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Prediction of Heating Value of Vegetable Oil-Based Ethyl Esters Biodiesel Using Artificial Neural Network

Bahman NAJAFI [1], Mahmoud ABBASI FAKHR [1], Shahram JAMALI [2]
[1]Faculty of Agriculture, Department of Agricultural Machinery, Mohaghegh Ardabili University, Ardabil-IRAN
[2]Computer Networks and Communication Systems, Department of Electrical and Computer Engineering, Mohaghegh Ardabili University, Ardabil-IRAN
m.fakhr2@yahoo.com

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Abstract: Biodiesel, defined as the mono-alkyl esters of vegetable oils, has undergone rapid development and acceptance as an alternative diesel fuel. The fatty acid composition of base oil predominantly affects the properties of the biodiesel produced from it. Determination of the properties of a fuel by an experimental procedure is a tedious job for the upcoming biodiesel production industry. Therefore, in this study a new approach based on Artificial Neural Networks has been designed to predict the heating value of various vegetable oil-based ethyl esters biodiesel. Biodiesel fuels were produced from transesterification of seven types of vegetable oils (sun flower, canola, corn, soybean, olive, rice-barn and grape seed oils) with ethanol. Gas chromatography**-**mass spectrometry analysis was used to determine the composition of fatty acid ethyl esters (FAEE) in produced biodiesels. The produced biodiesels were mixed with different and specified weight ratios and 240 biodiesel fuel samples were produced. Their heating value was measured by following American Society for Testing and Materials test methods. The FAEE composition of 240 samples (as input) and the experimental data (as output) were used to train the networks. The present work, applied a three layer back propagation neural network. The parameters that affect the development of the model are also discussed. ANN predicted heating values are found to be in good agreement with the experimental data. The correlation coefficient, mean square error and prediction accuracy were %97.25, 0.033 and 99.80 respectively. Hence, the developed ANN models can be used reliably for prediction of biodiesel heating value.
Key words: Biodiesel, fatty acid ethyl ester, heating value, artificial neural network

INTRODUCTION

Diesel engines dominate the field of commercial transportation and agricultural machinery due to its higher fuel efficiency. The consumption of diesel fuel is several times higher than that of petrol. Due to the shortage of petroleum products and its increasing cost, researchers are trying to develop alternative fuels especially for the full or partial replacement of the diesel fuel.

In recent years, biodiesel has received considerable attention, both as a possible renewable alternative fuel and as an additive to the existing petroleum-based fuels. It is a promising alternative to crude oil-derived diesel fuels because it significantly reduces particulate matter, hydrocarbon, carbon monoxide and life cycle net carbon dioxide emissions (Sheehan et al., 1998; McCormick et al., 2001). Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel production is commonly carried out through a transesterification reaction between a lipid source and an alcohol to produce an ester and a by-product, glycerol. Among the applicable oils and alcohols, vegetable oils and methyl and ethyl alcohol are most frequently used in the biodiesel production.
Biodiesel fuels derived from vary vegetable oils have different properties. These differences come from different feedstocks, climatic conditions of plant growth and process of oil production. But overall, biodiesel fuels include some of fatty acid ethyl (or methyl) esters that their compositions in fuel

predominantly affect on fuel properties. In the other hand, biodiesel properties depend on compositions of fatty acid ethyl (or methyl) esters including ethyl estearate, ethyl palmitate, ethyl oleat and ethyl linoleate.

Higher heating values

The higher heating value (HHV), which is one of the most important properties of a fuel, is the amount of heat released during the combustion of one gram of fuel to produce CO_2 and H_2O at its initial temperature and pressure. There are a number of formulae proposed in the literature to estimate the HHV of biomass fuels from the basic analysis data, i.e. proximate, ultimate and chemical analysis composition. Goering CE et al. (1982) measured Fuel properties including heat of combustion of eleven vegetable oils. They concluded that increased carbon chain lengths and reduced number of double bonds are associated with increased oil viscosity heating values. Sadrameli et el. (2008) Developed an equation to predict the HHVs for individual saturated fatty acids as a function of their molecular weight, density and carbon number. They found that the HHV of fatty acids increase with molecular weight and carbon number and decrease with their density. Freedman (1989) Obtained equations for calculating the heats of combustion of pure fatty esters including saturated methyl esters, saturated ethyl esters and unsaturated methyl esters. Their equations related heats of combustion to carbon number or chain length, electron number or number of valence electrons and molecular weight. Demirbas (1998) Investigated the physical, chemical and fuel properties of vegetable oils. Combustion heats, determined as HHVs, of vegetable oil samples obtained from different sources were determined experimentally and calculated from chemical analyses. The HHV (kJ g^{-1}) of the oils was calculated as a function of saponification value (SV) and iodine value (IV). The HHVs calculated from this equation showed a mean difference of 0.0067%. Demirbas (2009) Measured HHV of vegetable oils and their biodiesels and correlated using linear least square regression analysis. Tow equations were developed for the calculation of the HHV of vegetable oils and biodiesels from their viscosity (VS) and density (DN). Demirbas (1997) Determined calorific values (HHV) of 16 biomass samples obtained from different sources experimentally and calculated them from both ultimate and proximate analyses. The HHV (MJ kg^{-1}) of the biomass samples as a function of fixed carbon (FC, wt%) was calculated from an equation. The calorific values calculated from this equation showed a mean difference of 2.2%.

ANNs

A neural-network is a massively parallel distributed processor that has a natural propensity for storing experiential knowledge and making it available for use (Haykin, 1994).

ANN models may be used as alternative methods in engineering analyses and predictions. ANNs mimic somewhat the learning process of a human brain. They operate like a "black box" model, and require no detailed information about the system. Instead, they learn the relationship between the input parameters and the controlled and uncontrolled variables by studying previously recorded data, in a way similar to how a non-linear regression might be performed. Another advantage of using ANNs is their ability to handle large and complex systems with many interrelated parameters. They seem to simply ignore excess data that are of minimal significance, and concentrate instead on the more important inputs. Refs. Allen et al. (1999) Used mixture model to predict the viscosity of biodiesel based on its fatty acid composition. Kalogirou (2003) Reviewed the ANN-based engine combustion modeling, performance and emission characteristics analysis carried out by various researchers. Kalogirou (2001) Also reviewed the use of ANN in renewable energy applications such as solar energy and energy optimizations etc. Ramadhas (2006) Applied ANNs for the prediction of the cetane number of biodiesel. The application of ANN in engineering field is interesting and increasing one. In this study, an attempt made to predict the properties of biodiesel using ANN modeling. The various ANN models are tried for the prediction of the properties of the biodiesel. The comparison of predicted properties with actual properties is described in the following sections.

The present study, applies a feed forward back-propagation neural network in three layers. The input, hidden and output layers had 4, 7 and 1 neurons

respectively. The methodology of the approach used in this study is accomplished by means of Matlab Toolbox. This software has extensive neural net capabilities.

MATERIALS and METHOD

Samples preparation

It has been established that fatty acid compositions of feedstock predominantly affects the properties of the biodiesel. Fatty acid compositions of vegetable oils depends on the climatic condition and oil processing methods. For investigating the effects of fatty acid ethyl ester (FAEE) compositions on biodiesel properties, biodiesel prepared by transesterification of seven types of vegetable oils (sun flower, canola, corn, soybean, olive, rice barn and grape seed oils) using ethanol as alcohol source and sodium hydroxide as catalyst in a batch system. The reaction carried out using 99.7% excess ethanol, i.e., molar ratio of ethanol to oil was 6:1. The oil was heated until the desired temperature was reached (65^{o}C). At this point, a mixture of ethanol and sodium hydroxide (at same temperature) was added to the oil and the transesterification reaction began. The solution was kept at around 65^{o}C for 90min. For stirring, a mixer at 600 revolutions min^{-1} was used. At the end of the reaction period, the glycerol-rich phase was separated from the ethyl esters layer in a decantation funnel. The esters phase (crude biodiesel) was washed with water, with a HCl solution and again with water to provide a purified biodiesel.

Gas chromatography-mass spectrometry (GC-MS) analysis was used to determine the FAEEs compositions of produced biodiesels.

The produced biodiesels were mixed on different and specified mass fractions and 240 biodiesel fuel samples were produced. The FAEE compositions of 240 biodiesel fuel samples were calculated by knowledge of FAEE compositions of produced biodiesels.

Heating value measurement

The higher heating values of the fatty acids were measured by a Parr Adiabatic Model 1261 Oxygen Bomb Calorimeter using the instruction recommended in the Parr manual. An oxygen bomb was pressurized to 3.2 × 10^{6} N/m^{2} (450 psig) with an oxygen container. The bomb was fired automatically after the jacket and bucket temperatures equilibrated to within acceptable accuracy of each other. Data for corrections for the heat of formation of HNO_3 and fuse wire heat of combustion were entered to the system to calculate the final values of HHV. The calibration of the bomb calorimeter has been carried out using the standard benzoic acid samples which were obtained from Parr Instrument Co., Moline, IL, USA, with the higher heating value of 26.453 MJ/kg (6318.0 cal/g). A two-gram pellet sample of benzoic acid was placed in the center of the crucible and weighted with an accurate balance (±0.0001 accuracy). Hundred millimeter of the fuse wire was cut and threaded through the electrodes and configured in a v shape directly above the sample. One milliliter of distilled water was added to the bomb and the bomb was pressurized with pure oxygen and then placed in the calorimeter bucket which was filled with 0.2 m^{2} of tap water at 300–302 K. The bomb was slowly depressurized and the inside washed with distilled water. The wash water was then titrated with 0.0709 N sodium carbonate and methyl red indicator. The data including amount of sodium carbonate in milliliter, and the equivalent energy content for the remaining wire then entered to the system. The calorimeter energy equivalent constant calculated after testing of the benzoic acid sample. The above procedure was repeated with fuel samples except the mass of the fuel was reduced to 1 g . After each experiment the crucible was washed and cleaned with acetone.

Modeling with ANN

To improve the learning process, fatty acid ethyl ester compositions of biodiesel samples and measured Heating value of each sample were used as input and output parameters respectively. This fatty acid ethyl ester compositions include ethyl palmitate ($C_{16:0}$), ethyl stearate ($C_{18:0}$), ethyl oleate ($C_{18:1}$) and ethyl linoleate ($C_{18:2}$). Thus, a neural network was designed with four neurons in input layer and one neuron in output layer. The procedure to create and train a network using Matlab toolbox was as follows:

- Input (C16:0 wt%, C18:0 wt%, C18:1 wt%, C18:1 wt% and C18:2 wt%) and target (heating value) vectors entered in its suitable format in the workspace of Matlab.

- The vectors normalized independently to assign a number between -1 and 1 to each element of vectors by preprocessing function because inputs are sensitive in this range when sigmoid transfer function is used. On the other hand, inputs are normalized because the training domain may be biased toward one input variable or toward higher input. Furthermore, the sigmoid transfer function produces the output within the range of -1 to 1 and if the input is not normalized, bias may be generated.
- The early stopping technique was used to avoid from over fitting. In this technique Data set was divided to tree subset including train, test and validation subset.
- A three layer feed forward back propagation network created in the Matlab neural networks toolbar. This was done because back propagation uses gradient descent method and it allows the neural network to train with a higher degree of efficiency.
- Trainlm, traingda, traingdx and trainscg chose as training function and tansig and purelin chose as transfer functions in hidden and output layers respectively.
- Input and target vectors introduced to the created network and weight initialized.
- Training parameters such as the epochs and error goal adjusted.
- The specified network trained gradually. This process finished when the defined error was reached. During training the weights and biases of the networks were iteratively adjusted to minimize the network performance function.
- Post processing function used to obtain actual output.

The optimized number of hidden layer, number of hidden layer neurons and training function were determined during the learning and training processes by trail end error tests. The Mean Square Error (MSE) ,correlation coefficient (R) and prediction accuracy (P.A) were calculated from following equations and were used to characterise the network performance.

$$MSE = \frac{1}{Q}\sum_{k=1}^{Q} e_{(k)}{}^{2} = \frac{1}{Q}\sum_{k=1}^{Q} (t_{(k)} - a_{(k)})^{2} \quad (1)$$

$$R^{2} = 1 - \frac{\sum_{k=1}^{Q} (t_{(k)} - a_{(k)})^{2}}{\sum_{k=1}^{Q} a_{(k)}{}^{2}} \quad (2)$$

$$P.A = \left[1 - \left(\frac{1}{Q}\sum_{k=1}^{Q} \frac{\left|t_{(k)} - a_{(k)}\right|}{t_{(k)}}\right)\right] \times 100 \quad (3)$$

Where, a is the network output, t is the target and Q is the number of input vectors.

The correlation coefficient can vary between -1 and +1, but R values closer to +1 indicate a stronger positive linear relationship, while R values closer to -1 indicate a stronger negative relationship. Different numbers of hidden layers, hidden layer neurons and training function were tested, however since the performance did not change significantly with more layers and neurons, the simplest network was chosen.

RESULTS and DISCUSSION

The results of GC-Mass analyse are given in Table 2. For training the network, four training function (traingdx, traingda, trainscg and trainlm) was used. To enhance performance and prediction accuracy of trained network, the number of hidden layer neurons in first hidden layer was changed from 7 to 13 neurons and its effect on the MSE of the network was observed .The results are shown in Figure 1.

Table 1. Fatty acid ethyl esters compositions in base produced biodiesels

source of produced biodiesel	Compositions of fatty acid ethyl esters				Heating value (MJ/kg)
	stearate %	palmitate %	oleate %	linoleate %	
Sunflower	12.395	5.112	25.873	54.694	39.24
Grape seed	8.614	5.681	30.88	54.826	39.14
Rice-barn	9.148	11.653	27.692	51.341	39.45
Canola	9.473	6.250	32.935	51.344	39.03
Soybean	9.393	4.807	32.133	53.666	39.45
Olive	4.644	11/033	68.537	15.786	38.43
Corn	5.898	10.031	32.166	50.834	40.56

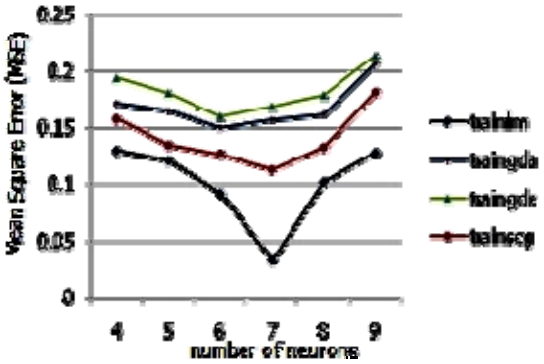

Figure 1. Effect of number of neurons in the first hidden layer on mean square error

As shown in Fig. 1, by increasing number of the neurons in hidden layer to a certain number, the MSE of the network reduced gradually. More increasing the number of neurons in this layer, increase the MSE of the network due to increasing in computations volume of the network. The optimum number of neurons in the hidden layer were determined 6, 6, 7 and 7 neurons, and MSE of the network were obtained 0.150, 0.160, 0.113 and 0.033 in traingdx, traingda, trainscg and trainlm training functions respectively. Number of hidden layers was increased from 1 to 2 layers and results were compared to the network with one hidden layer. Optimum number of neurons in second hidden layer was determined base on least MSE of the network. Total of 240 samples were used in this model, 50% of data set (120 samples) was randomly assigned as the training subset, 20% of data (60 samples) as validation subset and the remaining 20% of data (60 samples) are put aside for test subset. Obtained correlation coefficients of train, validation and test subset in training functions are given in Table 3.

Table 3. Summary of different networks evaluated to yield the criteria of network performance

Training function	Training subset R	Validation subset R	Test subset R	Total R	MSE
traingdx	0.90	0.88	0.89	0.89	0.18
traingda	0.84	0.80	0.85	0.83	0.27
trainscg	0.94	0.92	0.93	0.93	0.11
trianlm	**0.98**	**0.94**	**0.95**	**0.96**	**0.04**

As shown in table 3, trainlm function with 7 neurons in the hidden layer get better results compared to other training functions. The correlation coefficient was 0.972 in the analysis of the whole network, which implies that the model succeeded in prediction of the biodiesel heating value. The performance of the network in training process is shown in Fig. 2. Training of the network stop after 36 epochs with 'Validation stop' message. This ensured satisfactory results. The goal for the training was set to 10^{-3}.

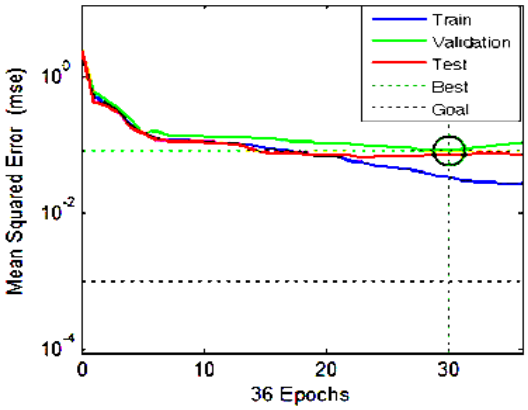

Figure 2. MSE curve of the network during training process using trainlm training function

To have a more precise investigation into the model, a regression analysis of outputs and desired targets was performed. As shown in Figure 3, there is a high correlation between the predicted values by the ANN model and the measured values resulted from experimental tests. The calculation of prediction accuracy was performed using Equation (3). it was 99.80% in prediction of heating value.

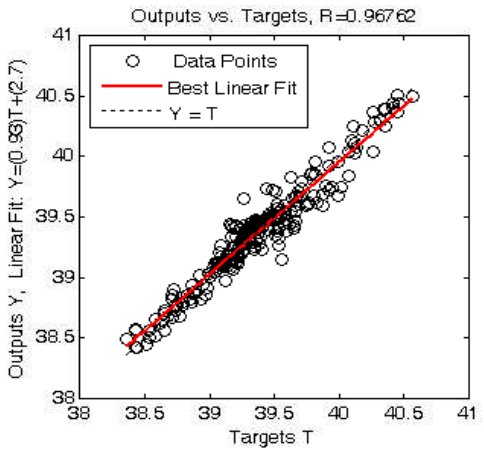

Figure 3. The predicted output vs. the measured Heating value

CONCLUSIONS

The climatic conditions and oil processing methods mainly determine the fatty acid composition of the feedstock (vegetable oil) that is used for the biodiesel production. The fatty acid composition of vegetable oil primarily affects the properties of its biodiesel. Determination of the properties of a fuel by an experimental procedure is a tedious and time consumer job for the upcoming biodiesel production industry. Therefore, in this study a new approach based on Artificial Neural Networks has been developed to predict the heating value of various vegetable oil-based ethyl esters biodiesel. The results show that ANN models can be used reliably to predict the heating value of biodiesel.

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