

# Modeling for Conversion of Two-phase Esterification for Biodiesel Production

Tanawan Pinnarat\*

Chemical Engineering Department, Faculty of Engineering, King Mongkut's Institute of Technology, Bangkok, Thailand

## ABSTRACT

The conversion of two-phase esterification was performed with the employment of two approaches whereby in the first approach, pseudo-homogeneous phase was assumed and deviation from the experimental data was noticeably observed; and to overcome the drawback, in the second approach, vapor-liquid equilibrium (VLE) was accounted for using ASPEN PLUS and the reaction was allowed to occur in small-time steps using the fatty acid catalyzed kinetics model prior to subsequent VLE calculation. It is assumed in the second approach that transfer between the phases would be faster than the reaction in the separate phases. The outcomes of the second approach show good agreement between the calculated conversion and experimental esterification data in the presence of two phases.

**Keyword:** Esterification, Biodiesel, Conversion Modeling, Vapor-Liquid equilibrium

## 1. INTRODUCTION

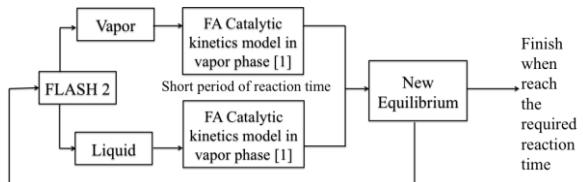
As reported in the work of Changi et al. [1], the fatty acid catalytic kinetics model can reasonably predict esterification conversion that takes place in one single phase. As an extension of the paper [1], the intention of this research is thus to expand the scope of study to encompass estimation of conversion of esterification with two phases present. Typically, esterification is studied in one phase either in a liquid phase with a catalyst or in a supercritical phase without catalyst. If the subcritical condition for esterification is employed, it is possible for the reaction to occur in two phases [2]. The subcritical esterification was introduced as an alternative method to lower the cost of biodiesel synthesis, using moderate temperature and pressure in the absence of catalyst. Previous kinetics studies however usually assumed the one-phase system. It is thus important to develop an accurate model of the two-phase system since the model could be applied to predict the conversion with precision. In addition, the model can

also be used to establish a proper condition for biodiesel production. Therefore, this paper introduces two simple approaches to calculating the conversion derived from the esterification with two phases present.

## 2. MATERIALS AND METHODS

The experimental data for comparison with the calculated conversion from the aforesaid model are from Pinnarat and Savage's [2]. The reactions at 230 °C and 250 °C at various molar ratio of ethanol to oleic acid were selected to conduct in this study because these conditions best represent the two phases reaction. The conditions used in this study are shown in Table 1. The ASPEN PLUS version 2006.5 process simulation software program was used for the model calculation. The fatty acid (FA) catalytic model [1] is the kinetics model used in this study to predict conversion of esterification reactions with two phases present. The details of the FA catalytic model were given in Changi et al.'s [1]. To calculate the conversion for conditions with the existence of two phases, two approaches were employed. In the first approach, the existence of two phases was ignored and the system was instead treated as a single pseudo-homogeneous phase when performing the kinetics model calculations. In the second approach, ASPEN (FLASH2 block) was used to calculate the vapor-liquid equilibrium (VLE) by which the amounts of the co-existing vapor and liquid phases and composition were determined. The results were then used in the FA catalytic kinetics model to calculate the reaction progress in each phase. The reaction was allowed to proceed for a short period of either five minutes or one minute. The reaction results from the kinetics model were inputs of ASPEN and subsequently updated the amounts of the vapor and liquid phases and composition at equilibrium. This new set of information was then used in the kinetics model to allow for the subsequent reaction to proceed for another five minutes or one minute. The procedure (flash, react, and mix) was repeated after each short reaction time until the desired final reaction time was reached. The flow diagram of this procedure is shown in Fig. 1.

\* Corresponding author, Email: kptanawa@kmitl.ac.th



**Figure 1.** The calculation procedure of second approach

The pressure of the system was calculated by trial and error using ASPEN PLUS. The FLASH2 block was used to perform vapor-liquid equilibrium calculations. These calculations provided estimates of the reactor pressure and composition and amounts of co-existing phases when multiple phases were present. As recommended by Carlson [3] for high-pressure, non-electrolyte systems, the PRMHV2 thermodynamic property option was chosen. This option employs the Peng-Robinson equation of state with modified Huron-Vidal mixing rules. Temperature, initial amounts of ethanol and oleic acid, and an assumed pressure were inputs of the process simulation software. Pressure was manually adjusted until the calculated results gave the total molar density of the mixture that was present under the experimental conditions.

### 3. RESULTS AND DISCUSSION

Esterification performed under subcritical conditions may exist in two phases: vapor and liquid. The ratio of vapor to liquid depends on the concentration of reactants, temperature, and system pressure. If the condition where the reactants could be separated from the products could be found, the equilibrium would shift and thereby more products would be produced. In selection of the proper condition, the kinetics model entailing two phases is a useful tool. This article nevertheless does not strive to locate such a proper condition but introduce two simple approaches for the kinetics model involving multiple phases, which can be viewed as a stepping stone to more advanced models.

The two approaches to calculating esterification conversion with two phases present were employed. In the first approach, the presence of two phases was disregarded and the system was rather treated as a single pseudo-homogeneous phase when the kinetics model calculations were performed. Since the first approach ignored the facts that two phases actually existed in the reactor and that the rates in separate phases were different, the accuracy of the model was thus not anticipated. To deal with the drawback, the vapor-liquid equilibrium (VLE) was taken into account in the second approach.

With respect to the first approach (pseudo-homogeneous phase model), the dash lines in Fig. 2-6 depict the results of the model calculations along with the experimental data for two-phase esterification experiments. The model prediction values are considerably below the experimental conversions, especially in the low-density experiment where  $f=0.04$ , as shown in Fig. 2 and 5. Note that  $f$  is a fraction of

reactant partially filling the reactor at room temperature, which in turn determines the system pressure.

Of different conditions with  $250\text{ }^{\circ}\text{C}$  and  $f=0.04$ , if the ratio of ethanol to oleic acid is greater than the stoichiometric ratio as shown in Fig. 2b and 5, the majority of the material added to the reactor is in the vapor phase (i.e. over 80% by mole). If the proportion of ethanol to oleic acid is identical to the stoichiometric ratio as exhibited in Fig. 2a, there will be more liquid portion. The limiting reactant or oleic acid is mostly in the liquid phase at the start of the reaction. In these runs, it was found that in liquid phase, the ethanol to oleic acid ratio was lower than the stoichiometric ratio ( $R_{\text{EtOH, Liq}} < 1$ ) as shown in Table 1. The conversion in the vapor phase was perhaps very rapid in the experiments because of a large excess of ethanol. As oleic acid in the vapor phase was depleted, more oleic acid from the liquid phase was transferred into the vapor phase to maintain the vapor-liquid equilibrium. Thus, the fast-reacting phase could be continually re-supplied by fast mass transfer from the slow-reacting phase. In addition, ethanol in the vapor phase can transfer to the liquid phase. The limiting reactant in the liquid phase, ethanol could become more abundant and thereby drive more reaction in that phase. This interplay of mass transfer, vapor-liquid equilibrium, and reaction kinetics could account for the high experimental conversions observed in this low-density, two-phase reaction system.

At a higher density ( $f = 0.26$ ), the model did a better job of predicting the experimental conversions when treating the system as one pseudo-homogeneous phase (Fig. 3b and 6). Under such a condition, both vapor and liquid phases not merely enjoyed a near equimolar split at  $t = 0$  (~50% mole in liquid phase) but also contained excess amounts of ethanol in both phases. This better level of agreement is probably due to the fact that the liquid and vapor phases are similar in composition and perhaps concentration. Both phases had a large excess of ethanol present. The model predictions were more accurate probably because the actual composition and concentrations in the two phases did not differ dramatically from those obtained by assuming a single phase. However, the model predictions still deviated from the experimental data in this Run. For the condition in Fig. 3a with  $250\text{ }^{\circ}\text{C}$  and  $f=0.26$ , the stoichiometric ratio of ethanol to oleic acid was used, and thereby more portion of liquid phase existed under this condition due to less ethanol compared to the previous two cases presented in Fig. 3b and 6. It could be said that deviation of the prediction from experimental data was the result of the lower ratio of ethanol to oleic acid in the liquid phase than stoichiometric ratio.

In the case of  $230\text{ }^{\circ}\text{C}$  with higher reactant fraction  $f=0.56$  as shown in Fig. 4a,b since the system was mostly in the liquid phase of more than 90%, the prediction assuming a single phase gave a close prediction to experimental data.

The comparison of model predictions assuming a single phase in the reactor with the experimental

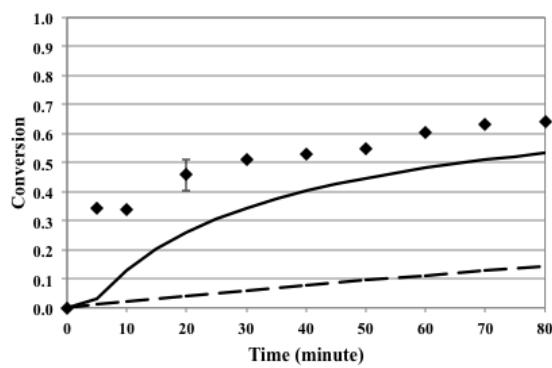
results for two-phase esterification shows that prediction is poor at low density in which one of the phases has a lower amount of ethanol than stoichiometric amount. Clearly, a more rigorous and more accurate treatment of the physics and chemistry governing these two-phase constant-volume batch reactions would require the use of a reliable thermodynamics model to handle vapor-liquid equilibrium, a mass transfer model to handle interphase transport of reactants and products, and a reaction engineering model to monitor the reaction progress in both phases. Taken collectively, these elements would allow for the computation of the composition and amounts of the co-existing phases at each time step throughout the reaction.

TABLE I. EXPERIMENT CONDITIONS OF FIGURES 2-7

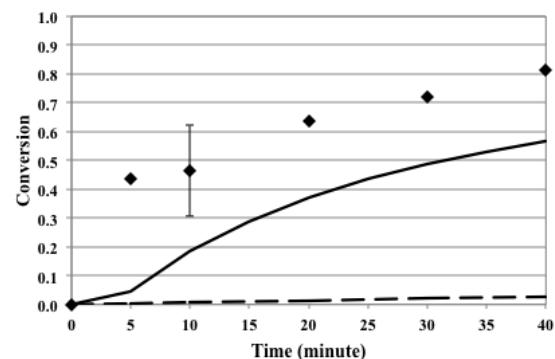
T (°C)	P (MPa)	f	R <sub>EtOH, total</sub>	R <sub>EtOH, Liq</sub>	R <sub>EtOH, Vap</sub>
250	1	0.04	1	0.16	150.83
250	1	0.04	7	0.25	196.84
250	2	0.26	1	0.45	244.94
250	5	0.26	7	3.29	141.88
230	2	0.56	1	0.86	517.16
230	4	0.56	5	4.88	405.32
250	2	0.04	10	0.43	243.13
250	6	0.26	35	20.14	108.95

TABLE I. (CON'T) EXPERIMENT CONDITIONS OF FIGURES 2-7

T (C)	P (MPa)	f	C <sup>0</sup> <sub>OA</sub>	Mol%	Ref. Fig.
			(mol/L)	Liquid	
250	1	0.04	0.22	59	Fig. 2a, 7
250	1	0.04	0.04	16	Fig. 2b
250	2	0.26	0.68	73	Fig. 3a
250	5	0.26	0.35	52	Fig. 3b
230	2	0.56	1.49	95	Fig. 4a
230	4	0.56	0.92	98	Fig. 4b
250	2	0.04	0.05	13	Fig. 5
250	6	0.26	0.11	49	Fig. 6

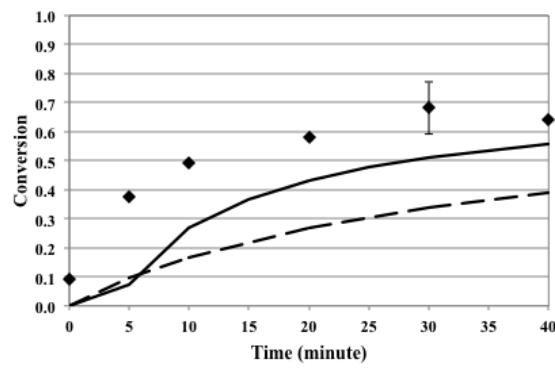


(a)

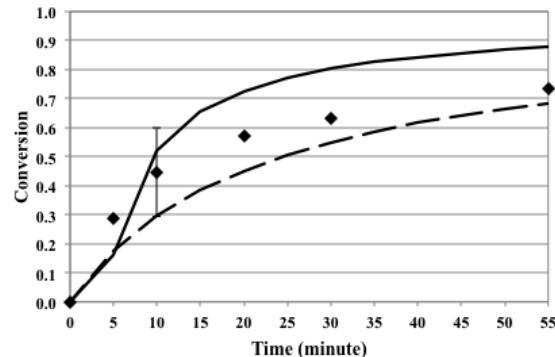


(b)

**Figure 2.** Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 250 °C,  $f = 0.04$  for two-phase esterification systems by treating the system as single pseudo homogeneous phase (dash line) and multi-phase (solid line) with 5-minute time step (a)  $C^0_{OA} = 0.22 \text{ mol/L}$ ,  $R_{EtOH} = 1$ ,  $P = 1 \text{ MPa}$ ; and (b)  $C^0_{OA} = 0.04 \text{ mol/L}$ ,  $R_{EtOH} = 7$ ,  $P = 1 \text{ MPa}$

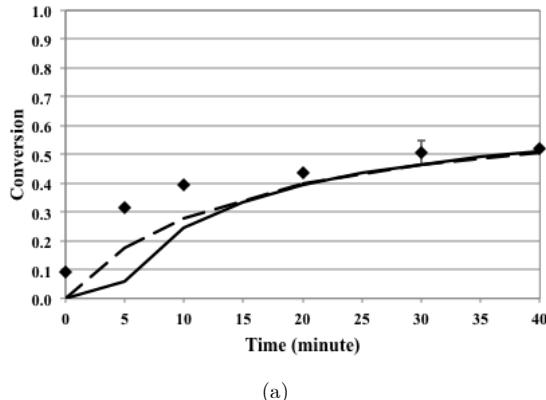


(a)

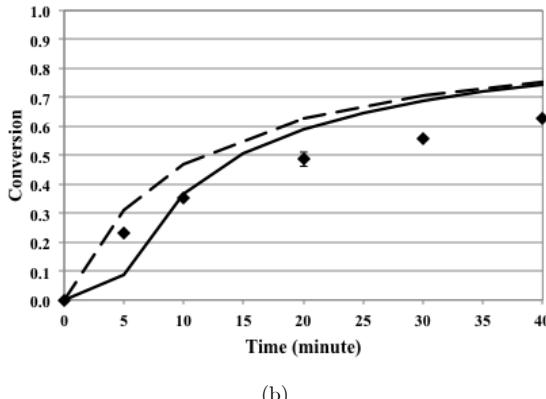


(b)

**Figure 3.** Comparison of conversions predicted kinetics model (curve) and measured by experiment (discrete points) at 250 °C,  $f = 0.26$  for two-phase esterification systems by treating the system as single pseudo homogeneous phase (dash line) and multi-phase (solid line) with 5-minute time step (a)  $C^0_{OA} = 0.68 \text{ mol/L}$ ,  $R_{EtOH} = 1$ ,  $P = 2 \text{ MPa}$ ; and (b)  $C^0_{OA} = 0.35 \text{ mol/L}$ ,  $R_{EtOH} = 7$ ,  $P = 5 \text{ MPa}$

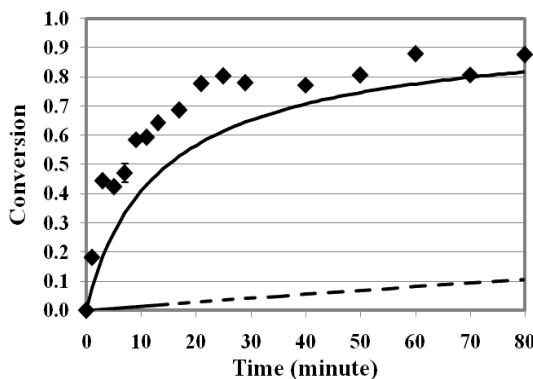


(a)

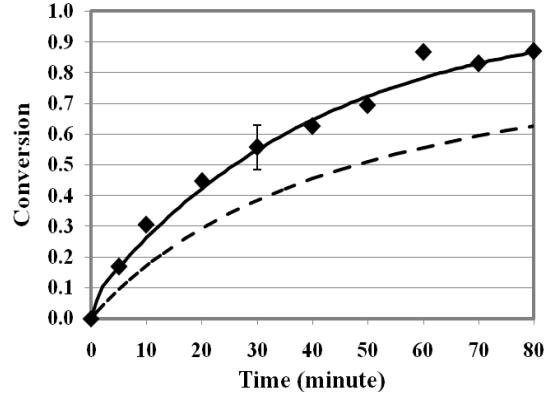


(b)

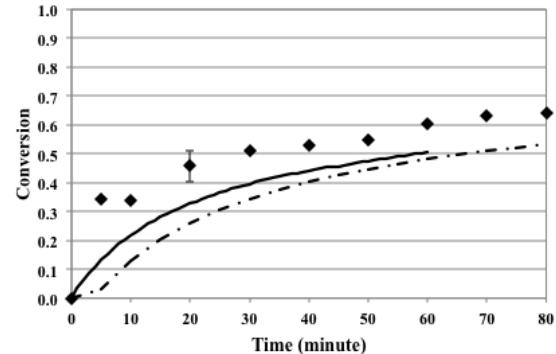
**Figure 4.** Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 230 °C,  $f = 0.56$  for two-phase esterification systems by treating the system as single pseudo homogeneous phase (dash line) and multi-phase (solid line) with 5-minute time step (a)  $C^0_{OA} = 1.49 \text{ mol/L}$ ,  $R_{EtOH} = 1$ ,  $P = 2 \text{ MPa}$ ; and (b)  $C^0_{OA} = 0.92 \text{ mol/L}$ ,  $R_{EtOH} = 5$ ,  $P = 4 \text{ MPa}$



**Figure 5.** Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 250 °C,  $C^0_{OA} = 0.05 \text{ mol/L}$ ,  $f = 0.04$ ,  $R_{EtOH} = 10$ ,  $P = 2 \text{ MPa}$  for two-phase esterification systems by treating the system as single pseudo homogeneous phase (dash line) and multi-phase (solid line)



**Figure 6.** Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 250 °C,  $C^0_{OA} = 0.11 \text{ mol/L}$ ,  $f = 0.26$ ,  $R_{EtOH} = 35$ ,  $P = 6 \text{ MPa}$  for two-phase esterification systems by treating the system as single pseudo homogeneous phase (dash line) and multi-phase (solid line)



**Figure 7.** Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 250 °C,  $f = 0.04$  for two-phase esterification systems by treating the system as multi-phase  $C^0_{OA} = 0.22 \text{ mol/L}$ ,  $R_{EtOH} = 1$ ,  $P = 1 \text{ MPa}$  using reaction time steps of 5 minutes (dotted line) and 1 minute (solid line)

Although a rigorous model would simultaneously account for reaction, mass transfer between phases, and vapor-liquid equilibrium (VLE), we opted for a simpler model that explicitly accounted for only reaction and VLE. Rather than treating mass transfer rigorously as a rate-based process, it is assumed that transfer between the phases would be swifter than the reactions in each phase. We accounted for VLE and reaction using ASPEN (FLASH2 block) as described in the Material and Method section. The results in Fig. 2-6 (solid lines) show that the predicted conversion shifted closer to the experimental data compared to when the system was treated as a single pseudo-homogeneous phase. The improvement was more pronounced in the low density conditions with lower ratio of ethanol to oleic acid than the stoichiometric ratio in liquid phase (Fig. 2a,b; 3a; 5). In addition, the second approach gives a good prediction for the remaining cases in which mere pseudo-homogeneous phase assumption calculation is adequate.

Two distinct time steps of five minutes and one minute were employed in the reaction step. The result shows that the conversion prediction improved in the case of one-minute reaction time compared to the five-minute reaction time step (Fig. 7).

Further tests were conducted to determine whether a smaller reaction time step would affect the prediction, and thereby the time step was reduced from 1 to 0.5 minute. However, the change portrayed no significant difference in the predicted conversions. Hence, one-minute time step appears to be adequate.

It was also observed that the molar density of the mixture changed after the reaction step because the composition changed while pressure was held constant in ASPEN. In reality, the molar density should remain unchanged since the reaction is equi-molar. Therefore, the pressure was adjusted in a trial and error fashion to keep the molar density constant. The new pressure was then used to calculate the composition in each phase by Flash 2. The results showed no significant difference in the calculations between the cases of adjusted pressure and constant pressure.

In predicting the results from the two-phase reaction system, the use of a small reaction time step (1 minute) in each phase allows the calculation to shift closer to the actual system and enables the model to better predict the conversion with two-phase conditions.

#### 4. CONCLUSION

Two simple approaches were introduced for conversion prediction of esterification with two phases present. The first approach assumed that the system was in the pseudo-homogeneous phase and the conversion prediction exhibited deviation from the experimental data, especially in the case that the ethanol to oleic acid molar ratio was lower than the stoichiometric value in liquid phase. In the second approach, we accounted for vapor-liquid equilibrium

(VLE) and reaction using ASPEN PLUS and the fatty acid catalyzed kinetics model. The calculated conversion improved and became more aligned with the experimental data. This study shows that the mass transfer between phases is important and has to be incorporated into the model to obtain an accurate prediction. Our study employed this simple approach by assuming that transfer between the phases would be faster than the reactions in each phase and accounted for VLE and reaction using ASPEN. A more advanced model involving simultaneous mass transfer between phases, VLE, and reaction is required for a better prediction. However, there exist few studies on VLE data of the esterification system and on solubility of oleic acid, ethanol, ethyl oleate, and water, the findings of which are necessary for development of a rigorous model.

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#### REFERENCES

- [1] S. Changi, T. Pinnarat, and P.E. Savage, "Modeling Hydrolysis and Esterification Kinetics for Biofuel Processes," *Industrial & Engineering Chemistry Research*, 2011.
- [2] T. Pinnarat and P.E. Savage, "Noncatalytic esterification of oleic acid in ethanol," *The Journal of Supercritical Fluids*, vol. 53, 2010, pp. 53–59.
- [3] E.C. Carlson, "Don't gamble with physical properties for simulations," *Chemical Engineering Progress*, vol. 92, 1996, pp. 35–46.



Dr. Tanawan Pinnarat  
Research Interests: Biodiesel from algae, Green and renewable energy, Techno-economic evaluation of biodiesel process