



## Optimization of Chemical Kinetics for Base Catalyzed Transesterification of *Eruca sativa* Oil

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Current study describes the optimization of time line kinetics for the base catalyzed transesterification of *Eruca sativa* oil for biodiesel production. Monitoring of transesterification was carried out using high performance liquid chromatography whereas optimization of kinetic was performed with the help of MATLAB-7. The observed order in terms of rate constants for the forward base catalyzed transesterification reactions of *Eruca sativa* oil was  $k^3 > k^2 > k^1$  whereas for the backward reactions the order of rate constant was  $k^{-3} > k^{-1} > k^{-2}$ .

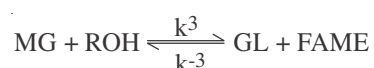
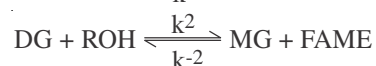
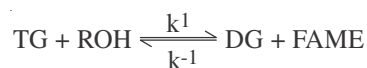
**Key Words:** *Eruca sativa* oil, NaOCH<sub>3</sub>, Transesterification, Optimization, Kinetics.

### INTRODUCTION

Ozone layer depletion and global warming along with many others environmental problems resulted from accelerated non-renewable fossil fuel (petrochemicals, natural gas and coal) consumption because of increase population, urbanization and industrialization lead to the depletion of fossil fuel reserves<sup>1-3</sup>. This uncertain situation regarding the availability of fossil fuel in future has directed the researchers worldwide towards the development of alternative and renewable fuels competitive with conventional, petroleum-based diesel fuels<sup>4,5</sup>.

Low volatility and high viscosity of vegetable oils prevent their direct use in diesel engines as an alternative fuel but biodiesel which is frequently produced by the transesterification with methanol of vegetable oils shows low viscosity and high volatility making it most suitable alternative fuel<sup>6,7</sup>. Biodiesel is proved to be a renewable, nontoxic, biodegradable and environment friendly fuel with superior fuel properties compared to conventional non-renewable diesel fuel<sup>8-10</sup> (Biodiesel: Development Status World-Wide, Report of the Austrian Biofuels Institute, Vienna, Austria).

Transesterification of vegetable oil involves three consecutive reversible reactions. Partial methanolysis of triglyceride (TG) results in the formation of diglycerides (DG) in first step, monoglycerides (MG) in second step whereas glycerol (GL) during the third and final step.



During each one of the reaction step fatty acid methyl esters (FAME'S) are also produced<sup>6,7,11,12</sup>. It is therefore, essential to study and understand the chemical kinetics of transesterification of vegetable oils for biodiesel production<sup>13</sup>.

Different researches have studied the kinetics of transesterification of vegetable oils. Freedman *et al.*<sup>14</sup> reported the transesterification kinetics of soybean oil, Erciyes *et al.*<sup>15</sup>, studied the kinetics of the esterification reaction between castor oil and oleic acid. Moore *et al.*<sup>16</sup>, investigated the kinetics of lipase-catalyzed inter-esterification of fats and oils. Nouredini and Zhu<sup>17</sup> described the kinetics of transesterification of soybean oil. Darnoko and Cheryan<sup>18</sup> studied the kinetics in a batch reactor for Palm oil transesterification. Karmee *et al.*<sup>19</sup>, reported the kinetic study of transesterification of monoglycerides from Pongamia oil. Debora De Oliveira *et al.*<sup>8</sup>, described the kinetics of enzyme-catalyzed transesterification of Soybean oil in *n*-hexane. Karmee *et al.*<sup>13</sup>, investigated the kinetics of base-catalyzed alcoholysis of triglycerides from Pongamia oil. Dantas *et al.*<sup>3</sup>, reported the kinetic and thermal

study of corn oil biodiesel using methanol and ethanol. Marta *et al.*<sup>20</sup>, investigated the dynamic kinetic for castor oil biodiesel production. Narvaez *et al.*<sup>11</sup>, reported the kinetics of palm oil methanolysis and Yun *et al.*<sup>21</sup>, reported the optimization and kinetic of transesterification reaction for biodiesel production catalyzed by combined lipases.

The present study was designed to study the kinetics of base catalyzed transesterification of *Eruca sativa* oil for the production of *Eruca sativa* oil fatty acid methyl esters (ESOFAME's) which may possibly be the first study.

## EXPERIMENTAL

*Eruca sativa* seeds were procured, verified and used for *Eruca sativa* oil extraction with a Soxhlet extraction method (AOCS, 1997) using *n*-hexane as an extracting solvent<sup>22,23</sup>. The extracted oil after required purification was subjected to base catalyzed transesterification. The alkaline catalyst used was NaOCH<sub>3</sub> procured from ACROS (New Jersey USA) whereas methanol was purchased from Merck Chemical Company (Darmstadt, Germany). The entire chemicals used were of analytical/research grade.

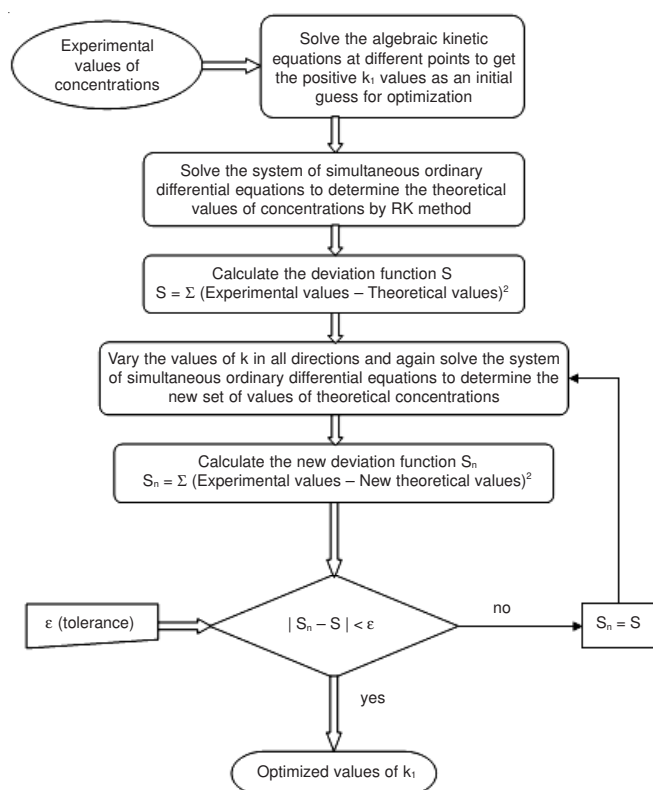


Fig. 1. Algorithm of MATLAB Program for the optimization of kinetics of base catalyzed transesterification of *Eruca sativa* oil

**Monitoring of transesterification:** Based catalyzed transesterification was executed in a flat bottom three necked flask assembled with a condenser, thermometer, heating plate, stirrer and a chiller<sup>24,25</sup>. Experiments were performed at optimized reaction conditions. 100 g *Eruca sativa* oil was taken in a three necked flat bottomed flask and temperature of the oil was maintained at 52 °C with the help of heating plate and a thermometer. 0.5 % NaOCH<sub>3</sub> catalyst was properly mixed in methanol and poured into the reaction flask containing *Eruca*

*sativa* oil. Methanol: oil molar ratio was maintained at 4.5:1. Transesterification reactions were carried out at a stirring rate of 600 rpm for 45 min.

A definite amount of sample from reaction mixture during the base catalyzed transesterification of *Eruca sativa* oil was taken after various time intervals, mixed in hexane and subjected to HPLC analysis for the estimation of triglyceride (TG), diglycerides (DG), monoglycerides (MG) and *Eruca sativa* oil fatty acid methyl esters (ESOFAME's) concentrations. Analytical HPLC system with a reverse phase C<sub>18</sub> column was used for the separation of various components of the reaction mixture, the mobile phase used in the present study was consisted of hexane, isopropanol and methanol in two reservoirs *i.e.*, methanol in reservoir (A) and a mixture of isopropanol and hexane (5 : 4 v/v) in reservoir (B) with a linear gradient elution from 100 % (A) to 50 % (A) + 50 % (B) and a flow rate of 1 mL/min, whereas detection was done using UV detector at a wavelength of 205 nm according to the method as developed by Jech-Wei and Wen-Teng<sup>26</sup> and Holcapek *et al.*<sup>27</sup>. The peaks of FAMES and TG were observed in HPLC chromatogram at retention times between 3-7 and 20-30 min, respectively, while diglycerides and monoglycerides peaks were observed in the region between the peaks of FAMES and TG. The glycerol (GL) concentration was calculated using the formula given below as described by Titipong<sup>28</sup> based upon the assumption *i.e.*, during transesterification no change in number of moles of glycerol is observed.

$$n_{TG0} + n_{DG0} + n_{MG0} = n_{TGi} + n_{DGi} + n_{MGi} + n_{GLi}$$

**Optimization of the kinetics for the base catalyzed transesterification of *Eruca sativa* oil:** The set of kinetic rate equations for the base catalyzed transesterification of *Eruca sativa* oil are given below:

$$\frac{dC_a}{dt} = -k'_1 C_a + k_{-1} C_b C_d$$

$$\frac{dC_b}{dt} = +k'_1 C_a - k_{-1} C_b C_d - k'_2 C_b - k_{-2} C_c C_d$$

$$\frac{dC_c}{dt} = +k'_2 C_b - k_{-2} C_c C_d - k'_3 C_c + k_{-3} C_e C_d$$

$$\frac{dC_d}{dt} = +k'_1 C_a - k_{-1} C_b C_d + k'_2 C_b - k_{-2} C_c C_d + k'_3 C_c - k_{-3} C_e C_d$$

$$\frac{dC_e}{dt} = +k'_3 C_c - k_{-3} C_e C_d$$

where  $k'_1 = k_1 C_1$ ,  $k'_2 = k_2 C_1$ ,  $k'_3 = k_3 C_1$  (as methanol is in excess therefore it is considered as constant).

Experimental data was subjected to the shape preserving inter polant type curve fitting using MATLAB-7 curve fitting toolbox (Fig. 1). Slopes at different points were determined while taking the derivation of concentrations with respect to time on the fitted curves. Taking into consideration the slopes and the concentration values in the kinetic rate equations a set of algebraic kinetic equations was derived. Inverse matrix method (A) was applied to solve the derived set of algebraic kinetic equations for the positive rate constant values as an initial guess for the optimization.

$$k_i = A^{-1}B \quad (A)$$

The initial guess of the rate constants ( $k_i$ ) was further used to solve a system of simultaneous ordinary differential equations by R-K method using ode45 function in MATLAB-7 and theoretical concentration values were obtained.

The deviation (S) among all the theoretical and experimental concentrations between upper and the lower limits of time were calculated to optimize the initial guess values of rate constant ( $k_i$ ) using following general formula (B).

$$S = \sum [\text{Experimental Values} - \text{Theoretical Values}]^2 \quad (B)$$

Further initial guess values of rate constants ( $k_i$ ) were varied by 20 % alternatively in all directions and new theoretical values of concentrations were calculated by RK method using ode45 function in MATLAB-7. Deviations among new theoretical and experimental values were calculated again using the same general formula (B). The values of rate constants ( $k_i$ ) with least value of deviation (S) provided the direction to get the final result of optimized rate constant values. Deviations (S) were further calculated by changing the rate constant values to higher % levels until the deviation was minimized. At this deviation the rate constant values were taken as the optimized rate constant values<sup>13,29</sup>.

## RESULTS AND DISCUSSION

The present study dealt with the optimization of kinetics for base catalyzed transesterification of *Eruca sativa* oil leading to biodiesel production. A characteristic curve showing the concentrations of triglycerides (TG), diglycerides (DG), monoglycerides (MG), fatty acid methyl esters (FAME) and glycerol concentrations at various time intervals during base catalyzed transesterification is presented in Fig. 2.

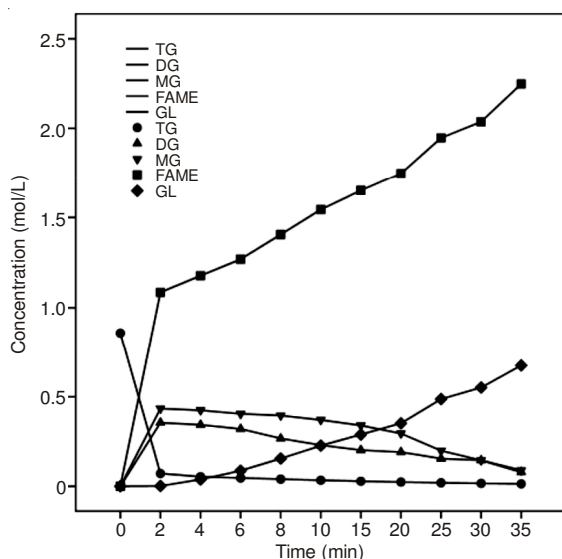


Fig. 2. Composition of reaction mixture during base catalyzed transesterification of *Eruca sativa* oil

Experimental results (Fig. 2) depict the variation in concentration (mol/L) of various components of the reaction mixture with respect to time (minutes) during base catalyzed transesterification of *Eruca sativa* oil. Initially, conversion of triglycerides to fatty acid methyl esters and intermediates *i.e.*,

diglycerides, monoglycerides *etc.* was found to be significantly faster than at the later stages of reaction times. An abrupt slowing of all the reactions was observed that may be attributed due to the formation of glycerol phase as  $\text{NaOCH}_3$  is more soluble in this phase. During base catalyzed transesterification of *Eruca sativa* oil for a time period of 35 min, a continue decrease in triglycerides concentration, ranging from 0.8595-0.013587 mol/L, with respect to time was observed, although the decrease was large at initial reaction times. As triglycerides are converted to diglycerides and diglycerides are converted to monoglycerides during the reaction steps along with the formation of fatty acid methyl esters, it was observed that diglycerides and monoglycerides concentrations after a reaction time *i.e.*, 2 min were 0.3553 and 0.4343 mol/L, which then decreased to 0.0787 and 0.0898 mol/L, respectively at 35 min reaction time, whereas a continuous increase in the *Eruca sativa* oil fatty acid methyl esters concentration was observed, maximum value of 2.2481 mol/L was achieved after 35 min reaction time.

Based upon experimental data correlation studies were carried out between triglycerides (TG), diglycerides (DG), monoglycerides (MG), fatty acid methyl esters (FAME) and glycerol (GL) concentrations (Table-1) during base catalyzed transesterification of *Eruca sativa* oil for biodiesel production. It was observed that for a reaction time of 35 min on the average there exists a significant person correlation between triglycerides and fatty acid methyl esters concentrations with  $p$ -value  $0.001 < 0.05$ , diglycerides and monoglycerides concentrations with  $p$ -value  $0.000 < 0.05$  and fatty acid methyl esters and glycerol concentrations with  $p$ -value  $0.001 < 0.05$ .

The optimized rate constants for the forward ( $k^1$ ,  $k^2$  and  $k^3$ ) and backward ( $k^{-1}$ ,  $k^{-2}$  and  $k^{-3}$ ) reactions during base catalyzed transesterification of *Eruca sativa* oil were 0.0205, 0.0723, 0.2851 and 0.0043, 0.008, 0.0396, respectively. From the Table-2, it is clear that in case of forward reactions, the rate constant  $k^3$  showed highest value whereas  $k^1$  showed lowest value. Similarly among the rate constant for backward reactions the highest value was found to be associated with  $k^{-3}$  while the lowest with  $k^{-2}$ . The observed order in terms of rate constants for the forward reactions was found to be  $k^3 > k^2 > k^1$  while for the backward reactions was  $k^{-3} > k^{-1} > k^{-2}$ . The order of the rate constants for the forward reactions was comparable to the order as described by Nouredini and Zhu<sup>17</sup> for base catalyzed methanolysis of soybean oil and Darnoko and Cheryan<sup>18</sup> for the transesterification of palm oil whereas varied than the results of Karmee *et al.*<sup>19</sup>, for transesterification of triglycerides from Pongamia oil and for transesterification kinetics of soybean oil<sup>14</sup>. The order of the rate constants for the backward reactions (Table-2) was found to be different than the order as described by Nouredini and Zhu<sup>17</sup> and Karmee *et al.*<sup>19</sup>. These differences may be because of different analytical methods used and different feedstock used for base catalyzed transesterification.

The weight percentages of fatty acids methyl esters (FAME) present in the product usually represent the purity (% wt) of the transesterification reactions of vegetable oils<sup>30</sup>. The % purity curve for the base catalyzed transesterification of *Eruca sativa* oil is shown in Fig. 3.

TABLE-1  
CORRELATION MATRIX BETWEEN TRIGLYCERIDES (TG), DIGLYCERIDES (DG), MONOGLYCERIDES (MG),  
FATTY ACID METHYL ESTERS (FAME) AND GLYCEROL (GL) CONCENTRATIONS

		Correlations matrix				
		TG	DG	MG	FAME	GL
TG	Pearson correlation	1	-0.566	-0.575	-0.833**	-0.429
	P-value	–	0.070	0.064	0.001	0.188
DG	Pearson correlation	-0.566	1	0.960*	0.021	-0.487
	P-value	0.070	–	0.000	0.950	0.129
MG	Pearson correlation	-0.575	0.960**	1	0.033	-0.485
	P-value	0.064	0.000	–	0.922	0.131
FAMEs	Pearson correlation	-0.833**	0.021	0.033	1	0.857**
	P-value	0.001	0.950	0.922	–	0.001

\*Correlation is significant at the 0.01 level (2-tailed).

TABLE-2  
OPTIMIZED RATE CONSTANTS FOR THE BASE CATALYZED  
TRANSESTERIFICATION OF *Eruca sativa* OIL AT 52 °C

Sr. No.	Optimized rate constant	Values (L mol <sup>-1</sup> min <sup>-1</sup> )
1	k <sup>1</sup>	0.0205
2	k <sup>-1</sup>	0.0043
3	k <sup>2</sup>	0.0723
4	k <sup>-2</sup>	0.0008
5	k <sup>3</sup>	0.2851
6	k <sup>-3</sup>	0.0396

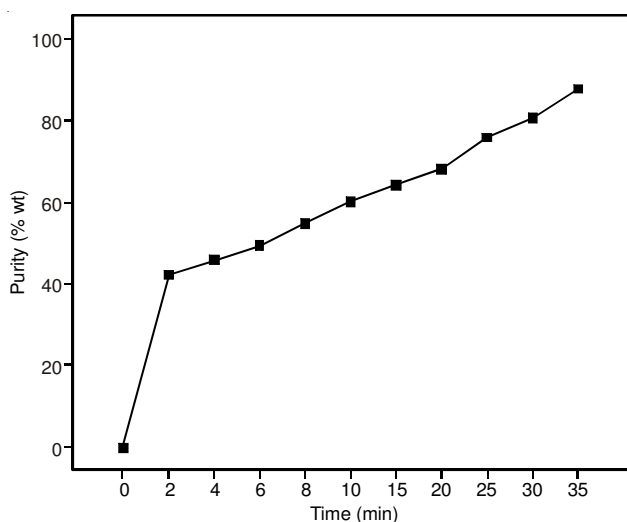


Fig. 3. Purity (% wt) with respect to time (min) for the base catalyzed transesterification of *Eruca sativa* oil

## Conclusion

From the described results it is concluded that *Eruca sativa* oil may be used as an alternative feedstock for the production of biodiesel with the optimized rate constants values with the order for forward and backward reactions  $k^3 > k^2 > k^1$  and  $k^{-3} > k^{-1} > k^{-2}$ , respectively.

## REFERENCES

- J. Tickell, From the Fryer to the Fuel Tank: The Complete Guide to Using Vegetable Oil as an Alternative Fuel, Tickell Energy Consultants, edn. 3, p. 162 (2003).
- A.B. Chhetri and M.R. Islam, *Energy Sources A*, **30**, 754 (2008).
- M.B. Dantas, M.M. Conceição, V.J. Fernandes Jr, N.A. Santos, R. Rosenhaim, A.L.B. Marques, I.M.G. Santos and A.G. Souza, *J. Thermal Anal. Calorim.*, **87**, 835 (2007).
- W. Kapila, C.S. Jeremiah, R.W. John, O.S. Steven and N.K.Y. Simon, *J. Am. Oil Chem. Soc.*, **85**, 1073 (2008).
- M.J. Haas, K.M. Scott, T.L. Alleman and R.L. McCormick, *Energy Fuels*, **15**, 1207 (2001).
- C.M. Simone, R. Elizabeth, R.S.V. Lachter, J.A. Nascimento, J. Rodrigues and G.R. Marcelli, *J. Am. Oil Chem. Soc.*, **82**, 9 (2005).
- F. Ma and M.A. Hanna, *Bioresour. Technol.*, **70**, 1 (1999).
- D. de Oliveira, M. Di Luccio, C. Faccio, C.D. Rosa, J.P. Bender, N. Lipke, C. Amroginski, C. Dariva and J.V. de Oliveira, *Appl. Biochem. Biotechnol.*, **122**, 553 (2005).
- M. Mittelbach and S. Gangl, *J. Am. Oil Chem. Soc.*, **78**, 6 (2001).
- M. Mittelbach, M. Wörgetter, J. Pernkopf and H. Junek, *Energy Agric.*, **2**, 369 (1983).
- P.C. Narvaez, S.M. Rincon and F.J. Sanchez, *J. Am. Oil Chem. Soc.*, **84**, 971 (2007).
- Schuchardt, U.R. Sercheli and R.M. Vargas, *J. Braz. Chem. Soc.*, **9**, 199 (1998).
- S.K. Karmee, D. Chandna, R. Ravi and A. Chadha, *J. Am. Oil Chem. Soc.*, **83**, 10 (2006).
- B. Freedman, R.O. Butterfield and E.H. Pryde, *J. Am. Oil Chem. Soc.*, **63**, 1375 (1986).
- A.T. Erciyes, L. Dandik and O.S. Kabasakal, *J. Am. Oil Chem. Soc.*, **68**, 639 (1991).
- S.R. Moore and J. Davies, *J. Am. Oil Chem. Soc.*, **71**, 526 (1994).
- H. Noureddini and D. Zhu, *J. Am. Oil Chem. Soc.*, **74**, 1457 (1997).
- D. Darnoko and M. Cheryan, *J. Am. Oil Chem. Soc.*, **77**, 1263 (2000).
- S.K. Karmee, P. Mahesh, R. Ravi and A. Chadha, *J. Am. Oil Chem. Soc.*, **81**, 425 (2004).
- M.M. Conceição, V.J. Fernandes Jr, A.F. Bezerra, M.C.D. Silva, I.M.G. Santos, F.C. Silva and A.G. Souza, *J. Thermal Anal. Calorim.*, **87**, 865 (2007).
- L. Yun, Y. Yunjun, H. Fang, Y. Anna, W. Zhicheng and W. Fuxiang, *AIChE J.*, **56**, 1659 (2010).
- U. Rashid and F. Anwar, *Fuel*, **86**, 265 (2008).
- U. Rashid, F. Anwar, M.A. Tariq, A. Muhammad and A. Mushtaq, *J. Chem. Technol. Biotechnol.*, **84**, 1364 (2009).
- J.M. Encinar, J.F. Gonzalez, J.J. Rodriguez and A. Tejedor, *Energy Fuels*, **16**, 443 (2002).
- U. Rashid and F. Anwar, *Energy Fuels*, **22**, 1306 (2008).
- C. Jech-Wei and W. Wen-Teng, *J. Biosci. Bioeng.*, **95**, 466 (2003).
- M. Holcapek, P. Jandera, J. Fisher and B. Prokes, *J. Chromatogr. A*, **858**, 13 (1999).
- I. Titipong, M.Sc. Thesis, Biodiesel Production from Fryer Grease, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Thailand, p. 104 (2006).
- A.S. Abdel-Latif and A.M.A. Lamiaa, *Am. J. Appl. Sci.*, **7**, 509 (2010).
- L. Theerayut, W. Worawut, P. Gumpon, T. Charktir and A. Michael, A Second Order Kinetics of Palm Oil Transesterification, The Joint International Conference on Sustainable Energy and Environment (SEE) 1-3 December, Hua Hin, Thailand, pp. 3-25, (2004).