller-is-better' SN ratio increases with the increase in catalyst loading, temperature and MR which directly implies that MG decreases in reaction mixture with the increase in these parameters. Figure 6b shows that in the minimization of MG, the MR has 48.43% contribution which is followed by temperature contribution as 40.97%. Contribution of catalyst loading is found to be 7.05% only (less than 10%) unlike the case of FAME, TG and DG where the impact of catalyst loading is large and contributes more than 40%. MR and temperature have important influence on MG minimization with 90% confidence level as F-value is > 9 and < 19 (table 6). F-value for catalyst loading is far less than 9 and thus, defined insignificant which means reduction in MG due to changes in the levels of catalyst loading is insignificant compared to the errors in the range of the parameters studied. Residual error is found to be 3.56% from the calculation of percentage relative contribution (see figure 6b).



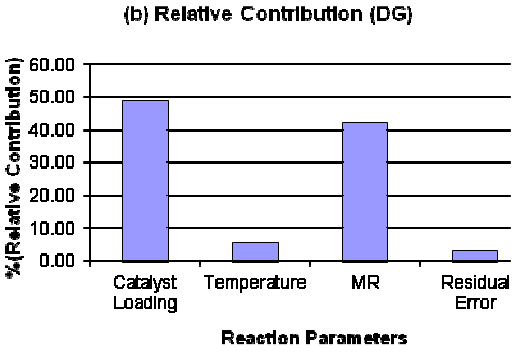


Figure-5

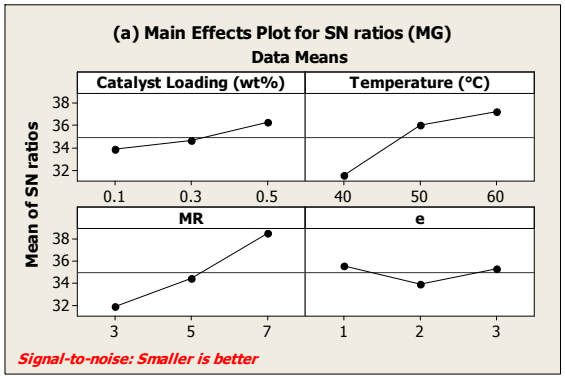
Effect of reaction parameters on DG after 60 minutes of reaction (a) Main effect plot for 'smaller-is-better' SN ratio analysis (b) Relative contribution of parameters within the range studied

Table-5

ANOVA table for 'smaller-is-better' SN ratio analysis of DG

Parameters	Degree of Freedom (*DF*)	Sum of Square (*SS*)	Variance (*V*)	F-value	
Catalyst loading	2	63.162	31.581000	14.914	Significant[b]
Temperature	2	7.367	3.683500	1.740	
MR	2	54.442	27.221000	12.855	Significant[b]
Residual error	2	4.235	2.117500		
Total	8	129.206			

[a] Significant at 95% confidence: F(0.05,2,2) = 19 (Bagachi)[8], [b] Significant at 90% confidence: F(0.05,2,2) = 9 (Bagachi)[8]



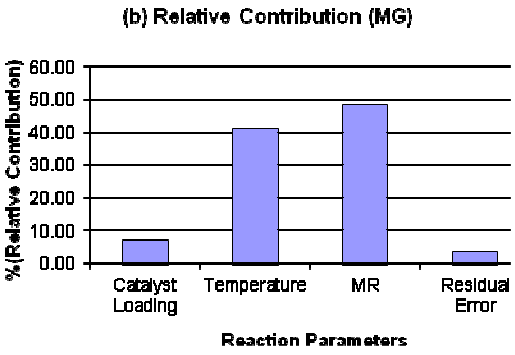


Figure-6

Effect of reaction parameters on MG after 60 minutes of reaction (a) Main effect plot for 'smaller-is-better' SN ratio analysis (b) Relative contribution of parameters within the range studied

Table-6
ANOVA table for 'smaller-is-better' SN ratio analysis of MG

Parameters	Degree of Freedom (*DF*)	Sum of Square (*SS*)	Variance (*V*)	F-value	
Catalyst loading	2	9.765	4.882500	1.981	
Temperature	2	56.769	28.384500	11.517	Significant[b]
MR	2	67.116	33.558000	13.617	Significant[b]
Residual error	2	4.929	2.464500		
Total	8	138.579000			

[a] Significant at 95% confidence: F(0.05,2,2) = 19 (Bagachi)[8], [b] Significant at 90% confidence: F(0.05,2,2) = 9 (Bagachi)[8]

Discussion and Verification Experiments: It is observed from Main effects plots (figures 3-6) for FAME, TG, DG and MG (in the reaction mixture after 60 minutes of reaction) that FAME increases with simultaneous decrease in TG, DG and MG with the increase in catalyst loading, temperature and MR. Increase in FAME with the increase in catalyst loading and temperature is also observed by Vicente et al.,[10]. Freedman et al.[15] observed that higher temperature is favored for trans-esterification of refined soybean oil and gave higher reaction rate and conversion to produce FAME at 6 MR and 1% NaOH. Yusup and Khan[3] reported that FAME increased over the course of temperature from 45 °C to 65 °C. In the same study of Yusup and Khan[3], it was found that FAME increased by increasing the amount of KOH from 0 to 2 wt% and FAME exceeded 98% after 5 h of reaction at 2 wt% while temperature and MR was kept constant at 55 °C and 8:1, respectively. Georgogianni et al.[16] used KOH catalyst in trans-esterification of sunflower seed oil at 2.0 wt% catalyst amount and FAME was produced close to 95%. Colucci et al.[17] reported 95% FAME as well using 2.2% KOH. Though high temperature and catalyst amount favor the FAME yield but higher MR at high catalyst amount causes soap formation[3]. Yusup and Khan[3] varied MR from 6 to 10 and catalyst from 0 to 2 wt%, and the optimized values are reported to be 8 MR and 2 wt% for the best result. In this study, MR ranges from 3 to 7 and KOH amount is used up to 0.5 wt%. Therefore, increase in FAME with the increase in MR and catalyst loading is found as shown by main effects plot (figure 3).

The residual error is found to be less than 5% in all the cases (ANOVA for SN ratio of FAME, TG, DG and MG) and hence, the total contribution of parameters studied to overall kinetics is more than 95% ─ which means that the kinetics are captured by the reaction parameters considered. Sequence of effects of parameters based on contribution is observed as follows catalyst loading > MR > temperature except for MG where the sequence is MR > temperature > catalyst loading. Based on F-value, the order of process parameters for FAME yield was also given by Wu and Leung[6] as catalyst amount > reaction time > molar ratio > temperature. However, in all the cases, contribution of MR is more than temperature. Except for MG, catalyst loading contribution to FAME, TG and DG is found more than 40% and the temperature contribution to FAME, TG and DG is found to be least. Also, according to the F-value criterion based on 90% and 95% confidence level, catalyst loading is found to be a significant control parameter for FAME, TG and DG whereas the effect of temperature is insignificant for TG and DG. However, temperature has the contribution of 40.97% and an important influence on the minimization of MG wherein catalyst loading is an insignificant parameter based on F-value criterion.

The combination of parameters over a range of experimental conditions, to achieve maximum yield and high purity of FAME, is searched through the prediction of FAME and MG using Taguchi additivity model (linear model analysis). As the reliability of the Taguchi analysis over a range of experimental conditions with sufficient degree of accuracy is found (discussed earlier), which means that the Taguchi additivity models can be used to predict FAME, TG, DG AND MG within the range of parameters studied. Based on discussion in the preceding paragraph, it can be deduce that (i) higher level of catalyst loading and MR is required for maximization of FAME and minimization of TG and DG (ii) higher level of temperature and MR is needed to minimize MG, which is important for high purity of FAME. Therefore, FAME and MG are predicted at different temperatures with fixed 0.5 wt% catalyst loading and 7 MR. FAME and MG are shown in percent by mole (mol%), which is calculated based on initial 0.228311 moles (200 g) of sunflower oil.

At 40, 50 and 60°C, the predicted values of FAME with 95% confidence interval are 87.00 (±4.65), 93.87 (±5.0) and 95.75 (±4.9) mol%, respectively, while predicted values of MG are 7.19 (±2.82), 4.21 (±1.65) and 3.67 (±1.44) mol%, respectively. Higher yield of FAME with minimum MG are predicted at 50 and 60°C. Therefore, the verification experiments at 50 and 60°C are performed only to prove the effectiveness of the Taguchi method and the validity of the observed results. Yield of FAME is found to be 94.45 and 96.32 mol% in the verification experiments at 50 and 60°C, respectively, wherein 3.39 and 2.90 mol% of MG is also found, respectively, in the reaction mixture. These experimental values are in good agreement with predicted values. However, it can be seen that there is small difference in mol% of FAME, as well as mol% of MG, between 50 and 60°C. Therefore, ~95% FAME can be yield with reasonable purity at the combination of parameters as 0.5 wt% catalyst loading, 50°C temperature and 7 MR. In trans-esterification of camelina seed oil, 98.4% FAME yield was obtained by Wu and Leung[6] at optimized experimental condition: 8 MR, 50°C temperature, 1 wt% KOH and reaction time of 70 min. The high yield of FAME obtained by Wu and Leung is due to the nature of the oil and the higher amount of catalyst used.

Conclusion

Fewer experiments are required using Taguchi method for KOH-catalyzed trans-esterification of sunflower oil to evaluate the effects of methanol-to-oil molar ratio (MR), reaction temperature and catalyst loading on fatty acid methyl esters (FAME), triglycerides (TG), diglycerides (DG) and monoglycerides (MG). Overall trans-esterification reaction consists of three consecutive second-order reversible reaction steps which are mathematically modeled and good fit with experiments is obtained. Main effects plots showed that FAME increases with simultaneous decrease in TG, DG and MG when catalyst loading, temperature and MR increase. Order of parametric effects based on relative contribution is observed as catalyst loading > MR > temperature except for MG where the sequence is MR > temperature > catalyst loading. However, relative contribution of MR is found to be more than temperature for all the cases, i.e. FAME, TG, DG and MG. Relative contribution of catalyst loading on FAME, TG and DG is found to be >40% and the temperature contribution is found to be least. Catalyst loading is found to be a significant control parameter for FAME, TG and DG wherein insignificant parameter for MG. The temperature is insignificant for TG and DG reduction wherein it has an important influence on the minimization of MG. The combination of parameters which yielded ~95% of FAME with reasonable purity is 0.5 wt% catalyst loading, 50°C temperature and 7 MR.

References

1. Xie W., Peng H. and Chen L., Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology, *Appl. Catal, A*, **300**, 67–74 (**2006**)

2. Ma F. and Hanna M.A., Biodiesel production: A review, *Bioresour. Technol.*, **70 (1)**, 1–16 (**1999**)

3. Yusup S. and Khan M.A., Base catalyzed transesterification of acid treated vegetable oil blend for biodiesel production, *Biomass Bioener.*, **34**, 1500–1504 (**2010**)

4. Ramezani K., Rowshanzamir S. and Eikani M.H., Castor oil transesterification reaction: A kinetic study and optimization of parameters, *Energy*, **35**, 4142–4148 (**2010**)

5. Antolin G., Tinaut F.V., Briceno Y., Castano V., Perez C. and Ramirez A.I., Optimisation of biodiesel production by sunflower oil transesterification, *Bioresour, Technol.*, **83**, 111–114 (**2002**)

6. Wu X. and Leung D.Y.C., Optimization of biodiesel production from camelina oil using orthogonal experiment, *Applied Energy*, **88**, 3615–3624 (**2011**)

7. Phadke M.S., Quality Engineering Using Robust Design, 1st Low Price edition, Pearson Education (**2008**)

8. Bagachi T.P., Taguchi Methods Explained: Practical Steps to Robust Design, Prentice-Hall of India Pvt. Ltd, New Delhi (**1993**)

9. Mahamuni N.N. and Adewuyi Y.G., Application of Taguchi method to investigate the effects of process parameters on the transesterification of soybean oil using high frequency ultrasound, *Energy Fuels*, **24**, 2120–2126 (**2010**)

10. Vicente G., Martinez M., Aracil J. and Esteban A., Kinetics of Sunflower Oil Methanolysis. Ind. Eng. Chem. Res., **44**, 5447–5454 (**2005**)

11. Noureddini H. and Zhu D., Kinetics of Transesterification of soyabean oil, *J. Am. Oil Chem. Soc*., **74**, 1457 – 1463 (**1997**)

12. Karmee S.K., Chandna D., Ravi R. and Chadha A., Kinetics of base-catalyzed transesterification of triglycerides from pongamia oil, *J. Am. Oil Chem. Soc*., **83 (10)**, 873-877 (**2006**)

13. Cao P., Tremblay A.Y. and Dube M.A., Kinetics of canola oil transesterification in a membrane reactor, Ind. Eng. Chem. Res., **48**, 2533–2541 (**2009**)

14. Freedman B., Butterfield R.O. and Pryde E.H., Transesterification kinetics of soybean oil, *J. Am. Oil Chem. Soc.*, **63**, 1375–1380 (**1986**)

15. Freedman B., Pryde E.H. and Mounts T.L., Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc*., **61**, 1638–1643 (**1984**)

16. Georgogianni K.G., Kontominas M.G., Pomonis P.J., Avlonitis D. and Gergis V., Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel, *Fuel Processing Technol.*, **89**, 503– 509 (**2008**)

17. Colucci J.A., Borrero E.E. and Alape F., Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing, *J. Am. Oil Chem. Soc*., **82**, 525–30 (**2005**)