



Modeling and Simulation of Reactive Distillation column for the Production of Biodiesel with the Effect of Liquid hold-up; MATLAB

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Abstract: Biodiesel, which is regarded as a promising alternative to a conventional petroleum-based diesel fuel, can be produced from transesterification of vegetable oils and alcohol in conventional batch and continuous reactors. Since the transesterification is an equilibrium-limited reaction, a large excess of reactants is usually used to increase the production of biodiesel, thereby requiring more expensive separation of unreacted raw materials. This study proposed the use of a reactive distillation for transesterification of soybean oil and methanol catalyzed by sodium hydroxide to produce biodiesel. In modeling, the overall mass balance equations and partial vapor-liquid equilibrium relations with kinetic used. Comparison of the predicted composition of the product components and temperature profiles along the tower with the experimental data reported in the literature, show that the proposed model is acceptable. The simulation results show that the reactive distillation tower case (which has 12 trays balance), the feed ratio of methanol to oil ratio of about 4 to 5.4, and the reflux ratio is approximately 6 adequate amounts comparatively.

Keywords: Modeling, Simulation, Distillation Tower, Biodiesel, Traditional

INTRODUCTION

In this study: with respect to the growing demand of the world, fossil sources, the need for renewable and renewable resources, It is increasing every day (Houge, 2013; Zenouzi and Ghobadian, 2007; Santandera et al., 2010).

Scientific research on biofuels began in the late 1970 s and early 1980 s in the United States and Europe with the objective of production. In 1988 (Fukuda, Kondo and Noda, 2001; Singh and Singh, 2010), the first commercially viable product (Mohammed, 2009) of biodiesel was produced from Rapeseed seed, and the first time in the United States was founded in 1992 by the American National Research Institute(Taylor and Krishna, 2000; Krishnamurthy and Taylor, 1985; Wilson and Deal, 1962; Renon and Prausnitz, 1968; HYSIS 2010; Abrams and Prausnitz, 1975; Smith and Van Ness, 1987; Drapcho, Nhuan and Walker. 2008; Al-Widyan and Al-Shyoukh, 2002).

In other words, biodiesel is ethyl ester or methyl ester produced from vegetable oils or animal fats and used as fuel in diesel engines or thermal systems (Raneses et al., 1999; Bender, 1999; Ghobadian, Khatamifar and Rahimi, 2005; Carra et al., 1979; Chang and Seader, 1988). Biodiesel can also be produced in addition to fresh oils ¹ (SVO), waste oils ^Â (WVO) (Alejski, 1991; Simandl and Svrcek, 1991; Ciric and Gu, 1994; Abufares and Douglas, 1995; Perez-Cisneros, Gain and Michelsen, 1997).

Different methods have been proposed in the world to produce biodiesel. The most important factors affecting the type of process are the type of feed used and the capacity of the process (Sawistowski and Pilavakis, 1979).

The problem of reactive distillation can be studied using various methods, including feasibility, simulation, modeling, design and empirical studies in laboratory and pilot. A combination of these methods will provide the right solution (Jianjun, Thomas and Bruce, 2004; Antti Pyhälähti, 2005). One of the most important aspects of predicting the behavior of these systems is the model used to design and simulate the process of reactive distillation (Simasatitkul et al., 2011; Drapcho, Nhuan and Walker, 2008; Issariyakul and Dalai, 2012; Geankoplis, 2003).

The present work aims to find the more preferable reactive distillation and downstream separation process following a process simulation approach to obtain a pure biodiesel fuel 99 wt. %. The currently most efficient distillation models considered, i.e., alkali and heterogeneous catalysts, for biodiesel (Ibrahim, 2007).

Productions were compared to determine the most cost-effective process (Abrams and Prausnitz, 1975)¹. Pure soybean oil was used as process feedstock due to its low free fatty acids content (less than 0.3%); which prevents the need of a pre-treatment process. The two processes are compared based on a detailed economic analysis (Halvorsen and Skogestad, 2000; Knothe, Krahl and Gerpen, 2010)².

Methodology

In the following, the modeling of the reaction distillation column of biodiesel production and its simulation is described. By simulating the effects of variables in the chemical process can be evaluated. The simulation of the steady state of the system involves solving algebraic equations, and dynamical simulation including solving differential equations. In this research, a summary of the principles of the dynamic mathematical model of reactive distillation is presented to describe the production of biodiesel. After modeling, simulation of reactive distillation using MATLAB software is dealt with. The schematic of the reactive distillation system shown in Figure below is presented (Mueanmas, Prasertsit and Tongurai, 2010). As stated in the figure, 12 equilibrium levels are considered. It should be noted that the reaction is not carried out in a condensing and boiling process (Mueanmas, Prasertsit and Tongurai, 2010). The operating conditions of the reactive distillation system are also presented in following Table (Mueanmas, Prasertsit and Tongurai, 2010).

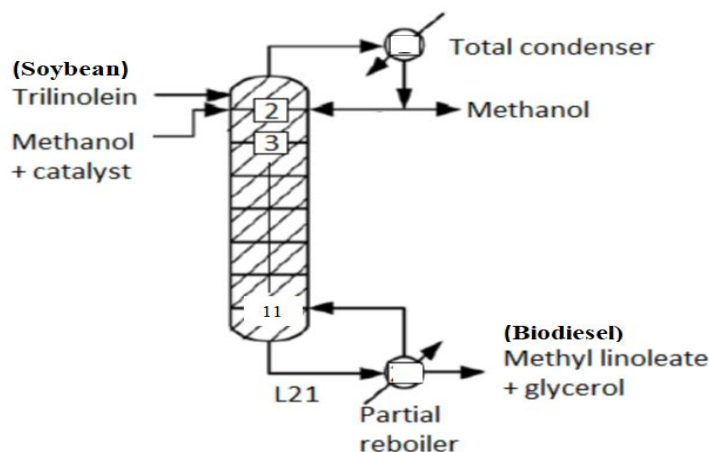


Figure 1: Biodiesel Reactive Distillation Process Scheme (Mueanmas, Prasertsit and Tongurai, 2010).

Table 1: Biodiesel Reactive Distillation Operating Conditions (Mueanmas, Prasertsit and Tongurai, 2010).

Amount	Value input variables
4: 1	Methanol-to-oil ratio in feed

¹ DIPPR 801 Database. Available from: <http://dippr.byu.edu/students/>.

² 1-Monolinoleoyl-rac-glycerol. Available from: <http://goo.gl/Ku39P>.

1,2-dilinoleoylglycerol. Available from: <http://goo.gl/45b0m>

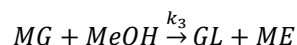
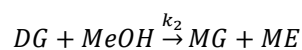
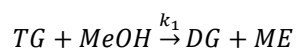
atm 1	Pressure
1	Feed Tray
12	Number of tray
6	Reflux ratio

In the reactive distillation model, the following assumptions have been made, which include:

1. Soybean oil only consists of Tri-glyceride.
2. The pressure drop and the heat losses between the trays in the column are ignored.
3. The amount of soap and hydrolysis reaction is negligible.
4. The reaction occurs only in the liquid phase.
5. The phase equilibrium is established on each tray and the gas phase is considered to be ideal.
6. The reaction occurs on all the trays of the column and the efficiency of each tray is 100%.
7. Gas hold-up is considered negligible.

Reaction kinetics:

Modeling requires a better understanding of the reactions. Oily and fat can be converted into biodiesel through a process of esterification or trans-esterification. The catalyst for this reaction can be either alkaline or acidic. The successive stages of the biodiesel production reaction are presented in following Equations (Drapcho, Nhuan and Walker, 2008).



The reaction rate balance for each of the materials is given in following equations (Mueanmas, Prasertsit and Tongurai, 2010).

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH]$$

$$\frac{d[DG]}{dt} = k_1[TG][MeOH] - k_2[DG][MeOH]$$

$$\frac{d[MG]}{dt} = k_2[DG][MeOH] - k_3[MG][MeOH]$$

$$\frac{d[ME]}{dt} = k_1[TG][MeOH] + k_2[DG][MeOH] + k_3[MG][MeOH]$$

$$\frac{d[GL]}{dt} = k_3[MG][MeOH]$$

$$\frac{d[MeOH]}{dt} = k_1[TG][MeOH] + k_2[DG][MeOH] + k_3[MG][MeOH]$$

[TG] concentration of tri-glyceride, [DG] concentration of di-glyceride, [MG] concentration of mono-glyceride, [GL] concentration of glycerin, [MeOH] concentration of methanol, and [ME] concentration of methyl ester or biodiesel.

The constant values of the reactions are calculated from the Arrhenius equation and the required parameters for obtaining the constant of the reactions are given in Table below (Mueanmas, Prasertsit and Tongurai, 2010).

$$k_i = A_i \exp\left(\frac{Ea_i}{RT}\right) \quad i = 1,2,3$$

Table 2: Kinetic parameters (Simasatitkul, 2011)

Ea_i [kJ mol ⁻¹]	A_i [m ³ kmol ⁻¹ h ⁻¹]	Reaction constant
33.870	7.46×10^{16}	k_1
29.850	1×10^{15}	k_2
19.470	6.17×10^8	k_3

The model equations are presented in an unstable state, which the stable state form the process model can be deduced by eliminating time derivatives. In the reactive distillation column, the number of moles is changing, and because of this, the molar equilibrium of the column's various portions is necessary. Because the column trays are equilibrium, so the vapor and liquid flows on the tray are in thermodynamic equilibrium. The following figures respectively show a reactive distillation column and a view of the equilibrium tray.

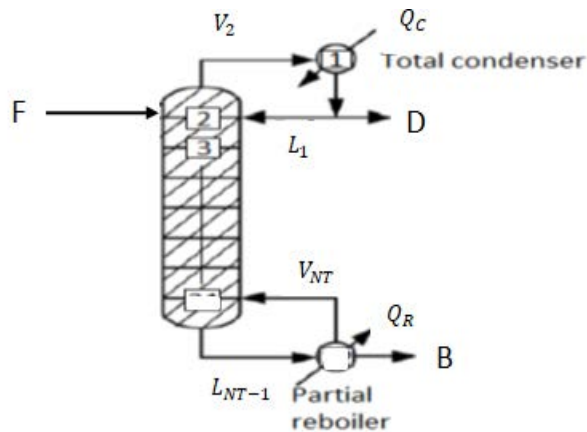


Figure 2: General view of the reactive distillation column

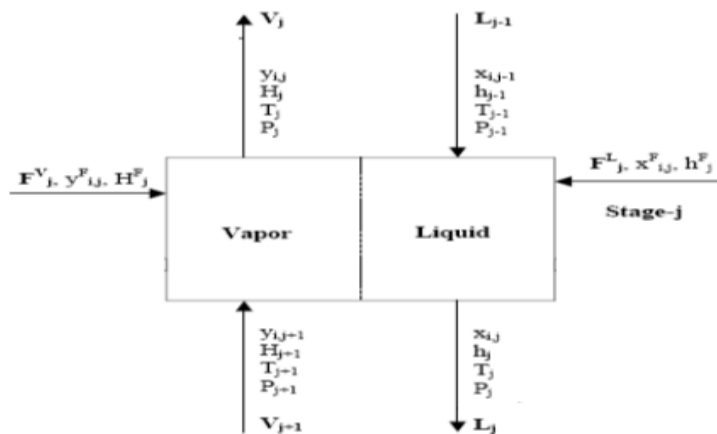


Figure 3: General view of the Equilibrium stage of the column

A reaction takes place in all the trays of the column, and as a result, the parameter ($M_{i,j}$), which produces component i by the reaction in the tray j , is considered in the mass balance. This parameter is defined as:

$$M_{i,j} = \varepsilon_j r_{i,j}$$

M_j is also defined as the parameter for the sum of the reactions as follows:

$$M_j = \sum_{i=1}^{NC} \varepsilon_j r_{i,j}$$

Where ε is the reaction volume and r is the reaction rate.

The overall and partial molar equilibrium in an unstable state for each tray is shown in the equations below.

$$\frac{dHR_j}{dt} = F_j^L + F_j^V + V_{j+1} - V_j + L_{j-1} - L_j + M_j$$

$$\frac{dHR_j x_{i,j}}{dt} = F_j^L x_{i,j}^F + F_j^V y_{i,j}^F + V_{j+1} y_{i,j+1} - V_j y_{i,j} + L_{j-1} x_{i,j-1} - L_j x_{i,j} + M_{i,j}$$

Where HR_j indicates the liquid hold-up on the j tray.

The differential form of the term of molecular aggregation of components is rewritten in the following equation.

$$\frac{dHRx}{dt} = HR \frac{dx}{dt} + x \frac{dHR}{dt}$$

To find changes in the mole fraction over time (dx/dt), the following equation is used which is simplified by the differential equation above.

$$\frac{dx}{dt} = \frac{\frac{dHRx}{dt} - x \frac{dHR}{dt}}{HR}$$

In the above equations, the thermodynamic equilibrium equation is used to calculate the molar fraction of the i component in the vapor phase that means:

$$y_i = \frac{\gamma_i P_i^*}{P_t} x_i \quad (*)$$

To calculate the vapor pressure of each component, the following equation is used which is generalized to the Antoine equation. The required parameters for calculating the vapor pressure of each material are given in the table below³.

$$P^* = F \cdot \exp\left(A + \frac{B}{T} + C \cdot \ln T + D + T^E\right)$$

That T is based on Kelvin's and P^* based on Pascal.

Table 3: Required Parameters to calculate the vapor pressure using the generalized Antoine equation ⁴

	MetOH	TG	DG	MG	GL	BD
A	82.718	234.71	-15.931	118.95	99.986	105.47
B	-6904.5	-34699	-2111	-20181	-13808	-14531
C	-8.8622	-27.250	2.4303	-14.318	-10.088	-10.980
D	7.4664×10^{-6}	1.5475×10^{-18}	8.0567×10^{-21}	9.1481×10^{-19}	3.5712×10^{-19}	2.5753×10^{18}
E	2	6	6	6	6	6
F	9.869×10^{-6}	9.869×10^{-6}	9.869×10^{-3}	9.869×10^{-3}	9.869×10^{-6}	9.869×10^{-6}

The coefficient of activity (γ_i) of each component can be calculated from the various activity equations. In this research, the UNIQUAC equation is used. UNIQUAC is a model made to describe the phase equilibrium by providing activity coefficients, which shows the ideal liquid behavior. The coefficients of activity are obtained

³ DIPPR 801 Database. Available from: <http://dippr.byu.edu/students/>.

⁴ DIPPR 801 Database. Available from: <http://dippr.byu.edu/students/>.

from the equation below, which includes the remainder term and the combined term (Abrams and Prausnitz, 1975).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

The combined term in the theory of networks is based on the difference in the shape of the molecules, which obtained from the equation below.

$$\ln \gamma_i^C = (1 - V_i + \ln V_i) - \frac{z}{2} q_i \left[1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right]$$

Here, Z is the number of coordinates related to the number of molecules in the close interaction around a central molecule that varies from 6 (cubic) to 12 (hexagonal). The average value of 10 was used in this study. The parameters V_i and F_i respectively represent the volume fraction and the surface ratio in the molar fraction of the mixture. These parameters are calculated in the following equations.

$$V_i = \frac{r_i}{\sum_j^{NC} r_j x_j}$$

$$F_i = \frac{q_i}{\sum_j^{NC} q_j x_j}$$

Where, r_i is the volume size of the molecule and q_i is the surface area parameter of the molecule. The values of these parameters are presented in Table below.

The remaining term is an enthalpy correction coefficient in the ideal mixture behavior. The remaining activity parameter is calculated by following Equation.

$$\ln \gamma_i^R = q_i \left[1 - \ln \left[\frac{\sum_j^{NC} q_j x_j \tau_{ji}}{\sum_j^{NC} q_j x_j} \right] - \sum_j^{NC} \left(\frac{q_j x_j \tau_{ij}}{\sum_k^{NC} q_k x_k \tau_{kj}} \right) \right]$$

Which NC is the number of components and τ_{ij} is the adaptability parameter.

The adaptability parameter τ_{ij} is obtained from Equation below.

$$\tau_{ij} = \exp \left(\frac{-\Delta u_{ij}}{RT} \right)$$

Which; Δu_{ij} is a dual interaction parameter. The values of these parameters for binary components are presented in Table below:

Table 4: Required data in the UNIQUAC equation for the reactive distillation mixture of biodiesel (Abrams and Prausnitz, 1975)

Dual interaction parameter data

Δu_{ij}	TG	DG	MG	BD	GL	MetOH
TG	0	-48.519	213.876	47.076	836.044	3030.060

DG	59.273	0	-79.159	26.437	757.300	-89.061
MG	-139.052	114.633	0	219.802	317.795	-113.482
BD	-45.259	-16.759	-125.764	0	823.302	0
GL	-266.224	-274.223	-60.390	-262.612	0	411.932
MetOH	-704.965	870.689	534.174	0	-267.337	0

Table 5: Molecular volume data

Component	TG	DG	MG	BD	GL	MetOH
r_i	39.6176	28.0103	16.403	13.5084	4.7957	1.4311

Table 6: Surface area data of the molecule

Component	TG	DG	MG	BD	GL	MetOH
q_i	32.094	23.032	13.97	11.11	4.908	1.432

The energy balance was not used in the modeling of the reactive distillation process of biodiesel production. Therefore, the equilibrium equation has been used as guessing and error to determine the temperature for each equilibrium stage.

Given that the pressure is constant, the temperature can be calculated on the basis of the liquid-vapor equilibrium equation given in Equation (*), depending on the concentration of the components. This method is guesswork and error in the following equation. To solve this guess and error, Newton-Raffon's algebraic solution method has been used.

$$0 = P - \sum_{i=1}^{NC} x_i \gamma_i P_i^*(T)$$

The following equations are used to calculate the amount of Tri-glyceride conversion and biodiesel production efficiency. These definitions depend on the amount of Tri-glyceride input (F_{TG}) and the biodiesel outflow from the bottom of the tower (B_{TG}).

$$Conversion = \frac{F_{TG} - B_{TG}}{F_{TG}}$$

$$Yield = \frac{B_{TG}}{F_{TG}}$$

The following figure shows the algorithm for solving the equations of the mathematical model of the reactive distillation column. In this solution, the detailed method of the tray to tray is used for the column. First, all the information needed to solve is given to software. Then, the initial conditions of composition of percentages are calculated. For the temperature variable, a preliminary guess has been done to solve the equations completely (saturation pressure from the generalized Antoine equation and the coefficient of activity of the UNIQUAC model). After obtaining the vapor pressure of the components and the coefficient of activity, the mass conservation equations and vapor-liquid equilibrium are solved, in which a mass flow of vapor and liquid is obtained on the tray. In the next step, the accuracy of the guessed temperature by the equilibrium law must be checked. If the mathematical relation is correct, outputs are extracted and otherwise a new temperature will be guessed. This method of guessing and error will continue until equality of the equilibrium law.

To solve the differential equation system in the mathematical model, the ode45 function is used in MATLAB software.

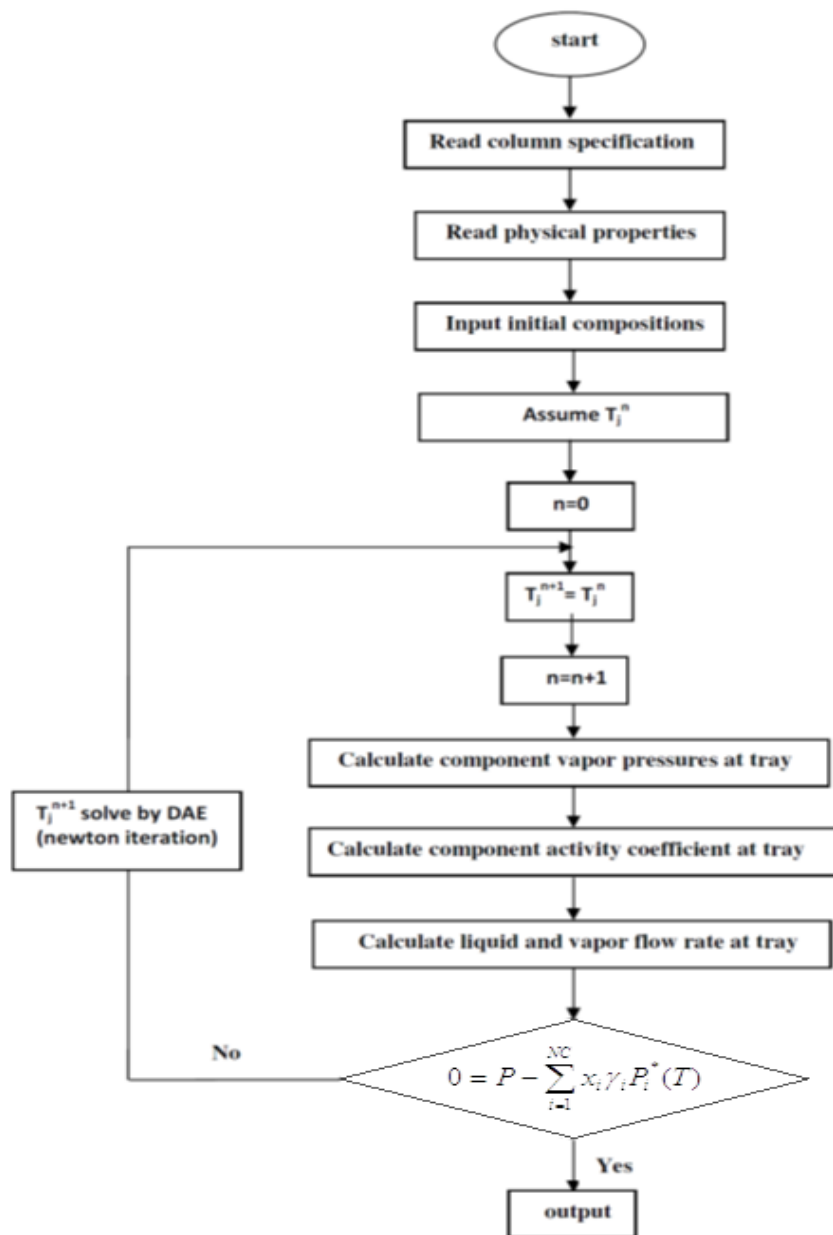


Figure 4: Algorithm of Solving Biodiesel Reactive Distillation Model

Results and Discussion

Comparison of simulation results with experimental data (Mueanmas, Prasertsit and Tongurai, 2010)

In this section, the results obtained from the weight composition of the components by solving the mathematical model in MATLAB software and the results of experimental data (Mueanmas, Prasertsit and Tongurai, 2010), are presented for the lower product of the column in a different feed ratio. These results are presented in the table below.

Table 7: Comparison of the mathematical model results with experimental data (Mueanmas, Prasertsit and Tongurai, 2010)

proportion of methanol to oil in feed	Weight composition									
	experimental data					Simulation results				
	biodiesel	Mono-glyceride	Di-glyceride	Tri-glyceride	Methanol	biodiesel	Mono-glyceride	Di-glyceride	Tri-glyceride	Methanol
3 : 1	79.9	2.3	3	12.7	2.1	76.9	2.44	3.24	14.8	2.62
3.5 : 1	79	1.4	3.6	14.6	1.4	81.9	1.44	2.92	12.9	0.84
4 : 1	92	0.4	0.9	5.8	0.9	92.24	0.49	0.88	5.78	0.61
4.5 : 1	93.8	0.6	0.7	3.4	1.5	94.35	0.33	0.68	3.48	1.16

For further understanding, in the following figure, the simulation results for the products composition of the bottom of column were compared with experimental data at in various molar ratios of methanol to oil of 3, 3.5, 4 and 4.5 by bar graph.

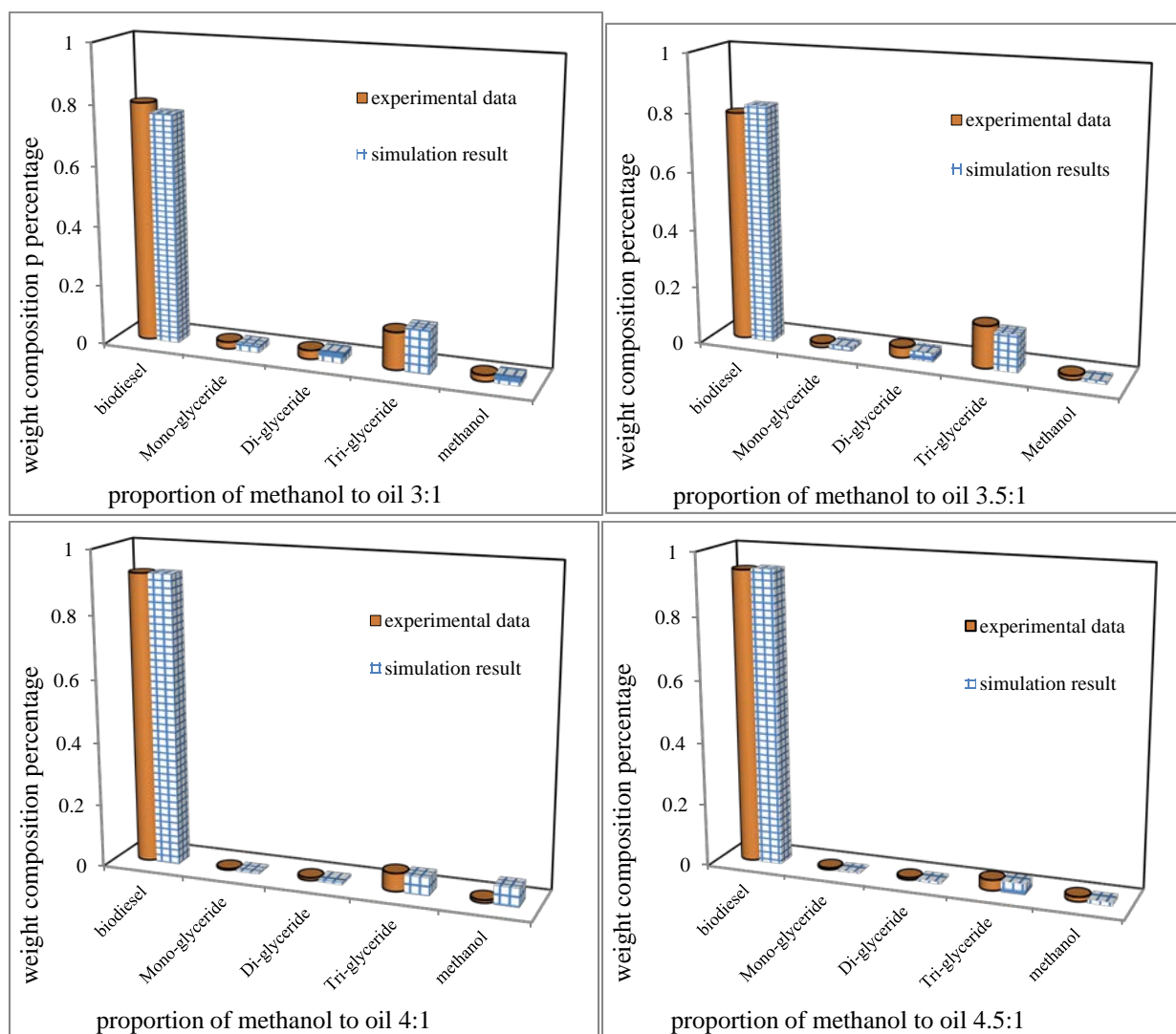


Figure 5: Comparison of the results obtained from the mathematical model with experimental data in the form of a bar graph

As it is clear, the proposed mathematical model predicts with acceptable accuracy the composition of the component in the outflow of the column. Of course, the error rate in the composition of the components is relatively high, which can be due to the constant assumption of the molar rate of flows (McCabe's assumption) in modeling.

The temperature variations along the column (different trays) are also can be compared with laboratory temperature data (Mueanmas, Prasertsit and Tongurai, 2010) in figure below. The maximum error is related to the second stage, which is less than 5 ° C. Therefore, the proposed model seems to have an acceptable ability to predict the temperature profile in the column.

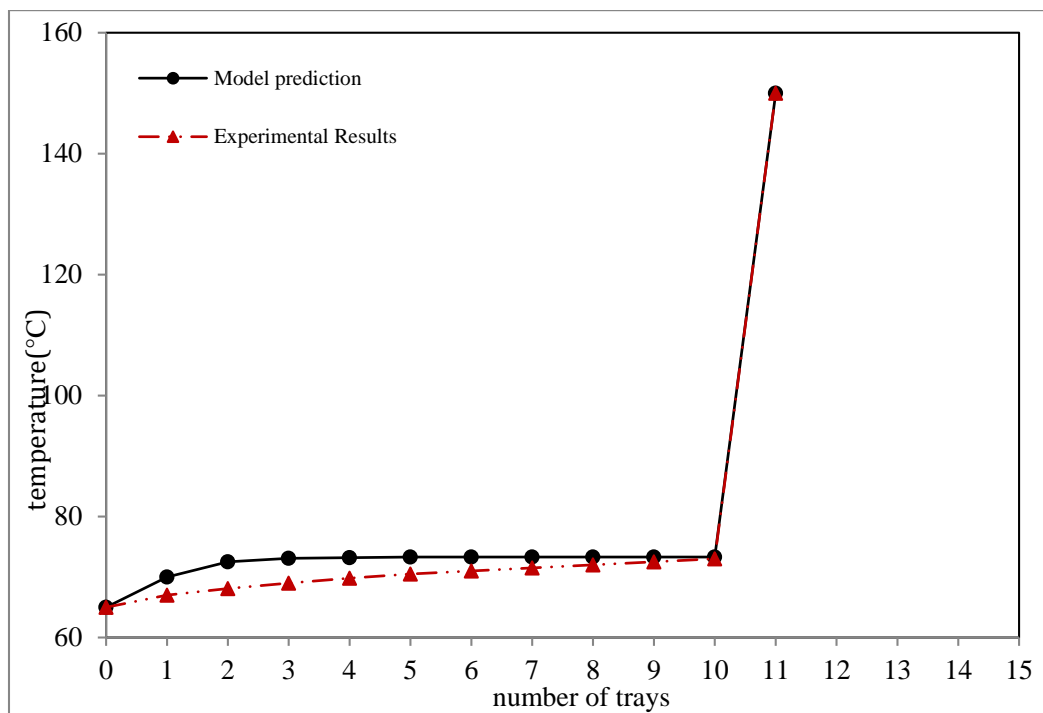


Figure 6: Comparison of predicted temperature by model with laboratory data (Mueanmas, Prasertsit and Tongurai, 2010)
(Feed ratio = 4: 1 and reflux ratio = 6)

Effect of number of reaction steps

To evaluate the effect of the number of equilibrium stages for the biodiesel weight composition, the number of stages of the reactive distillation column has been changed in the interval of 1 to 12 stages and the weight composition of biodiesel has been calculated.

The results are shown in the following graph for the two different feed ratios (methanol to oil ratio of 4 and 4.5 and reflux ratio 6). As can be seen, for the feed ratio of 4.5, the number of reaction steps required 7 and for the feed ratio 4 the number of required reaction steps is greater than 12.

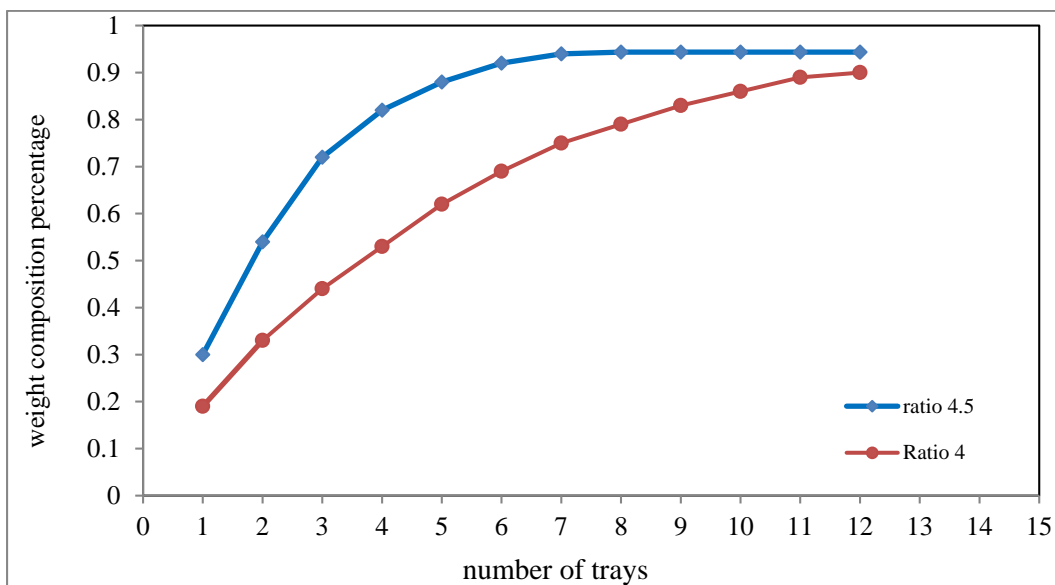


Figure 7: The biodiesel weight composition is based on the number of reaction steps for the feed ratio of 4 and 4.5 (Reflux ratio = 6)

Checking the effect of feed entry:

In order to investigate the effect of feeding site on the biodiesel weight composition, feed tray was changed from 1 to 11 and in each case the biodiesel weight composition was calculated.

The results are shown in the following graph (for feed ratios of 4 and 4.5 and reflux ratio 6). As you can see, in both cases, the first tray is the most suitable place for feed input. Of course, in a feed ratio of 4.5, given that the number of steps is greater than the required level (7 steps are required), the feed can also be entered from the lower stages (feed entry from step 1 to 5 will produce the same results). The above results indicate that there is no reaction in the trays above the tray, given the insignificant concentration of Tri-glyceride.

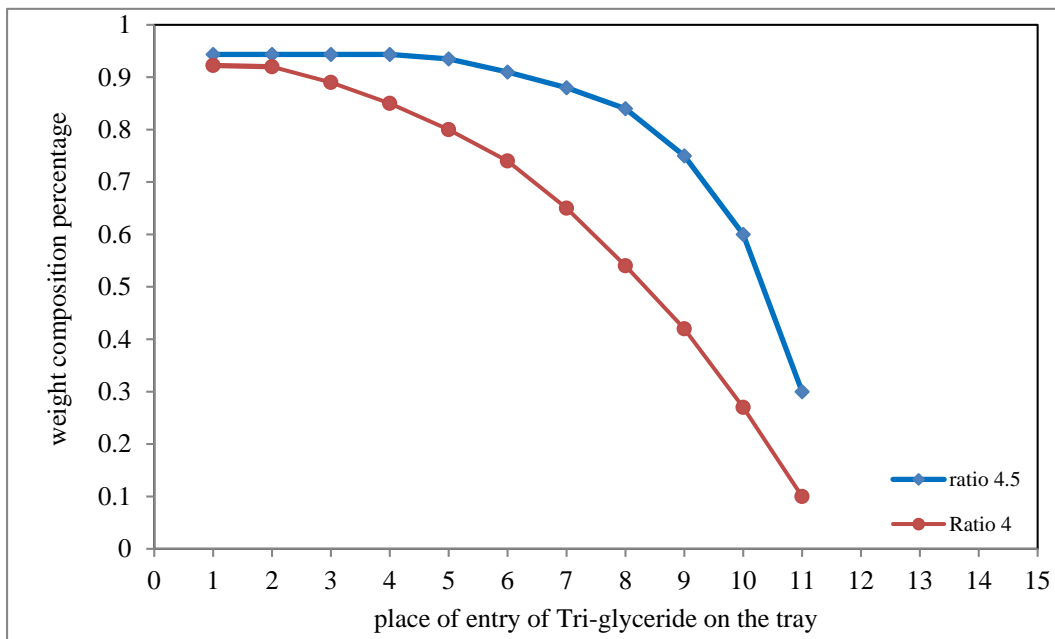


Figure 8: The biodiesel weight composition based on the input of Tri-glyceride feed for two feed ratios of 4 and 4.5 (Reflux ratio = 6)

Checking the effect of reflux ratio:

In order to investigate the effect of the reflux ratio on the amount of Tri-glyceride conversion (or, in other words, the amount of biodiesel production) in the lower product of the column, the reflux ratio has been changed in the range 2 to 10 with the step size one. The results are shown in the following graph. As can be seen, after reflux ratio 6, the slope of the conversion of the Tri-glyceride percentage is very small and it seems that the choice of reflux ratio greater than 6 is not economical.

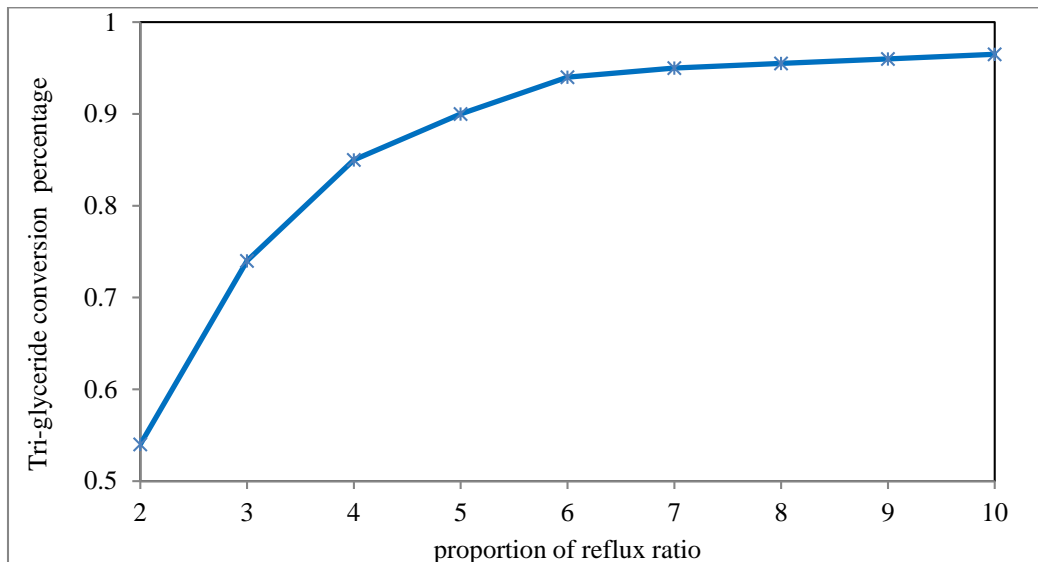


Figure 9: Tri-glyceride conversion percentage based on reflux ratio (Feed ratio = 4: 1)

Effect of ratio of components in feed:

Similarly, to investigate the effect of the methanol-to-oil molar ratio in the feed, the methanol-to-oil ratio ranged from 2 to 10 with a step increment of one unit. The change in the percent conversion of Tri-glyceride is shown in the figure below. Obviously after a feed ratio of 4.5, no significant change in conversion rate is observed therefore, it seems that the appropriate ratio of methanol to oil per unit feed is about 4 to 4.5.

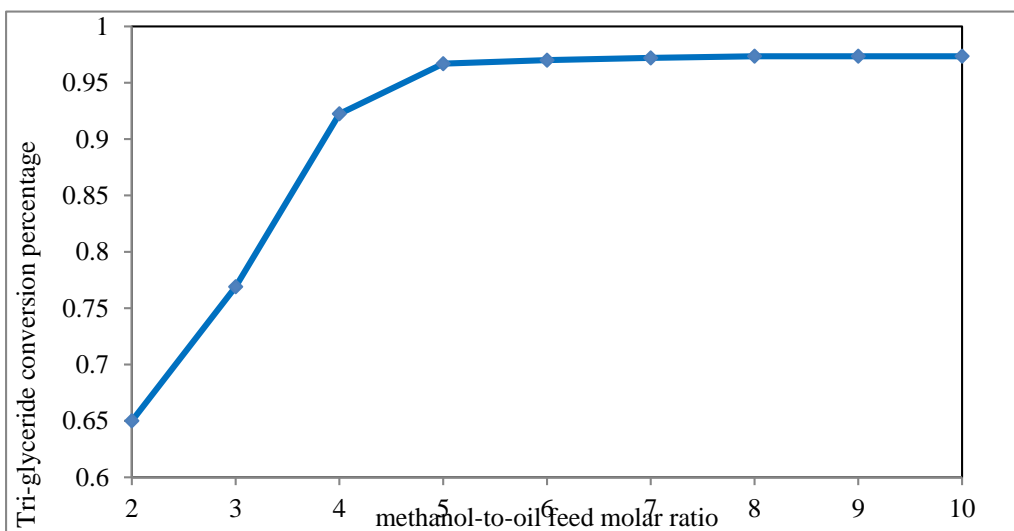


Figure 10: Tri-glyceride conversion percentage based on feed molar ratio (Reflux ratio = 6)

Conclusion

In this research, the biodiesel production process modeling was investigated through reactive distillation and the mathematical model for the above process was based on overall and partial mass balance and thermodynamic equilibrium. In order to check the validity of the model, the results were compared for the percentage of components in the bottom of the column, as well as how the temperature changes along the column were compared with the experimental data presented in reference (Mueanmas, Prasertsit and Tongurai, 2010).

An acceptable consistency was observed between model prediction and experimental data. Of course, the error in the prediction results may have occurred in the modeling of the column due to the use of McCabe's assumptions (the constant molar flow of gas and liquid in the column). The effect of the reflux ratio and the effect of methanol to feed oil on the purity of the biodiesel product were evaluated. The results showed that the reflux ratio 6 and the ratio of methanol to oil 4 to 4.5 were appropriate.

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