



A Mathematical Study on the Effect of Molar Ratios of the Reactants for Biodiesel Production in SC-CO₂ Medium

Arunabha Sengupta¹, Ashis Kumar Sarkar²

¹Senior Research Fellow, Department of Mathematics, Jadavpur University, Kolkata 700032, India.

²Professor, Department of Mathematics, Jadavpur University, Kolkata 700032, India.

ARTICLE INFO	ABSTRACT
Published online: 06 September 2023	The present global situation is so alarming that the conventional energy resources are decaying day by day. This adverse situation encourages us to introduce unconventional and sustainable energy resources like biodiesel. The main source of biodiesel is the non-edible vegetable oil (Jatropha curcas oil) and it is produced by chemical catalytic method. But recently supercritical method has also been proposed as an alternative cost-effective method for its production. A good quality of biodiesel can be produced in a Supercritical-Carbon dioxide medium. The productivity of biodiesel preparation through supercritical method depends on molar ratio of the reactants (water and methanol). In this research article, a set of nonlinear differential equations has been formulated based on concentrations of Triglyceride, Diglyceride, Monoglyceride, Methanol, Free fatty acid, Water, Glycerol and Biodiesel. Our study is based on the effect of the molar ratios of the reactants and how we can get a cost-effective production of biodiesel. The validity of our model is attained by experimental results. The analytical results are also verified by our numerical findings.
Corresponding Author: Arunabha Sengupta	
KEYWORDS: Jatropha curcas oil, Biodiesel, Supercritical, Molar ratio, Optimization, Cost-effectiveness.	

I. INTRODUCTION

Unlimited use of fossil fuels causes the reduction of petroleum reserves. It has already been predicted that we will surely run out of fossil fuels in this century. This adverse circumstance brings significant attention to introduce and develop new alternate plant-based fuels. Also increasing environmental pollution is another threat to the world. To overcome these threats biofuel is of utmost importance because it is environmentally friendly and secures future energy supplies. As a consequence, the production and usage of biodiesel is being tremendously researched worldwide. We can derive biodiesel from vegetable oils like Jatropha curcas oil that comprises triglycerides with methanol in various processes. Biodiesel is a renewable, non-toxic, biodegradable energy source. This clean renewable fuel is superior to diesel oil in terms of sulphur and aromatic content.

Lascaray [1, 2] showed that hydrolysis is mainly a homogeneous reaction occurring in the oil phase and only a minor portion of the reaction happens at the oil and water interface during the induction period. Hydrolysis of triglyceride (TG) from fats and oils to glycerol and free fatty acids (FFA) is an important reaction for the oleochemical

industry. Hydrolysis involves three stepwise reversible reactions. Triglyceride (TG) is first hydrolyzed to diglyceride (DG) and then to monoglyceride (MG) and glycerol respectively. At each step, we get one molecule of free fatty acid (FFA) which later reacts with methanol and produce biodiesel. The hydrolysis reaction rate is initially low and then gradually increases up to its normal level. This is due to an induction period that obscures the kinetics of the hydrolysis of oil [3].

Many research articles are published on biodiesel production through different processes like transesterification with chemical catalysts [4, 5], biochemical catalysts, SCMTR method [3, 4, 5, 6, 7], etc. The process of producing biodiesel from vegetable oils and animal fats with the aid of alcohols is called Transesterification. Alkaline catalysts processes form soap as a side product and reduce the production of biodiesel as Jatropha oil contains free fatty acids (FFAs) and water. Therefore, there are complex and energy-consuming separation and purification steps in the homogeneous chemical catalyst processes. It is observed that we also face difficulties in recovering glycerol due to the solubility of excessive methanol and catalyst [7].

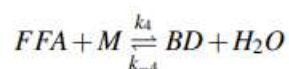
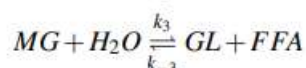
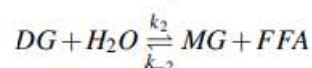
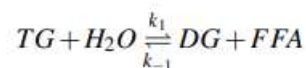
Nowadays we have motivated our research on the production of biodiesel by supercritical transesterification reaction without catalyst. Supercritical carbon dioxide (SC-CO₂) medium is also considered an important reaction medium for lipids [8, 9]. One of the advantages of conducting hydrolysis in SC-CO₂ medium is that the hydrolysis vessel can also serve as an extraction vessel for FFA [9]. Our primary motive to conduct this study is to investigate the hydrolysis reaction in SC-CO₂ medium as it eases the separation of the FFA from the product mixture [10].

Nowadays impulsive differential equations are being used to model a large number of biological phenomena [12, 14]. Recent research articles have reported that the stepwise addition of water enhances the reaction rate. The effect of water content on the initial reaction rate and conversion has been discussed thoroughly in many articles [13].

In this research article, a mathematical model for biodiesel production in a Supercritical carbon dioxide medium has been formulated. We have done a comparative numerical study based on mass transfer and reaction conditions for the production of biodiesel. Our study finds that hydrolysis reaction in SC-CO₂ medium is a better approach for FFA production and hence biodiesel in view of water to oil molar ratio and methanol to oil molar ratio. Previously Chowdhury et.al have shown that the required methanol to oil molar ratio for maximum production of biodiesel is 6 : 1 [14]. But here we have shown that due to the use of water in the extraction of the FFA stage, the ultimate required methanol to oil molar ratio is 3 : 1, which is half of the previous result. It also leads to the simpler separation and purification steps of biodiesel. For the cost-effective production of biodiesel, an impulsive strategy for adding water is proposed here. Thus, here an impulsive mathematical model for biodiesel production is formulated. Finally, we conclude our findings.

II. MODEL FORMULATION

The following schematic diagram shows our assumption to formulate our mathematical model.



• There are three stepwise consecutive and reversible reactions in the hydrolysis of *Jatropha curcas* oil.

- ❖ In the first step triglycerides (TG) is hydrolyzed to diglycerides (DG).

- ❖ In the second step diglycerides (DG) is hydrolysed to monoglycerides (MG).
- ❖ In the third step monoglycerides (MG) is hydrolyzed to glycerol.
- ❖ Each of these reaction steps produces one molecule of free fatty acids (FFA).
- ❖ At last methanol (M) reacts with this FFA and produces the required biodiesel (BD).

• Here $\{k_1, k_2, k_3, k_4\}$ and $\{k_{-1}, k_{-2}, k_{-3}, k_{-4}\}$ are forward and backward reaction rate constants respectively. These reaction rate constants follow Arrhenius equation [11],

$$k_i = a_i e^{-\frac{b_i}{T}} \quad (2.1)$$

where

T - reaction temperature,

a_i - frequency factor,

$$b_i = \frac{E a_i}{R} \quad (2.2)$$

in which

$E a_i$ - activation energy for each component

R - Universal Gas Constant.

Based on these assumptions the following system of differential equations has been formed.

$$\begin{aligned} \frac{dx_T}{dt} &= -k_1 x_T x_H + k_{-1} x_D x_F \\ \frac{dx_D}{dt} &= k_1 x_T x_H - k_{-1} x_D x_F - k_2 x_D x_H + k_{-2} x_M x_F \\ \frac{dx_M}{dt} &= k_2 x_D x_H - k_{-2} x_M x_F - k_3 x_M x_H + k_{-3} x_G x_F \\ \frac{dx_H}{dt} &= -k_1 x_T x_H + k_{-1} x_D x_F - k_2 x_D x_H + k_{-2} x_M x_F \\ &\quad - k_3 x_M x_H + k_{-3} x_G x_F + k_4 x_F x_{ME} - k_{-4} x_B x_H \\ \frac{dx_F}{dt} &= k_1 x_T x_H - k_{-1} x_D x_F + k_2 x_D x_H - k_{-2} x_M x_F \\ &\quad + k_3 x_M x_H - k_{-3} x_G x_F - k_4 x_F x_{ME} + k_{-4} x_B x_H \\ \frac{dx_{ME}}{dt} &= -k_4 x_F x_{ME} + k_{-4} x_B x_H \\ \frac{dx_G}{dt} &= k_3 x_M x_H - k_{-3} x_G x_F \\ \frac{dx_B}{dt} &= k_4 x_F x_{ME} - k_{-4} x_B x_H \end{aligned} \quad (2.3)$$

with the following initial conditions:

$$\begin{aligned} x_T(0) &= x_{T_0}, x_D(0) = 0, x_M(0) = 0, x_H(0) = x_{H_0} \\ x_F(0) &= x_{F_0}, x_{ME}(0) = x_{ME_0}, x_G(0) = 0, x_B(0) = 0. \end{aligned} \quad (2.4)$$

III. SYSTEM WITH IMPULSE ON WATER

In this section, we have considered the stepwise addition of water with time intervals t' and t'' for maximum biodiesel production. Therefore, the above system (2.3) becomes an impulsive system with an impulse on water. Hence the impulsive form of the above system is as follows:

$$\frac{dx_T}{dt} = -k_1 x_T x_H + k_{-1} x_D x_F \quad t \neq t_k$$

$$\frac{dx_D}{dt} = k_1 x_T x_H - k_{-1} x_D x_F - k_2 x_D x_H + k_{-2} x_M x_F \quad t \neq t_k$$

$$\frac{dx_M}{dt} = k_2 x_D x_H - k_{-2} x_M x_F - k_3 x_M x_H + k_{-3} x_G x_F \quad t \neq t_k$$

$$\frac{dx_H}{dt} = -k_1 x_T x_H + k_{-1} x_D x_F - k_2 x_D x_H + k_{-2} x_M x_F - k_3 x_M x_H + k_{-3} x_G x_F + k_4 x_F x_{ME} - k_{-4} x_B x_H \quad t \neq t_k$$

$$\frac{dx_F}{dt} = k_1 x_T x_H - k_{-1} x_D x_F + k_2 x_D x_H - k_{-2} x_M x_F + k_3 x_M x_H - k_{-3} x_G x_F - k_4 x_F x_{ME} + k_{-4} x_B x_H \quad t \neq t_k$$

$$\frac{dx_{ME}}{dt} = -k_4 x_F x_{ME} + k_{-4} x_B x_H \quad t \neq t_k$$

$$\frac{dx_G}{dt} = k_3 x_M x_H - k_{-3} x_G x_F \quad t \neq t_k$$

$$\frac{dx_B}{dt} = k_4 x_F x_{ME} - k_{-4} x_B x_H \quad t \neq t_k$$

and impulse is given by

$$x_H(t_k^+) - x_H(t_k^-) = r x_H \quad t = t_k \quad (3.1)$$

with the conditions

$$\begin{aligned} x_T(0) = x_{T_0}, x_D(0) = 0, x_M(0) = 0, x_H(0) = x_{H_0} \\ x_F(0) = 0, x_{ME}(0) = 0, x_G(0) = 0, x_B(0) = 0. \end{aligned} \quad (3.2)$$

Analytical study of the system

To get the approximate concentration profile for water by analytical method, we have considered the following subsystem here.

$$\begin{aligned} \frac{dx_H}{dt} = & -k_1 x_T x_H + k_{-1} x_D x_F - k_2 x_D x_H + \\ & k_{-2} x_M x_F - k_3 x_M x_H + k_{-3} x_G x_F + k_4 x_F x_{ME} - \\ & k_{-4} x_B x_H \end{aligned} \quad t \neq t_k$$

$$x_H(t_k^+) - x_H(t_k^-) = r x_H \quad t = t_k \quad (3.3)$$

Since the system is bounded, $\exists C \in \mathbf{R}^+$ such that $x_j < C$, (j stands for T, D, M, H, F, ME, G, B).

Also, by Arrhenius Principle k_1, k_{-1}, k_2, k_{-2} are finite quantities. Then for some positive real numbers M and N , it can be written that,

$$\begin{aligned} \frac{1}{2} M = & \min\{k_{-1} x_D x_F, k_{-2} x_M x_F, k_{-3} x_G x_F, k_4 x_F x_{ME}\} \\ \text{and } \frac{1}{2} N = & \min\{k_1 x_T, k_2 x_D, k_3 x_M, k_{-4} x_B\}. \end{aligned}$$

Then the system (3.3) becomes

$$\frac{dx_H}{dt} \leq M - N x_H, \quad t \neq t_k \quad (3.4)$$

$$\Delta x_H = r x_H \quad t = t_k$$

For maximum rate of change of water, the system is re-written as,

$$\frac{dx_H}{dt} = M - N x_H, \quad t \neq t_k \quad (3.5)$$

$$\Delta x_H = r x_H \quad t = t_k$$

Here m, n are some real constants. Therefore, for a single impulsive cycle $t_k \leq t \leq t_{k+1}$, solution of the system is -

$$\begin{aligned} x_H(t_{k+1}^-) = & \frac{M}{N} [1 - e^{-N(t_{k+1}-t_k)}] + \\ x_H(t_k^+) e^{-N(t_{k+1}-t_k)} \end{aligned} \quad (3.6)$$

The amount of water just before impulse and immediately after impulse are given by

$$x_H(t_k^-) \text{ and } x_H(t_k^+) \text{ respectively.}$$

Hence, we have

$$x_H(t_1^-) = \frac{M}{N}$$

$$\begin{aligned}
 x_H(t_1^+) &= \frac{M}{N} (1+r) \\
 x_H(t_2^-) &= \frac{M}{N} (1+r)e^{-N(t_2-t_1)} + \frac{M}{N} (1 - e^{-N(t_2-t_1)}) \\
 x_H(t_2^+) &= \frac{M}{N} (1+r)^2 e^{-N(t_2-t_1)} + \frac{M}{N} (1+r)(1 - e^{-N(t_2-t_1)}) \\
 x_H(t_3^-) &= \frac{M}{N} [(1+r)^2 e^{-N(t_3-t_1)} + (1+r)e^{-N(t_3-t_2)} \\
 &\quad - (1+r)e^{-N(t_3-t_1)} + 1 - e^{-N(t_3-t_2)}] \\
 x_H(t_3^+) &= \frac{M}{N} [(1+r)^3 e^{-N(t_3-t_1)} + (1+r)^2 e^{-N(t_3-t_2)} \\
 &\quad - (1+r)^2 e^{-N(t_3-t_1)} + (1+r) - (1+r)e^{-N(t_3-t_2)}] \tag{3.7}
 \end{aligned}$$

and so on.

Hence, we can write the general solution of the subsystem as

$$\begin{aligned}
 x_H(t_p^-) &= \frac{M}{N} [(1+r)^{p-1} e^{-N(t_p-t_1)} + (1+r)^{p-2} e^{-N(t_p-t_2)} + (1+r)^{p-3} e^{-N(t_p-t_3)} + \dots + 1 \\
 &\quad - (1+r)^{p-2} e^{-N(t_p-t_1)} - (1+r)^{p-3} e^{-N(t_p-t_2)} \\
 &\quad - (1+r)^{p-4} e^{-N(t_p-t_3)} - \dots - e^{-N(t_p-t_{p-1})}]
 \end{aligned}$$

For Fixed Time Interval

If water is given to the system in fixed time interval, then $t_n - t_{n-1} = \tau$ is constant. Hence, the general solution is:

$$\begin{aligned}
 x_H(t_p^-) &= \frac{M}{N} [1 + (1+r)e^{-N\tau} + (1+r)^2 e^{-2N\tau} \\
 &\quad + \dots + (1+r)^{p-1} e^{-N(p-1)\tau} - e^{-N\tau} \{1 + (1+r)e^{-N\tau} \\
 &\quad + (1+r)^2 e^{-2N\tau} + \dots + (1+r)^{p-2} e^{-(p-2)N\tau} \}] \\
 &= \frac{M}{N} \left[\frac{1-(1+r)^p e^{-Np\tau}}{1-(1+r)e^{-N\tau}} - \frac{e^{-N\tau}(1-(1+r)^{p-1} e^{-N(p-1)\tau})}{1-(1+r)e^{-N\tau}} \right] \tag{3.9}
 \end{aligned}$$

Taking limit,

$$\lim_{p \rightarrow \infty} x_H(t_p^-) = \frac{M}{N} \left[\frac{1-e^{-N\tau}}{1-(1+r)e^{-N\tau}} \right] \tag{3.10}$$

This is the long-term maximum value of the water (since the effect of the impulse is to be immediately reduced). To keep this under the threshold \widehat{x}_H , we have,

$$\frac{M}{N} \left[\frac{1 - e^{-N\tau}}{1 - (1+r)e^{-N\tau}} \right] < \widehat{x}_H$$

which implies $\tau < \frac{1}{N} \ln \left\{ \frac{M-N(1+r)\widehat{x}_H}{M-N\widehat{x}_H} \right\} = \tau_{\max}$ (say)

IV. NUMERICAL SIMULATION

In this section, we have numerically solved the model systems to show the effect of the molar ratio and also the impulsive effect of water in SC-CO₂ medium to maximize the production of biodiesel. The effect of changes in the reaction parameters are shown numerically by our model. Here the effect of the molar ratio of water and methanol on the system kinetics has been discussed.

Figure (I) represents the effect of water to oil molar ratio on the reaction. From 5:1, 10:1, 15:1, 20:1 water to oil molar ratios 15:1 water to oil molar ratio has been considered as the optimum molar ratio for the execution of the reaction because though for both 15:1 and 20:1 molar ratios we have the maximum production of FFA at the same time, but for 15:1 water to oil molar ratio the requirement of the amount of water is less and it increases the reaction rate.

Figure (II) compares the impulsive effect of adding the same amount of water to the reaction system for different time intervals. Here we can observe that adding water in the impulsive way with 2.5 minute interval is considerably more effective than adding water with 5 minutes interval as the reaction rate is enhanced more and ultimately results to a stable production of FFA, i.e., 3 moles/L, which is the maximum production.

Figure (III) shows the effect of methanol to oil molar ratio on the reaction rate for conversion of biodiesel production. We have seen that 3:1 methanol to oil molar ratio is optimum for biodiesel production in Supercritical method. Though for both 3:1 and 4:1 methanol to oil molar ratios, we get the same amount of biodiesel but for 3:1 methanol to oil molar ratio less amount of methanol is required than its requirement for 4:1 molar ratio which also justifies cost-effectiveness of the system.

Table 1 Kinetic parameter set for the reaction system [11]

Reaction rate constants, k_i	Values(unit)
k_1	0.0095 moles $L^{-1} min^{-1}$
k_{-1}	0.1219 moles $L^{-1} min^{-1}$
k_2	0.03 moles $L^{-1} min^{-1}$
k_{-2}	0.0011 moles $L^{-1} min^{-1}$
k_3	1.9514 moles $L^{-1} min^{-1}$
k_{-3}	0.1144 moles $L^{-1} min^{-1}$
k_4	0.1785 moles $L^{-1} min^{-1}$
k_{-4}	0.5744 moles $L^{-1} min^{-1}$

V. FIGURES

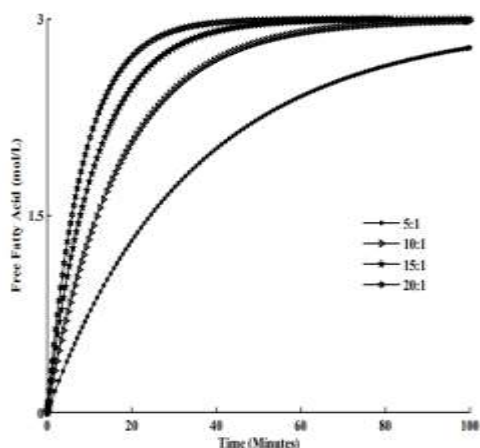


Fig. I. Effect of water to oil molar ratio in production of Free Fatty Acid through hydrolysis of Triglycerides, using parameter values given in Table 1.

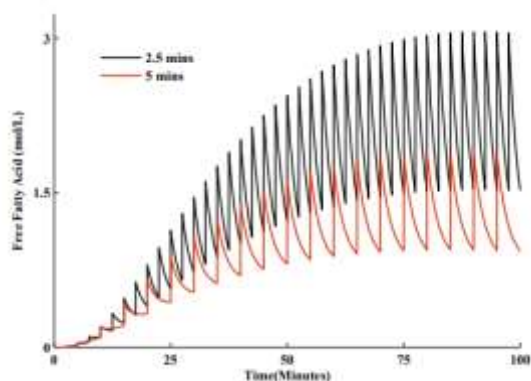


Fig. II. Concentration of Free Fatty Acid with respect to addition of water in 2.5 minutes and 5 minutes intervals, using parameter values given in Table 1.

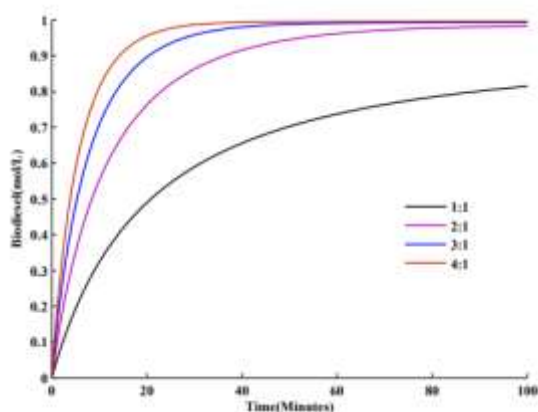


Fig. III. Concentration of biodiesel as a function of time for different methanol to oil molar ratios, using parameter values given in Table 1.

REFERENCES

1. L. Lascaray, Industrial fat splitting, Journal of the American Oil Chemists' Society, 29(9), 362-366, 1952.

2. L. Lascaray, Mechanism of fat splitting, Industrial & Engineering Chemistry, 41(4), 786-790, 1949.
3. L. Hartman, Kinetics of the Twitchell hydrolysis, Nature, 167(4240), 199, 1951.
4. A. Srivastava, R. Prasad, Triglycerides-based diesel fuels, Renewable and Sustainable Energy Reviews, 4(2), 111-133, 2000.
5. Y. Zhang, M. A. Dube, D. D. Mclean, M. Kates, Biodiesel production from waste cooking oil. 1. Process design and technological assessment, Bioresource Technology, 89(1), 1-16, 2003.
6. G. T. Ang, K. T. Tan, K. T. Lee, A. R. Mohamed, Optimization and kinetic studies of sea mango (Cerbera odollam) oil for biodiesel production via supercritical reaction, Energy Conversion and Management, 99, 242-251, 2015.
7. A. Demirbas, Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification, Energy Conversion and Management, 50(4), 923-927, 2009.
8. P. H. Moquin, F. Temelli, Kinetic modeling of hydrolysis of canola oil in supercritical media, The Journal of Supercritical Fluids, 45(1), 94-101, 2008.
9. K. Fujita, M. Himi, Hydrolysis of glycerol trioleate and extraction of its fatty acid under CO₂ supercritical conditions, Nippon Kagaku Kaishi, 79-79, 1995.
10. P. H. Moquin, F. Temelli, H. Sovova, M. D. Saldaña, A. R. Mohamed, Kinetic modeling of glycerolysis-hydrolysis of canola oil in supercritical carbon dioxide media using equilibrium data, The Journal of Supercritical Fluids, 37(3), 417-424, 2006.
11. U. Diwekar, P. Benavides, Optimal control of biodiesel production in a batch reactor Part I: Deterministic control, Fuel, 94, 218-226, 2012.
12. X. Liu, Ballinger, Permanence of population growth models with impulsive effects, Mathematical and Computer Modelling, 26(12), 59-72, 1997.
13. S. Al-Zuhair, K. V. Jayaraman, S. Krishnan, W. H. Chan, The effect of fatty acid concentration and water content on the production of biodiesel by lipase, Biochemical Engineering Journal, 30(2), 212-217, 2006.
14. J. Chowdhury, X. Cao, F. Al Basir, P. K. Roy, Effect of Mass transfer and Reaction Kinetics in Transesterification of Jatropha curcas oil, International Journal of Mathematical Models and Methods in Applied Sciences, 11, 130-138, 2017.