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Artificial neural network approach for modeling of ultrasound-assisted transesterification process of crude Jatropha oil catalyzed by heteropolyacid based catalyst

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ABSTRACT

Transesterification of crude Jatropha oil to fatty acid methyl esters in an ultrasound-assisted process was conducted in the presence of different heteropolyacid-based catalysts. Tungstophosphoric acid immobilized on activated carbon and gamma alumina as well as cesium salt of the heteropoly acid were prepared and characterized for elucidation of their properties. The experimental data collected from the central composite design were used to establish artificial neural network (ANN) model in order to predict the response in the reaction. The models were also optimized to identify the suitable network topology and training method. The results obtained from ANN models were compared with the results of the regression analysis and good agreement was obtained to suggest the good potential of ANN in the FAME yield prediction.

1. Introduction

Transesterification is the most popular way to convert vegetable oils or animal fats to biofuel [1]. The main product is a mixture of fatty acid methyl esters (FAME) better known as biodiesel. Theoretically, 3:1 molar ratio of alcohol to triglyceride is needed to complete a transesterification process. Practically, the presence of excess alcohol in the reaction mixture and a catalyst (acid or base) could accelerate and control the equilibrium to achieve a high yield of the ester [2]. This reaction can be catalyzed by basic or acidic catalysts. However, basic catalysts can result in higher reaction rate while acid catalysts are more preferred in the case of significant impurities present in the reactants [1].

Due to their unique physicochemical properties, heteropolyacids have been widely used as acid catalysts in various chemical reactions and oxidation processes [3]. Yet, the solubility problem and low surface area of the HPAs (1–5 m^2/g) [4] are the main reasons for the immobilization of the active acidic component on appropriate porous support materials. An appropriate technique to create major effects on the surface area, pore and solubility of the parent HPA by partial substitution of H^+ in HPA with alkaline cations can also be conducted [5]. HPA-based catalysts generally show higher tolerance to water and FFA that will enable the use of cheap and readily available feed stocks for the transesterification reaction [6–10] to improve the overall economy of the FAME production process.

The methods for elucidating the effects of process parameters on the response have shifted from the costly and time consuming trial and error searches to powerful, elegant, and cost-effective statistical methods. Design of experiment (DOE) is a systematic approach used to investigate a system or process. It consists of a series of designed tests that subject planned changes to the input factors on a process to assess the effects on the process output. This method can achieve the identification of the "best" experimental conditions to be adopted in the experimentation [11]. On the other hand, artificial neural network (ANN) is a powerful mathematical modeling tool designed for complex systems. Since 1940s, ANN methods have been successfully applied in different areas of engineering and science [12].

Neural network is a parallel distributed processor consisting of simple processing units called neurons which have tendencies for storing experimental knowledge and make it ready to use. ANN resembles human brain in two respects i.e. gaining the knowledge from its environment by learning process and storing the acquired knowledge using the strength of interneuron connections known as synaptic weights. The process used to conduct the learning process is called the learning algorithm which has the function of modifying the weights via a systematic fashion to address the required purposes [13].

Rajković et al. [14] compared the use of ANN with the topology 4–10–1 with the response surface methodology (RSM) for ultrasound-assisted sunflower oil transesterification using KOH

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Table 1
Properties of the crude Jatropha oil.

Property	Value
Density (kg/m^3)	921
Viscosity (cSt)	38.12
Molecular weight	870
Water content (wt.%)	0.161
FFA content (wt.%)	10.5

catalyst. Four input factors i.e. methanol/oil molar ratio, reaction temperature, catalyst loading and reaction time and one output response i.e. FAME yield were included into the optimization study. The ANN was proven to be a powerful tool for modeling and optimizing FAME production as less deviation between the experimental and simulated values was achieved compared to that in an RSM model.

In the present study, ultrasound-assisted transesterification process of crude Jatropha oil was studied. Particular focus has been given on the comparison between the regression analyses approach and ANN modeling to show the validity of the models in accurately expressing the process.

2. Experimental

2.1. Reagents and materials

Tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$), abbreviated as TPA in this manuscript, was supplied by Merck (Malaysia) while cesium chloride was purchased from Sigma–Aldrich (Malaysia). Gamma alumina support was purchased from Merck (Malaysia) and activated carbon (AC) support was purchased from Galcon Carbon Corporation (USA). Crude Jatropha oil was supplied by Telaga Madu Resources (Malaysia) and the properties of the crude Jatropha oil are tabulated in Table 1. Methanol used in the transesterification reaction was supplied by Thermo Fisher Scientific Inc. (USA) while ethanol (for catalyst preparation) and n-hexane (for product analysis) were purchased from Merck (Malaysia). Meanwhile, reference FAME standards were supplied by NuChek Prep. Inc. (Australia).

2.2. Catalysts preparation

TPA supported on activated carbon and supported on gamma-alumina catalysts were synthesized as discussed in [6,7]. For preparation of Cs-doped heteropolyacid catalyst, 0.1 M of C_S solution was first prepared by dissolving a pre-calculated amount of cesium chloride in 50:50 v/v of deionized water and ethanol solution. Milky suspension solution was formed during the drop wise addition of the Cs solution to 0.08 M TPA solution under constant stirring. The TPA solution was then prepared by dissolving a calculated amount of TPA in 50:50 v/v of deionized water and ethanol solution. After the addition, the white precipitate solution was left for aging without stirring for 12 h at ambient temperature. Then, the solution was evaporated in a rotary evaporator to collect the white powder which was then washed excessively using deionized water before drying in an oven at 110 °C for 2 h. The powder was then calcined at 200 °C for 4 h.

2.3. Catalysts characterization

Nitrogen adsorption–desorption isotherms and Brunauer–Emmet–Teller (BET) surface area for the synthesized catalysts were measured by means of an Autosorb 1C system. The BET surface area was calculated from the linear part of the adsorption plot between $0.0 < P/P_0 < 0.3$. The pore size distribution plots were obtained using the Barrett–Joyner–Halenda (BJH) model. The confirmation of the tungstophosphoric species after the catalyst preparation procedure was investigated by means of Raman spectroscopy. The Raman spectra of the supports and the synthesized catalysts were collected using a Raman Module (Jobin Yvon HR 800 UV) equipped with a CCD array detector. The samples were excited by an argon ion laser source with a wavelength of 514.55 nm. The catalyst samples were measured in the range of 200–1200 cm^{-1}. Surface acidity measurement for the prepared catalysts and the support materials was evaluated using titration method after a displacement reaction [15].

2.4. Transesterification reaction

The experimental setup and the equipment used to conduct the ultrasound-assisted reactions are described in detail elsewhere [6,7]. In a typical experimental run, the desired amount of oil was transferred into the reactor and placed in a water bath until it reached the desired reaction temperature. Then, a required preheated amount of methanol was added to the oil according to the desired molar ratio of the reactants followed by the desired amount of catalyst. At this point, ultrasonification was started and a condenser attached to the system was switched on to recover the evaporated methanol. Ultrasonic energy was supplied in a discrete pattern i.e. 10 s on and 3 s off at a certain percentage of the maximum power. After the required reaction time, the reaction mixture was quenched in cold water and the excess methanol was evaporated out. The reaction mixture was then separated into two layers by centrifugation at 3500 rpm for 25 min. The upper FAME layer was then collected for GC analysis. For all experimental runs, the water bath temperature was fixed at about 54 °C. In this system, the heat generated by the ultrasonic probe combined with the heat gained from the water bath successfully maintained the reaction temperature at 65 ± 1 °C. All the experiments were carried out in the presence of air under atmospheric pressure.

2.5. Product analysis

Analyses of the products were conducted using an Agilent gas chromatograph (GC) (7890 A). The GC unit was equipped with a flame ionization detector (FID) and fitted with a capillary column (Agilent Technologies, Inc. 19091 J-413 HP-5) with dimensions of 30 m × 0.32 mm × 0.25 μm. The system was operated using an auto-injector mode and controlled with a PC.

2.6. Experimental design

In order to optimize the reaction conditions for ultrasound-assisted transesterification reaction, Design Expert 6.0.6 software was used. The software was employed to generate the design matrix (central composite design or CCD) for four reaction variables to analyze the data and to create mathematical expressions that can predict the reaction response by statistically fitting of the experimental responses on appropriate mathematical terminology. The selection of the center values for the reaction variables was accomplished as discussed previously [6,7]. Coded and actual reaction variables used in the experimental design are presented in Table 2.

2.7. Artificial neural network modeling

The data collected from the CCD matrix and the experimental yield values for the three catalysts were used for network training to establish the network model that could compute the predicted yield values from the input reaction conditions using MATLAB R2011b software. All experimental data were divided randomly into three groups i.e. training (70%), validation (15%) and testing data (15%). The results of different networks architecture