Efficient bifunctional catalyst lipase/organophosphonic acid-functionalized silica for biodiesel synthesis by esterification of oleic acid with ethanol

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HIGHLIGHTS

- A novel bifunctional catalyst SG-T-P-LS was successfully developed.
- Esterification of FFA oleic acid on the bifunctional catalyst was investigated.
- Biodiesel synthesis process by esterification of oleic acid was optimized by RSM.
- Optimum parameters were 14.9 wt.% SG-T-P-LS at 28.6 °C and 1.05:1 (molar) ethanol:oleic acid.
- A maximum FFA conversion of 89.94% could be obtained under the optimized conditions.

GRAPHICAL ABSTRACT
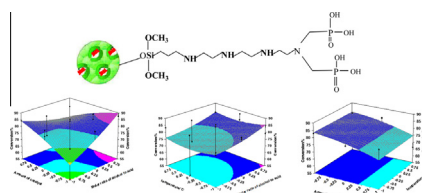
ABSTRACT

An efficient bifunctional catalyst lipase/organophosphonic acid-functionalized silica (SG-T-P-LS) has been successfully developed, and biodiesel production of fatty acid ethyl ester (FAEE) from free fatty acid (FFA) oleic acid with short-chain alcohol ethanol catalyzed by SG-T-P-LS was investigated. The process optimization using response surface methodology (RSM) was performed and the interactions between the operational variables were elucidated, and it was found that the molar ratio of alcohol to acid was the most significant factor. The optimum values for maximum conversion ratio can be obtained by using a Box–Behnken center-united design, and the conversion ratio could reach 89.94 ± 0.42% under the conditions that ethanol/acid molar ratio was 1.05:1 and SG-T-P-LS weight ratio was 14.9 wt.% at 28.6 °C. The research results show that SG-T-P and LS-20 could work cooperatively to promote the esterification reaction, and the bifunctional catalyst SG-T-P-LS is a potential catalyst for biodiesel production.

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1. Introduction

As one of the alternatives for fossil diesel, biodiesel fuel, which is usually defined as fatty acid methyl/ethyl ester, is gaining significant attention in recent years because of its advantages of cleaner engine emissions, biodegradable, non-toxic, renewable and superior lubricating properties (Alcantara et al., 2000; Kawashima et al., 2009; Lee and Saka, 2010; Son et al., 2011). These characteristics of biodiesel make it an excellent substitute or additive to conventional diesel fuels. Moreover, biodiesel could be derived from renewable and domestic resources, thereby relieving the reliance on petroleum fuel imports. However, biodiesel production costs are rather high compared to petroleum-based diesel fuel. The major obstacle to the commercialization of biodiesel from refined plant/vegetable oils or animal fats is primarily the high cost of raw materials in the global market (Corro et al., 2011). Low-grade oil such as waste cooking oil could be a better alternative, but the

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high free fatty acids content in waste cooking oil has been the main drawback for the potential feedstock (Lam et al., 2010). Therefore, an esterification step is required in which fatty acid methyl/ethyl ester could be produced using homogeneous, heterogeneous, and enzymatic catalysts. It has been found that there is the potential of heterogeneous acid catalysts and enzymes towards a more sustainable biodiesel industry because of their easily separation from reaction systems, the decreased amount of waste water and the excellent catalytic efficiency (Edgar et al., 2005; Kamini and Iefuji, 2007; Kawashima et al., 2009; Marchetti and Errazu, 2008). Therefore, the use of solid catalysts in the esterification reactions of FFA is very important in developing cleaner and friendly-economical processes for biodiesel production as they could reduce equipment needs and cost. But the main drawback of enzyme-catalyzed processes is the high cost of the lipases. To decrease the operational costs of the biocatalyst, the process must be optimized using an immobilized enzyme.

In the previous work, the esterification of FFA oleic acid with ethanol using organophosphonic acid-functionalized silica catalyst (triethylenetetramine bis(methylene phosphonic acid)-functionalized silica catalyst SG-T-P) was investigated using response surface methodology (RSM) to determine the optimum catalyst amount, molar ratio of ethanol to oleic acid and reaction temperature, and the conversion ratio of oleic acid reached 77.02 ± 0.62% under the optimal conditions. SG-T-P exhibits catalytic activity, and also adsorbs water from the reaction system at the same time (Yin et al., 2012). In order to make the biodiesel production process commercially feasible, its catalytic activity by synthesizing composite catalysts using SG-T-P has been tried to improve. It is well known, enzymes are biocatalysts with excellent prospects of industrial implementation, and they have excellent features such as high activity and selectivity under mild and environmental friendly conditions. Especially, lipases are among the most attractive and promising enzyme for industrial applications (Ramani et al., 2012). In the present work, the aim is to immobilize the lipase LS-20 over SG-T-P, and to develop the bi-functional catalyst lipase/organophosphonic acid-functionalized silica (SG-T-P-LS). The esterification reaction process has been optimized using response surface methodology (RSM), and the optimum values for maximum conversion ratio could be obtained by using a Box–Behnken center-united design with a minimum of experimental work.

2. Methods

2.1. Materials and instruments

The lipase LS-20 was obtained from Beijing Kaitai Co., Ltd. of China. Silica gel (SG) of chromatographic grade (80–100 mesh size) was obtained from Qingdao Silicon Create Fine Chemical Co., Ltd. Shandong Province of China. SG was activated with nitric acid ($HNO_3:H_2O = 1:1$) at refluxing temperature for 3 h, hydrochloric acid ($HCl:H_2O = 1:1$) at room temperature for 6 h, then filtered off, washed thoroughly with distilled water till acid-free and friendly calcined in a muffle at 160 °C for 10 h. Organic solvent toluene was redistilled just before use. 3-chloropropyltrimethoxysilane (CPTS) (Jianghan Chemicals Factory, Jinzhou, China), triethylenetetramine (TETA) (Shanghai Chemical Factory of China) and the other reagents were used without further purification. Infrared spectra (FTIR) of samples were obtained on a Nicolet MAGNA-IR 550 (series II) spectrophotometer, USA. Test conditions were as follows: scanning 32 times, KBr pellets in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1}. The morphology of the compounds was examined on JEOL JSF5600LV scanning electron microscope, JEOL Co., Japan.
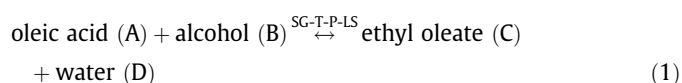
2.2. Synthesis of the bifunctional catalyst SG-T-P-LS

The synthetic route of the bifunctional catalyst SG-T-P-LS is shown in Fig. S1 (available in the Supplementary material). Under a nitrogen atmosphere, a mixture of 25.0 mL of triethylenetetramine and 15.0 mL of CPTS were stirred at 80 °C in the 150 mL of ethanol solution for 12 h, and then the product was distilled until there is no ethanol in it, and then 15.0 g of activated silica gel was added with 150 mL toluene as solvent. The mixture was stirred at 110 °C for 12 h, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as SG-TETA. 10.0 g of SG-TETA were added to 95 mL ethanol at room temperature for 12 h, then 2.5 g of paraformaldehyde, 6.9 g of phosphorous acid and 2.9 mL of hydrochloric acid were added. After being refluxed at 90 °C for 12 h, the solid catalyst (SG-T-P) was filtered off, then washed thoroughly with distilled water and finally dried under vacuum over 48 h at 50 °C. 3.0 g of the lipase LS-20 was dissolved in 50 mL of the buffer solution (pH 7.4), and then 1.0 g of SG-T-P was put in. The mixed system was oscillated for 24 h, and the product SG-T-P-LS was filtered off and dried at room temperature.

2.3. Esterification reaction

A biodiesel production from FFA oleic acid with ethanol was investigated in the presence of SG-T-P-LS catalyst, and the relevant esterification reactions were carried out under batch reaction conditions using a 100 mL flask fitted with a stirrer, a thermometer and a reflux condenser. A typical reaction mixture in the reactor contained 12 mL of oleic acid, and a certain amount of ethanol and the catalyst SG-T-P-LS. All the experiments were conducted for 10 h at a certain reaction temperature under the mechanical stirring conditions. After a certain time of reaction operation, the reaction mixture was filtered by vacuum filtration to separate the solid catalyst, and the product was transferred to a three-necked flask to remove water and ethanol by reduced pressure distillation.

The esterification reaction between oleic acid with alcohol can be represented as:

$$\text{oleic acid (A)} + \text{alcohol (B)} \overset{\text{SG-T-P-LS}}{\leftrightarrow} \text{ethyl oleate (C)}$$
$$+ \text{water (D)} \tag{1}$$

The amount of un-reacted oleic acid in the product mixture was obtained from the acid value (AV), which can be determined by titration method. The conversion of oleic acid can be calculated according to the equation,

$$x = (1 - AV_1/AV_0) \times 100\% \tag{2}$$

where AV_0 and AV_1 are the acid values of feed and product, respectively.

2.4. Experimental design and optimization by RSM

Response surface methodology (RSM) was employed to analyze the operating conditions of esterification to obtain a high percent conversion. RSM is a combination of mathematical and statistical techniques, it can effectively develop, improve and optimize the relative processes, and predict the best performance conditions and the extreme values using a minimum number of experiments. Moreover, it can evaluate the relative significance of some affecting factors even in the presence of complex interactions. Central composite rotatable design (CCRD) is a response surface methodology employed in the optimization process of esterification processes (Jeong and Park, 2006). The effects of three independent variables,