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Optimization of acidified oil esterification catalyzed by sulfonated cation exchange resin using response surface methodology

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ABSTRACT

The esterification of acidified oil with ethanol catalyzed by sulfonated cation exchange resins (SCER) was optimized using the response surface methodology (RSM). The effects of the molar ratio of ethanol to acidified oil, reaction time and catalyst loading on the conversion rate of free fatty acids (FFAs) were investigated at the temperature of the boiling point of ethanol. Results showed that the highest conversion rate of 75.24% was obtained at the molar ratio of ethanol to acidified oil of 23.2, reaction time of 8.0 h and catalyst loading of 35.0 wt.%. Moreover, the conversion rate of FFAs was increased to 98.32% by using a water adsorption apparatus under the RSM optimized conditions. Scanning electronic microscopic–energy dispersive spectrometric (SEM–EDS), X-ray diffractometric (XRD) and thermogravimetric–derivative thermogravimetric (TG–DTG) analyses confirmed that the morphology of catalysts did not change much and the mechanical and thermal stabilities were still good after the reaction. Furthermore, SCER exhibited a high catalytic activity and stability after being reused for five successive times. The fuel properties of the biodiesel were comparable to that of ASTM, EN and GB biodiesel standard.

1. Introduction

Along with the increasing global consumption of fossil fuels and the resulted environmental pollutions, particular attentions have been paid to the exhaustion of nonrenewable resources. Recently, developing sustainable alternative fuels have been prioritized in many countries. Biodiesel, consisting of long-chain fatty acid alkyl esters (FAAE), is known as a promising fossil fuel substitute due to the biodegradability, renewability, low greenhouse gas emission, non-toxic and superior lubricating properties [1–3]. Furthermore, biodiesel is superior to regular petroleum-based diesel fuels in the respects of flash point, cetane number and sulfur content [4,5].

Biodiesel, fatty acid methyl esters (FAME) or ethyl esters (FAEE), usually derived from renewable sources of vegetable oil and animal fats [6,7]. Recently, different vegetable oils such as palm, sunflower and soybean oil have been used to produce biodiesels [8–10]. However, China has the largest population in the world and consumes massive cooking oils to maintain the sustainable development of society and economy. As a result, non-edible sources and waste grease were favored to produce biodiesel, including the waste cooking oil (WCO), acidified oil and Jatropha curcas oil [11–13]. Therein, the acidified oil has been used as a cheap and environmentally friendly raw material for biodiesel syntheses in this study. Whereas, the high contents of free fatty acids (FFAs) in the acidified oil could cause saponification when alkali catalysts were employed, compromising the esterification using acidified oil as the feedstock. Therefore, the acid catalysts were used to reduce the acid value of FFAs to 2 mg KOH/g. Compared with the heterogeneous acid catalysts, the homogeneous acid catalysts had the separation, corrosive and environmental problems [14]. Hence, the heterogeneous acid catalysts aroused many researchers' interests for biodiesel syntheses [15–17]. Recently, ion-exchange resins have been preferable because they can catalyze the esterification under mild conditions due to the high concentration of acid sites. Furthermore, the toxicity, corrosion and separation difficulty of the catalysts could be eliminated [18–20]. Alcohols, as another kind of reactants, could be used as the acyl acceptor. For example, methanol and ethanol were commonly used in the esterification. Ethanol was preferable for the conversion of FFAs to ethyl esters from agricultural resources [21]. In other words, ethanol was renewable, environmental friendly and non-toxic [22]. Ethanol could also act both as an acid catalyst and a reactant under super critical conditions [23]. It could attain complete independence from petroleum-based alcohols. Besides, FAEE produced from ethanol has higher cetane number and heat

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content compared to FAME due to the increase of the number of carbon atoms of ethanol [24]. Thus, ethanol-based biodiesel appeared as a 100% renewable alternative [25].

In recent years, response surface methodology (RSM) as an empirical statistical tool for building mathematical models, optimizing multifactor experiments and evaluating the effects of several factors for desirable responses has been popular in the scientific community. RSM could not only get huge information from a small number of experiments but also provide the possibility of observing the effects of single variables and their interactions on the response [26,27]. Therefore, RSM was employed to optimize the various operating parameters such as the molar ratio of ethanol to acidified oil, reaction time and catalyst loading for biodiesel production in this study.

Chemically speaking, the esterification was a reversible reaction. The initial reaction rate was determined by the concentrations of the reactants. The rate of esterification can be improved markedly owning to the high concentrations of reactants at the beginning of reaction. As the esterification proceeded, FAAE and water were gradually formed. The concentrations of the reactants reduced correspondingly. The rate of forward reaction slowly decreased and the reverse reaction increased at the same time. The yield of FAAE cannot increase when the forward reaction rate was equal to the reverse reaction rate. However, the FAAE yield can be increased by removing water from the mixture continuously. Adsorbents can selectively remove water, such as the molecular sieve 4 Å. Lucena et al. studied the biodiesel production by esterification of oleic acid with methanol using a water adsorption apparatus filled with zeolite 3 Å. They had observed that oleic acid yield increased by 11.5% by using zeolite 3 Å [28].

In the present work, the esterification of acidified oil with ethanol catalyzed by sulfonated cation exchange resins (SCER) was explored by the RSM optimization. In order to increase the yield of FAEE, an adsorption column filled with the molecular sieve (4 Å) and connected to an isothermal batch reactor was employed to remove the side product of water selectively under the optimized conditions.

2. Experimental methods

2.1. Materials

The acidified oil was supplied by Zibo Jinxuan Resources and Environmental Technology Development Co., Ltd., Zibo, China. The acidified oil had an acid value of approximately 137.23 mg KOH/g after pretreatment (filtration and evaporation). SCER (Brand: CH-A; Form: H^+) was procured from Shandong Dongda Chemical Industry (Group) Company, Zibo, China. Physicochemical properties of SCER are listed in Table S1. The resins were washed using secondary deionized water and dried in a vacuum oven at 100.0 °C for 6.0 h before being used for the esterification [1]. Molecular sieve 4 Å, ethanol (purity > 99.7% w/w) and 95.0% (v/v) ethanol were purchased from Yantai Shuangshuang Chemical Company, Yantai, China. Prior to use, the molecular sieve 4 Å was activated in a muffle furnace at 500.0 °C for 6.0 h [29]. Petroleum diesel was commercially available. All other chemicals used were of analytical grade.

2.2. Experimental design and optimization by RSM

The effects of two single factors (molar ratio of ethanol to acidified oil and catalyst loading) on the conversion rate of FFAs with the reaction time belong to areas of single factor experimental. This traditional method involving the investigation of one-factor-at-a-time was tedious, laborious and time and energy consuming. Furthermore, the interactive effect of individual variables was also ignored [30]. Owing to the reasons above, new optimization method has become more significant. In this work, RSM in combination with Box–Behnken design (BBD) was used for conducting data analysis in order to optimize multiple experimental conditions with the minimum number of experiments for the maximum response. Therefore, RSM was developed to model the esterification of acidified oil with ethanol to produce FAEE. Three independent variables were applied to design the experiments, namely the molar ratio of ethanol to acidified oil (X_1), reaction time (X_2) and catalyst loading (X_3). The conversion rate of FFAs was the response of this design. The mathematical model, in the form of polynomial equation, was employed to predict the maximum biodiesel yield as a function of single variables and their interactions. The quadratic polynomial equation for the conversion rate of FFAs could be described by Eq. (1) [31].

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{i=1, i<j}^{k-1}\sum_{j=2}^{k}\beta_{ij} x_i x_j \quad (1)$$

where Y is the value of predicted response, $\beta_0, \beta_i, \beta_{ii}$ and β_{ij} are the regression coefficients (β_0 is the intercept coefficient (offset), β_i is the linear effect term, β_{ii} is the squared effect term and β_{ij} is the interaction effect term), x_i and x_j are the uncoded independent variables, and k is the total number of independent variables.

Analysis of variance (ANOVA) was used to check the adequacy of each factor for the response. In order to test the fitness of the experimental model, Fisher F-test in the form of F-value was performed. Generally, the calculated F-value was greater than the obtained F-value from the standard distribution table, indicating that the model could not only fit the experimental data, but also predict the results properly. The P-value test was also employed to explain the significance of these parameters for the response. The smallest P-value corresponded to the most significant effect on the response. The P-value of 0.05 meant the effect is significant at the 95.0% confidence interval [5].

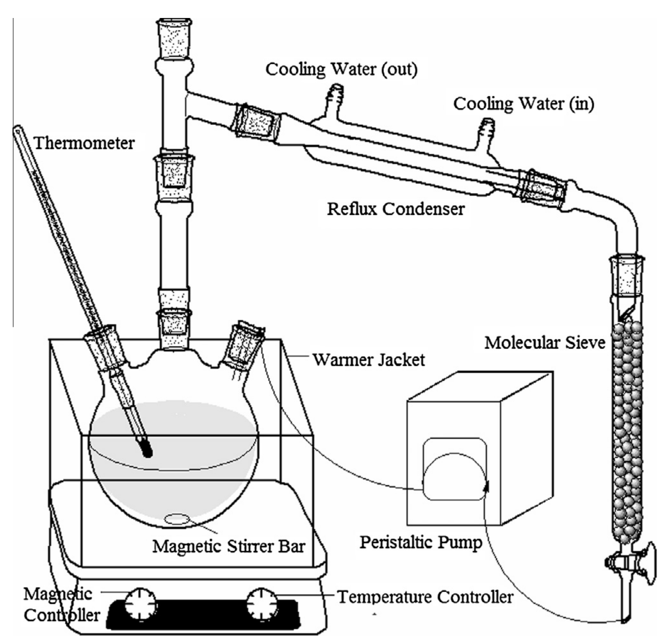

Fig. 1. The experimental setup for the esterification of acidified oil using the SCER catalyst.