Model Study on Transesterification of Soybean Oil to Biodiesel with Methanol Using Solid Base Catalyst †

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Modeling of the transesterification of vegetable oils to biodiesel using a solid base as a catalyst is very important because the mutual solubilities of oil and methanol will increase with the increasing biodiesel yield. The heterogeneous liquid—liquid—solid reaction system would become a liquid—solid system when the biodiesel reaches a certain content. In this work, we adopted a two-film theory and a steady state approximation assumption, then established a heterogeneous liquid—liquid—solid model in the first stage. After the diffusion coefficients on the liquid—liquid interface and the liquid—solid interface were calculated on the basis of the properties of the system, the theoretical value of biodiesel productivity changing with time was obtained. The predicted values were very near the experimental data, which indicated that the proposed models were suitable for the transesterification of soybean oil to biodiesel when solid bases were used as catalysts. Meanwhile, the model indicated that the transesterification reaction was controlled by both mass transfer and reaction. The total resistance will decrease with the increase in biodiesel yield in the liquid—liquid—solid stage. The solid base catalyst exhibited an activation energy range of 9–20 kcal/mol, which was consistent with the reported activation energy range of homogeneous catalysts.

1. Introduction

Biodiesel (fatty acid methyl esters, FAMEs) is synthesized from direct transesterification of vegetable oils with a shortchain alcohol in the presence of a catalyst; the reaction can be represented as eq $1.^{1}$

$$\begin{array}{ccc} \text{CH}_{2}\text{OOCR}_{1} & \text{CH}_{2}\text{OH} & \text{R}_{1}\text{COOCH}_{3} \\ \text{CHOOCR}_{2} + 3\text{CH}_{3}\text{OH} & \text{CHOH} + \text{R}_{2}\text{COOCH}_{3} \\ \text{CHOH} + \text{R}_{2}\text{COOCH}_{3} & \text{CH}_{2}\text{OH} + \text{R}_{3}\text{COOCH}_{3} \\ \text{CH}_{2}\text{OOCR}_{3} & \text{CH}_{2}\text{OH} + \text{R}_{3}\text{COOCH}_{3} \\ \text{CHCOLERIDE} & \text{GLYCEROL} & \text{FAME} \end{array}$$

$$(1)$$

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts, such as sulfuric acid, potassium hydroxide, calcium oxide, and enzymes.²⁻⁴ Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably costly to separate homogeneous catalysts from the reaction mixture.⁵⁻⁷ Heterogeneous catalysts are noncorrosive, environmentally benign, and present fewer disposal problems, and it is also much easier to separate them from liquid products. They can be designed to give higher activity and selectivity and a longer catalyst lifetime.^{8,9} Because of these advantages, research on solid bases as catalysts has increased over the past decade.¹⁰ Many types of heterogeneous catalysts, such as alkaline earth metal oxides, anion exchange resins, and various alkali metal compounds supported on alumina or zeolite have been studied.^{11–14} Alkaline earth metal compounds are slightly soluble in organic solvents, and it is possible to use them to catalyze transesterification reactions as solid base catalysts. Gryglewicz^{15,16} found calcium methoxide showed high catalytic activity in transesterification reaction. Our preliminary experiments studied calcium oxide, calcium methoxide, and calcium ethoxide as solid base catalysts in detail and found they are better for the transesterification reaction.^{17–19}

The transesterification process is complicated because the reaction system contains a methanol phase, an oil phase, and a solid phase when a solid catalyst is used. With the increase of biodiesel yield, biodiesel can change the phase equilibrium and promote the mutual dissolving of oils and methanol. When the produced biodiesel makes methanol dissolve all oils completely, the system becomes a liquid–solid reaction. Therefore, the reaction system contains a heterogeneous liquid–liquid–solid reaction stage and a liquid–solid reaction stage. However, reports on kinetics studies have focused on homogeneous catalysts. For example, Freedman et al. reported that the activation energy ranges of homogeneous base catalysts were 6.4-20 kcal/mol.^{20–22} However, few studies focus on kinetics using a solid base as the catalyst, especially on liquid–liquid–solid kinetics.

In this study, the authors established a heterogeneous liquid-liquid-solid model and a liquid-solid model on the transesterification of soybean oil to biodiesel with methanol using solid base catalysts, calculated the mass transfer coefficients and resistances, then analyzed the effects of mass transfer and reaction on the reaction rate. The activation energies were calculated according to the experimental data, and the model predictions and experimental data were compared.

2. Experimental Section

2.1. Materials and Catalyst Preparation. CaO was purchased from Beihua Fine Chemical Co., Beijing. It has a 0.56 m^2/g BET surface area. Ca(OCH₃)₂ was produced by a directed reaction of calcium with methanol in a glass reactor at 65 °C

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for 4 h. It has an average particle diameter of 42 μ m and a 19.02 m²/g BET surface area. Ca(OCH₂CH₃)₂ was produced using the same method as calcium methoxide. It has a 15.02 m²/g BET surface area. SrO was produced from calcinations of SrCO₃ in a muffle furnace at 1200 °C for 5 h. Its BET surface area is 1.05 m²/g. Refined soybean oil (SBO) was purchased at the Tianjin Jiali Oil Plant. The fatty acid composition consisted of palmitic acid 12.5%, stearic acid 5.2%, oleic acid 23.5%, linoleic acid 47.8%, linolenic acid 10%, and traces of other acids. Methanol was analytical reagent grade and purchased from Beihua Fine Chemical Co., Beijing.

2.2. Reaction Procedures and Phase Diagram. Transesterification reactions were carried out in a 100 mL glass reactor with a condenser.¹⁷ The magnetic stirring rate was 900 rpm. The reaction procedure was as follows: First, the catalyst was dispersed in methanol under magnetic stirring. Then the soybean oil was added, and the mixture was heated by hot water circulation. The dosage of soybean oil was 28 mL every time. After the reaction, the excess methanol was distilled off under vacuum, and the catalyst was separated by centrifugation. After removal of the glycerol layer, the biodiesel was collected for chromatographic analysis.

The phase boundary was determined by turbidimetric analysis using the titration method under isothermal conditions.²⁵ Biodiesel was titrated in the mixtures of different initial compositions of SBO and methanol. The points when the mixtures changed from turbid to transparent were considered to be the saturation points of biodiesel in SBO + methanol solutions. The quality was calculated by detecting the mass changes of the test tube with an analytical balance.

2.3. Analysis. The biodiesel samples were analyzed by a HP 5890 gas chromatograph equipped with a flame ionization detector and a capillary column HP-Innowax ($30 \text{ m} \times 0.15 \text{ mm}$). Four microliters of the upper oil layer was dissolved in $300 \,\mu\text{L}$ of *n*-hexane and $100 \,\mu\text{L}$ of internal standard solution (hepta-decanoic acid methyl ester/*n*-hexane solution) for GC analysis. Samples ($1 \,\mu\text{L}$) were injected by a sampler at an oven temperature of 220 °C. The oven was heated at 10 °C/min to 230 °C and held for 7.5 min. Nitrogen was used as the carrier gas at a flow rate of 2 mL/min measured at 20 °C, and the detector made up gas at a flow rate of 30 mL/min. The injector and detector temperatures were 300 and 320 °C, respectively. The biodiesel yield was calculated by eq 2.¹⁹

yield =
$$\frac{m_{\text{actual}}}{m_{\text{theoretical}}} \times 100\% \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\%$$

 $\approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100\% \approx \frac{C_{\text{esters}} \times n}{\rho_{\text{oil}}} \times 100\%$
(2)

3. Mathematical Modeling

The literature has reported that the solubilities of CaO, $Ca(OCH_3)_2$ and $Ca(OCH_2CH_3)_2$ in 100 g of methanol at 65 °C are 0.035, 0.04, and 0.011 g, respectively.^{17–19} However, the dissolved catalyst has little effect on the transesterification reaction, and those researchers believed that these catalysts acted mainly as heterogeneous catalysts.

Furthermore, triglyceride (TG) and methanol are partly soluble, and the produced biodiesel can also increase the mutual solubility of triglyceride and methanol. Figure 1 shows the phase diagram and tie lines of biodiesel + methanol + SBO. By calculation, it can be obtained that the ternary mixture becomes



Figure 1. Phase diagram and tie lines of the system biodiesel (FAME) + methanol + SBO at 65 °C.

a homogeneous solution when the biodiesel yield increases to 55% at 65 °C and a molar ratio of methanol to oil of 12. Therefore, the system is a liquid–liquid–solid reaction when the biodiesel yield is lower than 55% at these conditions. When the biodiesel yield exceeds 55%, triglyceride and methanol dissolve mutually, and the process becomes a liquid–solid reaction.

When the molar ratio of methanol to oil is fixed at 12, the distribution coefficient of triglyceride between the methanol phase and the oil phase can be expressed as a function of biodiesel yield (Y_{FAME}) by fitting the experimental data:

$$m_{\rm TG} = 0.00763 - 0.00428Y_{\rm FAME} + 0.26218Y_{\rm FAME}^{2}$$
(3)

The mass of the oil phase can also be expressed as a function of biodiesel yield by fitting the experimental data:

$$m_{\rm oil} = 0.7497 - 0.2933Y_{\rm FAME} + 0.4366Y_{\rm FAME}{}^2 - 2.35639Y_{\rm FAME}{}^3 \quad (4)$$

In the heterogeneous liquid—liquid—solid reaction stage, the reaction process can be described as follows: First, the catalyst is dispersed in methanol. The methanol wets the catalyst particles completely, and a methanol film on the liquid—solid (methanol—catalyst) interface is formed. Then the soybean oil is added into the system as a disperse phase, and it forms a large number of little oil drops. Oil film and methanol film are formed on the liquid—liquid (oil—methanol) interface according to the two-film theory. Triglyceride molecules must cross the liquid—liquid interface and partly dissolve in the methanol phase, then they cross the liquid—solid interface to the catalyst surface for a reaction to occur. Figure 2 depicts the concentration profiles of the reactants and products in the liquid—liquid—solid reacting system.

To develop the rate equation, let us draw on the two-film theory and make some assumptions as follows:

(i) The products consist of many kinds of fatty acid methyl esters (FAMEs), such as methyl palmitate, methyl oleate, methyl stearate, methyl linoleate, and methyl linolenate, which have similar physical and chemical properties. FAMEs are generally



Figure 2. Concentration profiles of the reactants and products in the liquid–liquid–solid reacting system.

named as biodiesel, which could be treated approximately as a component in this study.

(ii) The transesterification reaction is a three-stage reaction, which forms two intermediate products (diacyloglycerides (DG) and monoacyloglycerides (MG)). However, the effects of these intermediate products on biodiesel yield could be omitted. Therefore, only overall reaction is considered, and the biodiesel yield is postulated to equal TG conversion.

(iii) The byproduct of glycerol easily forms a new phase in the system and dissolves part of the reactants and biodiesel. To simplify the process, this study omits the effect of glycerol on the reaction process and mass transfer.

In the following, we detail the mass balances of TG from the oil phase to the surface of the catalyst particle.

In the oil phase, by diffusion, the molar flux of TG to the liquid–liquid interface can be expressed as eq 5.

$$\frac{1}{V}\frac{\mathrm{d}n_{\mathrm{TG}}^{\mathrm{oil}}}{\mathrm{d}t} = -J_{\mathrm{TG}}^{\mathrm{oil}}a \tag{5}$$

where, $n_{\text{tot}}^{\text{oil}}$ is the mole number of TG in the oil phase (which is equal to $[\text{TG}]^{\text{oil}}V_{\text{oil}}$), $J_{\text{TG}}^{\text{oil}}$ is the molar flux of TG out of the oil phase (kmol m⁻² s⁻¹), $[\text{TG}]^{\text{oil}}$ is the concentration of TG in the bulk of the oil phase (kmol m⁻³), *V* is the total liquid volume in the reactor (m_{tot}⁻³), V_{oil} is the volume of the oil phase (m_{tot}⁻³), and *a* is the oil-methanol interfacial area (m² m_{tot}⁻³).

At the oil-methanol interface, the following can be obtained,

$$aJ_{\rm TG}^{\rm oil} = aJ_{\rm TG}^{\rm Me} \tag{6}$$

where J_{TG}^{Me} is the incoming molar flux of TG from the oil-methanol interface (kmol m⁻² s⁻¹).

Considering a steady state in the methanol phase, expression 7 can be obtained,

$$aJ_{\rm TG}^{\rm Me} = a_{\rm S}J_{\rm TG}^{\rm S} \tag{7}$$

where J_{TG}^{S} is the incoming molar flux of TG from the methanol phase to the surface of catalyst particles (kmol m⁻² s⁻¹) and a_{S} is the liquid–solid interfacial area (m² m_{tot}⁻³).

Finally, taking into account that the mass flow of TG through the liquid—solid interface is identical to its total rate of reaction on the external surface of the catalyst (using the steady state approximation on the catalyst surface as well),

$$J_{\rm TG}^{\rm S} = R_{\rm TG}^{\rm S} \tag{8}$$

where R_{TG}^{S} is the reaction rate per (total) unit volume of liquid (kmol $m_{tot}^{-3} s^{-1}$).

The reaction is a pseudo-first-order kinetics at large molar excess of methanol (12:1 molar ratio of methanol to oil), so on the basis of the unit surface,

$$R_{\rm TG}^{\rm S} = a_{\rm S} k_{\rm hetero} [{\rm TG}]^{\rm S}$$
(9)

where $[TG]^{S}$ is the surface concentration of TG per unit volume of the methanol phase (kmol m⁻³), k_{hetero} is the heterogeneous reaction rate constant per unit of external surface of the solid base catalyst (m_{tot}³ m_S⁻² s⁻¹ = m s⁻¹).

Hence,

$$-\frac{1}{V}\frac{\mathrm{d}n_{\mathrm{TG}}^{\mathrm{oil}}}{\mathrm{d}t} = J_{\mathrm{TG}}^{\mathrm{oil}}a = J_{\mathrm{TG}}^{\mathrm{Me}}a = J_{\mathrm{TG}}^{\mathrm{S}}a_{\mathrm{S}} = R_{\mathrm{TG}}^{\mathrm{S}} \qquad (10)$$

$$-\frac{1}{V}\frac{dn_{TG}^{\text{oil}}}{dt} = -\frac{d[TG]^{\text{mix}}}{dt} = -\frac{1}{V}\frac{d[TG]^{\text{oil}}V_{\text{oil}}}{dt} = -\phi_{\text{oil}}\frac{d[TG]^{\text{oil}}}{dt} \quad (11)$$

$$[TG]^{oil} V_{oil} = [TG]^{mix} V$$
(12)

where $[TG]^{mix}$ is the concentration of TG in the mixture (kmol m^{-3}).

Approximately, the biodiesel yield equals to the conversion of TG.

$$Y_{\text{FAME}} = \eta_{\text{TG}} = \frac{[\text{TG}]_0^{\text{mix}} - [\text{TG}]_t^{\text{mix}}}{[\text{TG}]_0^{\text{mix}}}$$
(13)

where Y_{FAME} is the biodiesel yield, η_{TG} is the conversion of TG, and [TG]₀^{mix} is the initial concentration of TG in the mixture (kmol m⁻³).

Using mass transfer coefficients on each of the fluid interfaces (and recalling that the oil phase is dispersed into the methanol phase), we can write the following general rate equation based eq 11:

$$-\frac{d(1-Y_{\text{FAME}})}{1-Y_{\text{FAME}}} = \frac{1/\phi_{\text{oil}}}{\frac{1}{a}\left(\frac{1}{k_{\text{d}_{\text{TG}}}} + \frac{1}{m_{\text{TG}}k_{\text{c}_{\text{TG}}}}\right) + \frac{1}{a_{\text{S}}}\left(\frac{1}{m_{\text{TG}}k_{\text{S}_{\text{TG}}}} + \frac{1}{m_{\text{TG}}k_{\text{hetero}}}\right)} dt \quad (14)$$

where $k_{c_{TG}}$ is the mass transfer coefficient in the continuous phase (ms⁻¹), $k_{d_{TG}}$ is the mass transfer coefficient in the disperse phase (ms⁻¹); $k_{S_{TG}}$ is the mass transfer coefficient on the fluid side of the

 TABLE 1: Mass Transfer Coefficients, Mass Transfer Resistances, Reaction Rate Constant, and Reaction Resistance at Different Biodiesel Yields^a

		$k_{\rm d_{TG}}, 25$	$k_{\rm c_{TG}}, 0.115$	$k_{\rm S_{TG}}, 349$	$k_{\text{hetero}}, 4.13$
resistance, $\times 10^3$		$1/ak_{dTG}$	$1/am_{TG}k_{cTG}$	$1/a_{\rm S}m_{\rm TG}k_{\rm STG}$	$1/a_{\rm S}m_{\rm TG}k_{\rm hetero}$
biodiesel yield	0.1	0.0745	1683	7.9796	6.7446
	0.2	0.0805	1036	4.5414	3.8385
	0.3	0.0888	653	2.6180	2.2128
	0.4	0.0972	452	1.6377	1.3842
	0.5	0.1100	344	1.1035	0.9327

^a 65°C, a 12:1 molar ratio of methanol to oil.

liquid—solid interface (ms⁻¹); [TG]^{i,oil} and [TG]^{i,Me} are the interfacial concentration of TG on the oil and the methanol sides, respectively (kmol m⁻³); $m_{\rm TG} = ([TG]^{i,Me}/[TG]^{i,oil}$ is the distribution constant of triglyceride between the methanol and oil phases; and ϕ_{oil} is the volume fraction of the oil phase ($m_{oil}^{3} m_{\rm tot}^{-3}$). In addition, $1/ak_{\rm drg}$, $1/am_{\rm TG}k_{\rm crc}$, and $1/a_{\rm S}m_{\rm TG}k_{\rm Src}$ represent the mass transfer resistance in the oil—methanol interface, bulk of methanol phase, and methanol—catalyst interface, respectively. $1/a_{\rm S}m_{\rm TG}k_{\rm hetero}$ represents the resistance of reactivity on the catalyst surface. However, the biodiesel can promote the mutual solubility of oil and methanol, which causes the changes of *a*, $m_{\rm TG}$, $\Phi_{\rm oil}$, and $k_{\rm hetero}$ with the increase in the biodiesel yield. $\Phi_{\rm oil}$ can be calculated by the followed equations,

$$a = a_0 (1 - Y_{\text{FAME}})^{2/3} \tag{15}$$

$$\Phi_{\rm oil} = \Phi_{\rm oil0}(1 - Y_{\rm FAME}) \tag{16}$$

$$\Phi_{\rm oil0} = \frac{m_{\rm oil0}}{\rho_{\rm oil} \left(\frac{m_{\rm oil0}}{\rho_{\rm oil}} + \frac{m_{\rm me0}}{\rho_{\rm me}}\right)}$$
(17)

where a_0 is the initial interfacial area between the oil and methanol phases, which is calculated according to ref 23, and m_{oil} and m_{TG} are obtained by fitting the experimental data at the conditions of 65 °C and a 12:1 molar ratio of methanol to oil (eqs 3 and 4). The above diffusion coefficient and mass transfer coefficients can be calculated according refs 23 and 24. The calculated results of the mass transfer coefficient and resistance at different biodiesel yields are shown in Table 1.

From Table 1, we can see that the order of mass transfer resistances is $1/am_{TG}k_{c_{TG}} \gg 1/a_{S}m_{TG}k_{S_{TG}}) \gg 1/ak_{d_{TG}}$. If the reaction is so fast that the reactivity resistance $(1/a_{S}m_{TG}k_{hetero})$ can be negligible, we calculated the reaction time by employing the above equations using a 12:1 molar ratio of methanol to oil, a 2% mass ratio of calcium methoxide catalyst to oil, and 65 °C. The results indicated that the process was so slow that it will take 23.78 h to reach a 50% biodiesel yield. In fact, the experimental results indicated that the reaction was essentially completed within 3 h. Therefore, it suggested that the mass transfer resistance in a methanol phase should be neglected. Another possible explanation is that the distance between oil drops and the catalyst particle is very short, or the oil film directly contacts with the methanol film on the surface of the catalyst. Therefore, the rate equation can be written as follows:

$$-\frac{d(1-Y_{\text{FAME}})}{1-Y_{\text{FAME}}} = \frac{1/\phi_{\text{oil}}}{\frac{1}{ak_{\text{d}_{\text{TG}}}} + \frac{1}{a_{\text{S}}m_{\text{TG}}k_{\text{S}_{\text{TG}}}} + \frac{1}{a_{\text{S}}m_{\text{TG}}k_{\text{hetero}}}} dt$$
(18)



Figure 3. Plot of $\log_{10} k_{hetero}$ vs 1/T at 2% of mass ratio of calcium oxide to oil, 12:1 molar ratio of methanol to oil.

The heterogeneous liquid—liquid—solid model of the transesterification of soybean oil to biodiesel with methanol using a solid base catalyst was proposed (eqs 3, 4, 15–18). It can predict the correlations of biodiesel yield with the reaction time under particular conditions. However, the k_{hetero} must be calculated with an integral model equation by fitting the experimental data in different reaction conditions, and the reactivity resistance must be calculated with the reactivity rate constants.

From Table 1, it is indicated that the biodiesel yield is determined by both surface reaction and mass transfer. The transfer resistances are mainly on the liquid-solid interface. Moreover, the reaction resistance is slightly lower than the mass transfer. Therefore, the transesterification reaction is controlled by both the reaction and the mass transfer in the heterogeneous liquid-liquid-solid stage.

When the biodiesel yield exceeds 55%, the system becomes a liquid-solid reaction. The mass transfer resistance on the liquid-liquid interface disappears. A liquid-solid model can be used to depict the reaction, as shown in eq 19.

$$Y_{\text{FAME}} = 1 - (1 - Y_{\text{FAME}}) \exp(-3600k(t - t_0))$$
(19)

4. Results and Discussion

Calcium methoxide has high catalysis activity in the transesterification reaction. It mostly acts as a heterogeneous catalyst despite slight methanol solubility. The relationship between the reaction rate constant (k_{hetero}) and the temperature is given by the integrated form of the Arrhenius equation,

$$\log_{10} k_{\rm hetero} = -\frac{E_{\rm a}}{2.303RT} + C$$
(20)

where E_a is the activation energy, R is the gas constant in calories (mol⁻¹ deg⁻¹), T is the absolute temperature, and C is a constant.

Figure 3 gives the plot of $\log_{10} k_{hetero}$ vs 1/T for the transesterification reaction in the liquid—liquid—solid stage when calcium methoxide was used as a solid base catalyst. The E_a of 18.26 kcal/mol (76.34 kJ/mol) was calculated. Figure 4 compares the model predictions and experimental data in the transesterification of soybean oil to biodiesel using calcium



Figure 4. Comparison of model predictions and experimental data using calcium methoxide as a solid base catalyst.

 TABLE 2: The Activation Energy of Solid Base Catalysts in

 Liquid–Liquid–Solid Stage^a

catalyst	CaO	$Ca(OCH_3)_2$	$Ca(OCH_2CH_3)_2$	SrO
activation energy, kcal/mol	19.4	17.6	13.0	9.6

^{*a*} Mass ratio of catalyst to oil, 2%; molar ratio of methanol to oil, 12:1; 65°C.

methoxide as a solid base catalyst. In the initial stages of the reaction, the reaction rate was slow, then it increased with the increasing of biodiesel yield. The reason is that because the biodiesel promoted the mutual solubility of triglyceride and methanol, the content of triglyceride in the methanol phase and liquid—solid interface were increased. Both mass transfer resistances and reaction resistance decreased. Furthermore, the content of methanol in the oil phase also increased with an increase in the biodiesel yield. When the biodiesel yield exceeded 55%, the mass transfer resistance decreased, but the reaction rate decreased with an increase in the biodiesel yield. However, the liquid—solid model exhibits a good fit for the experimental data.

CaO, calcium ethoxide, and SrO have chemical properties similar to calcium methoxide, and they exhibited good catalysis activity.²⁶ The calculated activation energies in the liquidliquid-solid stage are shown in Table 2. They indicated that SrO has the lowest activation energy and exhibits a fast reaction rate. CaO has a higher activation energy, and it exhibites a lower reaction rate. In all, the four catalysts have an activation energy range of 9.6–19.4 kcal/mol. The reported activation energy range of the homogeneous base catalyst was 6.4-20 kcal/mol.^{20,22} Therefore, the solid base catalyst has almost the same range of activation energy as the homogeneous base catalyst; however, the solid base catalyst exhibited a slower reaction rate than that of a homogeneous catalyst, such as NaOH, KOH, and NaOCH₃. The reason is that the solid base catalyst provided a lower external surface area. Both mass transfer and reaction baffled the reaction. If a solid base catalyst with a high external surface area is adopted, the reaction rate can be improved distinctly.

Figures 5, 6, and 7 compare the model predictions and experimental data using CaO, calcium ethoxide, and SrO, respectively. These catalysts exhibit a similar change of reaction rate with time, which is slow in the initial state and then becomes fast due to the increase in mutual solubility in the liquid—liquid—solid stage. Meanwhile, in the liquid—solid stage, the reaction rate becomes slow gradually. It can also be seen that most of the solid bases need 1.5-2 h of reaction time to reach a 55% biodiesel yield. In contrast, only several minutes are required to reach the same biodiesel yield when homogeneous catalysts are used. Furthermore, because SrO has a stronger basicity and higher methanol solubility.





Figure 5. Comparison of model predictions and experimental data using CaO as a solid base catalyst.



Figure 6. Comparison of model predictions and experimental data using calcium ethoxide as a solid base catalyst.



Figure 7. Comparison of model predictions and experimental data using SrO.

a faster reaction rate is exhibited as compared to other solid base catalysts. It can also be interpreted that the reaction was catalyzed mainly by the dissolved SrO as a homogeneous catalyst, and it should not be seen as a solid base catalyst absolutely. Therefore, the proposed liquid—liquid—solid and liquid—solid models cannot fit the experimental data very well, and a new heterogeneous ration model should be developed.

5. Conclusions

By analyzing mass transfer and reaction processes, the heterogeneous liquid—liquid—solid reaction model was built, which was suitable in describing biodiesel yield as a function of time in the liquid—liquid—solid stage. The reaction was controlled by both mass transfer and reaction, but the mass transfer resistance was slightly higher than the reaction resistance. In detail, the main mass transfer resistances lay on the surface of the catalyst particle. Therefore, the reaction time could be decreased by increasing the usage of the catalyst or increasing the external surface area of the catalyst. When the surface area is big enough, the reaction will become a controlling step. In addition, the mass transfer resistance can be decreased, and the reaction time can also be reduced by

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adding biodiesel into the system at the beginning of the reaction. In the liquid-solid stage, the proposed liquid-solid model also exhibited a good fit to the experimental data. However, the proposed models are not fit well for the SrO catalyst because it acts in the roles of both a homogeneous catalyst and a heterogeneous catalyst at the same time.

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Appendix

Nomenclature

a	interfacial area between the oil and the methanol
	phases $(m^2 m_{tot}^{-3})$
a_0	initial interfacial area between the oil and methanol
	phases $(m^2 m_{tot}^{-3})$
$a_{\rm S}$	external area of the catalyst particles per unit total
	volume of the reacting system (m ² m_{tot}^{-3})
BET	Brunauer, Emmett, and Teller
C_{ester}	mass concentration of methyl ester which was acquired by GC (g/mL)
d^*	diameter number
d_{32}	mean Sauter diameter (m) = $(\Sigma n_i d_i^3)/(\Sigma n_i d_i^2)$
$d_{\rm p}$	mean diameter of the catalyst particles (m)
D_{a}	stirrer diameter (m)
DG	diacyloglyceride
D_{j}	diffusion coefficient compounds j in the L phase $(m^2 s^{-1})$
$E_{\rm a}$	activation energy, J/mol or cal/mol
FAME	fatty acid methyl ester
J_{j}	molar flux of compound j (kmol $m^{-2} s^{-1}$)
[j] ^L	concentration of compound j in the L phase (kmol
	m^{-3})
$k_{c_{TG}}$	mass transfer coefficient in the continuous phase $(m s^{-1})$
k.	mass transfer coefficient in the disperse phase
TG	$(m s^{-1})$
khetero	heterogeneous reaction rate constant per unit of
	external surface of the solid base catalyst (m s^{-1})
$k_{\rm L}$	mass-transfer coefficient in the L phase (m s^{-1})
$k_{S_{TG}}$	mass transfer coefficient on the fluid side of the
10	liquid—solid interface (m s^{-1})
mactual	actual mass of methyl ester (g)
MG	monoacyloglyceride
<i>m</i> _j	distribution constant of compound j ([j] ^{<i>i</i>,Me} /[j] ^{<i>i</i>,oil}), dimensionless
$M_{\rm i}$	molecular weight of compound j (kg kmol ^{-1})
$m_{\rm theoretical}$	theoretical methyl ester yield (g)
n	diluted multiple of methyl ester
na	stirring speed (s ⁻¹)
n _i	number of drops with diameter d_i of the disperse
	phase
n_{i}^{L}	number of moles of compound j in the L phase (kmol)
Р	power dissipated by the stirrer (kg $s^{-3} m^{-2}$)
R	reaction rate per unit total volume of liquid (kmol
	$m_{tot}^{-3} s^{-1}$
R	gas constant in calories $(mol^{-1} degree^{-1})$
SBO	soybean oil
t	reaction time (s)
Т	absolute temperature (K)

- V total liquid volume (m³)
- w mass ratio of catalyst by weight of soybean oil introduced in the reactor, dry basis $(kg_{\rm S}/kg_{\rm TG})$

We Weber number = $\rho_c n_a^2 D_a^3 / \sigma$

mass of compound j (kg) Wi

biodiesel yield Y_{FAME}

Greek Symbols

- conversion η
- viscosity (kg m⁻¹ s⁻¹) μ
- ρ density (kg m^{-3})
- dimensionless surface tension (N m⁻¹) σ
- Φ_{I} volume fraction of the L phase $(m_L^3 m_{tot}^{-3})$
- Ψ power number

Sub and Superscripts

eq	equilibrium
Me	methanol phase/methanol
i,Me	methanol phase interface
i,oil	oil phase interface
j	compound j
0	initial
oil	soybean oil phase
S	solid catalyst
TG	triglyceride
tot	total

Supporting Information Available: Mathematical derivations and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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