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# Simulation of Batch Reactive Distillation for Biodiesel Production from Oleic Acid Esterification

**Nada B. Nakkash[1] and Sarah R. Al-Karkhi[2]**
[1]Chemical Engineering Department, College of Engineering, University of Al-Nahrain, Baghdad – Iraq
[2]Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad – Iraq

## Abstract

The present work concerns with simulating unsteady state equilibrium model for production of methyl oleate (biodiesel) from reaction of oleic acid with methanol using sulfuric acid as a catalyst in batch reactive distillation. MESHR equations of equilibrium model were solved using MATLAB (R2010a). The validity of simulation model was tested by comparing the simulation results with a data available in literature. UNIQUAC liquid phase activity coefficient model is the most appropriate model to describe the non-ideality of OLAC-MEOH-MEOL-$H_2O$ system. The chemical reactions rates results from EQ model indicating the rates are controlled by chemical kinetics. Several variables was studied such as molar ratio of methanol to oleic acid 4:1, 6:1 and 8:1, amount of catalyst 0.6, 1.2 and 1.8 g sulfuric acid/g oleic acid, reaction time 36, 57 and 75 minutes, and reaction temperature 100, 120 and 130$^o$C. Taguchi method based on signal to noise ratio was used to determine the best operating conditions for biodiesel production.

**Keywords:** equilibrium model, UNIQUAC, biodiesel, oleic acid, rate of reaction

## Introduction

Biodiesel is an environmental friendly biofuels that consists of alkyl esters derived from the transesterification of triglycerides, esterification of free fatty acids and two-stage process (transesterification and esterification) with low molecular weight alcohols [1,2]. Biodiesel fuel has become more attractive because of its environmental benefits due to the fact that vegetable oils and animal fats are renewable biomass sources [3]. Biodiesel is considered to be renewable, since the carbon in the oil or fat originated mostly from carbon dioxide in the air. Tests show the use of biodiesel in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide and particular matter. The exhaust emissions of total hydrocarbons are on average 67% lower for biodiesel than diesel fuel, the exhaust emissions of carbon monoxide from biodiesel are on average 48% lower than carbon monoxide emissions from diesel and the exhaust emissions of particular matter from biodiesel are 47% lower than overall particulate matter emission from diesel. Emissions of nitrogen oxides stay the same or are slightly increased. Biodiesel emissions show decreased levels of polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (nPAH), which have been identified as potential cancer causing compounds [4-6].

The higher cost of biodiesel is due to its production mostly from expensive raw materials like edible oils, therefore non-edible oils are suitable for biodiesel production, because edible oils are already in demand and too expensive than diesel fuel. Non edible oil is considered to be the wonder biodiesel feed stock because of rapid in growth, higher seed productivity, suitable for tropical regions [7-10].

Reactive distillation (RD) is an innovating process which combines both distillation and chemical reaction into a single unit, which saves energy (for heating) and materials. Therefore, the RD technology offers many benefits as well as restrictions over the conventional process of reaction followed by distillation or other separation approaches. Reducing capital cost, higher conversion, improving selectivity, lower energy consumption, the reduction or elimination of solvents in the process and voidance of azeotropes are a few of the potential advantages offered by RD. This technique is especially useful for equilibrium-limited reactions such as esterification and transesterification reactions [11-21].

In the present work a simulation of batch reactive distillation for biodiesel production from oleic acid and methanol using sulfuric acid as a catalyst is considered.

## Theoretical Model

Consider the batch packed reactive distillation column and the schematic model of j$^{th}$ stage shown in Figure 1.

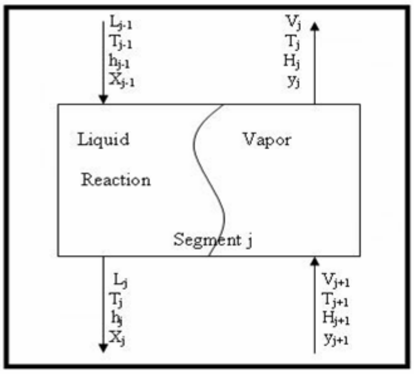

Fig. 1, Schematic diagram of equilibrium stage

The mathematical equilibrium model was formulated using the following assumptions:

1- Constant pressure drop across the column.
2- Hold-up per stage equal to liquid hold up on stage (i.e. vapor phase molar hold-up is neglected).
3- The chemical reactions occur only in the liquid phase.
4- Vapor-liquid equilibrium is achieved on each stage.
5- Each stage is considered as a continuous stirred-tank reactor (CSTR).
6- There is heat transfer in the reboiler and in the condenser, but the interior stages of the column are adiabatic.

Equations that model the equilibrium stage are given as MESHR equations:

M: Total and component material balances.

$$\frac{dM_j}{dt} = V_{j+1} + L_{j-1} - V_j - L_j + R_j \quad \ldots(1)$$

$$\frac{dM_j x_{ij}}{dt} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} - V_j y_{i,j} - L_j x_{i,j} + R_{i,j} \quad \ldots(2)$$

E: Equilibrium relation

$$y_{i,j} = K_{i,j} x_{i,j} \quad \ldots(3)$$

S: Summation equations

$$\sum_{i=1}^{c} x_{i,j} = 1, \sum_{i=1}^{c} y_{i,j} = 1 \qquad \ldots(4)$$

H: Enthalpy equation

$$\frac{dM_jH_j}{dt} = V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j + R_jHr \qquad \ldots(5)$$

R: Reaction rate equations [22, 23].

$$R_{OLAC} = -\frac{d[OLAC]}{dt} = k_1[_{OLAC}]*W_{cat} \qquad \ldots(6)$$

Where the kinetic constant $k_1$ in equation 6 is given by the Arrhenius equation [23]:

$$k_1 = 1.27\exp\left(\frac{-13300}{RT}\right) \qquad \ldots(7)$$

The concentration of oleic acid is replaced by activity, equation 6 becomes:

$$R_{OLAC} = k_1 a_{OLAC} * W_{cat} \qquad \ldots(8)$$

The activity of $i^{th}$ component was calculated using the following equation:

$$a_i = C_i\gamma_i \qquad \ldots(9)$$

The derivative of the rate reaction is found in Yadav, et. al. [24].

- **Vapor-Liquid Equilibrium Relation**

For non-ideal mixture additional variables such as $\gamma_i$ (activity coefficient) and $\phi_i$ (fugacity coefficient) appears to represent the degree of deviation from ideality.

$$y_i = \frac{K_i\gamma_i}{\phi_i}x_i \qquad \ldots(10)$$

The results of vapor fugacity coefficient by Redlich/Kowng and Peng-Robinson cubic equations of state show that the vapor phase has ideal gas behavior and the fugacity coefficient $\cong 1$.

For the present work the activity coefficient $\gamma_i$ has been calculated using NRTL, UNIFAC and UNIQUAC method. Parameters of NRTL and UNIQUAC are given in Tables A-1 and A-2.

- **Enthalpy Calculation**

Enthalpy of component in vapor phase is estimated through the integration the sensible heat from reference temperature to desired temperature

$$h_i = \int_{T_{ref}}^{T} Cp_i^V dT \qquad \ldots(11)$$

Evaluation of integral in equation 11 requires knowledge of the temperature dependence of heat capacity.

$$CP_i^V = [A + B[\frac{(\frac{C}{T})}{\sinh(\frac{C}{T})}]^2 + [\frac{(\frac{E}{T})}{\cosh(\frac{E}{T})}]^2] \qquad \ldots(12)$$

The constants A, B, C, and D for all components in vapor are given in Table A-3. The total enthalpy of vapor phase is:

$$h^V = \sum_{i=1}^{n} y_i \int_{T_{ref}}^{T} CP_i^V dT \qquad \ldots(13)$$

The enthalpy of component in liquid phase is estimated through the integral of heat capacity in vapor phase from reference temperature to desired temperature then substrate from heat of vaporization.

$$h_i = \int_{T_{ref}}^{T} Cp_i^V \, dT - \lambda_i \qquad \ldots(14)$$

The heats of vaporization at normal boiling point for each component is given in Table A-4.

The total enthalpy of liquid phase is given by equation 15:

$$h^L = \sum_{i=1}^{n} x_i \Big( \int_{T_{ref}}^{T} CP_i^V \, dT - \lambda_i \Big) + H_{mix} \qquad \ldots(15)$$

The heat of reaction at 298.15 K is given by equation 16:

$$Hr^\circ = \sum_{i=1}^{c} v_i \Delta H_{fi}^o (liq) \qquad \ldots(16)$$

The sign of stoichiometric ratio $v$ is positive for products and negative for reactants.

$$\Delta H_f^o(liq) = \Delta H_f^0(gas) - \lambda \qquad \ldots(17)$$

The heats of formation of vapor at 298.15K for each component are given in Table A-4.

The heat of reaction at any temperature is calculated by equation 18:

$$Hr = Hr^\circ + \int_{T_{ref}}^{T} \Delta Cp_i^V \, dT \qquad \ldots(18)$$

### - Vapor Pressure Calculation

The vapor pressure of each component for the present system was calculated using Antoine equation.

$$LnP^o = A - \frac{B}{T + C} \qquad \ldots(19)$$

Where vapor pressure $P^o$ in Pa and T in Kelvin. Parameters of Antoine equation for each component are given in are given in Table A-5.

### - Bubble Point Calculation

Temperatures of stages have been calculated using iterative procedure of bubble point until the summation in equation 20 equals to one.

$$\sum_{i=1}^{m} (K_{ij} x_{ij}) = 1 \qquad \ldots(20)$$

Where K is the distribution coefficient and it can be calculated using:

$$K_i = \gamma_i \frac{P_i^o}{P} \qquad \ldots(21)$$

### - Holdup

In the present work the equilibrium model was considered for tray columns, to change packed columns to the concept of the equilibrium stage, the idea of the Height Equivalent to a Theoretical Stage (HETS or HETP) was considered.

HETP value represents a certain bed length of a packing equivalent to one theoretical stage, HETP for the random packing [25].

$$HETP, ft = 1.5 D_P, in \qquad \ldots(22)$$

Molar holdups in condenser system and on the column stages based on constant volume holdups, $G_j$ :

$$M_j = \frac{G_j}{\sum_{i=1}^{N} \frac{x_i \cdot M_{w_i}}{\rho_i}}, \text{ Where j=1 to N-1} \qquad \ldots(23)$$

The holdup in reboiler based on the initial charge to the reboiler ($M^\circ$) and it is given by [25]:

$$M_N = M_N^\circ - \sum_{j=1}^{N} M_j - \int_0^t D_t \, dt \qquad \ldots(24)$$

Stages numbered down from top, consider N=1 for condenser.

## Solution of the Equilibrium Model

Theoretical model for an equilibrium stage is considered for batch unsteady-state distillation column consisting of a number of stages arranged in a counter current cascade, where the stages are numbered from top to the bottom. In this column, the reboiler and the condenser are assumed as an equilibrium stages. The determination of phase composition and its temperature can be done by solution of material balance equations. The solution of material balance equations are derived for the overhead condensing system, the column stages and reboiler as follow:

### 1. The Overhead Section

$$\frac{dx_{i,1}}{dt} = -[\frac{L_1 + D + \frac{dM_1}{dt}}{M_1}]x_{i,1} + \frac{V_2 K_{i,2}}{M_1} x_{i,2} + R_{OLAC} \qquad \ldots(25)$$

$$L_1 = R * D \qquad \ldots(26)$$

### 2. The Stage Section

$$\frac{dx_{i,j}}{dt} = [\frac{L_{j-1}}{M_J}]x_{i,j-1} - [\frac{L_j + K_{i,j}V_j + \frac{dM_j}{dt}}{M_j}]x_{i,j} + [\frac{V_{j+1}K_{i,j+1}}{M_j}]x_{i,j+1} + R_{OLAC} \qquad \ldots(27)$$

### 3. The Reboiler Section

$$\frac{dx_{i,N}}{dt} = [\frac{L_{N-1}}{M_N}]x_{i,N-1} - [\frac{K_{i,N}V_N + \frac{dM_N}{dt}}{M_N}]x_{i,N} + R_{OLAC} \qquad \ldots(28)$$

The matrix balance equations are reduced to a tri-diagonal matrix form for batch reactive distillation:

$$A = \begin{bmatrix} B_1 & C_1 & 0 & 0 & 0 \\ A_2 & B_2 & C_2 & 0 & 0 \\ 0 & A_j & B_j & C_j & 0 \\ 0 & 0 & A_{j-1} & B_{j-1} & C_{j-1} \\ 0 & 0 & 0 & A_N & B_N \end{bmatrix} \begin{bmatrix} x_{i,1} \\ x_{i,2} \\ x_{i,j} \\ x_{i,j-1} \\ x_{i,N} \end{bmatrix} = \begin{bmatrix} \frac{dx_{i,1}}{dt} \\ \frac{dx_{i,2}}{dt} \\ \frac{dx_{i,j}}{dt} \\ \frac{dx_{i,j-1}}{dt} \\ \frac{dx_{i,N}}{dt} \end{bmatrix} \qquad \ldots(29)$$

The general solution of such system is as follow.

$$x = C_1 \cdot e^{\lambda_1 t} \cdot V_1 + C_2 \cdot e^{\lambda_2 t} \cdot V_2 + \cdot \quad \cdot \quad \cdot + C_{12} \cdot e^{\lambda_{12} t} \cdot V_{12} \qquad \ldots(30)$$

Where

$C_1$ to $C_{12}$ is constants of equation.

$\lambda_1$ to $\lambda_{12}$ is eigenvalues of $A$ matrix $A$.

$V_1$ to $V_{12}$ is eigenvalues of $A$ matrix $A$.

This set of equations may be formally written as the following matrix equation:

$$A.X = \frac{dx_{i,j}}{dt} \qquad \ldots(31)$$

Where

$$A_1 = 0$$

$$B_1 = -\left[\frac{L_1 + D + \frac{dM_1}{dt}}{M1}\right], j=1 \qquad \ldots(32)$$

$$C_1 = \left[\frac{V_1 K_{i,1}}{M_1}\right] + R_{OLAC}, \quad j \qquad \ldots(33)$$

$$A_j = \left[\frac{L_j - 1}{M_j}\right], \quad 2 \le j \le N-1 \qquad \ldots(34)$$

$$B_j = -\left[\frac{L_j + (K_{i,j}V_j)}{M_j}\right], \quad 2 \le j \le N-1 \qquad \ldots(35)$$

$$C_j = \left[\frac{K_{i,j}V_{j+1}}{M_j}\right] + R_{OLAC}, \quad 2 \le j \le N-1 \qquad \ldots(36)$$

$$A_N = \left[\frac{L_{N-1}}{M_N}\right], \; j=N \qquad \ldots(37)$$

$$B_N = \left[\frac{V_N K_{i,N}}{M_N}\right] + R_{OLAC}, \; j=N \qquad \ldots(38)$$

$$C_N = 0$$

After calculating $\frac{dx_{i,j}}{dt}$ from algorithm matrix the mole fraction $x_{i,j}$ is calculated from Eigen-value. The values of mole fraction $x_{i,j}$ are corrected to provide better values of the assumed iteration variables for the next trial, therefore, for each iteration the computed set $x_{i,j}$ values for each stage will normalized using the following relation:

$$\left(x_{i,j}\right)_{normalized} = \frac{x_{i,j}}{\sum_{i=1}^{C} x_{i,j}} \qquad \ldots(39)$$

The modified H equations are obtained first by calculating the vapor phase enthalpy, and then the liquid phase enthalpy is calculated which depends on vapor phase enthalpy. Secondly calculate the vapor flow rate $V_j$ then the heat supplied to condenser.

$$V_j = \frac{Q_r}{\sum_{i=1}^{C} x_{i,j}\lambda_i} \text{, at initial mole fraction} \qquad \ldots(40)$$

$$V_{j+1} = \frac{1}{(h_{j+1}^V - h_j^L)}\left[V_j(h_j^V - h_j^L) - L_{j-1}(h_{j-1}^L - h_j^L) + M_j \frac{dh_j^L}{dt}\right] \qquad \ldots(41)$$

$$Q_c = V_2(h_2^V - h_1^L) - M_1 \frac{dh_1^L}{dt} \qquad \ldots(42)$$

A computer program to solve the MESHR equations has been developed using MATLAB (R2010a) to determine the composition of components, segments temperatures, condenser and reboiler duties, liquid and vapor flow rates along stages, and reaction rate profile.

The program begins with specify all parameters that consist of number of stages, reflux ratio, total pressure, feed compositions, distillate rate, batch time, step time, and mass of catalyst, as well as all physical properties of components. Time, and temperature loops were started, respectively over all stages. The temperature of each stage has been calculated by trial and error until the equilibrium relation applicable.

The new segments temperatures have been used in calculation of reaction rate, enthalpies of vapor, liquid and mixing. Then the liquid and vapor flow rates were calculated by total material and energy balances. A tridiagonal matrix was used to find the component compositions by solving the MESHR equations, solving the matrices by eigen value, and normalizing the new compositions for each component.

New sets of composition are obtained with the previous procedure for each step time of the batch time. When the compositions at different times are evaluated the program ended and the results plotted.

## Selection of Activity Coefficient Model

To simulate the non-ideal batch reactive distillation column, a good thermodynamic model is required to represent the VLE for the system used. The liquid phase activity coefficient model should be selected carefully to represent the non-idealities of the liquid phase.

NRTL, UNIQUAC and UNIFAC models have been used to calculate the activity coefficient to select the appropriate liquid phase activity coefficient model for OLAC-MEOH-MEOL-Water System; different activity coefficient models were compared with the experimental results taken from Oliveira, M.B., et. al. [26]. The experimental data was at atmospheric pressure. The experimental boiling point temperature of the system was compared with the predicted boiling point temperature from each of the activity coefficient models.

Figure 2 shows that the UNIQUAC points nearly fall on the diagonal, indicating that the UNIQUAC liquid phase activity coefficient model is the most appropriate model to describe the non ideality of OLAC-MEOH-MEOL-$H_2O$ system.

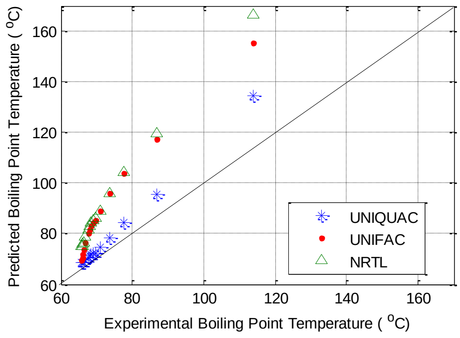

Fig. 2, Comparison between experimental and predicted boiling points

## Checking the Validity of the Unsteady State Equilibrium Model

The proposed unsteady state equilibrium model was consider for producing methyl oleate as a biodiesel by esterification process in batch reactive distillation column, the results of theoretical part with the experimental from the literature [22] were compared with the results of the developed model.

To the best of our knowledge, there is no information about the simulation of batch reactive distillation column for the production of Biodiesel (methyl oleate) is available in literature, so the experimental results obtained from the literature [22] have been checked with the results obtained from the unsteady state equilibrium model to give the validity of the model.

The comparison results give the ability of the model to predict the results of experiment performed with the same variables of experimental from the literature [22]. Figure 3 shows the points are nearly fall on the diagonal indicating that the developed model is in good agreement with the experimental work.

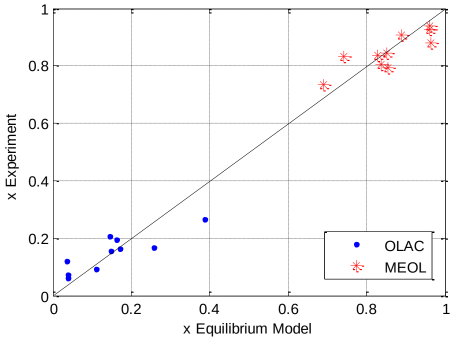

Fig. 3, Plot for the EQ model validation

Also the developed model was checked with experimental work from literature Kusmiyati et. al., [8] which provides the conversion of oleic acid in batch reactive distillation at molar ratio of methanol to oleic acid is 8:1, amount of catalyst is 1 g sulfuric acid/g oleic acid and time 90 min.

Even though the experimental temperature and time of reaction used by Kusmiyati et. al., [8] is not within the parameter ranges of the model, but the model still gives a nearly quantitative accurate prediction of the conversions.

## Equilibrium Model Results

The best conditions for the largest conversions of oleic acid were based on the S/N ratio [22] statistically analysis by Taguchi method [27-29], the best variables were feed molar ratio MEOH/OLAC 8:1, catalyst amount 1.2 g sulfuric acid/g oleic acid, Time 57 min and reaction temperature130°C. The biodiesel production system details were found in [22]. Figure 4 shows Experimental and equilibrium model results for composition profile of oleic acid and methyl oleate in the still for the best conditions.

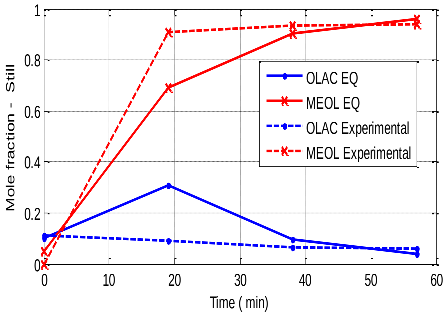

Fig. 4, Experimental and theoretical equilibrium model results for composition Profile in the still, molar ratio 8:1, catalyst amount 1.2, 57 min, 130 ˚C

Figure 4 shows that, at a first step time the composition of oleic acid increases due to the removal of methanol is removed by distillation, hence the oleic acid mole fraction increases (excess methanol), and the reaction temperature is higher than the boiling point of methanol.

Figure 5 shows the % conversion of oleic acid with time for experimental and theoretical equilibrium model.

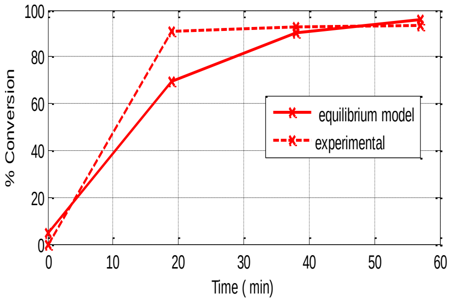

Fig. 5, % Conversion profile for equilibrium model for best conditions

Initial mole fractions and the operating conditions for different molar ratios, catalyst amounts, reaction time and reaction temperature for the equilibrium model are given in Tables 1 and 2.

Table 1, Initial mole fractions of equilibrium model

| Feed molar ratio MEOH/OLAC | mol% OLAC | mol% MEOH | mol% MEOL | mol% Water |
|---|---|---|---|---|
| 4:1 | 0.1875 | 0.75 | 0.03125 | 0.03125 |
| 6:1 | 0.1333 | 0.7998 | 0.03345 | 0.03345 |
| 8:1 | 0.1 | 0.8 | 0.05 | 0.05 |

Table 2, Operating conditions for proposed EQ Program

| | |
|---|---|
| Pressure (Pa) | 101325 |
| Hold up per each stage (ml) | 11.2 |
| D: Feed molar ratio D (gmol) | 0.66 |
| Reflux ratio (mol/mol) | 0.001 |
| Total stages | 4 |
| Boiler Heat duty (W) | 200 |

## Rate of Reaction

The chemical reaction of esterification is first order with respect to oleic acid and of zeroth order with respect to methanol due to the use of excess methanol. The reaction occurs in liquid phase, and because of the high boiling point of oleic acid the reaction takes place in the still, so the effect of reaction rate is studied in still.

Figure 6 shows that the average rate of esterification increases with increasing of catalyst amount, which gives an increase in conversion. From equation 8 the rate of esterification is proportional with amount of catalyst, which causes an increase in conversion, this indicate that the reaction is kinetically controlled [22].

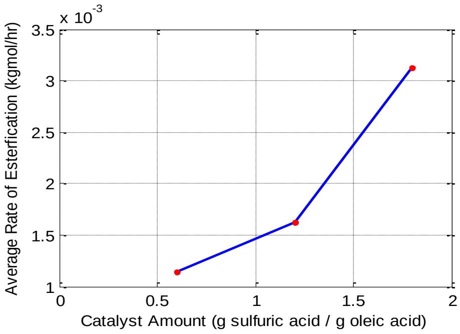

Fig. 6, Effect of catalyst amount on average rate of esterification reaction

Figure 7 show that the increases of molar ratio of methanol to oleic acid the average rate of esterification is decreased. This is because of the increasing of conversion of oleic acid to biodiesel, so the concentration of oleic acid decreases, and the rate of esterification is proportional with the concentration of oleic acid, equation 8.

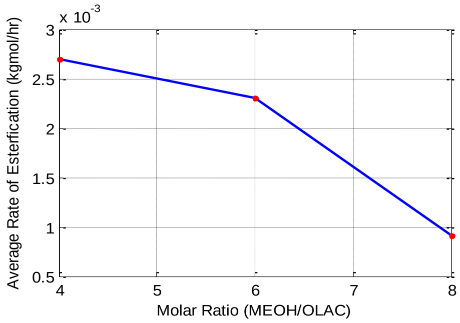

Fig. 7, Effect of molar ratio on average rate of esterification reaction

In general in all nine experiments the initial rate of esterification increases with increasing of time and then decreased, Figure 8. This is because the composition of oleic acid increases by removing of methanol by distillation.

Figure 9 shows that the average rate of esterification increases with the increasing of time of reaction. This is because of the long contact time between reactants.

Figure 10 shows that the average rate of esterification increases with increasing of temperature of reaction. This is because of the temperature of reaction is higher than boiling point of methanol, so the amount of methanol in reaction mixture decreases and the oleic acid remains increases (rate of reaction equation).

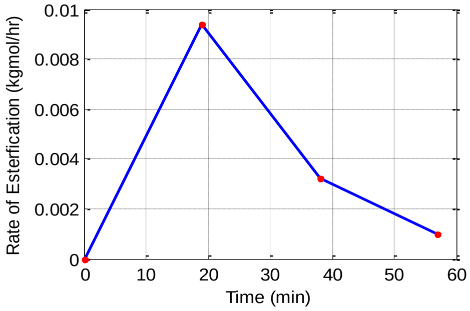

Fig. 8, Effect of Time on rate of esterification reaction, Best Experiment

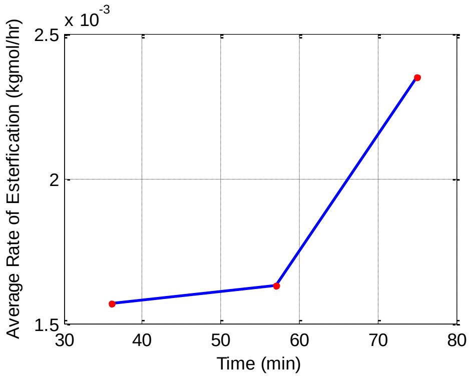

Fig. 9, Effect of time on average rate of esterification reaction

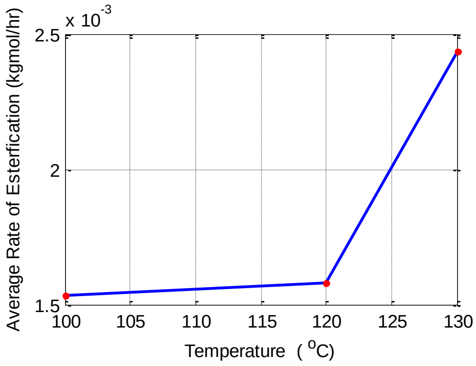

Fig. 10, Effect of reaction temperature on average rate of esterification reaction

The effect of variables studied in the present on the rate of esterfication show that the reaction is kinetically controlled.

## Conclusion

In the present work, the esterfication of oleic acid to produce biodiesel in batch reactive distillation column was simulated using MATLAB (R2010a).

The model results show a good agreement with results available in literatures. UNIQUAC liquid phase activity coefficient model is the most appropriate model to describe the non-ideality of OLAC-MEOH-MEOL-$H_2O$ system. The best operating conditions to produce biodiesel were feed molar ratio MEOH/OLAC 8:1, catalyst amount 1.2 g sulfuric acid/g oleic acid, time 57 min and reaction temperature130 °C. The average rate of esterification increases with increasing of catalyst amount, time of reaction and temperature which gives an increase in conversion indicating that the reaction is kinetically controlled.

## Nomenclature

| Symbols | Notation |
|---|---|
| $a_{ij}$ | Parameter for the interaction between components of the NRTL. |
| A | Constant |
| $B_{ij}$ | Parameter of the NRTL. |
| B | Constant |
| C | Constant |
| $CP^L$ | Specific heat of liquid |
| $CP^V$ | Specific heat of vapor |
| $D_p$ | Outside diameter of packing |
| D | Constant |
| E | Constant |
| $G_{ij}$ | Parameter of the NRTL equation. |
| $h_i$ | Enthalpy of component $i$ |
| $h^L$ | Total enthalpy of liquid phase |
| $h^V$ | Total enthalpy of vapor phase |
| $h_L$ | Liquid hold up in Packing. |
| $H_{mix}$ | heat of mixing |
| $H_r^o$ | Standard heats of reaction. |
| $H_r$ | Heats of reaction |
| $K_{i,j}$ | Equilibrium constant for component i in stage j |
| HETP | Height equivalent to theoretical plate |
| HETS | Height equivalent to theoretical stage |
| L | Liquid flow rate |
| $M_{cat}$ | Mass of catalyst |
| $M_{wi}$ | Molecular weight |
| $M_i$ | Molar hold up |
| $N_T$ | Number of stages |
| $N_c$ | Number of components |
| P | Pressure |
| $P^o$ | Vapor presure |
| Q | Heat duty |
| $q_i$ | Area parameter of component $i$ in UNIQAC and UNIFAC models |
| R | Gas constant = 8.314 |
| $R_{FFA}$ | Reaction rate |
| $R_{OLAC}$ | Reaction rate of olaic acid |
| $R^2$ | Coefficient of Multiple determination |
| r | Linear correlation coefficient for sample |
| $r_i$ | Volume parameter of component $i$ in UNIQUAC and UNIFAC models |
| $T$ | Temperature |
| $T_{ref}$ | Reference temperature |
| $u_{ij}$ | Parameter of interaction between component $i$ and $j$ in UNIQUAC model |
| $V$ | Vapor flow rate |
| $W_{cat}$ | Weight of sulfuric acid |
| $x_i$ | Liquid mole fraction |
| $y_i$ | Vapor mol fraction |

## Greek Letters

| | |
|---|---|
| $\nu$ | kinematic viscosity at 40°C |
| $\phi_i$ | Fugacity coefficient of component $i$ in mixture |
| $\gamma_i$ | Activity coefficient of component $i$ in mixture |
| $\alpha_{ij}$ | Non randomness parameter (NRTL parameter) – Empirical Constant |
| $\rho$ | Liquid molar density |

## Abbreviations

| | |
|---|---|
| FA | Fatty Aacid |
| FFA | Free Fatty Acid |
| FAME | Fatty Acid Methyl ester |
| MEOH | Methanol |
| MEOL | Methyl Oleate |
| NRTL | Nonrandom, two-liquid theory |
| OLAC | Oleic Acid |
| RD | Reactive Distillation |
| UNIFAC | UNIQUAC functional group activity cofficients |
| UNIQUAC | Universal quasi-chemical theory |

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Table A-1, NRTL parameters for the binary pairs of components in the reactive mixtures

| $i-j$ | $B_{ij}$ | $B_{ji}$ | $\alpha_{ij}$ |
|---|---|---|---|
| OLAC- MEOH | 199.884 | 479.688 | 1.1431 |
| MEOH- $H_2O$ | -24.4933 | 307.166 | 0.3001 |
| OLAC- MEOL | 37.63835 | 36.76161 | 0.2907206 |
| OLAC- $H_2O$ | -44.8289 | 2497.61 | 0.2250879 |
| MEOH-MEOL | 1388.564 | -240.4565 | 0.399494 |
| MEOL- $H_2O$ | 106.4762 | 2499.963 | 0.200312 |

Table A-2, UNIQUAC parameters for the oleic acid – methanol – methyl oleate – water mixture, cal/gmol

| $i-j$ | $u_{ij}-u_{jj}$ | $u_{ji}-u_{ii}$ |
|---|---|---|
| OLAC- MEOH | 952.028 | -149.181 |
| MEOH - $H_2O$ | 95.259 | -10.377 |
| OLAC- MEOL | 154.7875 | -133.418 |
| OLAC - $H_2O$ | 1123.794 | 403.7021 |
| MEOH- MEOL | -54.20368 | 1205.077 |
| MEOL - $H_2O$ | 1573.999 | 481.5153 |

Table A-3, Heat Capacity Constants in Vapor Phase in J/kgmol.K

| Component | A | B | C | D | E | Range Temperature K |
|---|---|---|---|---|---|---|
| OLAC | $3.2*10^5$ | $9.362*10^5$ | $-1.7431*10^3$ | $6.754*10^5$ | $7.825*10^2$ | 298.15-1500 |
| MEOH | $3.9252*10^4$ | $8.79*10^4$ | $1.9165*10^3$ | $5.3654*10^4$ | $8.967*10^2$ | 200-1500 |
| MEOL | $3.2997*10^5$ | $9.716*10^5$ | $-1.6456*10^3$ | $6.7448*10^5$ | $7.48*10^2$ | 300-1500 |
| Water | $3.3359*10^4$ | $2.6798*10^4$ | $2.6093*10^3$ | $8.888*10^3$ | $1.1676*10^3$ | 100-1500 |

Table A-4, Physical properties

| Component | Normal Boiling Point, K | $\Delta H^o_f$ (298.15K) [kJ /g.mol] of vapor | λ [kJ / Kg.mol At NBP |
|---|---|---|---|
| OlAC | 633 | -646.02 | 68131 |
| MEOH | 337.85 | -201.3 | 35278 |
| MEOL | 617 | -649.9 | 63625 |
| Water | 373.15 | -242 | 40683 |

Table A-5, Vapor pressure constants

| Component | Antonio Coefficient | | |
|---|---|---|---|
| | A | B | C |
| OlAC | 23.1373 | 5884.49 | -127.26 |
| MEOH | 23.4803 | 3626.55 | -34.29 |
| MEOL | 22.8313 | 5948.17743 | -96.15 |
| Water | 23.1964 | 3816.44 | -46.13 |