Biodiesel production from soybean oil by guanidinylated chitosan

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HIGHLIGHTS

- Guanidinylated chitosan, a novel alkaline catalyst for biodiesel production, was synthesized.
- The guanidinylated chitosan catalyst exhibited very high catalytic activity and stability.
- A kinetic model of the transesterification by the catalyst was established.

GRAPHICAL ABSTRACT
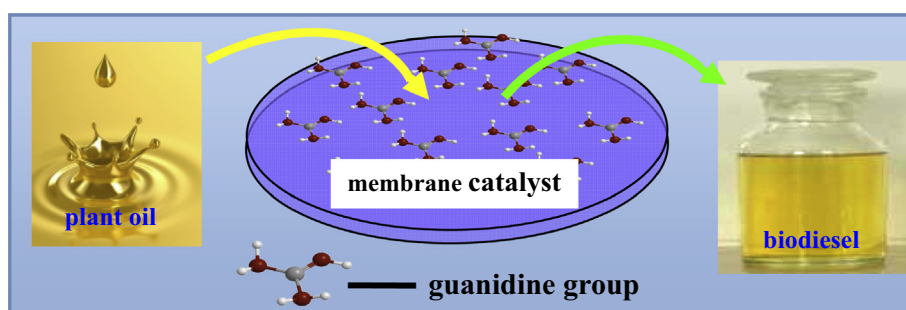
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ABSTRACT

Guanidinylated chitosan (GCS), as a heterogeneous alkaline catalyst for the transesterification of soybean oil with methanol, was synthesized by grafting aminoiminomethanesulfonic acid onto chitosan. The structure and properties of GCS membrane were investigated by Fourier transform infrared spectroscopy, thermogravimetry and X-ray photoelectron spectroscopy. The soybean oil conversion reached 98.8% at the first run and 96.6% at the fifth run under the reaction conditions: catalyst amount of 20 wt.%, methanol/oil mass ratio of 2.5:1 at 60 °C for 6 h. Results show that the transesterification mainly took place on the surface of the catalytic membrane. The kinetics study of the transesterification was undertaken in terms of pseudo-homogeneous model and performed as a first order reaction with an activation energy of 76.95 kJ/mol and pre-exponential factor of $7.94 \times 10^9 \, min^{-1}$.

1. Introduction

Biodiesel is an attractive substitute for petro-diesel fuel because it is renewable and biodegradable. Biodiesel (usually fatty acid methyl esters, FAME) was often derived from either the transesterification of triglycerides or the esterification of free fatty acids (FFAs) with methanol [1,2]. The most practical technique is the transesterification in the presence of homogeneous or heterogeneous alkaline catalysts. The homogeneous alkaline catalysts, such as NaOH, KOH and NaOCH₃, show a very high catalytic activity in general, but there are obvious disadvantages, namely severe equipment corrosion, difficult separation of product, and environmental

problem of waste water discharge [3,4]. The development of heterogeneous catalysts to overcome the disadvantages of homogeneous catalysts is of great importance [5,6].

Anion-exchange resins and Metal oxides have been widely used as heterogeneous alkaline catalysts in the transesterification. Anion-exchange resin (D261) was employed in a bed reactor to catalyze the transesterification of soybean oil with methanol in a continuous mode with a conversion of over 95% [7]. However, the catalytic efficiency dropped with running time due to the deactivation of the catalysts. Tantirungrotechai et al. [8] investigated alkali earth oxide Sr/MgO for the transesterification, a conversion greater than 90% was obtained within 30 min. An alkaline catalyst, CaO/KF supported on cinder was prepared for the production of biodiesel. The catalyst showed high catalytic performance within 20 min. But the catalytic sites were easily lost during the

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transesterification [9]. In fact, the deactivation and/or loss of solid heterogeneous catalyst are still a main challenge [10].

Being a heterogeneous catalyst, membrane catalyst is being explored and exploited for producing biodiesel. Membrane catalyst could be easily prepared by polymer hybridizing or blending with other active components. An organic–inorganic hybrid membrane as heterogeneous acid catalyst was prepared from zirconium sulfate ($Zr(SO_4)_2$) and sulfonated poly(vinyl alcohol) (SPVA). But the $Zr(SO_4)_2$ particles could also be leached from polymer matrix due to the weak interaction between $Zr(SO_4)_2$ and SPVA [11]. In order to solve the loss of catalyst, the catalytic groups, such as sulfonic groups ($—SO_3H$), were grafted on polymer chains as composite catalytic membranes used in the esterification. Shah and Ritchie [12] introduced sulfonic acid groups onto the pore surface of polyethersulfone (PES) nanofiltration membrane, catalyzing the esterification between ethanol and acetic acid. A residence time of 20 s gave a conversion of 16%. In our previous work [13,14], a blend membrane of sulfonated polyethersulfone (SPES) and PES was employed as an acid catalyst for biodiesel production from free fatty acid. A conversion of over 98% was kept within continuous running time of over 500 h [14].

Chitosan is obtained by deacetylation of chitin that is the second most abundant natural organic resource on the earth next to cellulose. The presence of both hydroxyl and amino groups on chitosan offers numerous modification possibilities, such as alkylation, acylation, carboxymethylation [15,16]. Guanidine is one of the strongest organic bases (pK_a = 13.6) [17]. And monosubstituted guanidine could be synthesized from the reaction of aminoiminomethanesulfonic acid (AIMSOA) with primary amines [18]. So it is possible to prepare an alkaline polymer alkaline catalyst from the reaction of chitosan with guanidine groups for transesterification.

The aim of the present study is to prepare guanidinylated chitosan (GCS) as a heterogeneous catalyst for the transesterification of soybean oil with methanol. The structure and properties of GCS were studied. The kinetics of the reaction was also investigated.

2. Methods

2.1. Materials

Chitosan was purchased from Shandong Hili Bioprodcut Co. Ltd., China. The deacetylation degree of chitosan is 85%. Aminoiminomethanesulfinic acid (AIMSA) was purchased from Aladdin. Soybean oil was purchased from COFCO in Tianjin, China. The other chemicals were all analytical reagent (AR) grade and used without further purification.

2.2. Preparation of GCS-OH

2.2.1. Preparation of AIMSOA

Firstly, 1.7 mL concentrated sulfuric acid (18.4 mol/L) and 65 mL hydrogen peroxide (10 mol/L) were added into a breaker to prepare acidic solution of hydrogen peroxide. Secondly, 10 mL acidic solution of hydrogen peroxide was put into a three-necked flask and kept at 55 °C. And 54 g AIMSA and all the other hydrogen peroxide solution were dropwise added into the flask within 80 min at 55 °C. After addition was completed, the mixture was stirred at room temperature for 2 h [19]. Finally the product was placed below 10 °C for 4 h and filtered to obtain the AIMSOA hydrate crystals with smooth and shiny surface, then dried in the lyophilizer under a vacuum degree of 10 Pa and a temperature of −50 °C for 12 h to obtain AIMSOA.

2.2.2. Preparation of GCS-SO_3H

9 g chitosan was dissolved in 400 mL hydrochloric acid solution (0.2 mol/L) under stirring. After complete dissolution, 17.3 g AIMSOA (AIMSOA/chitosan molar ratio of 2.5:1) was added gradually into the chitosan solution at 60 °C within 40 min under stirring. The reaction was kept at 60 °C for 15 min and then cooled to room temperature to stop the reaction. The mixture was poured into ethanol to obtain the precipitate. The precipitate was filtered off and repeatedly washed with ethanol three times, then dried at 55 °C and 1.33 kPa in vacuum drying oven to constant weight to obtain GCS-SO_3H [20]. The degree of substitution (DS) was determined through elemental analysis. The synthetic route of GCS-SO_3H was shown in Scheme 1.

2.2.3. Preparation of GCS-OH membrane

3 g GCS-SO_3H and 3 g sodium hydroxide (NaOH) were dissolved in 100 g distilled water by stirring to transform into GCS-OH (as Scheme 1). The GCS solution containing NaOH was cast on a stainless glass plate to form membrane and then dried at 55 °C under 1.33 kPa in a vacuum furnace. The obtained GCS-OH membrane was repeatedly washed by methanol to fully remove the free NaOH in the membrane. The ion exchange capacity (IEC) of GCS-OH catalytic membrane was determined according to the method reported by Shi et al. [13].

2.3. Characterization of GCS membranes

Fourier transform infrared spectra (FTIR) were recorded in powder form in KBr discs in the range of 4000–500 cm^{-1} on a BRUKER FTIR TENSOR 37 spectrophotometer.

Thermal stability of the samples was investigated with a NETZSCH STA-409 thermogravimetric analyzer. The sample of 7 to 10 mg was heated from 30 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

X-ray photoelectron spectra (XPS) were recorded with a ThermoFisher K-alpha X-ray photoelectron spectroscope employing a monochromated Al Ka X-ray source ($h\nu$ = 1486.6 eV). Survey spectra were recorded with a pass energy of 200 eV, and high resolution spectra with a pass energy of 50 eV.

2.4. Transesterification by GCS-OH membrane catalyst

Transesterification reaction was carried out in a three-necked batch reactor (a total volume of 100 ml) equipped with a reflux condenser to prevent the escape of methanol and a magnetic
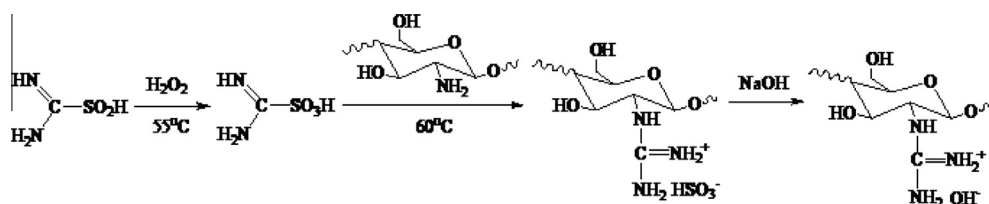
Scheme 1. The schematic representation of guanidinylated chitosan synthesis.