

Modeling of Biodiesel Reaction

By

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Abstract

Biodiesel is produced by a chemical reaction known as transesterification in which a triglyceride reacts with a primary alcohol to give an alkyl ester Biodiesel and a byproduct Glycerol. The reaction is said to proceed to completion only when the primary alcohol is in excess, but there has not been any Mathematical Model to support the claim. The problem statement as formulated and analyzed in this paper justifies the need to use excess primary alcohol for the reaction.

Introduction

Transesterification is a catalyzed chemical reaction between vegetable oil and an alcohol to yield fatty acid alkyl esters other-wise known as biodiesel. When vegetable oils, whose main components are triglycerides (tri acyl glycerols), react with an alcohol, in the presence of a catalyst, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters. The by-product of the reaction is glycerol², Figure 1.

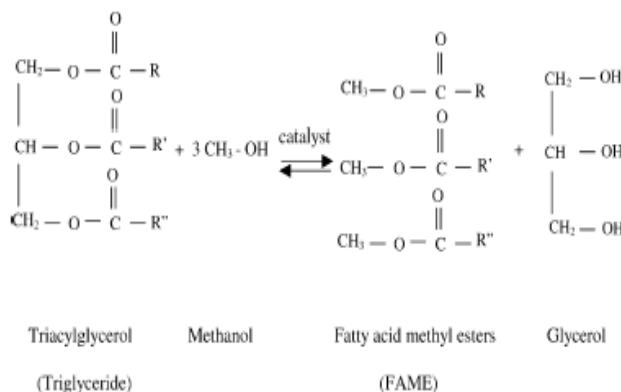


Figure 1: Transesterification reaction

The oil is heated to the required temperature and a mixture of the catalyst (to accelerate the rate of reaction through lowering of the activation energy) and an alcohol is added to the oil with thorough mixing. After a period of time the heating and mixing are stopped and the reaction mixture is allowed to settle. A successful reaction will yield two layers of products, the top layer being the crude bio-diesel and the bottom layer, glycerol.

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² Zhang Y, Dube M A, McLean D D, Kates, M, (2003a): Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Tech* 89 (1) 1-16

Residual methanol is removed immediately after separating the biodiesel and glycerine to forestall a reversal of the reaction. The methanol recovered is cleaned and reused for another transesterification reaction. The crude biodiesel is subjected to a series of purification steps to remove excess alcohol, residual catalyst and soaps by multistage washings with clean water before being dried and sent to storage.

The most frequently used alcohols for biodiesel production are short-chain alcohols, such as methanol (CH₃OH), ethanol (C₂H₅OH) and butanol (C₄H₉OH). Each of the alcohols has its attendant reaction kinetics. Nevertheless, the end-product, biodiesel, is considerably the same in terms of properties. Alcohol selection is based on cost, sustainability, and performance characteristics³. In Brazil, for example, ethanol is preferred because it is cheap and sustainable. Ethanol is also renewable, from agriculture. The un-reacted ethanol forms an azeotrope (a constant boiling mixture), more expensive to purify during recovery⁴. Methanol is much cheaper than ethanol and the literature on biodiesel production is replete with methyl esters rather than ethyl esters.⁵

The reaction rate is relatively slower when ethanol is used. The formation of the ethoxide anion is more difficult than that of the methoxide⁶. Ethanolysis leads to the formation of stable emulsions, making the separation and purification of the final product more complex. Emulsions formed in the methanolysis reaction are not very stable. They breakdown, quickly and easily, to form two layers in the reactor, lower glycerol-rich layer and the upper methyl ester-rich layer.⁷

³ Encinar J.M., Susan F.; Gonzalez J.F.; Rodriguez- Reinares A., (2007): Ethanolysis of used frying oils: Biodiesel preparation and characterization: *Fuel PNC. Tech.*, 88 (5) 513-522

⁴ Zhou W, Boocock D G B, (2006): Phase behavior of the base-catalyzed transesterification of soybean oil. *J Am Oil Chem Soc* 83 (12) 1041-1045

⁵ Alcantara, R., Amores, J.; Canoira, L.; Fidalgo, E.; Franco, M.J. and Navaro, A., (2000). Catalyst production of biodiesel from soya-bean oil used frying oil and tallow. *Biomass Bioenergy* 18 (3), 253-256.; Pinto A C, Gurieiro L N, L N, Rezende M J, Ribeiro N M, Torres E A, Lopes W A, Pereira P A, Andrade J B, (2005): Biodiesel: An Overview. *J Brazil Chem Soc* 16 (6B) 1313-1330; Encinar, J. M.; Gonzalez, J. F.; Rodriguez-Reinares, A., (2005): Biodiesel from used frying oil; variables affecting the yields and characteristics of the biodiesel. *Ind Engin Chem. Res.*, 44 (15), 5491-5499; Felizardo, P.; Correia, M.J.; Raposo, I. J. F.; Berkemeier, R.; Bordado J. M., (2006): Production of biodiesel from waste frying oils. *Waste Manage*, 26 (5), 487-494; Refaat A. A, Attia N K, Sibak H A, El Sheltawy S T, El Diwani G I, (2008a): Production optimization and quality assessment of biodiesel from waste vegetable oil. *Int J Environ Sci Tech* 5 (1) 75-82; Yuan X, Liu J, Zeng G, Shi J, Tong J, and Huang G, (2008): Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. *Renew Energ* 33 (7) 1678-1684.

⁶ Om Tapanes N C, Gomes Aranda, D A, de Mesquita Carneiro J W, Ceva Antunes, O A, (2008): Transesterification of jatropha *curcas* oil glycerides: Theoretical and experimental studies of biodiesel reaction. *Fuel* 87 (10-11) 2286-2295

⁷ Zhou W, Boocock D G B, (2006): Phase behavior of the base-catalyzed transesterification of soybean oil. *J Am Oil Chem Soc* 83 (12) 1041-1045; Encinar J.M., Susan F.; Gonzalez J.F.; Rodriguez- Reinares A., (2007): Ethanolysis of used frying oils: Biodiesel preparation and characterization: *Fuel PNC. Tech.*, 88 (5) 513-522

Methanol is easier to recover than ethanol, more easily recycled since it does not form an azeotrope. While it has a flash point of 10°C, that of ethanol is 8°C, even though methanol is more toxic⁸.

The alcohol-triglyceride molar ratio is a very important factor/ parameter in trans-esterification reactions. The stoichiometry requires the use of three mol of alcohol to react with one mol of triglyceride to produce three mols of fatty acid alkyl esters and one mol of glycerol. The trans-esterification is an equilibrium reaction. Hence to drive the reaction to the right, that is towards the formation of fatty acid methyl ester, FAME, and glycerol, an excess of alcohol is required. It however makes recovery of the glycerol difficult⁹.

A molar ratio of 6:1 for alcohol to triglyceride has been reported to be most acceptable for base-catalyzed trans-esterification reactions¹⁰. Higher molar ratios do not affect the conversion efficiency considerably. However they make the energy required for the recovery of the alcohol to increase¹¹. The extra alcohol, in addition to driving the reaction closer to the 99.7% yield of FAME, is required to meet the total glycerol standard of fuel grade biodiesel.¹²

It is clear therefore that excess alcohol is required for transesterification. Thus there is need to justify the claim mathematically.

Problem Formulation

Liquid triglyceride is to be trans-esterified batchwise by sparging methanol a primary alcohol in the presence of an alkali homogeneous catalyst into a reaction kettle containing the triglyceride. If the reaction kettle contains such an efficient agitator that the methanol which enters the reactor undergoes chemical reaction, and only glycerol is the other product, a mathematical model for

⁸ Van Gerpen J H; Shanks, B.; Pruszko, R.; Clements, D.; Knothe, G., (2004): Biodiesel Analytical Methods National Renewable Energy Laboratory, Colorado.

⁹Schuchardt U, Serchelia R, Vargas, R M, (1998): Transesterification of vegetable oils: A Review. *J Brazil Chem Soc* 9 (1) 199-210; Ma F, Hanna M A, (1999): Biodiesel production: A Review. *Bioresource Tech* 70 (1) 1-15.

¹⁰Saifuddin N, Chua K H, (2004): Production of ethyl ester from used frying oil: Optimization of transesterification process using microwave irradiation. *Malaysian Journal of Chemistry*, 6 (1) 77-82; Encinar, J M.; Gonzalez, J. F.; Rodriguez-Reinares, A., (2005): Biodiesel from used frying oil; variables affecting the yields and characteristics of the biodiesel. *Ind Engin Chem. Res.*, 44 (15), 5491-5499; Gupta A, Sharma S K, Pal Toor, A, (2007): Production of biodiesel from waste soybean oil. *J Petrotech Soc*, IV (1), 40-45; Meng X, Chen G, Wang, Y, (2008): Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Proc Tech* 89 (9) 851-857; Refaat A A, El Sheltawy S T, (2008): Comparing three options for biodiesel production from waste vegetable oil. *WIT Transactions on Ecology and the Environment, Waste Management and the Environment IV*, Vol 109, WIT Press, 133-140.

¹¹ Demirbas, A., (2009): Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. *Energy Convers Manage*: 50 (4), 923-927.

¹² Van Gerpen J H; Shanks, B.; Pruszko, R.; Clements, D.; Knothe, G., (2004): Biodiesel Analytical Methods National Renewable Energy Laboratory, Colorado;

the estimation of how much methanol must be added to give the maximum yield of Fatty-Acid Methyl Ester FAME, Bio-diesel, can be postulated.

Assumptions:

Let the following reactions be valid:



TG is the triglyceride, Me is methanol, DG is diglyceride, BD is Biodiesel, MG is monoglyceride, GL is glycerol. The k_1 , k_2 , and k_3 are the rate constants.

The reaction takes place isothermally at 55⁰C

The ratios of the specific reaction rate constants are

$$\frac{k_1}{k_2} = 0.734 \text{ and } \frac{k_2}{k_3} = 3.71$$

(Source: Akhiero, 2014¹³)

Basis: 1 mol TG fed into the reaction kettle at time 0 [adapted from “Chlorination of Benzene”, Jenson and Jeffreys (1963)]

Let there be

p mol fraction of Me present

q mol fraction of TG present

r mol fraction of DG present

s mol fraction of MG present

t mol fraction of GL present

¹³ Akhiero E.T. (2014): **Modeling of the Transesterification of *Jatropha curcas* Seed Oil**; Ph.D Thesis, Petroleum Technology Development Fund Chair in Renewable Energy, Department of Chemical Engineering, University of Benin, Benin City, Nigeria, October, 2014

Then $q + r + s + t = 1$ -----4

$p = r + 2s + 3t$ -----5

p is the total amount of methanol consumed

Let the reaction volume V = constant

Therefore, the rate of reaction of TG is given by

$V \frac{dq}{d\theta} = -k_1pq$ -----6

The rate of formation of each product is

$V \frac{dr}{d\theta} = k_1pq - k_2pr$ -----7

$V \frac{ds}{d\theta} = k_2pr - k_3ps$ -----8

$V \frac{dt}{d\theta} = k_3ps$ -----9

Eliminating the time θ as a variable by dividing equation 7 to 9 by equation 6 gives

$\frac{dr}{dq} = -1 + \frac{k_2r}{k_1q} = \frac{k_2r}{k_1q} - 1$

$\rightarrow \frac{dr}{dq} = \frac{r - \frac{k_1q}{k_2}}{\frac{k_1q}{k_2}} = \frac{r - Aq}{Aq}$ -----10

Let $(k_1/k_2) = A$; $(k_2/k_3) = B$

$\frac{\text{equation 7.8}}{\text{equation 7.6}} \rightarrow \frac{ds}{dq} = \frac{k_2pr - k_3ps}{-k_1pq} \rightarrow$

$\frac{ds}{dq} = \frac{k_3ps - k_2pr}{k_1pq} = \frac{s - (k_2/k_3)r}{(k_1/k_3)q}$

Or

$\frac{ds}{dq} = \frac{k_3 [s - (k_2/k_3)r]}{k_1q} = \frac{s - (k_2/k_3)r}{(k_1/k_3)q}$

$$\therefore k_1/k_3 = \frac{k_1}{k_2} \cdot \frac{k_2}{k_3} = A \cdot B$$

$$\therefore \frac{ds}{dq} = \frac{s}{ABq} - \frac{r}{Aq} \text{-----11}$$

Equation 10: $\frac{dr}{dq} = \frac{r-Aq}{Aq}$ is a first order homogeneous differential equation solvable by the substitution technique: Thus, let

$$r = vq \text{-----12}$$

$$\therefore \frac{dr}{dq} = v + q \frac{dv}{dq} \text{-----13}$$

Substituting equations 12 and 13 into equation 10 $\rightarrow v + q \frac{dv}{dq} = \frac{vq-Aq}{Aq}$

$$\begin{aligned} \rightarrow q \frac{dv}{dq} &= \frac{v-A}{A} - v \\ &= \frac{v-A-Av}{A} = \frac{v(1-A)}{A} - 1 \end{aligned}$$

Let $A = 1 + C$

$$\therefore 1 - A = -C$$

Hence

$$\begin{aligned} q \frac{dv}{dq} &= -\frac{vc}{1+C} - 1 \\ &= -\left[\frac{vc+(1+c)}{1+c} \right] \end{aligned}$$

Thus

$$\frac{dq}{q} = - (1+c) \frac{dv}{cv+(1+c)}$$

Integrating \rightarrow

$$\ln q = \frac{-(1+c)}{c} \ln(cv + (1+c)) + \ln K$$

$K =$ constant of integration

$$q = K [cv + (1 + c)]^{-\frac{1+c}{c}} \text{-----14}$$

$$q = K \left[c \frac{r}{q} + (1 + c) \right]^{-\frac{1+c}{c}} \text{-----14a}$$

At $\theta = 0, q = 1, r = 0$

$$\therefore 1 = K[1 + c]^{-\left(\frac{1+c}{c}\right)}$$

$$\text{Thus } K = (1 + c)^{(1+c)/c} \text{-----15}$$

Solution

Consider the case where $\frac{k_1}{k_2} = 0.734$, and $\frac{k_2}{k_3} = 3.71$

That is $A = 0.734 = 1 + C$

Thus $1 + C = 0.734$

$$\therefore C = -0.266$$

Substituting into equation 15

$$K = (0.734)^{\frac{-0.734}{0.266}} = (0.734)^{-2.7594}$$

$$\therefore K = 2.347$$

Recalling equation (14a) \rightarrow

$$q = 2.347 \left[0.734 - 0.266 \frac{r}{q} \right]^{2.7594} \text{-----16}$$

Rearranging equation 16 \rightarrow

$$\left(\frac{q}{2.347} \right)^{\frac{1}{2.7594}} = 0.734 - 0.266 \frac{r}{q}$$

$$q^{0.3624} (2.35^{-0.3624}) = 0.734 - 0.266 (r/q)$$

$$0.734q^{0.3624} = \frac{0.734q - 0.266r}{q}$$

$$0.734q^{1.3624} = 0.734q - 0.266r$$

$$\rightarrow 0.266r = 0.734q - 0.734q^{1.3624}$$

$$\rightarrow r = \frac{0.734}{0.266} [q - q^{1.3624}]$$

$$r = 2.7594 [q - q^{1.3624}] \text{ -----17}$$

$$\frac{ds}{dq} = \frac{s}{2.7231q} - \frac{r}{0.734q} \text{ -----18}$$

$$\text{Now } r = 2.7594[q - q^{1.3624}] \text{ -----17}$$

Substituting for r from equation 17 into 18→

$$\frac{ds}{dq} - \frac{s}{2.7231q} = -\frac{2.7594}{0.734q} [q - q^{1.3624}] = -3.7594[1 - q^{0.3624}]$$

$$\frac{ds}{dq} - \frac{s}{2.7231} \left(\frac{1}{q}\right) - 3.7594q^{0.3624} = -3.7594$$

$$\frac{ds}{dq} - \frac{s}{2.7231q} - 3.7594q^{0.3624} + 3.7594 = 0$$

$$\frac{ds}{dq} - \frac{[s+10.237^{1.3624}-10.237q]}{2.7231q} = 0$$

$$\frac{ds}{dq} - \frac{s}{2.7231q} = 3.7594(q^{0.3624} - 1) \text{ -----19}$$

Equation 19 can be solved by using the Integrating Factor method. Thus

Let R be the Integrating Factor→

$$\therefore R = \exp \int -\frac{dq}{2.7231q} \text{ -----20}$$

$$= \exp. \ln q^{-1/2.7231}$$

$$R = q^{-1/2.7231} \text{ -----21}$$

Hence

$$q^{\frac{-1}{2.7231}} \frac{ds}{dq} - \frac{q^{-1/2.7231}}{2.7231q} s = q^{-1/2.7231} [3.7594(q^{0.3624} - 1)]$$

$$\text{That is } d q^{-1/2.7231} s = 3.7594 \left(q^{-0.0048} - q^{-1/2.7231} \right) \text{ -----22}$$

Integrating →

$$s \ q^{\frac{-1}{2.7231}} = 3.7594 \left(\int \left(q^{-0.0048} - q^{1/2.7231} \right) dq \right) + \epsilon \text{ -----23}$$

where $\epsilon = \text{constant}$

$$s \ q^{\frac{-1}{2.7231}} = \frac{3.7594}{0.9952} q^{0.9952} - \frac{3.7594}{0.6328} q^{0.6328} + \epsilon$$

$$s = \frac{3.7594}{0.9952} q^{1.3624} - \frac{3.7594}{0.6328} q + \epsilon \ q^{0.3672} \quad 24$$

$$@ \theta = 0, s = 0; q = 1$$

$$\therefore 0 = 3.778 - 5.941 + \epsilon$$

$$\rightarrow \epsilon = 2.163 \quad 25$$

Hence

$$s = 3.778q^{1.3624} - 5.941q + 2.163 \ q^{0.3672}$$

$$s = 2.163q^{0.3672} - 5.941q + 3.778q^{1.3672}$$

$$= 2.163[q^{0.3672} - 2.747q + 1.747q^{1.3624}]$$

$$\mathbf{s = 2.163[q^{0.3672} - 2.747q + 1.747q^{1.3624}]} \quad \mathbf{26}$$

Thus for any value of q, Equations 17 and 26 can be used to determine the corresponding values of r and s, and then the value of t from Equation 4. The total amount of Methanol consumed can be determined from Equation 5: $p = r + 2s + 3t$

The following Table may now be set up:

TABLE 1: DATA PREDICTED FROM THE MODEL EQUATIONS

AMOUNT OF METHANOL CONSUMED ($p = r + 2s + 3t$)	MOL FRACTION TRIGLYCERIDE (q)	MOL FRACTION DIGLYCERIDE PRESENT (r)	MOL FRACTION MONOGLYCERIDE PRESENT (s)	MOL FRACTION GLYCEROL PRODUCED (t)	MOL FRACTION BIODIESEL PRODUCED ($\beta = p + \frac{1}{3}(q - t)$)
0.00000	1.00000	0.00000	0.00000	0.00000	0.00000
0.10720	0.90000	0.09300	0.00680	0.00020	0.40653
0.22960	0.80000	0.17140	0.02760	0.00100	0.49594
0.36900	0.70000	0.23420	0.06260	0.00320	0.59167
0.52830	0.60000	0.27980	0.11210	0.00810	0.72560
0.71140	0.50000	0.30640	0.17580	0.01780	0.87210
0.92370	0.40000	0.31180	0.25270	0.03550	1.04520
1.17420	0.30000	0.29270	0.34040	0.06690	1.25190
1.48120	0.20000	0.24380	0.43120	0.12500	1.50620
1.88930	0.10000	0.15610	0.49850	0.24540	1.84080
3.00000	0.00000	0.00000	0.00000	1.00000	2.66670

The data presented in Table 1 have been displayed in graphical form in Figure 1

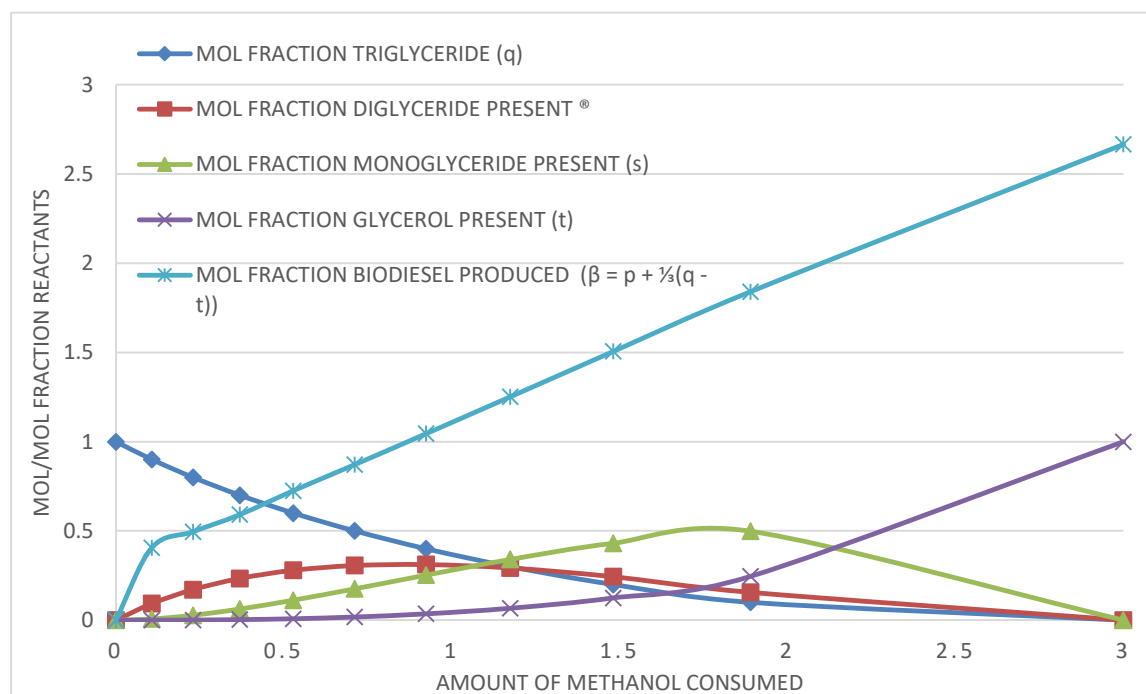


FIGURE 2: RATE EQUATIONS CONTROLLING THE TRANSESTERIFICATION REACTION

Conclusion

The trends observed in Figure 2 attest to the correctness of the model equations. For example, 1.0 mol of triglyceride reacts with 3.0 mol methanol to produce 1.0 mol glycerol. That 2.667 mol Bio-diesel instead of 3.0 mol predicted by the model equations was obtained reinforces the justification for the use of excess methanol for Trans-esterification.

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