Overall Transesterification Rate of Oil in Methanol-Oil Two-Phase System: A Simultaneous Diffusion-Reaction Model

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This short paper aims to clarify the main factor controlling overall transesterification rate of vegetable oil (triglycerides) with methanol catalyzed by homogeneous acid catalyst. In this reaction system, methanol droplets are dispersed in oil continuous phase. Most of the catalyst is existing in methanol droplets. The authors formulated a simultaneous diffusion-reaction model by focusing on the following processes: (1) dissolving of oil into methanol droplets at the oil-methanol interface, (2) inward diffusion of oil in methanol droplets, and (3) simultaneous transesterification of oil with the inward diffusion. In order to prove this model, firstly, the intrinsic transesterification kinetics were determined in methanol/oil/2-butanone/sulfuric acid system at 298, 308, and 323 K. 2-Butanone and sulfuric acid were used as a co-solvent and a catalyst, respectively. Secondly, transesterification of oil with methanol catalyzed by sulfuric acid was carried out in ordinary two-phase system at 298, 308, and 323 K. The authors successfully simulated the two-phase reaction results from the homogeneous kinetics by applying the model developed in this paper. It was found that the overall transesterification rate is controlled by the intrinsic kinetics.

Key Words
Methanol, Triglyceride, Intrinsic transesterification kinetics, Two phase transesterification, Diffusion of triglyceride, Homogeneous acid catalyst

1. Introduction
Fatty acid methyl ester (FAME) is one of a few successful biofuels in terms of industrial production. Although it is industrially successful, there are a few outstanding issues: one of them is how to formulate the overall reaction rate of transesterification of oil (triglyceride) with methanol catalyzed by homogenous catalyst. There have been a few studies for overall transesterification rate of oil with methanol with homogeneous catalyst 1) ~ 4). Richard et al.1) and Likozar and Levec.2) applied the double boundary layer model, which may be rather unrealistic for two-phase transesterification of oil with methanol. The main reason of its irrelevance is that the methanol phase can’t have internal boundary layer since the size of the droplets is too small to have an internal boundary layer. In
case of small droplets, stagnant molecular diffusion should be considered. Klofutar et al. only considered the external boundary layer at oil side, and they did not mention why they ignored the mass transfer in methanol droplets. Csernia and Hsu measured the mass transfer coefficient of methanol side. They could ignore the mass transfer of oil side boundary since they carried out their experiment at a lower range of oil conversion. This experiment is based on well-defined concept and the data looks reliable. Regrettably, they used a horizontal flat boundary layer experimental setup, but not suspension system. Therefore, their results can’t be applied for interpretation of ordinary two-phase transesterification results. In this paper, the authors are aiming to formulate a simultaneous diffusion-reaction model without any adjustment parameter for describing the overall transesterification rate in the two-phase system. In the model, oil dissolved in methanol droplet undergoes inward diffusion and transesterification in methanol phase, simultaneously.

2. Experimental

Cooking grade palm oil was used as oil. For methanol, 2-butanone and sulfuric acid, they were of all reagent grade.

For both the one-phase and two-phase transesterification of palm oil with methanol, reaction was carried out in a 500mL Pyrex three-neck round-bottom flask with a condenser, a thermometer and a sampling port. The reactor was maintained at a constant temperature (298, 308 or 323 K) by a water bath, and its content was agitated by a stirrer chip at 800 rpm. The reaction mixture sampled was analyzed by HPLC to measure the oil conversion and FAME yield. Table 1 shows the experimental conditions.

3. Model Description

Fig. 1 illustrates an overview of the model proposed in this paper. In this model, the boundary layer at the oil phase side is neglected by assuming vigorous agitation in the reactor. The methanol phase side is assumed to be stagnant since the methanol droplet size is very small.

Eq. (1) describes the mass balance of oil in methanol droplet.

\[
\frac{\partial C_T}{\partial t} + \frac{\partial (r C_T)}{\partial r} = -r_{T1}
\]

where \( C_T, r_{T1}, t, r \) are concentration of oil in methanol phase, molecular diffusion coefficient of oil in methanol phase, time and radial distance, respectively. It is likely that \( C_T \) change with time is quite slower than \( r_{T1} \) profile change with time. Then we can assume a pseudo steady-state for solving this equation. Eq. (1) can be thus re-written as Eq. (2) by also assuming the first order kinetics. The corresponding boundary conditions are Eqs. (3) and (4).

\[
D_T \left( \frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r} \frac{\partial C_T}{\partial r} \right) = k_v C_T
\]

\[
C_T = C_{T1, R} \quad \text{at} \quad r = R
\]

\[
\frac{\partial C_T}{\partial r} = 0 \quad \text{at} \quad r = 0
\]

where \( k_v \) and \( R \) are reaction rate constant of transesterification reaction and radius of methanol droplet, respectively. Eq. (2) with the conditions (3) and (4) can be solved analytically as follows:

\[
\frac{C_T}{C_{T1, R}} = \frac{\sinh(3\phi_s R)}{\sinh(3\phi_s)} \quad \phi_s = \frac{R}{3} \sqrt{k_v D_T}
\]

For analyzing the real reaction rate in droplets, it is convenient to use the effectiveness factor \( \eta \).

\[
\eta = \frac{\rho_{T1}}{\rho_{Real}} = \frac{\text{reaction rate when } C_T = C_{T1, R} \text{ [mol/s]} \sinh(3\phi_s)}{\text{ reaction rate when } C_T = C_{T1, R} \text{ [mol/s]} \sinh(3\phi_s) - \frac{1}{3\phi_s}}
\]

In this system (Fig. 1), the reaction rates \( \rho \) and \( \rho_s \) can be expressed by Eqs. (7) and (8), respectively.

\[
\rho = -\frac{dC_{T1}}{dt} V_1
\]

\[
\rho_s = k_v C_{T1, R} V_2
\]

where \( C_{T1}, V_1 \) and \( V_2 \) are concentration of oil in oil phase, oil phase volume and methanol phase volume, respectively. By combining Eqs. (6), (7) and (8), the following equation is obtained.

\[
-\frac{dC_{T1}}{dt} V_1 = \eta k_v C_{T1, R} V_2
\]
The variable $C_{CT,2}$ in Eq. (9) can be replaced to $C_{CT,1}$ by using the following distribution equilibrium.

$$C_{CT,2, \text{R}} = K_s C_{CT,1}$$

(10)

where $K_s$ is distribution constant of oil between methanol phase and oil phase. Finally, an apparent first order kinetic equation in terms of $C_{CT,1}$ is obtained as Eq. (11) below:

$$-\frac{dC_{CT,1}}{dt} = \eta k_v \frac{V_2}{V_1} K_s C_{CT,1} = k' C_{CT,1}$$

(11)

From the integrated form of Eq. (11), oil conversion vs. time can be calculated.

4. Results and Discussion

Fig. 2 shows the first-order kinetics plot for single-phase transesterification for initial oil concentration = 0.026 (a) and 0.052 (b) mol/L. As can be seen from Fig. 2, the linearity of the plots is good enough to assume the first order kinetics in this system. And the consistency of the reaction rate constant between 0.026 and 0.052 mol/L was observed to be good. Thus, the average value of the kinetic parameters was used for the model calculation in the present paper.

The proposed model relevancy was checked by comparing the measured data with the values calculated from Eq. (11) as shown in Fig. 3. The effectiveness factor $\eta$ used for Eq. (11) was unity since the corresponding Thiele modulus ranges from $5 \times 10^{-4}$ to $9 \times 10^{-4}$ as shown in Table 2.

The value of the rate constant $k_v$ used for Eq. (11) was determined in the following way. The transesterification rate of oil is expressed in first order in triglyceride concentration and first order in methanol concentration.

In this sense, $k_v$ in Eq. (11) is the product of the real reaction rate constant and the concentration of methanol. The single-phase transesterification was carried out at a methanol concentration of 7.5 mol/L, while the methanol concentration in the two-phase transesterification was 24.3 mol/L as listed in Table 1. Therefore, the value of $k_v$ in Eq. (11) (or the two-phase transesterification) was obtained by multiplying the rate constant from the single-phase transesterification by a factor of 24.3/7.5.

The values of $V_1$ and $V_2$ were 106.4 mL and 70.8 mL, respectively. The value of $K_s$ was taken from a previous report. As can be seen from Fig. 3, the calculated results (lines) fit to the empirical data (circle keys) well if we take the fact that this model does not have any adjustment parameter into account.

5. Conclusion

A simultaneous diffusion-reaction model was proposed for two-phase transesterification of oil with methanol in this paper. In this model, the major reaction zone was assumed to be methanol droplets. The external mass transfer of oil was assumed to be neglected since the conversion of oil is at a lower range. The internal mass transfer was formulated by assuming the stagnant diffusion from the oil-methanol interface to inside of the methanol droplets. The calculated results based on the model fit to the observed data well. Another important finding is that oil

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### Table 2: Calculation of the Thiele modulus

| Temp [K] | $k_v$, single [1/s] | Methanol factor | $k_v$ in Eq(11) [1/s] | $R$ [m] | $D_t$ [m$^2$/s] | $\phi$ |
|----------|---------------------|----------------|---------------------|--------|----------------|-------|
| 298      | $5.16 \times 10^{-3}$ | 243.75 | $1.68 \times 10^{-4}$ | $2.5 \times 10^{-6}$ | $4.63 \times 10^{4}$ | 5.0 $\times 10^{-4}$ |
| 308      | $1.05 \times 10^{-4}$ | 243.75 | $3.41 \times 10^{-4}$ | $2.0 \times 10^{-6}$ | $5.42 \times 10^{4}$ | 5.3 $\times 10^{-4}$ |
| 323      | $2.86 \times 10^{-5}$ | 243.75 | $9.34 \times 10^{-4}$ | $2.3 \times 10^{-6}$ | $6.95 \times 10^{4}$ | 8.9 $\times 10^{-4}$ |

*1: Calculated from the slope of linear plots in Fig. 2
*2: Measured by an optical microscope
*3: Calculated by the Wilke-Chang’s equation
diffusion in methanol droplets was not the rate-controlling factor under the conditions of the present study.

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