



Production of high quality biodiesel from waste acid oil obtained during edible oil refining using ion-exchange resin catalysts



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HIGHLIGHTS

- High quality biodiesel was produced in a continuous manner from waste acid oil.
- A simple method for pretreating the cation-exchange resin, was proposed.
- Biodiesel productivity with acid oil was higher than that with triglyceride-rich oil.

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ABSTRACT

This study was aimed at the continuous production of high quality biodiesel fuel, which fully satisfies international specifications, from waste acid oil with free fatty acids (FFA) content of >95 wt%. First, the effect of water on the esterification of FFA with the cation-exchange resin catalyst was discussed. Then, a simple method for pretreating the resin without drying, only supplying alcohol of 1.5 cm³/g (wet resin), was proposed. Second, the operating conditions for the continuous esterification of FFA to biodiesel were established. The complete conversion of FFA was achieved at the mole ratio of alcohol:fatty acid residue of 2:1 and sufficient residence time. Subsequent processing with an anion-exchange resin catalyst for the transesterification of triglycerides in the oil was necessary to produce high quality biodiesel. The biodiesel productivity with acid oil was about 8.5 times higher than that with triglyceride-rich oil. This process demonstrated a commercially feasible route to high quality biodiesel.

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1. Introduction

Refined edible oils with less than 1 wt% free fatty acids (FFA) are mainly used as feedstocks for industrial biodiesel production and the feedstock price is one of the most significant factors affecting the economic viability of fuel production [1–4]. The byproducts, such as soapstock, acid oils and deodorized distillates, obtained during the refining of edible oils have been suggested as alternative and cheaper feedstocks for biodiesel [5–7]. Especially, the crude oils of palm and rice bran have a high content of FFA and the amount of acid oils discharged during the refining of these edible oils, is large, at ca. 10–20 wt% refined oil output, e.g. 5.6–11 million tons for palm. The main components of acid oils are FFA, remainder comprising triglycerides, and hence the oils are almost solid at room temperature owing to the higher melting points of FFA. Such oils with a high FFA content could not be used as feedstocks using conventional processing methods, using homogeneous alkali catalysts.

Many researchers have studied biodiesel production from the waste acid oils [8–11]. One of the methods proposed is a two-step process, involving a homogeneously acid catalyzed esterification of FFA followed by the homogeneous alkali catalyzed transesterification of triglycerides [12–17]. This process (Fig. 1(a)) can smoothly convert both FFA and triglycerides present in the acid oil to biodiesel. However, drying/dewatering of the oil and the addition of excess alcohol (10–20 mol eq FFA) are required to shift the equilibrium toward the product because of the reversible nature of the esterification reaction. Subsequently, additional operations are required to remove the acid catalyst and the byproduct water and to add excess alcohol for transesterification. The additional steps result in increased production costs. There is no commercially feasible process to convert these acid oils to biodiesel, which fully satisfies international specifications.

We have proposed a simple continuous production process for obtaining biodiesel from oils with high content of FFA [18]. In the process (Fig. 1(b)), the expanded-bed reactor was packed with a cation-exchange resin catalyst for esterification of FFA and a second reactor loaded with an anion-exchange resin catalyst for

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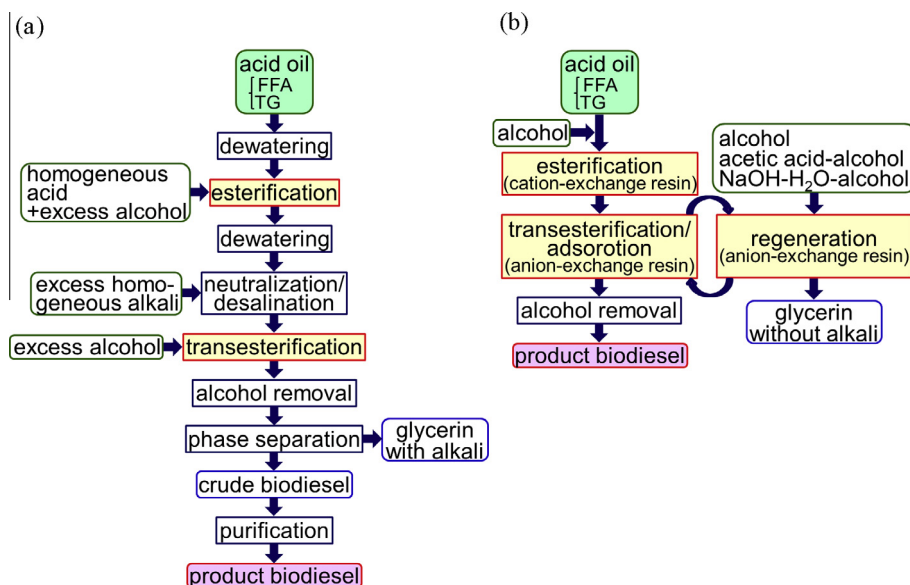


Fig. 1. Flow chart of biodiesel production process from acid oil with high FFA content, (a) process with homogeneous catalysts, (b) process with ion-exchange resin catalysts.

the transesterification of triglycerides was connected in series. By supplying a mixed solution of crude rice bran oil and alcohol to the process, the fatty acid ester was obtained with a high conversion of more than 98%. Additional operations, such as oil dewatering and removal of catalysts and byproducts were not required. However, the FFA content in the feed oil (ca. 14 wt%) was not particularly high. To apply the process to the acid oils with an FFA content of more than 95 wt%, it is necessary to optimize the operating conditions for complete conversion of the FFA to biodiesel. In addition, many researchers have reported the inhibiting effect of water on the esterification of FFA with cation-exchange resin catalysts. This means that the resins must be dried to completely remove moisture before use in the reaction [19–23]. A large amount of water is formed as a byproduct of the esterification of FFA in the acid oil, so that it becomes necessary to investigate the effect of water on the production process.

The purpose of this study is to continuously produce high quality biodiesel, meeting international specifications, from waste acid oil with a low environmental impact. First, batch esterification experiments were performed using a cation-exchange resin to investigate the effect of water on the reaction and to optimize the pretreatment of the resin. Next, continuous biodiesel production experiments were performed using a bench-scale unit, with two expanded-bed reactors separately packed with cation- and anion-exchange resins. Conditions required for the complete esterification of FFA to biodiesel were investigated and the behavior of each reactor was described. Finally, an assessment was made of the quality of the biodiesel obtained, in relation to international fuel specifications.

2. Experimental

2.1. Batch esterification using cation-exchange resin

The waste rice bran acid oil was kindly donated by Sanwa Yushi Co., Ltd., Tendo, Japan and recovered by distillation of FFA, liberated by acidulation of soapstock from the refining process applied to edible rice bran oil. The main component of the oil is FFA (>95 wt%), with triglycerides constituting the remainder.

The porous type cation-exchange resin with low crosslinking density, Diaion PK208LH was selected as the most active material

in the preliminary experiments. Its physical properties are listed in Table 1. The resin was kindly donated by Mitsubishi Chemical Co., Ltd., Tokyo, Japan and was in an activated H-form (>99 mol%) swollen with water. The lipid-soluble reactant did not easily diffuse into the resin, so that the resin, 60 g (wet basis), was packed with the column. Methanol (Wako Pure Chemical Industries, Ltd., Osaka, Japan, 1st grade, 99.5%) was supplied to the top of the column by a metering pump (Iwaki Co. Ltd., Tokyo, Japan, EHN-C21PP1R) at a flow rate of 2.5 cm³/min to remove water before the esterification step. The effluent from the column was collected at specific time intervals and the water concentration was determined using a Karl Fischer Moisture Titrator (Metrohm Japan Ltd., Tokyo, Japan, 852 Titrando) and HYDRANAL composite 5 titrating agent (Sigma-Aldrich Co. LLC., St. Louis, MO, USA).

Minimizing the volume of methanol used for the resin pretreatment is effective in reducing environmental impact and production costs. Therefore, batch esterification was performed using the resins pretreated with various volumes of methanol from 5.0 to 1.25 cm³/g (wet resin). The preheated mixed solution at the stoichiometric ratio of FFA:methanol of 1:1, and 33 wt% of resin were added to the glass bottle. The bottle was shaken at 150 rpm in a thermal bath (Yamato Scientific Co., Ltd., Tokyo, Japan, BW400 and BF200) at 50 °C. At specific time intervals, the sample solution was collected and the concentrations of the reactants were determined using an HPLC system equipped with a UV detector (Nihon Waters K.K., Tokyo, Japan, ACQUITY UPLC M-Class System) and an ACQUITY UPLC BEH C18 column (Nihon Waters K.K., particle size 1.7 μm, i.d. 2.1 mm, length 150 mm). Acetonitrile (HPLC AR Grade), 2-propanol (special grade) and ultrapure water were used as the mobile phase at a flow of 0.4 cm³/min by a gradient technique. These reagents were purchased from Wako Pure Chemical

Table 1
Physical properties of ion-exchange resins.

Diaion	PK208LH	PA306S
Character	Cation	Anion
Type of matrix	Porous	Porous
Crosslinking density [%]	4	3
Particle size [mm]	0.40–0.60	0.15–0.43
Ion-exchange capacity [mol/dm ³ -resin]	>1.2 × 10 ³	>0.8 × 10 ³

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