Simulation Model for Biodiesel Production using Non-isothermal (CSTR) Mode: Membrane Reactor

Rhoda Habor Gumus^{1*} Iwekumo Wauton², I Emmanuel Okekogene Efeonah³

- 1. Department of Chemical and Petroleum Engineering, Niger Delta University, Wilberforce Island. P.M.B 071. Bayelsa State . Nigeria email,
- 2. Department of Chemical and Petroleum Engineering, Niger Delta University, Wilberforce Island . P.M.B 071 Bayelsa State, Nigeria

Dayersa State, Nigeria

3. Department of Chemical and petroleum Engineering, Niger Delta University, Wilberforce Island. P.M.B 071. Bayelsa State. Nigeria

E-mail of the Corresponding author: rhodagumus@yaoo.com

Abstract

The immisicibility of vegetable oil in methanol provides a mass transfer challenge in the early stages of transesterification reaction in the production of biodiesel. A mathematical model capable of predicting the performance and behaviour of a membrane reactor operated in CSTR mode has been developed. The model utilized the mass balance of a typical multiphase reactor which accounted for the mass transfer rate term to generate the performance equation. Predicted concentration of species, yield and conversion of the membrane reactor were higher compared to that of conventional CSTR as shown in Table 1. The effect of temperature on yield, and conversion was also considered. The temperature at 40° C exhibited the highest yield and conversion of methyl ester compared to $25 \,^{\circ}$ C and $60 \,^{\circ}$ C

Keywords: biodiesel, mass transfer limitation, membrane reactor, modeling, vegetable oil

1 Introduction

Biodiesel, a mono alkyl esters of long chain free fatty acid has become increasingly attractive worldwide, because it is obtained from renewable resource, combined with high performance and environmental benefits (Damoko and Cheryan 2000; Qui et al., 2010; Bambase et al., 2007; Nye et al., 1983). In recent times, due the activities of man and technology, the world has been faced with many challenges such as global warming (Ataya et al., 2008; Kusdiana and Saka 2000). These challenges have led to the search for alternative fuels that have gained significant attention in recent times (Frascari et al., 2009). Biodiesel, derived from triglycerides of vegetable oils and animals have shown potential as substitute for petroleum-based diesel fuels [8]. Biodiesel fuel is derived from plant, has a more favourable combustion emission profile; such as low emission of CO, particulate matter, SO_x unburned hydrocarbons during the process and comparable properties to petroleum based fuel [Yamazaki et al., 2005; Lotero et al., 2006; Demirbas, 2002; Srivastava and Prasad 2000). Biodiesel is renewable, biodegradable and it does not contain sulfur, aromatic hydrocarbons, metal and crude oil residues because it is entirely made from vegetable oil or animal fats (Dube, 2007). The overall life cycle emission of CO₂ from 100% biodiesel (B100) is 78.45% lower than that of petrodiesel, and a B20 fuel reduces net CO₂ emission by 15.66%. Substituting B100 for petrodiesel in buses reduces the life cycle consumption of petroleum by 95% while a B20 fuel causes it to reduce by 19% (Fukuda et al ., 2005). It has a relatively high flash point (about 150 °C) which makes it less volatile and safer to transport or handle than petroleum diesel (Dube., 2007; Krawezyk., 2006) and provides lubricating properties that can reduce engine wear and extend., 2006 engine life (Krawezyk).

When adequately purified or blended, biodiesel can be used in operating motor vehicles, trains, and aircrafts, heating fuels in domestic and commercial boilers. Due to the oxygenated nature, a better lubricant, many countries are introducing biodiesel blends to replace the lubricating effect of sulfur compounds in low sulfur diesel fuels (Marjanovic *et al.*, 2010). Many research groups have attempted to produce biodiesel using different reactor types. A pseudo homogenous system in batch reactor with lewis acid catalyst, active, with no mass transfer limitations has been proposed [Noureddini and Zhu., 1997). Generally, a reaction mechanisms consisting of an initial mass transfer

controlled region followed by kinetically controlled region has also been identified (Zhang and Dube., 2000). The immiscibility of methanol and vegetable oil leads to mass transfer resistance in the trans-esterification reaction. The conventional base-catalyzed trans-esterification is characterized by slow reaction rates at initial and final stages limited by mass transfer between polar methanol/glycerol phase and non- polar oil phase (Klofutsr *et al.*, 2010).

Several research groups (Ataya et al 2008) acid catalyzed (Frascari et al., 2009), mechanical agitation, (Watanabe et al., 2001), laboratory batch reactor with separation set up (Kusdiana and Saka., 2000), treated in supercritical methanol and enzymatic conversion (Watanabe et al., 2001) in fixed bed reactor have been used to produce biodiesel. The acid catalyzed reaction is slow due to mass transfer limitation though active. Yet another drawback to acid catalyzed proccess is the high alcohol to oil ratios necessary to promote the conversion of oil to FAME (Freeman et al., 1986). The higher amount of alcohol increases the reactor size; associated with cost. Despite the slower reaction rate this approach has several advantages over the base-catalyzed method (Marjanovic et al., 2010), it employs one-step process as opposed to a two-step, because it can handle feedstock with high Free fatty acid content; easy downstream separation of the biodiesel and high quality glycerol by-product is produced. Another drawback of the acid-catalyzed process is the requirement for the reactor to withstand an acidic environment. The base catalyzed reaction could be performed under mild conditions to achieve significant conversion with minimal side reaction and reaction time. However, there is also this general problem, the presence of water and free fatty acid in feedstock, the cost associated with pre-treatment unit. The inherent water need to be reduced since it favours the formation of free fatty acid, which in the presence of base catalyst speeds up formation of soap that may partially consume the catalyst, thereby lowering the yield and renders the downstream separation difficult (Bam et al., 1995). A common challenge *that* plagues biodiesel production is the removal of residual TG and glycerol from the product. An attempt to drive the reaction as close to completion may also not be possible since trans-esterification is an equilibrium reaction. Also employing multiple washing of the product stream may give rise to serious waste water implications. The most important factor in biodiesel production is miscibility, because the conventional method results in a two-phase reaction, causing mass transfer limitation: the vegetable oil and methanol are not miscible. In order to solve the above, suggestions have been made to add solvent during washing and the use of solid adsorbent (activated carbon) for the product purification (Hayafuji et al., 199); Mei et al., 2013). Recent times, studies on biodiesel production using membrane reactor to alleviate the problem of mass transfer limitation is on the increase. This approach involves the use of membrane separation technologies, which exploit the immiscibility of the oil and methanol. The principle of membrane reactor operation is the physical characteristics, which permits the membrane reactor to separate FAME from TG, by formation of emulsion with dispersed oil droplets /micelles in the continuous MEOH rich phase This allows efficient transesterification at the surface of the oil droplets suspended in the MEOH. The product FAME and glycerol are then diffused from the oil droplets and dissolved in the MEOH rich phase (Mei et al., 2013). A mathematical model based on the modified Stefan-Maxwell with the incorporation of the effects of chemical phase equilibrium (CPE) and thermodynamic suitable for biodiesel production, on tubular plug flow reactor has been considered (Mei et al., 2013). A semi-batch two-phase membrane reactor with pore size of 0.05 micron, both model and experimental methods, with high conversion and purity biodiesel has also been reported (Marjanovic et al., 2010). But, the CSTR mode of membrane reactor to alleviate the immiscibility challenge is scare in literature. Therefore, in this paper, a CSTR mode of carbon membrane reactor model with pore size of 0.05 um based on twophase process was developed that involved *in-situ* separation to solve the challenges of immiscibility of biodiesel production. Simulation was conducted on both conventional CSTR and CSTR mode membrane reactor with experimental rate constant (k) values from literature (Zhang and Dube., 2000) for comparison, using MATLAB 7.5 Software package.

2. Model Formulation

The membrane reactor describes a number of different types of reactor configuration that contains a membrane. The reactors can be used to increase the conversion when the reaction is thermodynamically limited as well as to increase the selectivity when multiple reactions are occurring. In the reactor above, two phases are separated by a wall through which only one species can permeate. A significant assumption is that our catalyst is within the membrane so we can achieve reaction and separation simultaneously. This is a multiphase reactor with a specified wall area $A^{\alpha\beta}$ between phases.

2.1 Kinetics of Trans esterification Reaction

The kinetics of trans-esterification reaction is a three step process involving a set of reversible intermediates shown as;

$$TG + 3A \xleftarrow{Catalyst} 3ME + G$$
 (1)

But this reaction passes through three stepwise set of reversible intermediate reactions stated

TG + ROH
$$K_1$$
 DG + ME
DG + ROH K_3 MG + ME (2)
MG + ROH K_5 GL + ME,
K₆

For the rate expression to be derived, they have to be resolved into their individual elementary reactions which contain the rate constants and the corresponding conversions and activation energies.

$$TG + A \xrightarrow{K_1} DG + ME,$$

$$DG + ME \xrightarrow{K_2} TG + A,$$

$$DG + A \xrightarrow{K_3} MG + ME,$$

$$MG + ME \xrightarrow{K_4} DG + A,$$

$$MG + A \xrightarrow{K_5} G + ME,$$

$$G + ME \xrightarrow{K_6} MG + G,$$
(3)

Hence the rate expression for each elementary reaction in terms of conversion and concentration are as follows.

$$-r_{1} = K_{1}C_{TG}C_{A}$$

$$-r_{2} = K_{2}C_{ME}C_{DG}$$

$$-r_{3} = K_{3}C_{DG}C_{A}$$

$$-r_{4} = K_{4}C_{ME}C_{DG}$$

$$-r_{5} = K_{5}C_{MG}C_{A}$$

$$-r_{6} = K_{6}C_{ME}C_{G}$$
(4)

Now the rate expression for each component can be written as thus without the Shunt reaction scheme.

$$r_{TG} = \frac{d}{dt}C_{TG} = r_2 - r_1$$

$$r_A = \frac{d}{dt}C_A = r_2 - r_1 - r_3 - r_5 + r_4 + r_6$$

$$r_{ME} = \frac{d}{dt}C_{ME} = r_1 - r_2 + r_3 - r_4 + r_5 - r_6$$
(5)
$$r_G = \frac{d}{dt}C_G = r_5 - r_6$$

$$r_{DG} = \frac{d}{dt}C_{DG} = r_1 - r_2 - r_3 + r_4$$

$$r_{MG} = \frac{d}{dt}C_{MG} = r_3 + r_6 - r_4 - r_5$$

Substituting equation 4 into 5 gives

$$-\tau_{TG} - \frac{d}{dt}C_{TG} - -K_{1}C_{TG}C_{A} + K_{2}C_{DG}C_{ME}$$

$$-\tau_{A} = \frac{d}{dt}C_{A} = -K_{1}C_{TG}C_{A} + K_{2}C_{DG}C_{ME} - K_{3}C_{DG}C_{A} + K_{4}C_{MG}C_{ME} - K_{5}C_{MG}C_{A} + K_{6}C_{ME}$$

$$-\tau_{ME} = \frac{d}{dt}C_{ME} = K_{1}C_{TG}C_{A} - K_{2}C_{DG}C_{ME} + K_{3}C_{DG}C_{A} - K_{4}C_{MG}C_{ME} + K_{5}C_{MG}C_{A} - K_{6}C_{ME}C_{G}$$

$$\tau_{G} = \frac{d}{dt}C_{G} = K_{5}C_{MG}C_{A} - K_{6}C_{ME}C_{G}$$

$$-\tau_{DG} = \frac{d}{dt}C_{DG} = K_{1}C_{TG}C_{A} - K_{2}C_{D2}C_{ME} + K_{3}C_{DG}C_{A} - K_{4}C_{MG}C_{ME}$$

$$(6)$$

$$-\tau_{MG} = \frac{d}{dt}C_{MG} = -K_{3}C_{DG}C_{A} - K_{4}C_{MC}C_{ME} - K_{5}C_{ME}C_{G}$$

2.2 Model Assumptions

To achieve very high conversions, one of the reaction products is selected through a semi permeable membrane from the reaction mixture. The membrane is a novel technology with in-built membrane wall and technique for driving reversible reactions to the right toward completion Therefore the following assumptions are made. A membrane reactor with CSTR configuration A permeable interfacial area A separates the reaction into two homogeneously distinct phases. The reactor divides into two perfectly mixed phases. There is no fouling effect and a negligible resistance across membrane wall. No stable emulsions within the reactor, as the molecules are in purely homogeneously liquid phase. No density change in the reactor, thus: $v_0 = v$. The entering and leaving specific heat capacities are equal: $c_{p0} = c_p$

Pressure in the reactor is kept constant, and there is no constant hold-up in the system. The work done in the system is not considered as the system is already well stirred. The Reactor is equipped with a very efficient stirring mechanism so that there is no concentration gradient in the reactor: $\frac{d}{dt}n_i = 0$. Sum of entering and leaving densities are equal: $p_0 = p$. Heat transfer coefficients of the reaction are equal. The membrane reactor is a multiphase reactor; as such a significant mass transfer between phases is encountered. Thus a mass balance is taken for entering and leaving species together with a description of the mass transfer rate and interfacial area between phases describe the reactor performance. The mass balance also accounts for the chemical reaction and reaction rates taking place in the reactor. Thus, the expression for the mass balance is given as



Since the membrane reactor is a multiphase, it divides the reaction into two phases, with α and β respectively. The α -phase collects the feed and allows a residence time for completion of the reaction, while the β -phase collects the permeate species throughout the reaction. For each species; the following expression therefore gives the mass balance for the input, intermediate and the output species:

$$V \frac{dc_T}{dt} = v_0 C_{TG0} - v C_{TG} + r_{TG} V \tag{8}$$

$$V \frac{dC_A}{dt} = v_0 C_{A0} - v C_A + r_A V \tag{9}$$

$$V \frac{ac_{DG}}{at} = v_a C_{DGa} - v C_{DG} + r_{DG} V \tag{10}$$

$$V \frac{dC_{MG}}{dt} = v_{c}C_{MG} - vC_{MG} + r_{MG}V$$
(11)

$$V \frac{dC_{ME}}{dt} = v_a C_{MEa} - v C_{ME} + r_{ME} V + A K_m (C_{NE}^{\mathcal{L}} - C_{ME}^{\beta})$$
(12)

$$V \frac{dC_G}{dt} = v_o C_{Go} - v C_G + \tau_G V \tag{13}$$

Where **A** is the interfacial area of membrane, K_m is the mass transfer coefficient, v_a is the volumetric flow rate, **a** is the retentate phase and **b** is the permeate phase. Assuming steady state, the performance equation can be given in terms of reactor volume as:

$$0 = v_0(C_{TG0} + C_{A0}) - v(C_{TG} + C_A + C_{DG} + C_{ME} + C_{MG} + C_G) + V_R \sum_{j=1}^{N_j} \tau_j - AK_M (C_{ME}^{g} - C_{ME}^{\beta})$$
(14)

Simplifying and making V_R subject of formula gives the performance equation:

$$V_{R} = \frac{v(c_{TG}+c_{A}+c_{DG}+c_{MG}+c_{MG}+c_{G}-c_{TGU}-c_{AL})-AK_{N}(c_{MK}^{\alpha}-c_{ME}^{\beta})}{\sum_{j=1}^{T}\tau_{j}}$$
(15)

2.3 Space time

This is the time required to process one reactor volume of feed at specific conditions (Fogler., 2008). It is the ratio of the volume of the reactor to the volumetric flow rate of species in the reactor:

$$\tau = \frac{\mathbf{v}_{\mathbf{R}}}{\mathbf{v}} \tag{16}$$

$$\boldsymbol{\tau} = \left\{ \frac{(c_{TG} + c_{A} + c_{DG} + c_{ME} + c_{MG} + c_{G} - c_{TG0} - c_{AD}) - (\frac{AE_{M}(c_{ME}^{T} - c_{ME}^{\beta})}{2})}{\Sigma_{j=1}^{q} r_{j}} \right\}$$
(17)

2.4 Space Velocity

This describes the number of reactor volumes of feed treated at specified conditions which can be reacted in unit time, the reciprocal of space time.

$$\mathbf{f} = \frac{\mathbf{v}}{\mathbf{v}_{\mathbf{g}}} \tag{18}$$

$$S = \frac{1}{\tau} = \left\{ \frac{\sum_{j=1}^{q} \tau_{j}}{(C_{TG} + C_{A} + C_{DG} + C_{ME} + C_{MG} + C_{G} - C_{TG0} - C_{A0}) - \left(\frac{AK_{M}(C_{ME}^{q} - C_{ME}^{p})}{*}\right)} \right\}$$
(19)

2.5 Energy balance

Using the same principle, the energy balance equation is stated thus

$$\begin{bmatrix} Accumulation of energy \\ system \end{bmatrix} = \begin{bmatrix} Input of energy \\ to system \end{bmatrix} + \begin{bmatrix} Output of from \\ system \end{bmatrix} + \begin{bmatrix} Re \ action \ taking \ place \\ in \ system \end{bmatrix} - \begin{bmatrix} Heat \ given \ up \\ by \ system \end{bmatrix} - \begin{bmatrix} Work \ done \\ in \ system \end{bmatrix}$$
(20)

Taking into consideration the assumptions made in the development of this model, and for q multiple reactions and m species:

Input term is given as $\sum_{z=1}^{m} \Theta_z v_z c_{Pz} T_z$ (21)

Output ==
$$\sum_{i=1}^{m} \Theta_i v_i c_{Pi} T_i$$
 (22)

Accumulation =
$$V_R \sum_{i=1}^{m} \Theta_i v_i c_{Pi} \frac{d}{dt} I_i$$
 (23)

Heat =
$$Q$$
 (24)

Generation =
$$V_R \sum_{i=1}^{q} r_{ij} \Delta H_{Rij}(T)$$
 (25)

2.6 Heat Absorbed

Substituting equations (21), (22), (23), (24) and (25) into (18) gives

$$V_{R}\sum_{i=1}^{m}\Theta_{i}v_{i}c_{Pi}\frac{c}{dt}T_{i} = \sum_{z=1}^{m}\Theta_{z}v_{z}c_{Pz}T_{z} - \sum_{\ell=1}^{m}\Theta_{\ell}v_{\ell}c_{P\ell}T_{\ell} - V_{R}\sum_{i=1}^{q}\tau_{ij}\Delta H_{Rij}(T) - Q$$
(26)

Simplifying and making Q subject of formula gives the equation of heat absorbed.

3 Results and Discussion

3.1 Effect of mass transfer on biodiesel production

The immiscibility of methanol and vegetable oil leads to a mass transfer resistance in the trans-esterification of vegetable oil for biodiesel production (Guan *et al.*, 2009). However, in membrane reactor, the formation of twophase (emulsified) system is necessary for high conversion and separation. The model prediction on component concentrations is presented in Table 1 for comparison. From Table 1, it can be seen that, with the same initial concentration of Triglyceride and Alcohol species at the same reacting conditions, the final concentration obtained in conventional CSTR was higher especially for alcohol 0.34 and 0.19 respectively. Both conversion and the yield of the Methyl ester specie was higher (90 % and 2.36) using a membrane reactor compared to that of the conventional CSTR (60 % and 1.62). This is because the membrane reactor provides an interfacial area that helps to increase the permeability and separation of the methyl ester specie which reduces the mass transfer limitation encountered in trans-esterification reaction in conventional CSTR (0.01) which is in good agreement in literature (Marjanovic *et al.*, 2010), that the oil droplets are too large to pass through the pores of the membrane while the small molecular size of FAME, will pass through the membrane.

3.2 Effect of temperature on concentration of species

Fig. 2 shows the concentration profile of each species against time at a temperature of 25° C. The profile showed an increase in concentration of the Methyl esters (ME) and Glycerol (G) species with time and a corresponding decrease in the Triglyceride (TG) and Alcohol (A) species. This is an indication that conversion increases with increase in time. It is obvious from Fig. 2 that at this temperature, it takes a longer time (900 min) to achieve maximal Methyl ester production. This is so because trans-esterification reaction is kinetically-control. From Fig. 3, the reaction temperature is significantly affected the conversion. At 40 °C with the same alcohol-to-oil ratio, (3:1) the reaction time reduced drastically (600 min) to achieve high methyl ester, which agreed favourably in literature (Liu., 1994). This revealed that, a shorter time used to achieve maximum methyl ester production, indicates higher concentration of methyl ester production at 60° C. At this temperature, a much higher conversion of the alcohol specie was indicated as seen in the final concentration value. Although the reaction rate is significantly increased, a drawback, using this temperature is that the backward reaction is favoured as the backward rate constants are more affected by increased temperature.

3.3 Effect of temperature on yield and conversion

Fig. 5 shows the influence of various temperatures on methyl esters yield with time. The maximum yield of methyl esters at 25°C is achieved at a longer time, and the yield profile curve is lower compared to those of higher temperatures. The yield at 40°C is noticeably higher than that of 25°C and is achieved at a reduced time interval. However, from Fig.5, it is observed that while the maximum yield at 60°C is achieved at very short interval compared to other lower temperatures, yet, with the increased time the yield is reduced below that at 40° C. This is because a higher reaction temperature would results into lower maximal methyl ester production due to reversible reaction step (thermodynamic effect), which is in good agreement with literature (Marjanovic., 2010). Fig. 6 shows the effect of temperature on the Methyl esters conversion in vegetable oil with time. The temperature of reaction mixture dictates the maximum conversion itself and the rate of trans-esterification which affects the reaction time required to achieve maximum conversion. From Fig. 6, it follows that after 100 min the conversion to methyl ester was about 0.35, 0.65 and 0.85 at 25°C, 40°C, and 60°C, respectively. After 1200 min the conversion was about 0.7, 0.85, and 0.9 at 25°C, 40°C, and 60°C, respectively. The results obtained, also indicates that conversion is quite sensitive to temperature (Ahiekpor and Kuwornoo., 2010). Figure. 7 shows the increase in conversion with an increase in the volume of reactor. This is due to the formation of methyl esters, glycerol and other intermediate species together with other unreacted reactants left in the reactor. At higher temperatures, the conversion increases faster even at low reactor volume. With a maximum volume of 250 m^3 , conversions of 0.9, 0.8 and 0.7 were achieved at 60° C, 40° C and 25° C respectively.

4. Conclusion

A reactor model representing a CSTR with integrated membrane reactor mode based on two-phase process was developed to predict concentration profile, yield and conversion of methyl ester (FAME). The membrane integrated reactor significantly increased the conversion as well as yield and concentration of methyl esters species compared to conventional CSTR. It was also found out that temperature greatly affected the transesterification of oil and methanol reaction, in increasing both the yield and conversion at reduced time, from 900 min to 600 min to achieve maximal conversion of 90 %. A consistent increase in yield was observed at 40 ° C compared to 60° C where the yield decreased with increase in time which may be due to the reversible reaction at higher temperatures. A recommended range of temperature would be 40 °C-50 °C as this will increase the rate of forward reaction, limit the formation of by-products, reduce the concentration of intermediate species and prevent reversibility of reaction pathway noticed for very high reaction temperature. The model was found to be efficient and comprehensive for a CSTR novel membrane reactor that accounts for reducing mass transfer limitations encountered by conventional reactors for trans-esterification for biodiesel production with 3:1 molar ratio.

Acknowledgments

The authors would like to gratefully acknowledge The Niger Delta University for financing and providing the enabling environment to carry out this research work.

Nomenclature

- K_1 Reaction rate constant for elementary reaction 1 (min¹)
- K_2 Reaction rate constant for elementary reaction 2 (min¹)
- K_3 Reaction rate constant for elementary reaction 3 (min¹)
- K_4 Reaction rate constant for elementary reaction 4 (min¹)
- K_5 Reaction rate constant for elementary reaction 5 (min¹)
- K_6 Reaction rate constant for elementary reaction 6 (min¹)
- - \mathbf{r}_1 reaction rate for elementary reaction 1 (mol L⁻¹min⁻¹)
- - \mathbf{r}_2 reaction rate for elementary reaction 2 (mol L⁻¹min⁻¹)
- $-r_3$ reaction rate for elementary reaction 3 (mol L⁻¹min⁻¹)
- $-\mathbf{r}_4$ reaction rate for elementary reaction 4 (mol L⁻¹min⁻¹)
- - r_5 reaction rate for elementary reaction 5 (mol L⁻¹min⁻¹)
- r_6 reaction rate for elementary reaction 6 (mol L⁻¹min⁻¹)
- r_{TG} Reaction rate for triglyceride (mol L⁻¹ min⁻¹)
- Reaction rate for diglyceride (mol L⁻ min⁻¹) r_{DG} reaction rate for monoglyceride (mol L^{-1} min⁻¹) r_{MG} Reaction rate for Alcohol (mol L⁻min⁻¹) \mathbf{r}_{A} Reaction rate for methyl ester (mol L^{-1} min⁻¹) r_{ME} Reaction rate for glycerol ($mol L^{-1} min^{-1}$) r_G Reaction rate for species $J \pmod{L^{-1} \min^{-1}}$ $r_{\rm T}$ Final concentration of triglyceride (mol L⁻¹) C_{TG} Final concentration of diglyceride (mol L⁻¹) C_{DG} Final concentration of monoglyceride (mol L⁻¹) C_{MG} C_A Final concentration of alcohol (mol L⁻¹) Final concentration of methyl ester (mol L⁻¹) C_{ME} C_{TG0} Initial concentration of triglyceride (mol L^{-1}) Initial concentration of diglyceride (mol L⁻¹) C_{DG0} Initial concentration of monoglyceride (mol L⁻¹) C_{MG0} C_{A0} Initial concentration of alcohol (mol L⁻¹) Initial concentration of methyl ester (mol L⁻¹) C_{ME0} Specific heat capacity of outlet species (Cal K⁻¹ Kg⁻¹ mol⁻¹) C_{pi} $\begin{array}{c} C_{p0} \\ V_R \end{array}$ Specific heat capacity of inlet species (Cal K⁻¹ Kg⁻¹ mol⁻¹) Volume of reactor (L)

- v_0 Inlet volumetric flow rate (L min⁻¹)
- v Outlet volumetric flow rate (L min⁻¹)
- τ Space time (min)
- S Space velocity (min⁻¹)
- Q Heat absorbed (Cal mol⁻¹)
- T_i Temperature of outlet species
- T_0 Temperature of inlet species

REFERENCES

[1] D. Darnoko, and, M. Cheryan 'Kinetics of Palm Oil Trans-esterification in a Batch Reactor', JAOCS. 77, 2000, pp 1167-117

[2] Z.Y., Qui, L.N. Zhao, and L. Weather, "Process Intensification technologies in continuous biodiesel production". *Chemical Engineering and Processing 49, 4,* 2010, Pp (323-330), 0255-2701.

[3] M.E., Bambase, N., Nakamura, J., Tanaka, M., Matsumura ''Kinetics of hydroxide-catalysed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters''. *J. Chem. T echnol. Biotechnol 82 (3)*, 2007, Pp 273-280

[4] M. J., Nye, T. W., Williamson, S., Deshpande J. H., Schrader, and W.H., Snively. "Conversion of used frying oil to diesel fuel by trans- esterification: preliminary test". J. Am. Oil Chem. Soc. 60, 1983, Pp 1598-1601.

[5] F. Ataya, M.A., Dube and M. Ternan. "Variables affecting the induction period during acid-catalyzed trans esterification of canola oil to FAME". *Energy and Fuels 22* 2008, p 679.

- [6] D. Kusdiana, and S. Saka 'Kinetics of Trans-esterification reaction in rapeseed oil to biodiesel fuel as treated in supercritical methanol''. *Fuel 80*, 2000, Pp 693-698.
- [7] D., Frascari, M., Zuccaro, A paglianti and D. Pinelli, "Optimazation of mechanical agitation and evaluation of the mass – transfer resistance in the oil trans esterification reaction of biodiesel production". *Industrial and Engineering Chemistry research.* 48, 16. 2009, Pp (7540-7549), 0888-5885.
- [8] H. Fukuda, A. Kondo, and H Noda 'Biodiesel Fuel Production by Trans-esterification of oils'. J. Biosci. Bioeng 92 (5), 2001, Pp 405-416.
- [9] R., Yamazaki, S., Iwamoto, H., Nabetani, K., Osakade, O., Miyawaki, and Y. Sagara "Economic Assessment on practical application of Non catalytic Alcoholysis for Biodiesel Fuel Production". *Japan. J. Food Eng.*, 6. 2005, Pp 113-120.
- [10] E, Lotero, J..G, Goodwin, D.A, Bruce, K, Suwannakarn, Y, Liu and D.E. Lopez "The catalysis of biodiesel synthesis". *Catalysis 19*: 2006, Pp 41-83.
- [11] A.Demirbas, 'Biodiesel from vegetable oils via trans-esterification in supercritical methanol''. *Energy Conversion & Management, 43*, 2002 Pp 2349-2356.
- [12] A, Srivastava, R. and Prasad. "Triglycerides-based diesel fuels". *Renew Sustain Energy Rev* 4: 2000, Pp 111-133
- [13] T. Krawczyk, Biodiesel Alternative fuel makes in roads but hurdles remain INFORM 7: 2006, Pp 801-829.
- [14] W,Von, *Technical handbook for marine biodiesel in recreational boats*. National Renewable Energy Laboratory, Department of Energy, USA 1999.

- [15] M.A. Dube, A.Y. Tremblay and J. Liu., 'Biodiesel production using membrane reactor '' Bioresource Technlogy 98, 2007 639-647.
- [16] A. V., Marjanovic, O. S., Stamenkovic, Z. B., Todorovic, M. L., Lazic and V. B. Veljkovic, "Kinetics of the base-catalysed sunflower oil ethanolysis". *Fuel 89, 3,* 2010, Pp (665-671), 0016-2361.
- [17] H., Noureddini, and D. Zhu, "Kinetics of trans-esterification of Soybean Oil". Journal of the American Chemists Society, 74: 1997, Pp 1457-1463
- [18] Y., Zhang, M.A. Dube, D.D McLean. and M. Kates "Biodiesel production from waste cooking oil: 1. Process design and technological assessment". *Bioresource Technology* 89: 2000, Pp 1-16.
- [19] B., Klofutar, J., Golob, B., Likozar, C., Klofutar, E., Zagar, and I. Poljansek, "The transesterification of rapeseed and waste sunflower oils: Mass-transfer and kinetics in a laboratory batch reactor and in an industrial-scale reactor/ separator setup". *Bioresource Technology*, 101, 10, 2010, Pp (3333-3344), 0960-8524.
- [20] B. Freedman, E.H. Fryde and T.I, Mounts 'Variables affecting the yields of fatty esters from transesterified vegetable Oils ''Journal of American Oil Chem Society 61, 1984 1638-1643
- [21] Y., Watanabe, Y., Shimada, A., Sugihara and Y. Tominaga. 'Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed bed bioreactor' *Journal of the American oil Chemists' Society* 78: 2001, Pp 703-707.
- [22] N., Bam, D. C., Drown, R., Korous, D.S., Hoffman, T.G., Johnson, J. M., Washam. 'Method for purifying alcohol esters'. US Patent No. 5, 1995, Pp 424, 467.
- [23] S., Hayafuji, T., Shimidzu, S., Oh, and H., Zaima "Method and apparatus for producing diesel fuel oil from waste edible oil". US Patent No. 5, 1999, 972, 057. S., Hayafuji, T., Shimidzu, S., Oh, and H., Zaima "Method and apparatus for producing diesel fuel oil from waste edible oil". US Patent No. 5, 1999, 972, 057.
- [24] M.F. Chang, J. Chen, P.P. Oh and Z.-S. Chen "Modeling Analysis of membrane Reactor for Biodiesel production AIChE J. 59. 1. 2013 Pp 258271.
- [25] H.S. Fogler *Elements of Chemical Reaction Engineering Fourth Edition*, Prentice-Hall of India. 2008 203-3416-8
- [26] G. Guan, K., Kusakabe, N., Sakurai, and K. Moriyama 'Trans esterification of biodiesel fuel using acid catalysts in the presence of vegetable oil to dimethyl ether'. *Fuel* 88: 2009, Pp

81-86.

- [27] K. Liu Preparation of fatty acid methyl esters for gas-chromatograhic analysis of lipids in biological materials J Am Oil Chem. Soc. 71, 1994 1179-1187
- [28] J.C. Ahiekpor and D.K. Kuwornoo Kinetics of palm kernel oil and ethanol transesterification International Journal of energy and Environment 1, 6. 2010 Pp 1097-1108



Figure 1: A two-phase Membrane reactor with reactants TG and A in one phase and ME in permeate phase

Table 1 Comparison of values between Conventional CSTR and CSTR mode membrane reactor

Components	Conventional CSTR		Membrane Reactor	
	Initial value	Final Value	Initial value	Final Value
C _{TG}	0.25	0.01910044	0.25	0.0207386
C _A	0.75	0.3446087	0.75	0.1883408
C _{ME}	0	0.4053919	0	0.5909052
Yield	0	1.6215654	0	2.3636207
Conversion	0	0.6359824	0	0.9170456





Figure 2 A Plot of concentration against time at 25°C for 3:1 molar ratio



Figure 3 Plot of concentration against time at 40°C for 3:1 molar ratio

Chemical and Process Engineering Research ISSN 2224-7467 (Paper) ISSN 2225-0913 (Online) Vol.8, 2013



www.iiste.org

Figure 4 Plot of concentration against time at 60°C for 3:1 molar ratio



Figure 5 Yield of methyl ester versus time

Chemical and Process Engineering Research ISSN 2224-7467 (Paper) ISSN 2225-0913 (Online) Vol.8, 2013





Figure 6 Plot of conversion versus time



Figure 7 Plot of Conversion versus Reactor volume

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage: <u>http://www.iiste.org</u>

CALL FOR PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** <u>http://www.iiste.org/Journals/</u>

The IISTE editorial team promises to the review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library, NewJour, Google Scholar

