



Biodiesel production by pervaporation-assisted esterification and pre-esterification using graphene oxide/chitosan composite membranes



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ABSTRACT

In this study, a series of novel graphene oxide/chitosan (GO/CS) composite membranes was successfully synthesized and fully characterized. The performance of GO/CS composite membrane was then evaluated by integrating with the esterification of acetic acid with ethanol or the pre-esterification of palmitic acid with methanol, both essential in biodiesel production. Typically, esterification and pre-esterification are reversible reactions, which are limited by chemical equilibrium, resulting in a low product yield. In our study, reaction and separation were conducted in two separated steps or in a single one by means of a catalytic membrane. The preferential removal of water through the membrane in a PV-assisted process enhanced the conversion. The results show clearly that temperature, wt% of embedded GO within a polymeric CS-based membrane, and initial ratio of alcohol/acid are important parameters to enhance conversion because it acts on the kinetics of both pervaporation and esterification/pre-esterification. The enhanced catalytic membrane of the PV-assisted pre-esterification can only be observed when a proper amount of Amberlyst-15 catalyst is used. Additionally, the results of PV-assisted esterification/pre-esterification show that the ratio of water removal (by membrane) and water production (by esterification) rates play a significant role in evaluating the catalytic membrane. Under specific conditions, the conversions of PV-assisted esterification and pre-esterification by the catalytic membrane could be higher than those without PV-assisted up to 8% and 20%, respectively. This process could offer a key technology for biodiesel production in the future.

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1. Introduction

To date, pervaporation (PV) is the core and key point of current membrane research. PV could effectively shift its equilibrium position toward higher conversion by selectively removing one or more product species from the reaction mixture [1,2]. It has found practical applications for PV that could be classified under three categories: (a) dehydration with solvents, (b) separation of anhydrous organic mixtures, and (c) removal of water from aqueous solutions [3]. Among their applications, a hybrid PV-assisted esterification process that applied to the production of eco-friendly biodiesel is an effective and a potential method for producing esters [4–6]. This technique, in the corresponding experiment without membrane-assistance, is possible to shift the equilibrium toward higher

conversion by selectively removing the water produced. To have a better potential for biodiesel production at reasonable costs, much interest has been taken in using low-quality plant oil as the cost advantageous feedstock. However, the low-quality plant oil has a significant amount of free fatty acids (FFA, 2–7 wt% in the feedstock) which might cause several serious concerns, such as a slowdown of the base-catalyzed transesterification, loss of the produced biodiesel [7]. Therefore, the pre-esterification is often considered before the transesterification to reduce the amount of FFA by esterifying FFA into their methyl esters preliminarily (target of 0.5 wt% FFA). In this work, it would be quite valuable to explore the biodiesel production by both PV-assisted esterification and pre-esterification.

In PV process, the non-toxic and biodegradable polysaccharide polymer, chitosan (CS), is extensively applied across a material membrane. Several advantages have been offered by CS-based polymers such as naturally abundant, appreciable hydrophilic, high chemical stability, excellent forming ability, and facile filming

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process [8,9]. However, polymer-based membranes, in general, still face a lot of concerns, such as weak mechanical strengths and easy swelling after the long-term operation, resulting in reducing the separation performance [10]. A promising strategy for improving the physical properties of CS-based membranes is embedding inorganic nanoparticles within a polymeric phase, such as silica [11], calcium aluminosilicate [12], titanium dioxide [13], iron oxides [14–16], silver [17], and graphene oxide [18–21]. Among inorganic fillers, graphene oxide (GO) has attracted intensive attention. It contains various groups of oxygen functional, e.g., hydroxyl, epoxide, diol, ketone, and carboxyl, which chemically react to the amine group of CS to form a bond between GO and biopolymer (CS) [20,21]. It is important that GO also exhibits remarkable mechanical strength, relatively large surface area, and low costs [22]. In this study, a novel modified graphene oxide/chitosan-based (GO/CS) composite membrane is developed. We expect that GO/CS membrane could give advantages of both organic–inorganic membranes, such as high chemical and thermal stability, outstanding mechanical properties, and free of swelling.

In summary, to develop membranes with the desired physicochemical properties and long-term stability, a different amount of GO within a polymeric CS-based membrane was successfully embedded and analyzed by FTA-32 goniometer, FE-SEM, TGA, FT-IR. Amberlyst 15, among the best commercial heterogeneous acid catalysts with distinct advantages including inexpensive, high physicochemical stable, environmentally benign, nontoxic [23], and easily recyclable [24]. It is used to evaluate the efficiency of GO/CS composite membranes in catalytic esterification of acetic acid (AcOH) with ethanol (EtOH) and pre-esterification of palmitic acid (PamOH) with methanol (MeOH) reactions. Additionally, the optimization of the experimental conditions, including temperature, the amount of Amberlyst-15 catalyst and initial ratio of alcohol/acid, is also explored. To the best of our knowledge, such a diverse study that evaluates different wt% of GO within a polymeric CS-based membrane in PV-assisted esterification and pre-esterification for biodiesel production has not been reported before.

2. Experimental

2.1. Preparation of graphene oxide/chitosan (GO/CS) composite membrane

A series of graphene oxide/chitosan (GO/CS) composite membranes (1, 2, 3, and 4 wt% GO embedded CS) was prepared by using a doctor-blade method. Firstly, chitosan powders (Sigma-Aldrich, 200–800 cps) were dissolved in deionized water with 2 wt% acetic acid (J.T. Baker, >99.7%). To remove the impurities, the solution was subsequently filtered by the paper of a pore size of 6 μm. Then, a given amount of GO (E WAY Technology Co., LTD, China) was added into the as-prepared CS solution and stirred vigorously for 3 h. Next, a 1:33 dilution of cross-linking glutaraldehyde (GA) solution was prepared by dissolving glutaraldehyde (Sigma-Aldrich, 50 wt% in H₂O) in deionized water with 1 wt% H₂SO₄ (Sigma-Aldrich, 95–99%). As follows, the formed casting solution was reacted with a certain amount of 2.5 wt% GA dilution solution for 30 min. Afterward, the casting solution was carefully poured over the glass plate, then it was cast to form a membrane with a thickness of several micrometers. As follows, the membrane was slowly dried at 50 °C for 8 h, then peeled from the glass plate. Finally, the membrane is trimmed to fit the size of the PV module (39 mm circular diameter). For comparison, the pristine CS composite membrane was also prepared by the similar method.

2.2. Characterization of membranes

The contact angle between water and membrane surface is widely used to understand the hydrophilic property of membrane. Herein, the water contact angle was measured by the sessile drop method using an FTA-32 goniometer (First Ten Angstroms, USA). The fracture surface morphology on top and cross-section views of membranes were observed by Field Emission Scanning Electron Microscopy (FE-SEM). The composition and changes in thermal stability of the membranes were determined by the Thermogravimetric analyzer (TGA, Pyris 1 TGA, Perkin-Elmer, USA) at a heating rate of 10 °C/min up to a final temperature of 600 °C under the inert nitrogen flow rate of 20 ml/min. Chemical functional groups of membranes were analyzed using a Fourier transform infrared spectroscopy (FT-IR, Nexus 670 spectrometer, Thermo Nicolet, USA).

2.3. Experimental apparatus

The experiments of PV-assisted esterification were performed in the combination of a three-neck round-bottom flask reactor and a membrane module, as shown in Scheme 1. The flask reactor (130 ml) was equipped with a reflux condenser and thermocouple in a temperature-controlled oil bath. The initial reaction mixture of EtOH: AcOH (1:1, 2:1, and 3:1 in mol/mol) was heated to the desired reaction temperature (50–70 °C). The reaction was started by adding a desired wt% of Amberlyst 15 solid catalyst (1.50–2.25 wt%) to the flask reactor. The vacuum was the drive-force used for permeation while the retentate was circulated by a peristaltic pump. The membrane module (PV module) was made of 316 stainless steel and the composite membrane with an effective membrane area 706.9 mm² (39 mm circular diameter). The PV temperature was maintained at the same value of esterification temperature by an electric heating coil wound around the PV module.

For the PV-assisted pre-esterification, the initial reaction mixture of MeOH: PamOH (20:1 in mol/mol) was heated to the desired reaction temperature (50–60 °C). The reaction was started by adding a desired wt% of Amberlyst 15 solid catalyst (5–10 wt%) to the flask reactor. 4 wt% GO/CS composite membrane was used to evaluate the performance. The PV temperature was maintained at the same value of pre-esterification temperature.

During the PV-assisted reactions, the product samples were taken from the three-necked flask and analyzed every 2 h. The product and reactant compositions were determined by using a Hewlett Packard gas chromatograph (HP 6890) equipped with an HP-INNOWAX capillary column (0.32 mm in ID and 30 m in length) and flame ionization detector. It notes that the amount of acetic acid, which was removed by a membrane, was negligible. The conversion and flux were defined as follows.

$$\text{Conversion (\%)} = \left(1 - \frac{\text{detected acid}}{\text{initial acid}}\right) \times 100\% \quad (1)$$

$$\text{Total flux (\%)} = \frac{\text{Permeate weight}}{\text{Membrane area} \times \text{Time}} \quad (2)$$

$$\text{Partial flux of } i = \text{Total flux} \times \text{wt\% of } i \quad (3)$$

3. Results and discussion

3.1. Characterization of GO/CS composite membrane

The contact angles of all the different wt% of graphene oxide in the membrane were measured to evaluate the hydrophilicity of membranes. Fig. 1 clearly shows that 2 wt% of GO has the smallest contact angle (66.4°) among the membranes, suggesting that

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