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Research Article

Activated Charcoal Modified with Chromium Oxide as Catalyst for Groundnut Oil *Transesterification*

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Abstract

A gradual shift to biofuels development was considered advantageous in reducing the pollution and other challenges associated with fossil fuels. Specifically, biodiesel production is one of those options prioritized in the literature. Herein, we demonstrated how a modified activated charcoal sample and chromium oxide can catalyze the upgrading of groundnut oil into fuel-grade biodiesel at the laboratory scale via trans-esterification with methanol. The charcoal-based catalyst was characterized mainly at mole ratio: 3:1 (methanol: oil) reaction time of 1hr and reaction temperature at 60 ℃. The yield of biodiesel produced were found 71.50% for activated modified charcoal, 59.30% for chromium oxide and 49.45% for charcoal only, which is a little lower than that obtained by some researchers, and the density was found to be 0.56/cm^3 for active modified charcoal, 0.43g/cm^3 for chromium oxide and 0.33g/cm^3 for charcoal only which is within the ASTM approved limits. The viscocity was found to be 3.39mm^2/s, 2.52 mm^2/s and 1.85 mm^2/s for modified activated charcoal chromium oxide and charcoal respectively at 40 ℃. The free fatty acid was found to be 0.01%, 0.04% and 0.02% for modified activated charcoal, chromium oxide and charcoal respectively and the values are within the range approved by ASTM. The saponification values obtained were 0.56mgKOH/g, 0.84mgKOH/g and 1.12mgKOH/g for modified activated charcoal, chromium oxide and charcoal respectively. Trans-esterification method is found to be good in producing by biodiesel from groundnut oil as corroborated by several investigations.

Keywords

Charcoal Sample, Chromium Oxide, Activated Charcoal, Trans-esterification, Biodiesel

1. Introduction

The depletion of world petroleum reserves and increased environmental concerns have stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand [1]. In recent years, research has been directed towards exploring plant-based fuels, and plant oils and fats as fuels show great promise [2]. Among these, biodiesel, which is the fatty acid methyl esters of seed oils and fats, has become the most widely developed and used fuel in diesel engines. Biodiesel is known to be environmentally safe, non-toxic, and biodegradable [3].

Among the various biofuels, biodiesel is seen as the best option in this era of climate change and the depletion of petroleum reserves [4]. According to a study [5] biodiesel has emerged as an acceptable alternative to petroleum-derived diesel, ensuring energy and economic security. Biodiesel has the ability to reduce carbon emissions, increase biodegradabil-

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ity, lower environmental toxicity, and improve cetane ratings [6]. Biodiesel derived from plant oils is a suitable substitute for fossil diesel due to its high energy yield [7]. The production temperature significantly impacts the biomass pyrolysis during biodiesel production from oil plants [8].

Biodiesel can be manufactured using various methods [9]. The laboratory method used is transesterification, which involves replacing the alcohol group in an ester with another alcohol. The aim of this research work is to examine the effectiveness of activated charcoal modified with chromium oxide as a catalyst for biodiesel production from groundnut oil. The specific objectives include modifying and characterizing activated charcoal as a catalyst for biodiesel production, determining the impact of reaction time, temperature, oil to methanol ratio, and catalyst ratio on the production of biodiesel from groundnut oil using activated charcoal modified with chromium oxide as a catalyst.

2. Materials and Methods

2.1. Sample Collection

Charcoal sample was collected from charcoal sellers in Gusau, opposite Bebeji Plaza, Zamfara State. The sample was poured in to a cleaned and dried plastic bottle. Accurately weighed 200g of the sample was crushed into a fine powdery substance and sieved to micron sizes and was kept under laboratory conditions prior to the experiment.

Also, fresh groundnut oil was obtained from local groundnut oil producers, around an area called low cost Gusau, Zamfara State. It was also poured in to a cleaned and dried plastic bottle. It was repeatedly filtered five times to remove impurities and later stored under laboratory conditions before the experiment.

2.2. Preparation of Catalyst Precursor

10g of the charcoal powder was measured and transferred into a beaker. 100ml of 0.5M H_2SO_4 was measured and transferred into the same beaker. The solution was then stirred for 30minutes to obtain a homogenous mixture. The mixture was allowed to stand for 24 hours. It was then filtered. The filtrate was then allowed to dry for 2 hours.

2.3. Preparation of Catalyst

Exactly 9g of activated charcoal was dissolved in to the solution of Cr_2O_3 and distilled water and then stirred for about 20-30 minutes. The solution was then filtered and the residue is allowed to dry for 3 hours.

2.4. Methods

The methods used in this work were described and recommended by Association of Official Analytical Chemists (AOAC).

2.4.1. Transesterification Procedure

0.3g of the catalysts (charcoal, chromium oxide and modified activated charcoal) were added to a mixture of 100ml of methanol and 20ml of the groundnut oil produced, and placed inside a flat bottom conical flask. All were done individually at various molar ratios. The mixtures were stirred at constant speed of 400 revolutions per minute (rpm), at a temperature of 60 ℃ for duration of 1h. At the end of the reaction time, the products were poured in a separating funnel and left to stand under gravity for 24 hrs so that the reaction can continue and reach equilibrium and for the biodiesel produced and glycerol to separate into distinct layers. Then the crude biodiesel was dried in a water bath at 80 ℃ for 1 h. It was further purified to remove any soluble components. The biodiesel yield was calculated from Equation below: [10].

$$\text{Percentage Yield} = \frac{weight\ of\ the\ biodisel}{weight\ of\ the\ groundnut\ oil} \times 100\%$$

2.4.2. Density Determination

Density of biodiesel was determined by gravimetric analysis by measuring a volume of 25ml biodiesel with a glass cylinder and weighing the sample on the electronic scale [11]. The density was calculated using:

$$P = m/v$$

Where: m = weight of sample in g and v = volume of the sample in cm^3.

2.4.3. Selection of Reaction Temperature

The boiling point of methanol is 64.7 ℃ and in order to avoid alcohol evaporation, reaction temperature has to be less than 64.7 ℃. The optimal temperature runs between 50 and 60 ℃. Increasing the temperature will reduce the viscosity of the oil which leads to a sufficient contact at the active site of catalyst surface between the oil and the methanol [12].

2.4.4. Effect of Time

On biodiesel yield in a batch reactor through was studied by changing the reaction period. Generally, the effect of reaction time inside a reactor can be calculated by using the residence time distribution method (RTD) to compute the expected conversion with time. There will be different reaction times due to different RTD [13].

2.4.5. Determination of Viscosity.

The viscosity of biodiesel was measured using a digital viscometer Unlike the Falling-ball viscometer; the Digital viscometer automatically displays the viscosity of fluids; so no further calculation was done.

2.4.6. Determination of Saponification Value

Saponification number is the amount of mg KOH required to completely saponify 1g of oil. The oil was treated with excess alcoholic KOH, it was then saponified and the excess KOH is titrated against 0.1 N HCl. 1.0g of the oil and was weighed in a quick-fit-reflux flask and 10ml alcoholic KOH was added. It was refluxed for 30 mins, so that it gets simmer. The flask was cooled and 3 drop of phenolphthalein indicator was added and titrated against 0.1 N HCl. [14] the value was calculated thus;

$$\frac{56.1 \text{ x } (b - a) \text{ x } N}{W}$$

Where W= weight of sample, b = blank titre value, a = sample titre value, and N = Normality of HCl.

2.4.7. Determination of Free Fatty Acid

The Three (FFA) is the percentage of free acids present in the biodiesel which includes, modified activated charcoal, chromium oxide only and the charcoal is the percentage by weight of a specified fatty acid for example percentage oleic acid acids value and FFA may be converted from one to the other using a conversion factor is calculated after knowing the acid value. The fatty acid methyl ester is one of the key factors that determined the suitability of any feed stock for used in biodiesel fuel production [15].

$$\text{FFA} = \frac{(V-b)\times 0.5\times 28.2}{W}$$

Where: V - Titer value; W - Weight of biodiesel
b – Blank
N – Concentration of KOH

3. Result

Table 1. *Physicochemical Properties of Oil.*

Characterization	Charcoal only	Chromiumoxide only	Modified Activated charcoal	ASTM Limit D6751
Saponification (mgKOH/g)	1.12	0.84	0.56	3 Max
Free fatty Acid %	0.02	0.04	0.01	3 Max
Viscosity mm ²⁄s at 37.8 ℃	1.85	2.52	3.39	1.90-6.0
Density g/cm^3	0.33	0.43	0.56	0.910-0.915
Temperature ℃	60	60	60	65
Percentage yield of oil	49.45	59.3	71.5	%

4. Discussions

From the result above it can be deduce that biodiesel yield increases gradually with an increase in catalytic activity i.e the yield of the oil produced using modified activated charcoal is greater than the yield of the biodiesel produced using chromium oxide catalyst which is in turn greater than the biodiesel produced using charcoal only.

The saponification value: is a measure of the tendency of oil to form soap during transesterification reaction (i.e. define as the number in milligram (mg) of KOH required to saponified 1g of the sample fat). High saponification values indicate the presence of high percentage of fatty acids which might lead to soap formation and hence low biodiesel yield [16]. The saponification value obtained for sample of groundnut oil using charcoal, chromium oxide and modified activated charcoal were 1.12mgKOH/g, 0.84mgKOH/g and 0.56mgKOH/g which are within the ASTM Limit D6751 respectively.

Free Fatty Acid: This is the quantity of base required to titrate a sample to a specified end point. It is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can corrode metal components and may be a symptom of water in the fuel, inadequate washing or evidence of oxidative degradation. Excessive free fatty acid in the fuel can inhibit the transesterification process and lead to soap formation [17]. The groundnut oil had a free fatty acid of 0.02%, 0.04% and 0.01% using charcoal, chromium oxide and modified activated charcoal respectively. The values obtained are within the approval range.

Vscosity: is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel or leakage at high temperature when too thin [14]. The kinematic viscosity of biodiesel produced using chromium oxide and modified activated charcoal catalysts were 1.85mm ²⁄s, 2.52 mm ²⁄s and 3.39 mm ²⁄s respectively,

which are within the 1.90-6.0 limit. Similarly, the findings presented in the above table revealed that the biodiesel viscosity ranged between 1.85 mm⁄s, 2.52 mm⁄s and 3.39 mm⁄s. Furthermore, the results depicted that charcoal catalyst produced biodiesel that had the least viscosity, while the modified activated charcoal catalyst produced biodiesel with the highest viscosity.

Density: from the results above the biodiesel density varied between 0.33 g/cm^3, 0.43 g/cm^3 and 0.56 g/cm^3 using charcoal, chromium oxide and modified activated charcoal respectively, It was observed from the results that the biodiesel produced using modified activated charcoal as catalyst had the highest density (0.56 g/cm^3), while the biodiesel produced using charcoal as a catalyst had the lowest density, [16] reported similar results from biodiesel produced from different catalyst concentration. Density is an important liquid fuel property, as slight alteration in the density can significantly affect the engine's performance [18].

The findings of this study had affirmed previous reports of [19], that improved catalysts tend to produce biofuel with better fuel properties. According to [19], biodiesel produced from improved catalysts had better fuel properties, when compared to the biodiesel produced from normal catalysts. The poor fuel properties observed in this study can be improved on as stated by [6] to enhance their performance characteristics.

5. Conclusions

Biodiesel was effectively generated by utilizing activated charcoal modified with chromium oxide as a catalyst through the process of transesterification of groundnut oil. The fuel properties of groundnut biodiesel demonstrated comparability to those of diesel and met the standards set by ASTM. The research findings indicate that the yield of biodiesel increases progressively with an elevation in catalytic activity. Furthermore, it was observed that the yield of biodiesel obtained using modified activated charcoal surpassed that of biodiesel produced using a catalyst with chromium oxide, which in turn was higher than that obtained through using charcoal alone.

Abbreviations

ASTM: American Society For Testing and Material
RTD: Resident Time Distribution
FFA: Free Fatty Acid

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Conflicts of Interest

The author declares no conflict of interest.

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