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Recoverable and reusable hydrochloric acid used as a homogeneous catalyst for biodiesel production

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HIGHLIGHTS

- The recoverability and reusability of several acid catalysts was studied.
- HCl was the only recoverable and reusable catalyst for the reaction.
- The reaction factors for HCl-catalyzed esterification were optimized.

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ABSTRACT

Several homogeneous acid catalysts (nitric, sulfuric, and hydrochloric acids), were selected to investigate their recoverability and reusability for esterifying enzyme-hydrolyzed FFAs and methanol to produce biodiesel. Although all of the three catalysts drove the reaction at high yield, hydrochloric acid is the only recoverable and reusable catalyst, as indicated by partitioning data. Hence, esterifying FFAs and methanol was catalyzed using hydrochloric acid; and the reaction conversion, which was affected by the reaction conditions, was optimized using response surface methodology. A maximal reaction conversion of 98.19% was obtained at 76.67 °C, at a methanol/FFAs molar ratio of 7.92, a catalyst concentration of 0.54 M, and after a reaction time of 103.57 min. The catalyst could be reused at least five times to drive the reaction to a conversion of 97%. This study demonstrated that recoverable and reusable hydrochloric acid is promising for potential applications, including biodiesel production.

1. Introduction

Since the industrial revolution, fossil fuels have been exploited and used to promote economic development and to improve quality of life. However, continuously consuming these resources causes energy shortage and global warming. To relieve the reliance on fossil fuels, many countries have begun planning a series of measures to develop alternative fuels [1]. Biodiesel is well known to be a promising alternative biofuel in place of petro-diesel, because it is clean, nontoxic, and fully compatible with diesel engines [2]. In addition, biodiesel is a renewable biofuel because the feedstock used in biodiesel production can be derived from plants and oleaginous microorganisms [3–5]. Because of such benefits, numerous researchers have been engaged in developing efficient, economic, and eco-friendly processes for biodiesel production.

Biodiesel, fatty acid methyl ester, is produced by the transesterification of plant oils with short chain alcohols in the presence of catalysts [6–8]. Methanol is commonly employed as the preferred alcohol reactant because of its low cost and superior reactivity [9,10]. Currently, transesterification of virgin edible oil with methanol catalyzed by alkali catalysts is the most common commercial process for biodiesel production [11,12]. However, using refined oil as the feedstock for biodiesel production makes the process expensive and creates a negative effect on food supplies [13]. To solve the aforementioned problems, one possible solution involves using less expensive and inedible feedstocks, such as waste oils or crude plant oils, to produce biodiesel [14–16]. Such inedible oils, which are of considerable interest to recent biodiesel research, are mainly composed of triglycerides, diglycerides, monoglycerides, and a high level of free fatty acids (FFAs) [17].

Biodiesel derived from inedible oils via transesterification in a single-step process catalyzed by alkali, acidic or enzyme catalysts has been studied comprehensively [18,19]. Some studies have shown that lipase enzymes can simultaneously transesterify triglycerides and esterify FFAs with methanol to biodiesel [20]. However, economic concerns arising from high cost of enzymes and enzymes inactivated by methanol limit applications of the enzyme-catalyzed process

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[21,22]. Alternatively, alkali and acid catalyzed processes have received considerable attention because of their short reaction time and low cost, as compared with the enzyme-catalyzed processes. However, alkali catalysts, such as KOH or NaOH are highly sensitive to the presence of FFAs in raw feedstock. Neutralizing the alkali catalyst with FFAs causes catalyst loss and difficulties in purifying products [18]. Furthermore, in acidic processes, harsh reaction conditions, including high temperature, high pressure, and excess methanol, are required to drive the reaction at high yield [23]. Consequently, the aforementioned obstacles hamper the commercialization of biodiesel using the single-step strategy.

Hence, a two-step process has been developed to produce biodiesel from inedible feedstocks [24,25]. The first step involves converting FFAs into biodiesel using acid-catalyzed esterification. The FFA content is reduced below 0.5% (w/w) [24]. Subsequently, the pretreated oil is subjected to base-catalyzed transesterification to produce biodiesel and glycerol. Sulfuric acid and NaOH (or KOH) are commonly used to catalyze both reactions [24]. Although inedible oil can be converted effectively into biodiesel in a reasonably short time with high conversion, the drawbacks of this integrated process include effluent of wastewater and complicated purification of salt-containing products, which increase the cost of producing biodiesel [18,26].

Recently, a novel two-step process consisting of enzyme-catalyzed hydrolysis, followed by acid-catalyzed esterification, has been proposed for producing biodiesel [18,27]. In the first stage, tri-, di- and monoglycerides are hydrolyzed using lipase to produce salt-free FFA and glycerol [27]. The hydrolytic stage using lipase as catalyst has advantages over the common process for hydrolyzing oil and grease that uses extreme high temperature and pressure conditions [28]. Enzyme hydrolysis uses milder reaction conditions, resulting in the formation of fewer undesirable byproducts and improved energy conservation [27]. The hydrolyzed FFAs are then esterified with methanol to produce biodiesel in the presence of acidic catalysts [18]. This process reduces the effluent of wastewater and can produce salt-free glycerol [18,27]. However, sulfuric acid, the most commonly used catalyst in the later stage of this process, disperses into the product phase during the esterification reaction [29], generating additional cost for purifying biodiesel. Although some studies have used solid acidic catalysts to drive esterification in manufacturing a high yield of biodiesel [22,30], the high cost of such solid catalysts must be addressed [31].

This study confirmed that hydrochloric acid was completely retained in the reactant phase rather than in the product phase after esterification, thus reducing the process cost of biodiesel purification. Therefore, to produce high quality biodiesel using low cost catalysts, hydrochloric acid was used to esterify enzyme-hydrolyzed FFAs. To effectively analyze the factors affecting the reaction, an empirical modeling technique, that is, response surface methodology (RSM), was used to optimize the acid-catalyzed esterification of FFAs with limited experiments while maintaining high statistical significance among the results [32]. After esterification, the reactant phase containing hydrochloric acid and methanol was recovered and used to examine its reusability. Hydrochloric acid is considered as a promising catalyst to catalyze the esterification of FFAs and methanol for biodiesel production, as indicated by the experimental results.

2. Materials and methods

2.1. Materials

Soybean oil was purchased from Uni-President Enterprises Corp. located in Tainan County, Taiwan. Potassium hydroxide, calcium chloride, silver nitrate, lipase from *Candida rugosa*, and HPLC grade methanol and ethanol, were obtained from Sigma–Aldrich Co. (Missouri, USA). Sulfuric acid, hydrochloric acid, and nitric acid, used as homogeneous acid catalysts for biodiesel production, were purchased from Merck KGaA (Darmstadt, Germany).

2.2. Preparation of FFAs

Soybean oil was mixed with aliquots water under vigorous agitation using a magnetic stirrer to form an oil–water emulsion. The initial molar ratio of water to oil was 6:1. The hydrolysis reaction was initiated by adding an appropriate amount of enzyme solution (50 mg free lipase per milliliter of distilled water). To ensure complete conversion, the reaction was conducted overnight at room temperature. After the reaction, the acid value of the reaction mixtures was 201 mg KOH/g oil, indicating that 100% FFA was prepared from the hydrolysis of soybean oil [22]. Enzyme-hydrolyzed FFAs were collected using centrifugation at 10,000 rpm for 10 min at room temperature. The collected FFAs were used as feedstock to investigate biodiesel production through acid-catalyzed esterification.

2.3. Recoverability experiments

For this experiment, FFAs (3 g) and methanol (3.38 g) were mixed by stirring with several acidic catalysts (sulfuric acid, hydrochloric acid, and nitric acid) in a closed system. The initial molar ratio of methanol to FFAs was 10:1. To compare the catalytic efficiency, the catalyst loadings of sulfuric acid, hydrochloric acid, and nitric acid were set at 6.53 wt.%, 4.83 wt.%, and 8.40 wt.% with respect to FFAs, respectively. At those levels, the number of moles equals 4 milli-equivalent (mEq) because of differences in molecular weight. The reaction was conducted in a water bath in which the temperature was maintained at 70 °C. After 2 h of esterification, the reaction mixture was separated into oil and methanol layers by centrifugation. Free fatty acid conversion was analyzed by titration, and the amount of catalyst retained in the methanol layer was determined to evaluate the recoverability of these catalysts.

2.4. Optimization of esterification using RSM

A three-level and four-factorial Box–Behnken design was employed to investigate the reaction factors affecting FFA conversion from the esterification of enzyme-hydrolyzed FFA and methanol. Experiments using various molar ratios of methanol to FFA (1:1–10:1), hydrochloric acid concentrations (0.1–1 M), reaction temperatures (60–90 °C), and reaction times (30–120 min) were performed in a 50 mL closed system with stirring. The esterification reaction with methanol was conducted at temperatures greater than the atmospheric boiling point of methanol. This indicates that the total pressures among tested temperatures are different. The effect of pressure difference on the reaction was ignored in this study because in this liquid-phase reaction, the concentration of reactants is insignificantly affected, even when relatively large changes occur in the total pressure [33].

Free fatty acid conversion was determined from the sample withdrawn from the reaction mixtures. The response function of interest was the FFA conversion. The function was approximated using the following quadratic equation:

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \\ & + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 \\ & + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \end{aligned} \tag{1}$$

where Y is the FFA conversion; X_1 is the reaction temperature; X_2 is the methanol/FFAs molar ratio; X_3 is the catalyst concentration; X_4 is the reaction time; β_0 is the offset term; β_1–β_4 are linear parame-