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

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ABSTRACT

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 (Berchmans 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 is 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

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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 catalysts was applied to the reactions catalyzed by ion exchange resins, 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 catalytic membrane was little reported.

In this study, a sulfonated polyethersulfone (SPES)/polyethersulfone (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 reactant. 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-exchanged solution was titrated with 0.1 mol/l potassium hydroxide (KOH) solution using phenolphthalein as an indicator. The IEC value of the membranes was calculated using Eq. (1):

$$\mathrm{IEC} = \frac{C_{\mathrm{KOH}} V_{\mathrm{KOH}}}{W_{\mathrm{dry}}} \tag{1}$$

where IEC is ion exchange capacity value (meq/g), C_{KOH} is the concentration of KOH (mol/L), V_{KOH} is the volume of KOH used (ml), W_{dry} is the weight of the dry membrane (g).

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:

$$\mathrm{RCOOH(A)} + \mathrm{CH_3OH}(B) \leftrightarrow \mathrm{RCOOCH_3(C)} + \mathrm{H_2O}(D)$$

The reaction rate can be described as:

$$-\frac{dc_{\mathrm{RCOOH}}}{dt} = Kc^{a}_{\mathrm{RCOOH}} c^{b}_{\mathrm{CH_3OH}} - K' c^{c}_{\mathrm{RCOOCH_3}} c^{d}_{\mathrm{H_2O}} \tag{2}$$

where $c_{\mathrm{RCOOH}}, c_{\mathrm{CH_3OH}}, c_{\mathrm{RCOOCH_3}}, c_{\mathrm{H_2O}}$ 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.

$Kc^{b}_{\mathrm{CH_3OH}}$ 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:

$$-\frac{dc_{\mathrm{RCOOH}}}{dt} = kc^{n}_{\mathrm{RCOOH}} \tag{3}$$

$$c_{\mathrm{RCOOH}} = c_{\mathrm{RCOOH_0}}(1-X) \tag{4}$$

X and $c_{\mathrm{RCOOH_0}}$ refer to the conversion and the initial concentration of FFAs. Eq. (3) can be converted to Eq. (5)

$$\frac{dx}{dt} = \frac{k}{c_{\mathrm{RCOOH_0}}}[c_{\mathrm{RCOOH_0}}(1-X)]^n = k_1[c_{\mathrm{RCOOH_0}}(1-X)]^n \tag{5}$$

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