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Two-step esterification of palm fatty acid distillate in ethyl ester production: Optimization and sensitivity analysis

Utaiwan Kanjaikaew*, Chakrit Tongurai, Sininart Chongkhong, Kulchanat Prasertsit

Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

Low-cost palm fatty acid distillate (PFAD) feedstock to produce biodiesel is of interest. Single step esterification of PFAD is effective but requires large amounts of chemicals. Removal of water in a two-step process increases the effectiveness of FFA conversion with methanol, but ethanol has yet to be investigated and hence was proposed. Effects of parameters: ethanol to FFA molar ratio, temperature, time and catalyst amount, were investigated. In the first step, catalyst amount was kept constant; and for the second-step, the reaction temperature was fixed. RSM coupled with sensitivity analysis enabled parameters to be optimized. Optimal conditions for the first step were: 4:1 M ratio, 343 K and 15 min, resulting in 88% FFA conversion. In the second step, the conversion reached 86.8% under these conditions: 27:1 M ratio, 53 min and 35.3 wt% catalyst amount. Under these two sets of optimal conditions, the overall FFA conversion of 98.44% was comparable to other studies. The attempt on the use of ethanol to produce ethyl ester in a two-step process of PFAD is quite successful: ethanol, renewable and more environmental friendly, is a contending effective alternative.

1. Introduction

Current environmental issues and resource demands are driving the global development of renewable energy, inclusive of biodiesel. Typical raw materials of biodiesel production: canola oil, soybean oil, sunflower oil and palm oil, are edible oils [1]. Although, these suitable feedstocks establish successfully the final biodiesel, such biodiesel production relates to price rising of edible feedstocks from competition with food crops [2–4]. The cost of feedstock constitutes about 75–80% of biodiesel production [5–7]. The use of feedstock with low FFA, which is more expensive, would lead to even higher production cost. Therefore, commercialized lower quality raw materials containing high FFA content, such as used cooking oils, soapstock, palm fatty acid distillate (PFAD), are very attractive as alternative feedstocks.

PFAD is one of by-products generated during the crude palm oil refining process, 3–5% of PFAD which rich FFA content is obtained [8]. The price of PFAD is lower than other feedstocks and its volume has enough for the utilization [9,10]. The use of PFAD in the biodiesel industry would be very beneficial, and support a sustainable production of biodiesel. A number of researches, nevertheless, have been reported on the production of biodiesel using PFAD, which not only reduces cost of the production but also adds to the value of PFAD [11–14].

Methanol is commercially used in the production of biodiesel due to its fast reaction. However, methanol is derived from petroleum and has to be imported because not locally produced, especially in Thailand. Many researchers have attempted to develop biodiesel production using ethanol as an alternative alcohol [15–19], because it is obtained from the fermentation of crops and vegetation [20]. Thus, biodiesel produced with ethanol is completely a resource of sustainable and renewable energy, and also reduces the needs for methanol import.

Esterification is generally a pretreatment process to reduce FFA [21–24]. Since esterification is reversible, after it approaches equilibrium the rate of forward reaction is drastically slow, leading to a low ester yield. In case PFAD, consisting of over 70% FFA, is selected as the raw material, single-step catalyzed esterification process would need large amounts of chemicals plus a lengthy reaction time in order to obtain a high yield [25–28]. Hence, "*two-step esterification*" has been of interest in this study. This process is performed by removing water produced in the first-step esterification, that has the tendency to shift equilibrium to the product side, in order to achieve higher conversion in the second-step

* Corresponding author.
E-mail address: utaiwank@yahoo.com (U. Kanjaikaew).

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[29,30]. In addition, operation with milder conditions together with a simple set-up can be applied in actual biodiesel production. Many studies on biodiesel production from FFA with alcohols via esterification could be found on single-step esterification employing either methanol or ethanol, or on two-step esterification employing methanol [19,28,29,31]. The use of ethanol remains a technical challenge since the reaction with ethanol usually causes yields to be lower than with methanol [32–34]. No studies have yet to be found on two-step esterification of PFAD using ethanol, and hence our proposed study.

One other underlying reason in our proposed research using ethanol is that this more environmentally friendly chemical [35,36], if it could produce similar or possibly better outcome, would contribute greater benefits to society as a whole. In our two-step esterification with ethanol on PFAD, effects of variables involved in the process investigated concern the relationship between individual parameters to establish equation models in order to predict optimal conditions using response surface methodology (RSM). Sensitivity analysis of FFA conversion was also deployed to identify the more important factor influencing esterification in each step.

2. Materials and methods

2.1. Materials

PFAD was supplied by Chumporn Palm Oil Industry PCL., Thailand. The raw material consisted of 93 wt% FFA, the rest comprised triglycerides, diglycerides, monoglycerides and traces of impurities. Sulfuric acid (98 wt% H_2SO_4 purity) was obtained from Merck Ltd., Thailand, while commercial grade ethanol (99.5 wt%) was acquired from Union Intraco PCL.

2.2. Methodology

This study of two-step esterification for ethyl ester production was designed based partly on our preliminary results conducted using single-step esterification [37]. It was found in those results that FFA conversion increased due to the rise of all variables, but slowed down drastically when reaction approached equilibrium due to the effect of water produced. In the first step of this two-step process a set of milder conditions, i.e., smaller end ranges of ethanol and very brief reaction times, were employed to convert FFA before the equilibrium stage was reached. Water was then removed before the second-step reaction was performed. In each step optimal conditions and sensitivity analysis were investigated, as mentioned earlier near the end of the introduction section.

2.2.1. The first-step experiment

Fractional factorial design was used for the experiment in this study. This part aimed to produce a low FFA that could be further converted with a high conversion rate, and to assess significant effects of each factor. First-step esterification was conducted with 2.4:1, 3:1, 3.6:1 and 4:1 ethanol to FFA molar ratios. Reaction temperatures experimented were: 343, 348 and 353 K, designed to include both lower and higher than the boiling point value of ethanol (351 K). The reaction times were 5, 10 and 15 min, using sulfuric acid 2 wt% of FFA (1.86 wt% of oil) as catalyst.

2.2.2. The second-step experiment

Results from the earlier first-step were evaluated. Taking into consideration significant factors affecting esterification, in this second-step esterification new levels of molar ratio of ethanol to FFA were chosen (9.3:1, 17:1, 24.7:1 and 30:1). Reaction times of 10, 35 and 60 min were also opted. Acid catalyst concentrations were now varied (9.7, 21, 32.3 and 40 wt% of FFA), and the reaction temperature was fixed at 343 K. Justification of this choice is detailed under Section 3.1.3 “Optimum condition for the first-step esterification”. Selection of these independent variables and their ranges was also based on several outside sources and our preliminary laboratory results [37,38].

2.2.3. The esterification method

The method for the first-step esterification was thus: A measured quantity of solidified PFAD was first melted, heated and maintained to the desired temperature of each experiment. Each calculated mixture of ethanol and sulfuric acid was added to the molten PFAD and stirred continuously in a refluxed batch reactor to minimize losses of ethanol, and maintained at a designated reaction temperature. After each specified reaction time, the esterified mixture was settled for 60 min in a separating funnel. The lower aqueous phase (water plus alcohol) was removed, and the upper phase (the esterified PFAD) was purified by washing with warm water and dried at 378 K for 30 min.

For method in the second-step esterification, the process was carried out similarly to the first-step except that the input now is not the raw PFAD, but the esterified PFAD prepared from optimal conditions obtained from the first-step. The reaction temperature was fixed at 343 K, a constant associated with the chosen set. Other variable amounts were as detailed in Section 2.2.2. Each second-step experiment was run according to the set of parameters designed. After the reaction, the esterified mixture was settled, separated and purified, same as that conducted in the first-step, to obtain the biodiesel.

2.3. Analysis

After purification of the products of both the first and the second-step reactions, each residual FFA was determined by titration according to AOCS Ca 5a-40. Conversion of FFA was calculated using Eq. (1).

$$\text{FFA conversion } (\%) = (1\text{-}A/A_0) \times 100 \quad (1)$$

where A_0 and A are, respectively, the initial FFA of the material and the residual FFA of the product.

2.4. Optimization through response surface methodology

Responses of reactions in terms of percent FFA conversion are the main criteria in the optimization procedure. Response surface methodology (RSM) was employed to evaluate the conversion of FFA in the two-step esterification and to seek the optimized operating conditions. Multiple regression analysis and analysis of variance (ANOVA) were employed to evaluate the effect of each independent variable and their interaction to the response, and an equation model was derived, demonstrated in a general second-order polynomial equation in Eq. (2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \varepsilon \quad (2)$$

where Y is the predicted response; β_0, β_i, β_{ii} and β_{ij} are constant coefficients; X_i and X_j are the values of independent variables; k is the number of variables studied in the experiment, and ε is the error.