Esterification of acidified oil with methanol by SPES/PES catalytic membrane

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A B S T R A C T

A sulfonated polyethersulfone (SPES)/polyethersulfone (PES) blend catalytic membrane was prepared and used as a heterogeneous catalyst in the esterification of the acidified oil (acid value 153 mg KOH/g) with methanol for producing biodiesel. The results showed that the free fatty acids conversion reached 97.6% using SPES/PES catalytic membrane under the optimal esterification conditions. Meanwhile, the SPES/PES membrane with 20.3% degree of sulfonation showed a good catalytic stability. A pseudo-homogeneous kinetic model was established. The results indicated that the reaction rate constant increased with increasing methanol/acidified oil molar ratio, the loading of catalytic membrane and reaction temperature. The reaction order was 2 and the activation energy decreased from 74.65 to 21.07 kJ/mol with increasing catalytic membrane loading from 0 to 0.135 meq/g(oil). It implies that the esterification is not diffusively controlled but kinetically controlled. The predicted results were in good agreement with the experimental data.

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1. Introduction

Biodiesel fuel consists of the simple alkyl esters of fatty acid produced through esterification and/or transesterification of vegetable oils and animal fats. As it is made from renewable sources, it has attracted much attention as an alternative to diesel fuels (Berkhams and Hirata, 2008; Lee and Saka, 2010). However, it is currently not cost competitive with conventional diesel fuel due to high costs of raw material and production (Haas et al., 2006). To reduce the cost of biodiesel, in general, the selection of oil feed is very critical. The oil feeds containing high free fatty acids (FFAs), such as waste fats or non-edible type oils, are far cheaper than vegetable oils, such as soybean or rapeseed oil (Feng et al., 2010; Ni and Meunier, 2007). At the same time, the main problem involved in the utilization of these low-cost feedstocks is represented by the high content of FFAs, which can form soap under alkaline catalysis (Liu et al., 2010). The FFAs are often firstly carried out esterification by homogeneous strong acid catalyzing, such as sulfuric or hydrochloric acid, which is very effective from the view point of catalyzing (Liu et al., 2006). But new problems arose, such as difficult separation from the reaction medium and serious environmental and corrosion-related problems. The methods of enzyme catalyst and supercritical methanol of catalyst-free could overcome the above problems. The methods however have also been limited because of the high cost and deactivation of enzyme by methanol (Halim et al., 2009) as well as the harsh conditions of high pressures and high temperature needed in the supercritical method (Chongkhong et al., 2009).

Functional membranes with strong acid groups, as one form of solid acid catalysts, have attracted considerable attention because functional membranes are capable to eliminate equipment corrosion by comparison with liquid acid and reusable without any treatment so as to diminish wastewater effluent (Shi et al., 2010; Zhu et al., 2010). Further, functional catalytic membranes could be easily prepared by polymer blending or hybridizing with other active components (Castanheiro et al., 2006; Hasanoglu et al., 2009; Shah and Ritchie, 2005; Zhu et al., 2010) and employed in esterifications of small molecular acids (David et al., 1992; Korkmaz et al., 2009; Liu et al., 2001). And that, Nguyen et al. (2003) compared the catalytic activity of membranes obtained by blending polyvinyl alcohol (PVA) with different ionic polymers for the esterification reaction between n-propanol and propanoic acid. However, there are few reports regarding polymeric blend membrane as a catalyst in the preparation of biodiesel.

Besides the selection of the catalysts, the kinetics of the esterification is also very important in analyzing the reactive process and controlling the reaction parameters so as to evaluate the potential industrial applicability of the catalysts and production cost. The kinetics for the esterification catalyzed by homogenous catalysts such as sulfuric acid and hydrochloric acid was early investigated (Berrios et al., 2007; Liu et al., 2006). The kinetics of the heterogeneously catalyzed process recently also received much attention in
order to elucidate the reactive mechanism (Dwiarti et al., 2010; Mazzotti et al., 1997; Tesser et al., 2010; Sanz et al., 2002; Slinn and Kendall, 2009; Zhang et al., 2010). The pseudo-homogeneous (P-H) model as one of the classical models for heterogeneous catal-
yst was applied to the reactions catalyzed by ion exchange res-
sins, lipase and solid acids to study the kinetics of the esterification (Lee et al., 2000; Shu et al., 2009; Goddard et al., 2000; Tesser et al., 2005). The P-H model was found to fit the experimental data fairly well. For example, Su et al. used the cation-exchange resin as the acidic catalyst to investigate the esterification kinetics under different conditions (Su et al., 2008). The results showed that the optimal operating condition for obtaining FFAs conversion of 0.99 could be predicted by the P-H kinetic model. The agreement between the predicted and experimental results demonstrated that the proposed model was appropriate (relative error of 0.5%) for the reaction systems under the catalysis of ion exchange resins. However, the kinetics of the esterification of high FFAs oil with catal-
lytic membrane was little reported.

In this study, a sulfonated polyethersulfone (SPES)/polyeth-
sulfone (PES) blend catalytic membrane was prepared and used as a heterogeneous catalyst in the esterification of the acidified oil with methanol for producing biodiesel. A P-H kinetic model was also developed to predict the kinetics of the esterification by using the SPES/PES catalytic membranes.

2. Methods

2.1. Materials

PES (Ultrason® E3010P) was obtained from BASF. SPES was synthesized using information in the literature (Guan et al., 2005). Three SPES samples with 9.7%, 20.3% and 39.1% of degrees of sulfonation (DS) were obtained when increasing the amount of chlorosulfonic acid in the reagent. The acidified oil with an acid value of 153 mg KOH/g (0.03 wt% water) was supplied by Hubei Haolin Bioenergy Company, China. The other chemicals were all AR grade and used without further purification.

2.2. Preparation of catalytic membranes

1.5 g PES was dissolved in 14 g N-methyl-2-pyrrolidone (NMP) by stirring to form a homogeneous solution. 1.5 g SPES was added into PES solution and the SPES/PES solution obtained was cast carefully onto a glass plate. The plate was then dried by evaporation at atmosphere for 24 h to obtain SPES/PES membrane. The same process was used to prepare the pure SPES membrane.

2.3. DS and ion exchange capacity (IEC)

The sulfonation level is commonly expressed using DS and IEC. DS is defined as the average number of sulfonated groups per repeat unit. IEC indicates the number of milli-equivalents of ions (H+) in 1 g of dry polymer. The DS of the membranes was determined by a titration method (Dai et al., 2007). The IEC of the membranes was obtained as follows:

The membrane samples were soaked in 10 ml sodium chloride aqueous solution (0.1 mol/l) to equilibrate for 24 h. Then the ion-

2.4. Esterification by SPES/PES catalytic membranes

Esterification reaction was carried out in a three-necked batch reactor (total volume 100 ml) equipped with a reflux condenser to prevent the escape of methanol and a mechanical agitation. The system contained a warmer jacket to control reaction temperature. The catalytic membrane was cut into pieces to achieve better contact with reactants. The basic reaction conditions were as follows if not specially stated: the acidified oil amount 20 g, methanol 40 g (equivalent to the molar ratio 1:13.5 of FFAs to methanol); the reaction time 300 min; the reaction temperature 338 ± 1 K; the loading of catalytic membrane 1.35 meq (equivalent to 0.068 meq/g(oil)). After completion of this reaction, the product was purified by pressure distillation to remove the excess methanol and water produced. The FFAs conversion to methyl esters is defined as the ratio of change of acid value of the acidified oil before and after reaction to the initial acid value the same as the literature (Shi et al., 2010). The acid value was determined by titration according to China Standard GB/T 5530-2005: animal and vegetable fats and oils—determination of acid value and acidity.

The catalytic stability of the membrane was also investigated with a number of experiments performed at methanol/acidified oil molar ratio 13.5:1; the reaction time 300 min and the reaction temperature 338 K. The catalytic membrane was reused in the next run without any treatment. The sulfur content in the oil and biodiesel obtained was detected by Micro-coulometric Analyzer (WK-2D, Jiangfen Electroanalytical Instrument Co., Ltd., Jiangsu, China).

3. Kinetic model

The esterification reaction of FFAs with methanol for producing fatty acid esters and water in the presence of catalytic membranes is given as follows:

\[ \text{RCOOH}(A) + \text{CH}_3\text{OH}(B) \rightarrow \text{RCOOCH}_3(C) + \text{H}_2\text{O}(D) \]

The reaction rate can be described as:

\[ -\frac{dc_{\text{RCOOH}}}{dt} = K_{c_{\text{RCOOH}}}c_{\text{CH}_3\text{OH}}^a - K'c_{\text{RCOOCH}_3}c_{\text{H}_2\text{O}}^d \]  

where \( c_{\text{RCOOH}}, c_{\text{CH}_3\text{OH}}, c_{\text{RCOOCH}_3}, c_{\text{H}_2\text{O}} \) denote the concentration of FFAs, methanol, fatty acid esters and water, respectively; \( a, b, c, d \) refer to their reaction orders; \( K \) and \( K' \) are the kinetic constants for the forward and reverse reactions, respectively.

The kinetic model was built on the following assumptions:

(1) The rate of the non-catalyzed reactions can be neglected as compared with the catalyzed ones;
(2) The catalytic activity of all sites at the catalyst surface is the same; and
(3) The whole reaction system is taken into account as an ideal solution.

\[ K_{c_{\text{CH}_3\text{OH}}}^b \] can be a constant as the concentration of methanol is much higher than that of other components in our experimental conditions. \( K \) is far larger than \( K' \) (Su et al., 2008), so Eq. (2) can be simplified as follows:

\[ -\frac{dc_{\text{RCOOH}}}{dt} = k_{c_{\text{RCOOH}}}^n \]

\[ c_{\text{RCOOH}} = c_{\text{RCOOH}_0}(1 - X) \]

\( X \) and \( c_{\text{RCOOH}_0} \) refer to the conversion and the initial concentration of FFAs. Eq. (3) can be converted to Eq. (5)

\[ \frac{dx}{dt} = \frac{k}{c_{\text{RCOOH}_0}}[c_{\text{RCOOH}_0}(1 - X)]^n = k_l[c_{\text{RCOOH}_0}(1 - X)]^n \]
where \( k_1 = \frac{k}{[RCOOH]_0} \). When \( n = 1 \), Eq. (5) can be integrated to

\[
\ln(1 - x) = -kt
\]  

(6)

When \( n \neq 1 \), Eq. (6) is integrated to

\[
(1 - x)^{(1-n)} = 1 + (n - 1)k_1C_0^{1-n}[RCOOH]_0 t
\]  

(7)

To consider the effect of reaction temperature on the kinetic model, the Arrhenius equation is listed as:

\[
k = A \exp \left(-\frac{E_a}{RT}\right)
\]  

(8)

The plots of \( \ln k \) can be used as a function of the reciprocal temperature:

\[
\ln k = -\frac{E_a}{RT} + \ln A
\]  

(9)

Both the frequency factor \( A \), and the activation energy \( E_a \), were obtained by non-linear regression.

4. Results and discussion

4.1. Catalytic performance of SPES/PES membrane

4.1.1. Effect of methanol/acidified oil molar ratio

The relationship between conversion and methanol/acidified oil molar ratio was investigated. The dependence of FFAs conversion on the methanol/acidified oil molar ratio (from 3.3:1 to 54:1) was shown in Fig. 1. The conversion increased considerably with an increase in the ratio. When the ratio was 13.5:1, the conversion reached 97.6%. Further increasing in the molar ratio to 54:1, the conversion only slightly increased. In this work, the optimum methanol/acidified oil molar ratio to produce methyl esters was 13.5:1.

4.1.2. Effect of the loading of catalytic membrane

The effect of the loading of catalytic membrane on the reaction was illustrated in Fig. 2. It was observed that the rate of FFAs conversion increased with an increase in catalytic membrane loading from 0.034 to 0.135 meq/g(oil). At 60 min, the conversion of FFAs increased from about 48.1% to 74.9% with increasing in catalyst loading from 0.034 to 0.135 meq/g(oil). For 0.135 meq/g(oil) catalytic membrane loading, the equilibrium conversion of FFAs reached within 120 min. However, for 0.034 meq/g(oil) catalytic membrane loading, it took about 240 min to reach equilibrium conversion. The higher the catalyst loading, the sooner the equilibrium was reached because of the increase of the total number of acid sites available for the reaction.

4.1.3. Effect of temperature

The effect of temperature on FFAs conversion is very important for a heterogeneous catalyzed reaction. The information is useful to calculate the activation energy of the esterification reaction. Moreover, the reaction rate constant is a strong function of temperature. Fig. 3 presents the variation of conversion of acidified oil in the temperature range 328–348 K at 13.5:1 methanol/acidified oil molar ratio and 0.068 meq/g(oil) of catalytic membrane loading. It shows that increasing the temperature is apparently favorable for the acceleration of the reaction. The higher the temperature, the higher the conversion was. The highest conversion was up to 97.6% when being esterified at 338 K (the boiling point of methanol).

4.2. Catalytic stability of the membrane

A key factor in catalytic application for the industrial process is the catalytic stability as it directly affects the efficiency (Choi et al., 1996). The catalytic stability of SPES/PES membranes with DS of 9.7%, 20.3% and 39.1% in the same loading of catalytic membrane (0.068 meq/g(oil)) was investigated. The FFAs conversions obtained by the membranes with DS of 20.3% and 39.1% were 97.8% and 97.6% at the first run, respectively. After five runs, the FFAs conversion decreased to 84.1% and 74.4% for the membrane with DS of 20.3% and 39.1%, respectively. It indicated that the SPES/PES membrane with 20.3% DS showed a better catalytic stability. As compared with the membrane with 20.3% DS, the FFAs conversion obtained by the membrane with 39.1% DS declined more than 9.7% after five runs. This may be because the DS of the SPES/PES membrane (39.1% DS) was so high that the –SO3H groups in the membrane easily absorbed water produced during the esterification and became easily lost. It is noted that the loss of SPES in
the membrane could bring some adverse impacts. The loss of the –SO₃H groups from SPES membrane could contaminate the product oil. It was found that the sulfur content in the product oil obtained by the SPES/PES membrane with 20.3% DS (217 ppm) is slightly higher than that in the acidic oil (190 ppm). However, both the sulfur contents is much lower than that in the ASTM standard D6751 (500 ppm) even though there is a little loss of the –SO₃H groups from SPES membrane into the production of biodiesel during the esterification.

By contrast, the FFAs conversion was only 56.1% for the SPES/PES membrane with 9.7% DS at the first run. It decreased from 56.1% to 20.1% after five runs. The reason is that the SPES/PES membrane with 9.7% DS has not enough acidic sites for the esterification. In sum, the SPES/PES membrane with 20.3% DS showed a better catalytic stability.

4.3. Kinetic parameters of the process

4.3.1. Reaction order

The kinetic parameter values were determined by minimization of the sum of squared errors between all experimental data from the kinetic model. The reaction order fitted with Eq.(7) at different temperatures and the reaction order was calculated to be 2 in average. Thus, Eq. (7) can be changed to Eq. (10).

\[ \frac{x}{1-x} = k \frac{C_{ROOH_0}}{C_1} t \]  

4.3.2. Reaction rate constants

By solving the model and optimizing the objective function, the kinetic parameters for each experiment were determined. The reaction rate constant is performed by a linear regression. Fig. 4 shows a linear relationship between \( \frac{x}{1-x} \) and \( \frac{C_{ROOH_0}}{C_1} t \). The reaction rate constant \( k \) can be obtained from the slope of each straight line as shown in Table 1. The reaction rate constants increased with an increase in methanol/acidified oil molar ratio, the loading of catalytic membrane and reaction temperature. Besides, the straight line fitted well with the experimental data (Fig. 4). This is a clear indication that the P-H kinetic model is valid.

4.3.3. Activation energy and pre-exponential factor

The dependence of the reaction constants on reaction temperature is described by the Arrhenius equation (Eqs.(9) and (10)). The activation energy of the reaction under 0–0.135 meq/g(oil) of catalyst loading and a temperature range of 318–348 K was calculated and summarized in Table 2. The plot of ln \( k \) vs. \( 1/T \) can be represented by a straight line and the activation energy was obtained from the slope of the line. As can be seen in Table 2, the activation energy decreased from 74.65 to 21.07 kJ/mol with increasing in catalytic membrane and reaction temperature. Besides, the straight line fitted well with the experimental data (Fig. 4). This is a clear indication that the P-H kinetic model is valid.

![Fig. 4. The reaction rate constants obtained at (A) methanol/acidified oil molar ratio, (B) catalytic membrane loading, and (C) reaction temperature.](image)

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Methanol/acidified oil mass ratio</th>
<th>Catalytic membrane loading (meq/g(oil))</th>
<th>Rate constant ( k ) (1 mol⁻¹ min⁻¹)</th>
<th>Rate constant ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3:1</td>
<td>13.5:1</td>
<td>54:1</td>
<td>0.0302</td>
<td>0.9997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.034</td>
<td>0.0366</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.068</td>
<td>0.0550</td>
<td>0.9966</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.135</td>
<td>0.0819</td>
<td>0.9981</td>
</tr>
<tr>
<td>Rate constant ( k ) (1 mol⁻¹ min⁻¹)</td>
<td></td>
<td>0.0366</td>
<td>0.0550</td>
<td>0.0819</td>
</tr>
<tr>
<td>Rate constant ( R^2 )</td>
<td></td>
<td>0.9942</td>
<td>0.9966</td>
<td>0.9981</td>
</tr>
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</table>
4.3.4. Model prediction

The parameters of the kinetic model were determined and based upon the experimental data of the esterification of FFAs obtained under the conditions of (i) catalytic membrane loading (0.034–0.135 meq/g(oil)), (ii) reaction temperature (318–348 K), and (iii) methanol/acidified oil molar ratio (3.3:1–54:1). The conversion is predicted according to the following equation:

\[ x = 1 - 1/(1 + kc_{\text{COOH}, f}) \]  

(11)

The goodness-of-fit of the experimental data to the proposed model was assessed by comparing the experimental FFAs conversion with the theoretical prediction from Eq. (11) at a methanol/acidified oil molar ratio of 13.5:1 as shown in Fig. 1. It was found that three-fourths of the experimental data were reproduced with an error of less than 5% (see Fig. S2 in Supplementary information). It demonstrated that the proposed kinetic model was consistent with the experiment results.

5. Conclusions

A SPES/PES blend catalytic membrane as a heterogeneous catalyst in the esterification of the acidified oil with methanol for producing biodiesel has been successfully prepared and showed a high FFAs conversion and stability. A P-H kinetic model was also developed to predict the kinetics of the esterification using the catalytic membranes. The reaction order calculated was 2. The modeling results showed that the reaction rate constant was associated with methanol/acidified oil molar ratio, the catalytic membrane loading and reaction temperature. The experimental data were consistent with the predicted results.

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Appendix A. Supplementary material


References