



Biodiesel production from soybean oil by quaternized polysulfone alkali-catalyzed membrane



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HIGHLIGHTS

- APSF was synthesized by chloromethylation, quaternization and alkalization.
- The effects of water (below 5%) and FFAs (below 2.5%) were not obvious by APSF for biodiesel.
- Hexane was best suitable co-solvent for the transesterification by APSF membrane.
- The membrane kept a conversion of 93.2% by using five runs.

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ABSTRACT

A series of alkalinized polysulfones (APSF) were synthesized by several chemical reactions (chloromethylation, quaternization and alkalization). Among these reactions, chloromethylation and quaternization are two key reactions and have been studied in detail regarding the optimization of both chloromethylation and quaternization. FTIR and ¹H NMR spectrum confirmed the successful preparation of chloromethylated polysulfone. The best IEC of APSF was obtained for 1.68 meq g⁻¹ under reaction time of 10 h and reaction temperature of 45 °C. The APSF membrane as a heterogeneous catalyst for the transesterification of soybean oil with methanol was prepared through the method of solvent evaporation phase inversion. The effects of co-solvent types, mass ratios of soybean oil/co-solvent, water content and free fatty acids (FFAs) content in soybean oil on the conversions using the APSF membrane during transesterification were studied. The reusability of the APSF membrane and the kinetics of the reaction catalyzed by the APSF membrane were also investigated.

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1. Introduction

In view of the gradual exhaustion and the recent steep increase of the petroleum cost, biodiesel has been one of the most attractive alternatives to the traditional diesel fuel which is derived from the petroleum refinery (Farobie and Matsumura, 2015; Song et al., 2015). Biodiesel is commonly manufactured by homogeneously catalyzed transesterification of vegetable oil using the alkaline homogeneous catalysts (such as NaOH and KOH) (Sakai et al., 2009). Base-catalyzed transesterification is much faster than acid-catalyzed. Although homogenous base catalysts have fast reaction rate under mild reacting condition, some severe drawbacks of the catalysts are still obvious, such as the separation difficulties of the reaction medium, strong equipment corrosion and

the adverse effects of the homogenous base catalysts on environment (Dang et al., 2013; Vicente et al., 2004).

Solid-base catalysts (such as MgO, CaO, ZrO₂, calcined MgAl hydrotalcites, rehydrated hydrotalcites, anion-exchange resin and alkali-exchanged zeolite) have great potential for biodiesel production with several advantages over homogeneous acid catalysts (Gurunathan and Ravi, 2015), while the corrosion problems can be effectively avoided. Tantirungrotechai et al. (2013) investigated the application of alkali earth oxide Sr/MgO in the transesterification process and a conversion about 90% was obtained within 30 min. Liu et al. (2012) prepared a cinder supported CaO/KF particle catalyst for biodiesel production. The catalyst showed high catalytic performance within 20 min. But the catalytic sites were easily lost during the transesterification process. In fact, the loss of catalytic sites in the solid-base catalysts is still a main challenge.

Functional membranes with catalytic active components have recently attracted considerable attention in biodiesel production (Radiojevic et al., 2008). Functional membrane catalyst could be

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easily prepared by polymer hybridizing or blending with other active components (Schmidt and Schomäker, 2007). Lopez et al. (2006) immobilized sodium tungstate (Na_2WO_4) on plasma-treated poly(vinylidene difluoride) (PVDF) membrane surface for the oxidation of secondary amines to nitrones. The amine conversion of 100% was achieved within less than 3 h. In our previous work, an organic–inorganic hybrid membrane as heterogeneous acid catalyst was prepared from zirconium sulfate ($\text{Zr}(\text{SO}_4)_2$) and sulfonated poly(vinyl alcohol) (SPVA) (Shi et al., 2010). However, the inorganic particle could be easily lost from the polymer chains in the organic–inorganic catalytic membrane matrix. Based on these, polyethersulfone (PES) chemically grafted sulfonic acid groups ($-\text{SO}_3\text{H}$) as solid catalytic membranes have been used to produce biodiesel. The solid catalytic membranes exhibited excellent stability by comparison with organic–inorganic catalytic membranes (Shi et al., 2011). Besides, sulfonic acid groups were successfully grafted onto the pore surface of PES nanofiltration catalytic membrane through a post-sulfonation and the catalytic membrane was used to catalyze the esterification reaction of acetic acid with ethanol (Shah and Ritchie, 2005).

Polysulfone (PSF) is a high-performance polymer with good thermal and chemical stability. And the modification of this polymer is available to prepare functional catalytic membrane (Park et al., 2006). The aim of the present study is to prepare APSF as a heterogeneous catalyst for the transesterification of soybean oil with methanol. The synthesis of alkalized polysulfone (APSF) involves several chemical reactions: chloromethylation, quaternization and alkalization. Among them, chloromethylation and quaternization are two key reactions and have been studied in details regarding the optimizations of both chloromethylation and quaternization. The APSF catalytic membrane was prepared through the method of solvent evaporation phase inversion and was used as the catalyst for biodiesel production. The effects of water and FFAs in the feedstock on the transesterification were examined. And the kinetics of the reaction catalyzed by the APSF membrane was also investigated.

2. Methods

2.1. Materials

PSF (PSU P-3500) was purchased from SOLVAY (America). Chloromethyl ether, anhydrous zinc oxide, trimethyl ammonium, N-methyl-2-pyrrolidone (NMP), potassium hydroxide and methanol were purchased from Tianjin Kermel Chemical Reagents Limited Company (Tianjin City, China). The chemicals were all analytic reagent (AR) grade and used without further purification. Soybean oil was purchased from Tianjin Jiali grainoil Co. Ltd., Tianjin City, China.

2.2. Preparation of quaternized polysulfone

The preparation process of quaternized polysulfone includes two steps: chloromethylation and quaternization. The procedures were briefly described as follows: PSF was first dissolved in dichloromethane and stirred for 0.5 h to form a homogeneous solution. Then, chloromethyl ether and anhydrous zinc oxide were added into the solution and stirred to catalyze the reaction. The resulted mixture was precipitated with methanol. The product was dried at 343.15 K under vacuum for 24 h and chloromethylated PSF (CMPSF) was finally obtained. The degree of chloromethylation (DC) was determined through ^1H nuclear magnetic resonance (^1H NMR) analysis. CMPSF was dissolved in 35% trimethyl ammonium solution at temperature range from 298.15 to 328.15 K for several hours.

2.3. Preparation of APSF membrane

The APSF membrane was prepared through the method of solvent evaporation phase inversion. The quaternized polysulfone was completely dissolved in NMP until a homogeneous polymer solution was formed. The polymer solution was cast on a stainless glass plate by a stainless steel scraper and then immediately dried at 328 K under 1.33 kPa in a vacuum furnace. The nascent APSF membrane was soaked in a 1.0 M potassium hydroxide aqueous solution at room temperature for 24 h, followed by washing with deionized water several times and immersing in deionized water prior to use.

2.4. Membrane characterization

A thermogravimetric (TG) analyzer (Mettler Toledo TGA/SDTA851e, Netzsch company, Germany) was used to test the thermal stability of PSF, CMPSF and APSF. The samples were heated from 100 to 700 °C at a heating rate of 10 °C/min. Prior to the test, the sample was vacuum-dried for 24 h at 50 °C to remove moisture. ^1H NMR spectroscopy (Bruker company, Switzerland) was used to confirm the synthesis of CMPSF and also to determine the DC of CMPSF. ^1H NMR spectra of PSF and CMPSF were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz. About 1 wt% PSF and CMPSF solutions were directly prepared by dissolving polymers into $\text{DMSO}-d_6$, respectively, where tetramethylsilane (TMS) was used as the internal standard in all cases. The DC of CMPSF was calculated using Eq. (1).

$$\text{DC} = \frac{3I_{\text{CH}_2\text{Cl}}}{2I_{\text{CH}_3}} \quad (1)$$

where DC is the numbers of chloromethyl group in each unit of PSF (Theoretical value is 2.); $I_{\text{CH}_2\text{Cl}}$ is the integration area of the protons of the chloromethyl group; I_{CH_3} is the integration area of the methyl protons. The factors 3 and 2 derive from the fact that the methyl group possesses three protons and the chloromethyl group has two attached protons.

2.5. Ionic exchange capacity (IEC)

The ionic exchange capacity (IEC) was characterized by the classical back titration method (Zeng et al., 2010). The weight of dried APSF membrane was first obtained. Then the membrane was soaked into a 100 mL of 0.1 M HCl solution for 48 h to undergo an ionic exchange process. Finally, the solution together with the membrane was black titrated with a 0.1 M KOH solution. The IEC values ($\text{meq}\cdot\text{g}^{-1}$) are calculated using the following relationship:

$$\text{IEC} = \frac{M_{0,\text{HCl}} - M_{e,\text{HCl}}}{m_d} \quad (2)$$

where $M_{0,\text{HCl}}$ and $M_{e,\text{HCl}}$ are the milliequivalents (meq) of HCl acquired before and after equilibrium, respectively. m_d is the mass (g) of the dried membrane.

2.6. Transesterification by APSF membrane

Transesterification was carried out in a three-necked batch reactor equipped with a reflux condenser and a mechanical agitation. A water bath was employed to control reaction temperature. The APSF membrane was cut into pieces to achieve better contact with reactants. The reaction conditions were as follows if not specially stated: 10 g soybean oil, 10 g methanol, 5 g hexane as co-solvent, the reaction time of 4 h, the reaction temperature of 60 °C and the amount of APSF membrane 2.5 g (equivalent to 25 wt% related to soybean oil mass). After reaction completion,

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