Transesterification rate of model vegetable oil in heterogeneous system with a stirred vessel

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ABSTRACT

The transesterification of triglyceride with methanol using alkali catalyst was experimentally measured to study the reaction rate of the transesterification in the heterogeneous system. The liquid–liquid dispersions were measured under the various conditions to examine the effects of the agitation conditions on the drop size distributions. The Sauter-mean diameters were obtained to estimate the specific surface area of the liquid–liquid dispersions during the transesterification. Then the model of transesterification rate in the heterogeneous system was shown, and the reaction rate constants were obtained based on the measurement of the transesterification rates. The constant of the first reaction was the smallest, and the first reaction was found to be rate-limiting in transesterification. The activation energies of formation in the transesterification were measured to be positive; the reactions of the transesterification were endothermic. The obtained constant was correlated in terms of temperature and concentration of alkali catalyst.

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1. Introduction

Production of biofuels has been focused to meet the renewable energy requirements for support of sustainable society, and biodiesel fuel has been intensively studied as an alternative to petroleum-derived diesel fuel. Biodiesel fuel, consisting of long-chain fatty acid methyl ester (FAME), is produced through transesterification of vegetable oils or animal fats with methanol using alkali, acid or enzyme catalyst [1]. The considerable research activities have been reported to develop the effective production methods.

The quality of the biodiesel fuel is specified by the standards for pure biodiesel fuel and for blend stocks of diesel fuel. The biodiesel phase obtained from transesterification should contain some impurities, such as free glycerol, soap, metals, methanol, free fatty acids, water, unreacted glycerides and so on. To remove these impurities, treatment of the biodiesel phase is necessary and some research works have been presented. Some adsorbents, such as activated carbon and silica, were suggested to remove free fatty acid and water [2–4]. Washing with distilled water at 323 K was so effective to remove residual compounds of methanol, glycerol, sodium and soap. Most of the impurities in biodiesel phase were

effectively removed by simple washing and adsorption, however it was difficult to reduce unreacted glycerides in biodiesel phase. Then, it is necessary to reduce the concentration of glycerides in the biodiesel phase to a sufficiently low level at the transesterification operation. The favorable operation or conditions of the transesterification should be studied for the effective transesterification to reduce unreacted glycerides. According to the work done by Hayashi et al. [5], the reaction equilibrium constants of the respective transesterification with methanol were measured. The required amounts of methanol to meet the specification of glyceride concentration in the biodiesel fuel were estimated and it was suggested that the required amounts of methanol could be reduced by two-staged counter current contact reactor.

There have been many papers published on the analysis of the transesterification mechanism, and in most cases, the system of the mixture of feed oil and methanol was considered as homogeneous one [6–10]. As Stamenkovic et al. pointed out [11,12] the transesterification model with the homogeneous system was impossible to take into account mass transfer effects on the reaction rates, and they suggested the reaction model in the heterogeneous system. The liquid–liquid dispersion in the heterogeneous system was incorporated in the model of transesterification, and methanolysis of sunflower oil was studied to clarify the effects of the stirring velocity on the transesterification reaction rate. The transesterification should generally consist of

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Nomenclature

A_i	frequency factor ($m^4 \, kmol^{-1} \, h^{-1}$)
a	specific interfacial area (m^{-1})
$C_{j,i}$	concentrations in bulk ($kmol \, m^{-3}$)
$C^*_{j,i}$	concentrations at interface ($kmol \, m^{-3}$)
D	impeller diameter (m)
d_{32}	the Sauter mean diameter (m)
E_i	activation energy ($kJ \, kmol^{-1}$)
k_i	reaction rate constant ($m^4 \, kmol^{-1} \, h^{-1}$)
$k_{j,i}$	mass transfer coefficient of component i in phase j ($m \, h^{-1}$)
MR	molar ratio of methanol to feed oil ($-$)
N	stirring velocity (h^{-1})
r	reaction rate ($kmol \, m^{-3} \, h^{-1}$)
T	reaction temperature (K)
t	reaction time (h)
We	Webber number ($-$)
α_i	correlation constant ($kJ \, m^3 \, kmol^{-2}$)
β_i	correlation constant ($kJ \, kmol^{-1}$)
φ_j	volume fraction of phase j ($-$)
σ	interfacial tension ($kg \, m^{-1} \, h^{-2}$)
ρ_i	density of phase j ($kg \, m^{-3}$)
c	continuous phase
d	dispersed phase
DG	diglyceride
FAME	fatty acid methyl ester
GL	glycerol
i	component i
j	phase j
MeOH	methanol
MG	monoglyceride
org	organic phase
pol	polar phase
TG	triglyceride

three regimes; an initial mass transfer controlled regime, a chemically controlled regime, and a final regime close to equilibrium. Stamenkovic et al. [13] suggested the reaction model for each step, and analyzed the transesterification rate.

In this study, more generalized model of transesterification would be suggested to study the reaction mechanism incorporating the mass transfer effects in the heterogeneous system. The transesterification of the model vegetable oil was carried out in the ordinary stirred vessel to examine the effects of operating conditions on the reaction and mass transfer in the liquid–liquid dispersion system. Triolein, a major component in crude jatropha oil, was used as the model feed oil, and it was transesterified with methanol by using sodium hydroxide as alkali catalyst. The effects of the temperature, catalyst concentration, stirring velocity and methanol concentration on the reaction and mass transfer rates were studied.

2. Theoretical background

The transesterification reaction of triolein with methanol can be expressed as,

$$TG + MeOH \underset{k_2}{\overset{k_1}{\rightleftarrows}} DG + FAME \tag{1}$$

$$DG + MeOH \underset{k_4}{\overset{k_3}{\rightleftarrows}} MG + FAME \tag{2}$$

$$MG + MeOH \underset{k_6}{\overset{k_5}{\rightleftarrows}} GL + FAME \tag{3}$$

where TG, DG, MG, GL and FAME mean triglyceride, diglyceride, monoglyceride, glycerol and fatty acid methyl ester, respectively. This sequence of reactions is reversible and the reaction equilibrium constants, K_is, were defined as;

$$K_1 = \frac{C_{org,DG} \times C_{org,FAME}}{C_{org,TG} \times C_{pol,MeOH}} \tag{4}$$

$$K_2 = \frac{C_{org,MG} \times C_{org,FAME}}{C_{org,DG} \times C_{pol,MeOH}} \tag{5}$$

$$K_3 = \frac{C_{pol,GL} \times C_{org,FAME}}{C_{org,MG} \times C_{pol,MeOH}} \tag{6}$$

The kinetic model of transesterification in the homogeneous system has been fully developed [2–4] and in this study the reaction rate model in the heterogeneous system would be discussed. Then the equations of the reaction rates were derived with the following assumptions: I. the system always consists of two phases, such as organic and polar phases, II. the organic and polar phases consist of glycerides and fatty acid methyl ester, and methanol and glycerol, respectively, i.e. the dissolutions of glycerides and methyl ester in the polar phase, and of methanol and glycerol in the organic phase are neglected, III. the transesterification is equilibrium reaction, IV. the reaction rates are expressed by the second order reaction, and the reactions occur only at the organic-polar interface, V. only transesterification occurs and other side reaction, such as saponification, is neglected, VI. pseudo steady state is always valid. Then an example of the distribution of the concentrations of the respective components can be expressed as Fig. 1 when the triglyceride was major component in the organic phase. Triglyceride should diffuse from bulk solution to the interface of the organic and polar phases through the boundary layer in the organic phase, react with methanol at the interface, and the generated diglyceride and FAME should diffuse from the interface to the bulk organic phase. Di- and mono-glycerides should be generated at the interface and react with methanol to produce FAME. Simultaneously unreacted di- and mono-glycerides should diffuse to the bulk organic phase. The generated glycerol should also diffuse from the interface to the bulk polar phase. The transesterification is reversible and the generated glycerides and glycerol should react with FAME. The generation rates of each component can be expressed with the concentrations at the interface, C^*_i, as follows.
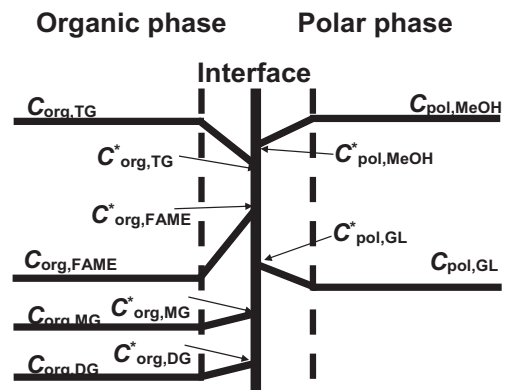

Fig. 1. Concentration profile of respective components around polar-organic interface when triglyceride was major component in organic phase.