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Optimization of the methanolysis of lard oil in the production of biodiesel with response surface methodology

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Methanolysis of lard oil to biodiesel was optimized using central composite design (CCD) of response surface methodology to delineate the effects of five levels, four factorson the yield of biodiesel. A total of 30 individual experiments were conducted and designed to study these process variables. A statistical model predicted that the highest conversion yield of lard biodiesel would be 96.2% at the following optimized reaction conditions: reaction temperature of 65 °C, catalyst amount of 1.25%, time of 40 min, methanol to oil molar ratio of 6:1 at 250 rpm. Experiments performed at the predicted optimum conditions yielded 96% which was in good agreement with the predicted value. This study shows that lard oil as a low cost feedstock is a good source of raw material for biodiesel production and a sustainable biodiesel production could be achieved with proper optimization of the process variables.

1. Introduction

Petroleum derived fuels have been the major source of energy globally. This source is finite and at the current rate of consumption emanating from the global population explosion, it will get depleted in the near future. In addition, the soaring prices due to uncertain political situation in some oil-producing countries, scarcity, and environmental concerns have necessitated the research for an alternative and renewable energy sources.

Our society is highly dependent on petroleum for its activities and Nigeria is not left out. This has led to numerous challenges and untold hardship to the citizens which would have been mitigated if there were sustainable alternative fuels. A viable alternative is biodiesel. An alternative fuel must be technically feasible, economically acceptable and readily available [1].

Biodiesel consists of the simple alkyl esters of fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat. It is oxygenated, sulphur free, biodegradable, nontoxic and environmentally friendly alternative automotive fuel [2]. Its use does not require any major modifications in the existing diesel engine. The advantage of this bio-fuel over the conventional diesel fuel also includes high cetane number, higher heating value, low smoke and particulates, low carbon monoxide and hydrocarbon emissions.

Biodiesel fuels are attracting increasing attention worldwide as a blending component or direct replacement for diesel fuel in vehicle engines. The major constraint in wide spread use of biodiesel is the production cost which includes the costs of raw materials and the process operation. The cost of raw materials represents approximately 60–75% of the total cost of biodiesel production [3–5]. As a future prospective, biodiesel has to compete economically with petroleum diesel fuels. One way of reducing the biodiesel production costs is to use the less expensive/low cost feed stock containing fatty acids such as animal fats, inedible oils, restaurant waste oil, frying oil, products of the refining vegetable oil instead of from the edible vegetable oil which could lead to food crisis [6–8]. These low cost feed stocks are more challenging to process because they contain high amount of free fatty acids (FFA) but could be overcome by improving on the production process by the use of two stage processes (esterification and transesterification)and using the optimum reaction conditions for maximum biodiesel yield.

Several processes have previously been developed for the production of biodiesel via acid, alkali, enzyme catalyzed and non-catalyzed processes. The process of transesterification with an alkali catalyst and short chain alcohol as most often conducted tends to yield the highest productivity in the shortest time. Most of the studies show best properties of biodiesel was obtained by

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using KOH as catalyst. Methanol is commonly and widely used in biodiesel production due to its low cost and availability. Other alcohols such as ethanol, isopropanol, and butanol may also be used. Ethanol is derived from renewable biomass, thus relatively cheap. However, ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. Also, the yield of fatty acid ethyl esters is less compared to methyl esters as well as separation of glycerol is the main constrains in the process of ethanolysis. A key quality factor for the primary alcohol is the water content which interferes with the transesterification reactions and can result in poor yields and high level of soap, free fatty acids (FFA) and triacylglycerols (TAG) in the final fuel [9,10]. Unfortunately, all the lower alcohols are hygroscopic and are capable of absorbing water from the air.

According to Enweremadu et al. [11], transesterification reaction involves some critical parameters which strongly influence the final yield. These parameters are peculiar to transesterification of triglycerides in general. From the review of the transesterification methods, the most relevant variables are namely; free fatty acid and water content in the oil, reaction temperature, molar ratio of alcohol to oil, type of catalyst, type/chemical structure of alcohol, amount/concentration of catalyst, reaction time, intensity of mixing (rpm), use of co solvents. However, Leung et al. [12] reported that, there are four primary/main factors affecting the yield of biodiesel namely; alcohol/oil quantity, Reaction time, Reaction temperature, and catalyst concentration.

The traditional one factor at a time method of analysis is time consuming and does not take into consideration the interaction effects between the factors hence optimization method with respect to design of experiment such as central composite design of response surface methodology to establish best conditions for biodiesel production, in addition to studying the main and interaction effects of the process factors thereby providing the best approach in establishing a model correlating the response variable and the independent variables. Response surface methodology (RSM) is a widely used statistical tool which has been applied in research into complex variable processes and has great advantage in the optimization of reaction conditions and the study of interactions among experimental variables within the range studied, allowing a better understanding of the process while reducing the experimental time and costs [13]. The central composite design (CCD) of response surface methodology was suitable approach for simultaneous study of effects of process variables on the biodiesel production and has previously been successfully applied in the study and optimization of biodiesel production with rapeseed oil, soybean oil, cotton seed oil, et cetera and in several biotechnological and chemical processes [14–16].

Aiming to achieve increased knowledge on previously described study specifically on biodiesel production from animal fat as raw material, the present work focused on assessing the effects of five levels, four factors and the correlation among the process variables within the range of temperature (50–70 °C), catalyst concentration (0.5–1.5 wt% of fat), time (20–100 min) and molar ratio of methanol to oil (3:1–15:1) and evaluating optimum parameters for the biodiesel yield by using Response surface methodology (RSM).

2. Materials and methods

2.1. Materials

Methanol (CH_3OH, 99.8% purity) and potassium hydroxide were bought from Cornraws Company Ltd., Enugu and of analytical grade, unless otherwise stated. Mixed pork lard was obtained from new market in Enugu and was rendered according to the method of Dias et al. [17]. The pork lard was rendered using dry-rendering method by subjecting it to heating in a pan without the presence of water at 110 °C for 1 h (under atmospheric pressure to avoid any degradation) to remove water, the waxy, and other suspended and residual matters. Melted fat was then filtered to remove the insoluble materials (such as meat and bone particles) known as cracklings. The processed pork fat was stored in air tight opaque plastic jars to prevent oxidation. The lard oil was characterized to determine the acid value, specific gravity, viscosity, water content, saponification and iodine values so as to ascertain the appropriate pre-treatment method to be used for the oil before used for the reaction.

2.2. Experimental methods

2.2.1. Transesterification procedure

A batch reactor of 500 ml capacity equipped with a reflux condenser and magnetic stirrer was charged with the desired amount of oil (50 ml) heated to 65 °C in a water bath with agitation. A measured amount of catalyst (potassium hydroxide) was then thoroughly mixed in known quantity of methanol till it dissolved completely to give potassium methoxide. The potassium methoxide was added to the reactor and the reaction timed immediately after the addition of the potassium methoxide. It was transferred into separating funnel and allowed to settle for an hour. Two distinct layers were observed; a thick brown layer (glycerol) at the bottom and a yellowish colour layer constituting the upper layer (biodiesel). FAME layer (Biodiesel) was washed with distilled water to remove unreacted catalyst, methanol and residual glycerol and heated slightly to remove any residual water in it.

The percentage yield was taken.

$$\%\ \text{Yield} = \frac{\text{Weight of Fatty Acid Methyl Ester}}{\text{Weight of Oil Used}} \times 100 \qquad (1)$$

The transesterification was carried out at optimum rotation speed of 250 rpm based on literature data to achieve maximum conversion. The reaction parameters were chosen as follows: temperature ranged from 50 °C to 70 °C, mass ratio of catalyst to oil from 0.5% to 1.5%, time from 20 min to 100 min, molar ratio of methanol to oil from 3:1 to 15:1. The procedures above were used for each experiment executed at different parameters using the experimental design matrix in Table 2.

2.2.2. Biodiesel characterization

Standard procedures were used to characterize the properties of lard biodiesel; acid value (A.V), viscosity (μ), specific gravity (S.G), saponification value (S.V), iodine value (I.V), cetane number (C.N), higher heating value (HHV), flash point, cloud point and pour point of the biodiesel. The determined fuel properties were compared with the ASTM standards for fuel. Most of the properties analyzed determine the efficiency of a fuel for diesel engines. There are other aspects or characteristics which do not have a direct bearing on the performance, but are important for reasons such as environment impact etc.

2.2.3. FTIR spectroscopy analysis

The various functional groups present in the raw oil and biodiesel sample were determined with Fourier Transform infrared (FTIR).

2.3. Design of experiment

The experimental design selected for this study is Central Composite Design (CCD) and the response measured which is the dependent variable is the yield of biodiesel.

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