



Full Length Article

Continuous transesterification to produce biodiesel under HTCC/ Na₂SiO₃/NWF composite catalytic membrane in flow-through membrane reactor



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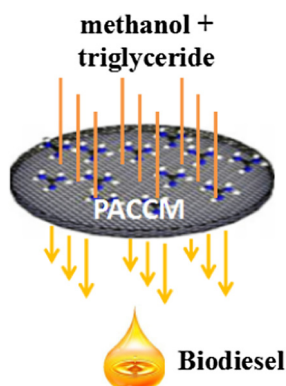
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HIGHLIGHTS

- A novel HTCC/Na₂SiO₃/NWF composite catalytic membrane was prepared.
- PACCM showing an excellent catalytic activity and stability.
- A kinetic model of the continuous transesterification by the PACCM was established.

GRAPHICAL ABSTRACT

A novel polymer-based alkaline composite catalytic membrane (PACCM) was employed to catalyze the transesterification of soybean oil with methanol in a flow-through membrane reactor, showing an excellent catalytic activity and stability.



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ABSTRACT

A novel polymer-based alkaline composite catalytic membrane (PACCM) for the transesterification of soybean oil with methanol in a flow-through mode, was prepared with sodium silicate (Na₂SiO₃) and N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride supported into polypropylene non-woven fabric by nonsolvent induced phase separation. The transesterification with a conversion of above 97.0% was achieved under the PACCMs in a membrane reactor under a molar ratio of methanol/soybean oil of 9:1 and residence time of 3913 s at 60 °C. External mass-transfer resistance in the PACCM could be neglected when the flow rate was beyond 1.0 ml min⁻¹. The transesterification in the membrane reactor was kinetically controlled. The PACCMs showed a good catalytic activity and stability. And the PACCMs could tolerate less than 3.0 wt.% water or less than 1.5 wt.% FFA in the feedstock at which the conversion reached above 90%.

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1. Introduction

Biodiesel, as a kind of clean and renewable energy, was often synthesized through transesterification reaction of plant oils, animal fats or waste cooking oil with low-grade alcohol under acid, alkali or enzyme catalyst [1–3]. Alkaline catalysts, including homogeneous and heterogeneous catalysts, more widely used due to its better catalytic performance compared with acid and enzyme catalysts [4–6]. Homogeneous alkaline catalysts, such as NaOH and KOH [7–9], showed high efficient catalytic activity under mild reaction conditions. However, the homogeneous catalysts had their own demerits, such as severe corrosion, separation difficulty of catalyst from the product and the environmental problem derived from the liquid wastes discharge [10,11]. In recent years, the heterogeneous alkaline catalysts were widely focused on due to easier separation of the heterogeneous catalyst from the reaction mixture and lower consumption in post-treatment process in comparison to the homogeneous systems [12,13]. The heterogeneous catalysts, such as alkaline earth metal oxides including BaO, SrO, CaO and MgO, showed a high catalytic activity after calcination at high temperature and were easily recovered to reuse through centrifuging the reaction mixture after completing transesterification process [14–17]. Very recently, a magnetic Ca/Fe₃O₄@SiO₂ nanocatalyst was prepared via combination of sol-gel and incipient wetness impregnation methods for biodiesel production [18]. The nanocatalyst also showed high catalytic activity with a conversion of 97%. Interestingly, the nanocatalyst could be simply recovered by using an external magnetic field. Although the solid inorganic oxides often had high catalytic activity and easy separation from the product, the preparation process of the catalysts was often complex and need high energy consumption. And the catalytic particles with a nano-scale size were easy to drain and kept in the product, which had a bad effect on the performance of the product [19].

Polymer-based solid catalysts, such as alkaline anion exchange resin, might be one of good candidates to overcome the shortcomings of the inorganic oxides catalysts because the catalytic active groups were chemically attached onto the polymer chains. As an example, D261 anion-exchange resin as a heterogeneous catalyst for the transesterification of soybean oil with methanol in a fixed bed showed high chemical stability of the catalytic active groups. The high conversion to biodiesel reached 95.2% and high quality of the product was obtained [20]. But the resin needed to regenerate every several hours interval. This was mostly because the fouling of organic substances (triglyceride and glycerol) blocked the nanopores or covered the active sites in the resins and then decreased the catalytic activity of the resin [21]. A membrane-shape catalyst with a porous structure could alleviate the fouling of catalyst in a flow-through mode [22].

In our previous study [23], a novel hybrid catalyst of Na₂SiO₃ and N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTCC) blend membrane with porous structure, was prepared through a conventional nonsolvent induced phase separation (NIPS) method. It was found that Na₂SiO₃ was chemically bridged on HTCC chains through epichlorohydrin (ECH) and well dispersed in HTCC matrix in a nanometer size. A good catalytic performance (higher than 97.0%) achieved in a batch mode.

In the present work, the composite catalytic membrane (PACCM) was prepared from Na₂SiO₃/HTCC blend supported into polyethylene (PP) non-woven fabrics (NWF) by NIPS and employed to catalyze the continuous transesterification of soybean oil with methanol in a flow-through mode to produce biodiesel. The reaction process parameters, as well as the stability of PACCMs were investigated. Furthermore, The kinetics of the reaction was also studied.

2. Methods

2.1. Materials

HTCC with an ammonium substitution degree of 95.6% was purchased from Nantong Lvshen Bioengineering Co., Ltd., China. Sodium silicate pentahydrate (Na₂SiO₃·5H₂O, 28.0–30.0 wt.% Na₂O, the weight ratio of Na₂O/SiO₂ = 1.03 ± 0.03), polyethylene glycol (PEG) (analytical reagent (AR), molecular weight 600) and epichlorohydrin (ECH) (99.0%) were purchased from Kernel Corp., Tianjin, China. Refined soybean oil from Fu-hong Corp., Liaoning, China was purchased from local supermarket. The other chemicals are all analytical reagent (AR) grade and used without further purification. The PP NWF were purchased from Tianjin Xinfu Spinning Co. (China). The NWF was pretreated by immersing into 5 wt.% PEG solution under ultra-sonication for 30 min at room temperature and dried in air to improve hydrophilicity of PP fiber.

2.2. Preparation and characterization of HTCC/Na₂SiO₃/NWF membrane

A flat sheet PACCM of HTCC/Na₂SiO₃/NWF was prepared by NIPS. The procedure was briefly described as follows: 6.0 g ECH was firstly dropwise added into Na₂SiO₃ aqueous solution (14.0 g Na₂SiO₃·5H₂O in 30 ml water) at 65 °C for 4 h under stirring to obtain Na₂SiO₃/ECH aqueous solution. Next, 10.0 g HTCC and 10 ml sodium hydroxide (NaOH) solution (0.067 mol/L) were added into Na₂SiO₃/ECH aqueous solution at 65 °C for 6 h to get a homogeneous HTCC/Na₂SiO₃/ECH casting solution. Then the pretreated PP NWF by PVA was immersed into the HTCC/Na₂SiO₃/ECH casting solution in vacuum deaeration for 12 h, and put in the ultrasonic treatment for 4 h. Finally, the HTCC/Na₂SiO₃/NWF was immediately put into the ethanol coagulation baths at room temperature. The HTCC/Na₂SiO₃/NWF PACCM was obtained and kept in ethanol as standby.

The morphologies of PACCM sample were observed by a scanning electronic microscope (SEM, Hitachi S-4800, Japan). The samples for SEM observation were coated by gold sputtering at 20 mA for 180 s. The porosity of PACCM sample is defined as the ratio of pore volume to geometrical volume of composite membrane samples [24]. The known-weight composite membrane samples was sufficiently immersed into butyl alcohol for 12 h, and weighed under wet state after mopping butyl alcohol on the surface. The porosity ε (%) was calculated using Eq. (1).

$$\varepsilon = \frac{m_w - m_d}{AL\rho} \times 100\% \quad (1)$$

where m_w (g), m_d (g) are the weights of wet and dry composite membrane samples, respectively. A (cm²), L (cm) and ρ (g ml⁻¹) are the PACCM area, the PACCM thickness, and butyl alcohol density, respectively.

The specific surface area and average pore diameter of PACCM were measured by a fully automated physical and chemical adsorption (Kangta instrument corporation, Autosorb iQ.C).

2.3. Continuous transesterification reaction

The continuous transesterification was carried out in a flow-through catalytic membrane reactor made from stainless steel for acid/alkali resistance [25]. The PACCM of 3.5 mm thickness was cut into round sheet with a diameter of 68 mm and fixed into the reactor, equipped with a mechanic agitation over the PACCMs and a warmer jacket to heat the reactants. The reactants with initial molar ratios of methanol/soybean oil in the range from 3:1 to 15:1 were pumped into the membrane reactor from the upper inlet

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