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Glycerolysis of palm fatty acid distillate for biodiesel feedstock under different reactor conditions

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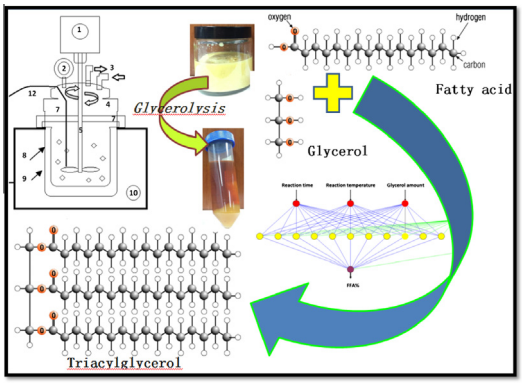
HIGHLIGHTS

- Glycerolysis of palm fatty acid distillate at different reaction conditions was reported.
- Optimization was using artificial neural network based on the genetic algorithm.
- Glycerolysis in open reactor system with inert gas flow option is much-preferred.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper deals with the comparative study on glycerolysis of palm fatty acid distillate (PFAD) in a solvent free system at different reaction conditions in an attempt to get maximum degree of FFA% reduction for biodiesel feedstock. Initially, optimization of varied reaction parameters was performed under all the different reaction conditions using artificial neural network (ANN) based on the genetic algorithm (GA). It has been found that the reduction of acidity varies with varying reaction conditions with maximum reaction rate observed in case of reaction carried-out in open reactor system with inert gas flow, followed by the reaction in open reactor system without inert gas flow and then in case of reaction under the close reactor system. In the most favorable case, 1.5 mg_{KOH}/g_{PFAD} of FFA (free fatty acid) was achieved after 90 min of reaction time with an excess glycerol of 4% at 220 °C. The results from the ANN model show good agreement with experimental results. Thus, the glycerolysis in open reactor system with inert gas flow (N_2) option is much-preferred option compared to acid esterification for the same biodiesel plant capacity, particularly for high-FFA feedstocks.

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1. Introduction

The utilization of waste oil reduces the feedstock cost and increases the sustainability of biodiesel production by minimizing resource consumption. Depending on the cooking process and subsequent storage, the used oils may contain impurities such as water, food residues, and high concentration of free fatty acid (FFA) [1]. The major technical challenge of making biodiesel from used oils and greases is the high percentage of free fatty acids (FFAs) content in the feedstock. FFA is undesirable during the alkali transesterification process due to the formation of soap, yield loss, and increased difficulty in product separation [2].

The acid-catalyzed transesterification can directly convert both FFA and oil into biodiesel. However, it is not much practiced by the biodiesel producers due to the longer reaction time and lower yield [3]. Instead, the two-step conversion process: an acid-catalyzed esterification pretreatment to lower the FFA content followed by the traditional alkali-catalyzed transesterification is widely used in both industry and laboratory [4]. While the acid pre-treatment is effective in reducing FFAs, multiple steps may be needed to reduce them to acceptable levels, generating even more acidic, wet methanol. After neutralizing the acidic methanol, drying requires multistage distillation with significant reflux rates, resulting in very high energy use [5]. Another approach is to produce high biodiesel from oils and greases by the reaction under supercritical conditions (275–325 °C and high pressure). Though, very low quality feedstocks can be processed by this method, the requirement of heavy-duty reaction vessels and extreme reaction conditions limit its applicability in industry [2].

One technique that has gained popularity recently is esterification with glycerol to reduce FFA content from low-grade oils without use of acid or methanol. This process was able to reduce the FFA content by converted it into glycerides rather than removing FFA. Several catalysts have been reported to be efficient in the esterification of free fatty acids with glycerol, mainly based on metal oxides of variable basicity [6–8], which suffer the drawback of difficult separation from the reaction medium. It was reported that the separation processes represent more than half of the total investment in equipment for the chemical and fuel industries [9]. Further, lipase-catalyzed esterification of fatty acids with glycerol was reported to be environmental friendly reaction which requires considerably lower reaction temperature (40–70 °C). However, reaction may take hours to days depending on enzyme loading and the reaction system employed [10,11]. In addition, enzymatic processes are expensive and not very efficient because of enzyme reusability issues. While other studies have investigated the effect of reaction variables including acid catalyst type, alcohol type, alkaline catalyst type on glycerolysis [1,7,8,12], a study of the effect of reactor conditions on the direct esterification reaction with glycerol in a solvent free system to get maximum the degree of FFA reduction from PFAD feedstocks have to the best of our knowledge, not yet been conducted. For the optimization, we used Artificial Neural Network (ANN) as a tool since it enables the evaluation of multiple parameters alone or in combination on response variables. The modeling and optimization of the results was performed by the Neural Power software version 2.5.

2. Materials and methods

2.1. Experimental set-up

Glycerolysis reactions were conducted in a 300-ml stirred batch reactor (BERGHOF) as shown in Fig. 1(a). The equipment consists of a high pressure cylindrical chamber, an inlet and out let for gas, a heater and a stirrer. For a typical experiment, 400 ml of PFAD was added into the flask and heated to the desired temperature. The glycerol and oil are immiscible so the agitating speed was kept at 500 rpm (rpm) to ensure efficient mixing [6]. The flow rate of the inert gas (N_2) was maintained 20 ml/min to keep inert condition of the reactor. The acid number of the initial PFAD or after the glycerolysis reaction was determined according to the ASTM D 664 international standard method [13]. The conversion of the FFA is defined as the fraction of FFA that reacted during the glycerolysis reaction at different reactor conditions. In this study, the initial acid value of the used cooking oil was 85 ± 2 mg_{KOH}/g_{oil}. Both the acid value and the FFA conversion rate can be used to indicate the completion of glycerolysis reaction. The conversion of FFA was determined from the acid number ratio using the following equation:

$$\text{FFA conversion} = \frac{\text{Initial FFA} - \text{Final FFA}}{\text{Initial FFA}} \times 100\%$$

where

Initial FFA is initial acid value of the PFAD (mg KOH/g).

Final FFA is final acid value after glycerolysis (mg KOH/g).

2.2. Experimental design and model

To study the influence of the several experimental variables on the glycerolysis reaction, an artificial neural network (ANN) was used with 3 factors of excess % of glycerine (4–16%), reaction temperature (180–240 °C), and reaction time (1–400 min) to define the effects of process parameters on the consumption of free fatty acid (%). An average molecular weight of 267 g mol^{-1} for PFAD was used to calculate glycerol/oil molar ratios. ANN is especially important in the beginning of an experimental study and they reveal high precision with minimum experimental effort and they enable detection of factor interactions [14]. In addition, the effect of reactor conditions on the consumption of FFA (%) in air (open reactor system) and N_2 flow system was studied at the optimum conditions. The reaction time was changed in the experiment matrix to check the rate of glycerolysis reaction. As well, all experiments were conducted at the same reaction temperature and glycerol amount. All the reactions were performed in three different reactor conditions including open reactor conditions, close reactor conditions, and open reactor with N_2 flow systems, as shown in Fig. 1 (b)–(d).

In this study, a feed forward back propagation ANN was developed for the prediction of the optimum conditions of reaction. Genetic algorithm (GA) was conducted for training of the ANN 66% of the entire data set of 106 experiments was used for training of the ANN and 33% of the data set was selected for testing and validation of the ANN model. The sigmoid function was selected as an activation function and the number of neurons in the hidden layers was obtained by trial and error. Reaction time, reaction temperature, and glycerol amount were used as inputs of the ANN and the reduction percentage of free fatty acid was used as the output. Training and testing performances of the network was evaluated with the root mean square error (RMSE). The lower value of RMSE and higher value of coefficient of determination (R^2) mean a better performance of the developed ANN.

An example of a perceptron, which is the most common neuron, is shown in Fig. 2 for three input variables, where $\{x_i\}_{i=1}^{3}$ are the input variables, $\{w_i\}_{i=1}^{3}$ the weights, b the bias, and y the output variable. Perceptron applies a linear combination of its inputs, obtaining the variable, $= \sum_{i=1}^{3} x_i \cdot w_i + b$, and then applies a function f, which is called the transfer function, to this intermediate variable v to obtain the output variable. Sigmoid functions are commonly used as the transfer function to give the perceptron a nonlinear behavior.