



Continuous biodiesel production from acidic oil using a combination of cation- and anion-exchange resins



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ABSTRACT

A continuous process was developed to produce biodiesel from acidic oil containing soybean oil and oleic acid, which combined esterification by cation-exchange resin NKC-9, online separation and transesterification by anion-exchange resin D261. The esterification was carried out with soybean oil/oleic acid weight ratio of 5/5, methanol to oleic acid weight ratio of 1.5/1, reaction temperature of 338 K and residence time of 126.6 min. After the reaction, the mixture was settled to online separate into two layers, and the methanol-water-oleic acid mixture at the top layer was reclaimed. The bottom layer, mainly containing soybean oil and methyl oleate, was transesterified under methanol/soybean oil weight ratio of 1/3 and n-hexane/soybean oil weight ratio of 1/2 at 323 K for the residence time of 112.0 min. The high conversions of oleic acid (above 98%) and soybean oil (92.3%) were achieved. The yield of biodiesel in this process reached up to 95.1%. The main parameters of the product met the Chinese Standard of biodiesel.

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1. Introduction

Biodiesel, as an alternative of the conventional fossil fuel, has received considerable attention in recent years because it has lower greenhouse gas emissions and higher net energy gain compared with fossil diesel [1]. However, biodiesel is not economically competitive with fossil diesel fuel in the market due to its high cost [2]. An effective way to reduce biodiesel cost is using cheap feedstocks, such as waste cooking oil and vegetable or animal oil distillates [2,3], but such cheap oil feedstocks usually contain significant amount of free fatty acids (FFAs). These feedstocks cannot be directly transesterified by alkaline catalysis to produce biodiesel because FFAs can react with alkali to form soap [4,5]. To resolve this problem, acid catalysts were adopted to simultaneously esterify FFAs and transesterify triglycerides in the acidic oils [6–8]. Unfortunately, the reaction conditions of the acid-catalyzed transesterification were very harsh, such as long reaction time and high reaction temperature [7,8].

Another method is to use a two-step process, combining acid-catalyzed esterification with alkali-catalyzed transesterification for the oil feedstock with high FFA content. This kind of method was investigated by some groups [9,10]. Berchmans et al. [9] reported a batch mode to produce biodiesel by an esterification reaction using 1 wt.% sulfuric acid as acid catalyst followed by a transesterification reaction using sodium hydroxide as alkaline catalyst, with a biodiesel yield of 90%. The liquid acid and alkali was washed out by water, respectively, which would produce a plenty of waste acid or alkali water and increase production

cost. Wang et al. [10] prepared biodiesel from waste cooking oil via the two-step process in a batch mode. Ferric sulfate as acid catalyst and potassium hydroxide as alkali catalyst were employed. The conversion to biodiesel reached 97.0%. However, the separation step of catalysts from the reaction mixture would produce waste water containing ferric sulfate and alkali and increase the cost [10].

In recent years, cation- or anion-exchange resins as solid catalysts have been widely investigated to produce biodiesel in a batch or continuous mode. Compared with homogeneous acid/base catalysts, the resin catalysts exhibit less corrosion, less environmental problem and easier separation. Tesser et al. [11] investigated the cation-exchange resin Relite CFS to produce biodiesel for 150 h with a conversion of over 95%. Our group [12] investigated the cation-exchange resin NKC-9 to catalyze the esterification of oleic acid with methanol, which maintained a conversion of above 98% within continuous running for 500 h. Shibasaki-Kitakawa et al. [13] investigated an anion-exchange resin (PA360s) packed in a fixed bed reactor to continuously catalyze transesterification of crude triolein with ethanol, which obtained a conversion of about 80%. Anion-exchange resin D261 was also reported to continuously transesterify soybean oil with methanol in a fixed bed reactor with a high conversion [14]. Although the esterification process under cation-exchange resins or transesterification under anion-exchange resins as an individual process was well independently explored, a continuous process of biodiesel production combining cation- and anion-exchange resins for the feedstock containing triglycerides and FFAs is still challenging. This is because the product mixture from esterification process is not suitable to be directly fed into the transesterification process due to existence of water produced from esterification process and residual FFAs in the esterification product.

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Table 1
Characteristics of ion-exchange resins of NKC-9 and D261.

	Form	Total exchange capacity (mmol/g)		Bead size ($\geq 95\%$, nm)	Average pore size (nm)	Density (wet, g/ml)		Surface area (m^2/g)
		Dry	Wet			True	Apparent	
NKC-9	$-\text{SO}_3\text{H}$	≥ 4.7	≥ 1.5	0.40–1.25	56	1.20–1.30	0.70–0.80	77.0
D261	$-\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	≥ 3.6	≥ 1.1	0.32–1.25	17.8	1.06–1.11	0.65–0.75	64.9

Moreover, the process to remove the water and residual FFAs is often time and energy consumption.

In the present study, we developed a continuous process to convert acidic oil into biodiesel. This process combined an esterification reaction of FFAs catalyzed by cation-exchange resin NKC-9 with a transesterification reaction of triglycerides catalyzed by anion-exchange resin D261. The water produced and the residual FFAs in the esterification product were removed online by a simple separation step. The effects of several variables, such as the concentration of oleic acid in the esterification feedstock, residence time and the contents of water and FFAs in transesterification feedstock, on the continuous process were investigated. Two addition manners of co-solvent (n-hexane) into the feedstocks were compared. Finally, an optimal process of esterification–online separation–transesterification was suggested.

2. Materials and methods

2.1. Materials

The feedstock used in this work is a mixture of pure oleic acid and pure soybean oil with weight ratios from 9:1 to 5:5, named acidic oil herein. The soybean oil was purchased from China Oil Food Co. and distilled to remove water before use at 90 °C under 1.33 kPa. Oleic acid, methanol and n-hexane (as co-solvent) are all of analytical grade and purchased from Tianjin Kermel Chemical Reagent Co. (China). Cation-exchange resin NKC-9 and anion-exchange resin D261 (Table 1) were purchased from the Tianjin NanKai Hecheng S&T Co. (China) and selected as catalysts due to their high catalytic activity (see supporting information). The pretreatment procedures of NKC-9 and D261 were referred to the literatures [14] and [15], respectively.

2.2. Continuous production process of biodiesel

The continuous biodiesel production from acidic oil with methanol was carried out in two fixed bed reactors for esterification and transesterification, respectively. The setup is shown in Fig. 1. The reactors were composed of a water-jacketed stainless steel column with an internal diameter of 25 mm and a height of 450 mm. The continuous esterification was performed in a reactor packed with 87.5 g NKC-9. Acidic oil and methanol were mixed and preheated in a feedstock tank (1) and then fed to the esterification reactor using a peristaltic pump to esterify. In this operation unit, methanol to oleic acid weight ratio is 1.5/1, reaction temperature is 338 K and feed flow rate is 0.6 ml/min if not specially stated.

The esterification product mixture from the esterification reactor was introduced into tank (2) to settle for about 30 min; and the mixture was separated into two layers due to no adding co-solvent. The upper layer mainly containing methanol, water produced and residual oleic acid with a small amount of biodiesel and oil was piped into tank (7) to further reclaim. Moreover, the bottom layer mainly containing soybean oil and biodiesel, which is named transesterification feedstock, was pumped into the feedstock tank (5). Methanol and n-hexane as a co-solvent in the tank (3) and (4) were replenished into the tank (5). The weight ratios of methanol/soybean oil and n-hexane/soybean oil are fixed at 1/3 and 1/2 (as discussed in the supporting information), respectively. Then, the mixture was preheated and continuously pumped to the transesterification reactor packed with 80 g D261 resin (as shown in Fig. 1) at 323 K and flow rate of 0.6 ml/min. Finally, the effluent mixture from the reactor was collected into the tank (6). After reaction completion, the mixture in the tank (6) was disposed by rotary evaporation to remove excess methanol and co-solvent at 90 °C under 1.33 kPa. And then the mixture was settled to separate glycerol and crude biodiesel product. The crude product was further purified to

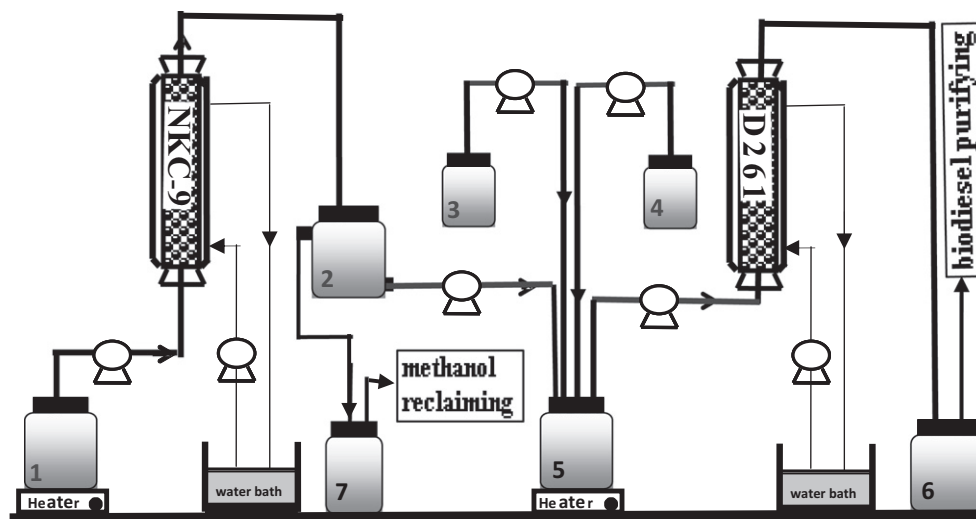


Fig. 1. Scheme of the experimental apparatus for the continuous production of biodiesel. (1) Tank of feedstock. (2) Tank of esterification product mixture. (3) Tank of methanol. (4) Tank of n-hexane. (5) Tank of transesterification feedstock. (6) Tank of product mixture. (7) Collecting tank.

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