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

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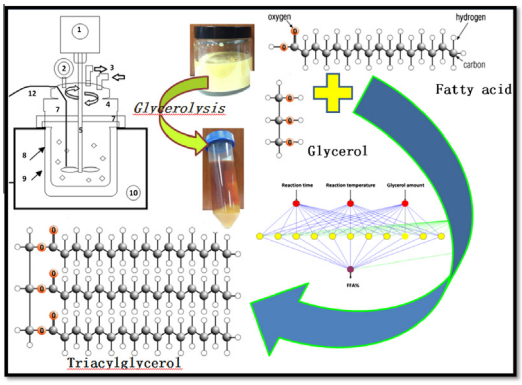
HIGHLIGHTS

- 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.

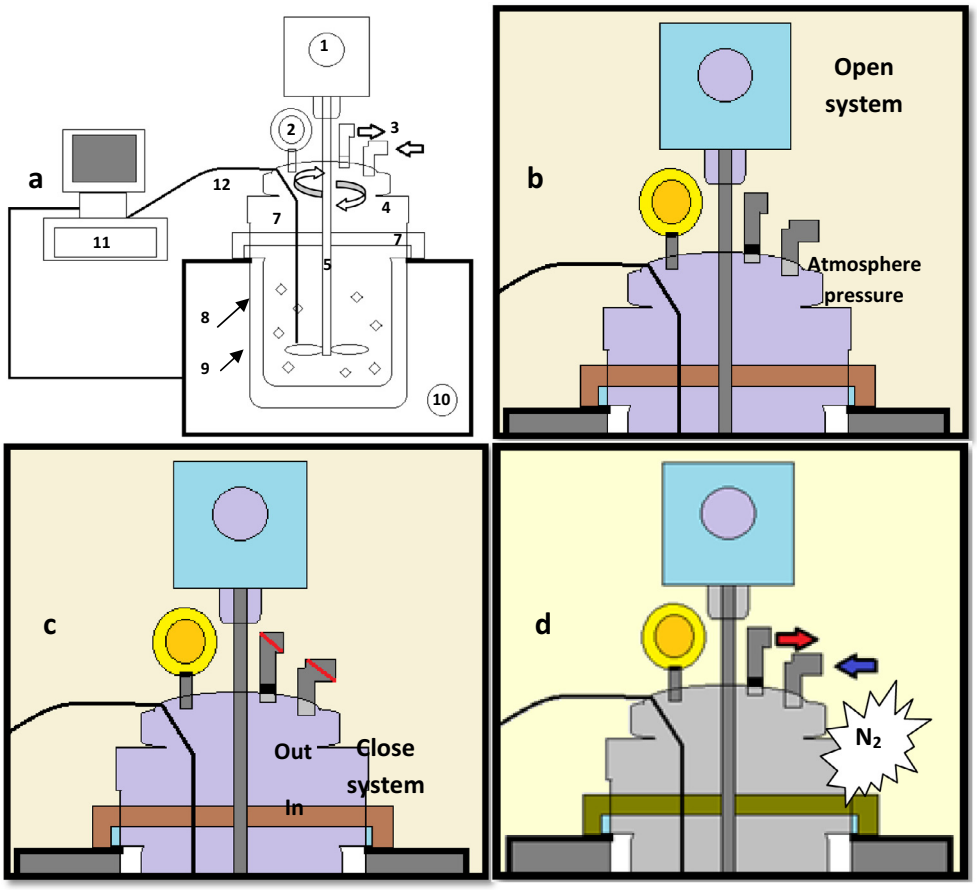

Fig. 1. Schematic diagram the glycerolysis reaction of JCO (a), with open vial system (b), close vial system (c) and N_2 atmosphere (d). 1-Stirrer motor, 2-pressure measurement, 3-standard fitting (N_2 inlet and outlet), 4-reactor lid, 5-PTFE cover stirrer, 6-K-type thermocouple, 7-PFTE seal, 8-PFTE insert, 9-reactor vessel, 10-safety temperature controller, 11-temperature controller, and 12-thermocouple connector line.

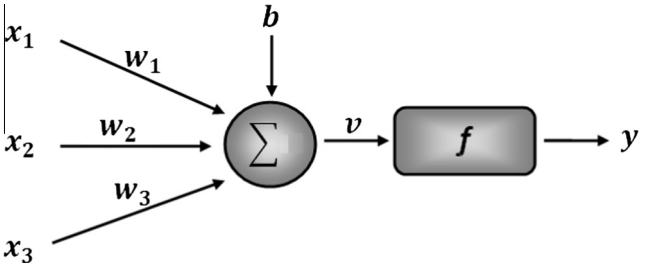

Fig. 2. Example of a perceptron with three input variables, where x are the input variables, w the weights, b the bias, f the transfer function and y the output signal.

A GA is an iterative search heuristic based on the process of natural selection and it is employed to solve optimization problems efficiently. GA belongs to the larger class of evolutionary algorithms and it combines randomized information exchange methods, which incorporate the survival of the fittest strategy, to find optimal solutions to the problem. The design of a GA involves the choice of the way the solutions should be represented, the design of a function which evaluates the fitness of the solution, the choice of the selection strategy to evolve the population, and the design of the information exchange methods [14]. In this optimization study, the final model was validated by 15 random experiments. Experimental values were compared with the predicted values to check the adequacy of the final models. Recommended optimum process parameters were also performed to verify the optimum response values predicted by the model.

3. Results and discussion

3.1. Optimization by neural network model

Finding the number of neurons in the hidden layer is necessary to develop the multilayer feed-forward ANN as it has significant effects on the performance of the network. The stop criterion has been selected on the basis of root mean squares error as a network performance function for the training data sets. The total number of neurons in the hidden layer has been varied from 1 to 15 to reach the best ANN architecture with optimum neuron numbers. Variation of RMSE as a function of the number of neurons in the hidden layer has been shown in Fig. 3. A network with the lowest values of RMSE gives the best ANN architecture. It is evident from Fig. 3 that the optimum neuron numbers in the hidden layer has been found to be 11. Too many hidden neurons may cause the neural network to be over learned and on the other side, fewer hidden neurons will not provide sufficient freedom for the network to accurately learn the problem behavior. The optimal architecture has been also shown in Fig. 4.

The regression graphs of training, testing, and validation sets are presented in Fig. 5. The experimental data of validation set were also tabulated in Table 1. The comparison between predicted value and the experimental result in optimum conditions presents the maximum relative standard error (RSE) of 0.0370 which indicates good agreement between the experimental results and the relation's outputs. The value of the FFA% for the presented relation indicates that this relation has a good ability to estimate thermal reaction time, reaction temperature, and amount of excess glycerol (%).

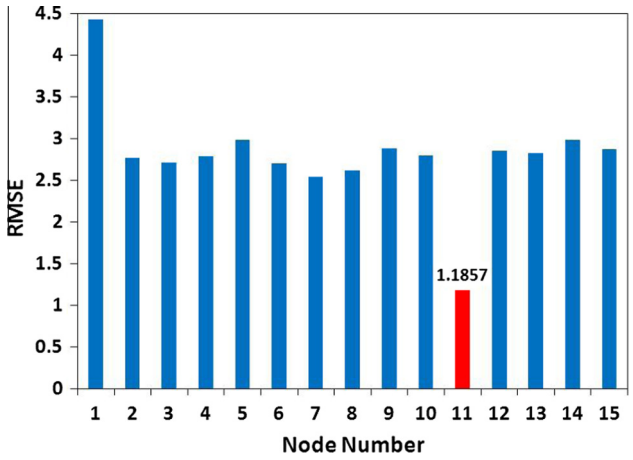

Fig. 3. Performance of the network at different hidden nodes *versus* RMSE using genetic algorithm.

The optimum reaction condition is needed to achieve the desired degree of conversion of the raw feedstock. A conclusion has been reached by several researchers [15–17] that esterification with glycerol at high temperature can caused undesired side reactions or consecutive reactions resulting part of the converted materials produce undesired by product at the end. To find out the conditions leading to a high reduction of FFAs, the esterification with glycerol in different reactor conditions including open, close, and open with inert conditions were evaluated in this study.

3.2. Glycerolysis in close system reactor

The rate of glycerolysis in a close reactor system was determined by the initial concentration of FFA and reaction temperature. The percentage of glycerine excess of 4% and stirring speed of 500 rpm were kept constant for studying the effect of the reaction temperature. The progress of reaction, monitored in terms of the change in FFA%, at different operating temperatures has been shown in Fig. 6(a). It has been observed that final acid value reduced with an increase in the reaction temperature from 180 to 220 °C but a further increase in the temperature up to 240 °C did not yield any significantly higher benefits. The reaction rate is maximum at 220 °C and the FFA (%) decreases from an initial value of 85–4.4 mg_{KOH}/g_{PFAD} after a reaction time of 180 min. It is clear that the acid value greatly reduced with the increase in reaction temperature from 180 °C to 220 °C. The results showed that the elevated reaction temperature enhanced the reduction of FFA. Similar trend for existence of optimum reaction temperature has also been reported for acidulated soap-stocks, where an optimal reaction temperature of 230 °C was found to be sufficient for reducing the FFA% value from 80 to 6.4 mg_{KOH}/g_{oil} [18]. A similar decrease in the FFA value of oil in the animal fat from 12 to 1 mg_{KOH}/g_{oil} at 200 °C using the glycerolysis approach [12]. The optimal temperature of 200 °C was reported to require for reducing the acid value from 18.6 to 1.2 mg_{KOH}/g_{oil} during the glycerolysis of Nagchampa oil. It should also be noted that the solubility of glycerine is rather limited in triglycerides. This was consistent with the fact that a high reaction temperature is necessary to increase the solubility of glycerol in oil for glycerolysis as described for the conventional process. From the results, it can be concluded that the higher reaction temperature favors the enhancement the reduction of FFA%, which can be attributed to better homogeneity of the reaction mixture.

However the operation temperature at 240 °C, the final acid value did not reach to below 4% after 180 min of reaction time as can be seen in Fig. 5(a). As earlier reported [19], the reduction of acid value for Nagchampa oil has not been improved further when glycerolysis was performed at 220 °C. Presumably, this phenomenon can be associated with the decomposition of glycerol forming acrolein at 240–250 °C, although such relationship has not been established on the basis of present evident. Therefore, the appropriate reaction temperature for the glycerolysis performed at close reactor system was 220 °C. It was noted that all of the batches could never quite reduce the remaining FFA below 2.5 mg_{KOH}/g_{PFAD}. Tuning the glycerolysis process occurring at different reaction temperature, it was reported [20] that residual mole fraction of water remaining in the reaction liquid may restrict the reaction kinetics at the end of the reaction although other researchers [21] concluded from their work that any remaining water shifts the equilibrium toward the formation of FFA by hydrolyzing the ester linkages, leading to decrease in FFA reduction. A conclusion has been reached that the presence of trace water produced during glycerolysis could decrease the rates of FFA reduction due to the hydroscopic nature of glycerol [22].

The availability of glycerol for interaction with FFA measured with the concentration of glycerol in the FFA phase is the factor of primary interest. Owing to the reversibility of the glycerolysis reactions, the presence of glycerol in excess of the stoichiometric required amount is widely believed to enhance the formation of monoacylglycerol**s** (MAGs). The balanced stoichiometric molar ratio for an ideal reaction between glycerol (G) and PFAD is 1:1, from which 1 mol of MGA is formed. MAG is known to be the main reaction products, but diacylglycerols (DAGs) and triacylglycerols (TAGs) are also formed during the reaction as shown below:

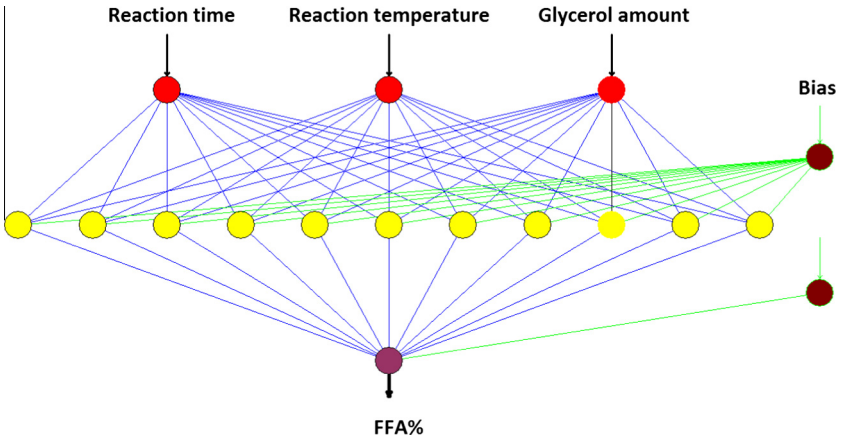

Fig. 4. Schematic representation of a multilayer perceptron feed forward network of ANN consisting of three inputs, one hidden layer with 11 nodes and one output.

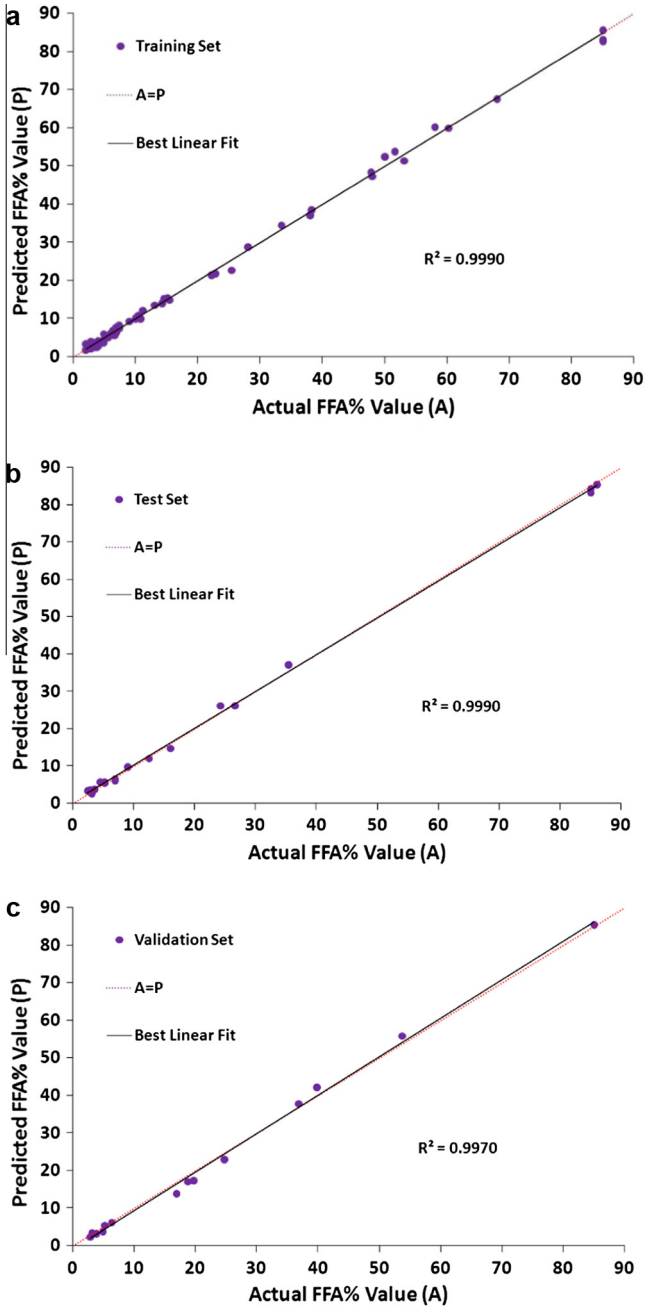

Fig. 5. The regression graphs of the correlation for (a) training set, (b) testing set, and (c) validation set.

$$G + FFA' \rightleftharpoons MAG + H_2O$$

$$MAG + FFA'' \rightleftharpoons DAG + H_2O$$

$$DAG + FFA''' \rightleftharpoons TAG + H_2O$$

In order to study the effect of glycerine excess on the glycerolysis reaction, some tests were performed in a close reactor system. The results are presented in Fig. 5(b). It can be seen that the maximum reduction rate of FFA% was obtained with the excess glycerol of 4%. With a further increase in the excess glycerol to 16%, no significant reduction in FFA% was observed. It is observed that the excess glycerol 8% and reaction time of 170 min is sufficient to reduce the FFA% value from 85 to 4.3 mg_{KOH}/g_{PFAD}. In previous reports using an immobilized *Candida antarctica* lipase B for glycerolysis, it was found that a large excess of glycerol was not altered the glycerolysis acylglycerol composition [23]. A similar observation has been made by the researchers [18] who have reported that the higher excess glycerol/oil molar ratio was not shown any

Table 1
Validation set for the glycerolysis reaction.

Run no.	Independent variables			FFA (%)	
	Reaction time (min)	Reaction temperature (°C)	Glycerol amount (%)	Actual value	Predicted value
1	1	220	8	85	85.6
2	57	180	4	39.8	42.2
3	54	220	8	24	23
4	330	240	4	6.3	6.2
5	1	220	12	85	85.5
6	240	200	4	5.2	5.5
7	152	220	8	4.9	3.8
8	54	220	12	19.7	17.4
9	36	180	4	53.7	55.9
10	330	200	4	3.8	3.2
11	240	220	8	2.8	2.7
12	54	220	16	16.9	13.9
13	150	180	4	18.7	17
14	50	200	4	36.8	37.8
15	150	220	16	3.3	3.4

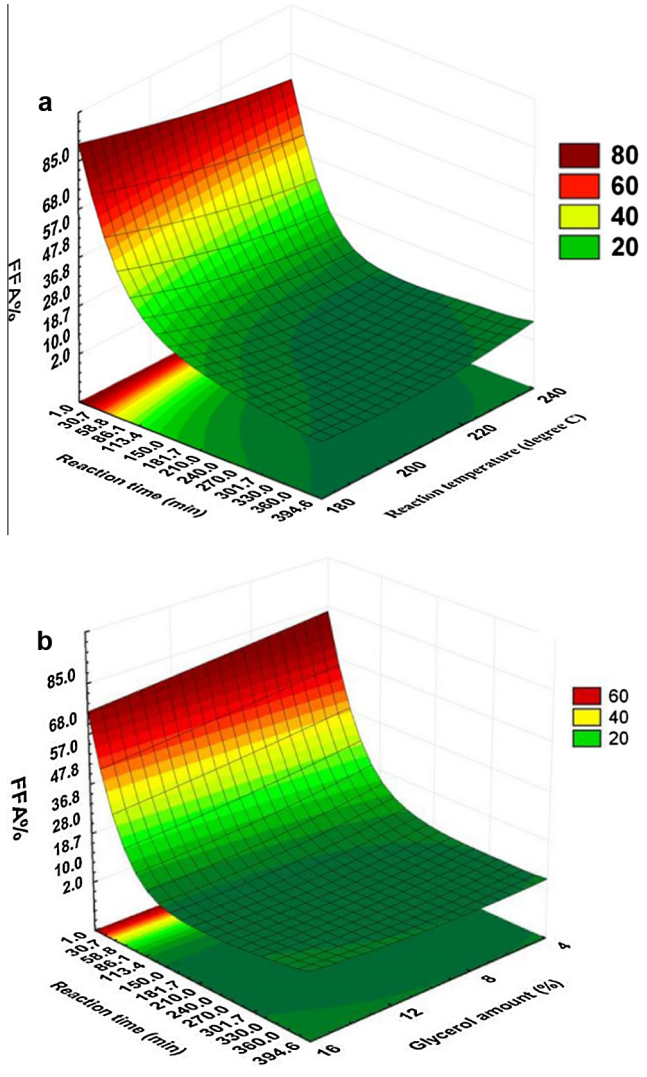

Fig. 6. Effect of temperature on the rate of glycerolysis reaction.

Table 2
Optimum conditions derived by ANN based on genetic algorithm model for the glycerolysis reaction.

Independent variables			FFA (%)	
Reaction time (min)	Reaction temperature (°C)	Glycerol amount (%)	Actual value	Predicted value
240	220	8	2.8	2.7

significant changes in the reduction of FFA. The readily available alcohol groups of glycerol can react with FFAs at the minimum excess amount of glycerol due to minimal steric hindrance [19,24]. Therefore, the sufficient degree of solubility of the hydrophilic glycerol in the hydrophobic FFA phase may be the key to the success of the glycerolysis. In addition, the results obtained from optimum conditions of reaction and the fitting model's outputs are compared in Table 2. Fig. 6 represents the relative importance of the inputs calculated by weights on the FFA% of glycerolysis reaction. The weights are coefficients between the artificial neurons, which are analogous to synapse strengths between the axons and dendrites in real biological neurons. Therefore, each weight decides what proportion of the incoming signal will be transmitted into the neuron's body. The neural net weight matrix can be used to assess the relative importance of the various input variables on the output variables. The importance of effective parameters was calculated by software base on the Garson equation for the percentage of removal. The FFA% of PFAD was reduced from 85 to 2.8 mg_{KOH}/g_{PFAD} in the close system reactor system at 220 °C with 4% of excess glycerol. Therefore, further reaction was compared to their respective optimized parameters in open reactor without and with inert gas flow system to see if it could be improved after optimization.

3.3. Comparison of glycerolysis in open reactor system without and with inert gas flow system

The change in FFA% with the reaction time on the glycerolysis was compared without and with inert gas flow system reactor at optimized reaction temperature of 220 °C with a glycerine excess of 4% and stirring speed of 500 rpm. The results are presented in Fig. 7. The FFA% was reduced in a closed system to 2.6 mg_{KOH}/g_{PFAD} after 120 min of reaction time while the acidity reduced to 1.5 mg_{KOH}/g_{PFAD} after 90 min of reaction time in an open with inert gas flow system. 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 reactor system with inert gas flow, followed by the synthesis in open reactor system without inert gas flow and then in case of reaction under the close

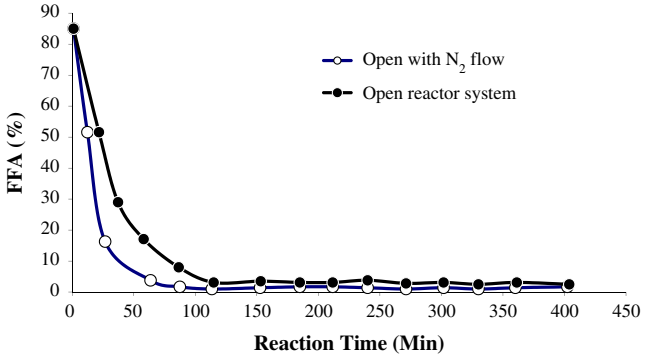

Fig. 7. Glycerolysis of PFAD at different reactor conditions at 220 °C with 4% of excess glycerol.

reactor system. The result has been reported for castor oil based process where the time required for reducing the initial acid value of oil from 55 to 15 mg_{KOH}/g_{oil} at constant molar ratio of 1:1 was 7 h [7]. The acid value of acidulated soap-stocks was reported to reduce from 80 to 7.8 mg_{KOH}/g_{oil} after 200 min of reaction time [18]. Performing the glycerolysis of animal fat with a glycerol/oil molar ratio of 1:2 it was found that the reaction time of 150 min required reducing FFA% value from 12 to 1 mg_{KOH}/g_{oil} [25]. The comparison of the obtained results with earlier studies [7,25] indicates that FFAs reduction rates obtained from the open with N_2 flow system in this study were better than those obtained in conventional glycerolysis. Several workers [18,7,25] in their discussion on the reduction of FFA have emphasized the influence of temperature, the present work suggest that reaction rate of glycerolysis can be increased by driven out of remaining traces of water effectively under the open system reactor with N_2 flow system. The strong dependency of reaction rate on removing the trace of water seems to suggest that molecular friction and collisions in absence of water could accelerate the reaction in a short time. A combination of heat and nitrogen purging would be likely to become a more efficient approach to enhance the reaction rate of glycerolysis. Thus, the glycerolysis option with open reactor system under N_2 flow is a much-preferred option compared to acid esterification for the same biodiesel plant capacity, particularly for high-FFA feedstocks.

4. Conclusion

The present work demonstrated the efficient approach for the treatment of free fatty acid containing sustainable biodiesel feedstock. It was possible to reduce the FFA (%) of PFAD from 85 to 1.5 mg_{KOH}/g_{PFAD} after 90 min of reaction at 200 °C. The advantage offered by this approach is the significant reduction in the reaction time from 180 min to 90 min even without the addition of any catalyst. The high reaction rate results of this laboratory batch study can be used to scale up the glycerolysis process to industrial design. Using the GA-based learning method to adjust the ANN weights and biases, it is possible to improve the reduction rate and to reduce the reaction time needed to perform the glycerolysis operations. Thus, a combination of heat and nitrogen purging reactor system can be used with great success to convert high FFA feedstock to biodiesel.

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