

Exploring the Prospects of Different Activated Charcoal Systems as Low-Cost Materials for Upgrading Groundnut Oil into Biodiesel

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Received on: January, 2024

Revised and Accepted on: March 2024

Published on: March 2024

ABSTRACT

The escalations in fuel consumption associated with rapid growth in human population and industrialization has accounted for consistent interest in search for alternative fuel sources. Valorization of biomass feedstock for fuels and chemicals production is one of those approaches given priority. In line with this global perspective, the current study investigated the prospects of different modified charcoal catalysts (i.e. H-C, Na-C and Cr – C) for biodiesel production from groundnut oil. One important noticeable feature was the possible creation of adequate surface for reactants adsorption-desorption over the developed catalysts. Specifically, the catalyst H-C formed from H₂SO₄ modification of charcoal was very active and yielded up to 95.70% methyl esters (i.e. biodiesel) and was stable for several reaction cycles. The overall activity of the catalysts followed the trend H-C > Na-C > Cr – C. Similarly, the produced biodiesel exhibited properties that were in good agreement with those reported in international databases for fuel specifications. **Keywords:** Activated Charcoal; Catalysts; Transesterification; High Quality; Active Sites.

1.0 INTRODUCTION

The increase in human population has continued to pose serious challenges as predicted by experts around the world. Statistical evidences projected the population to increase from seven (7) billions in 2020 to ten (10) billions by the end of 2050. This trend had an impact on several other economic parameters. One of these critical parameters is the energy demand because the production of goods and services, home-based and industrial activities, transportation, communication and other sectors of human sustenance require energy as an essential parameter. According to a recent analysis published by Energy Information Administration (EIA, 2023), the global rise in human population caused a tremendous rise in manufacturing processes elevated standards of living in different global regions and consequently posed elevation in energy consumption.

For instance, the world wide electric-power requirement had been predicted to grow in the range of 50-100%. Accordingly, electricity generation alone could rise by 30-76% in line with the EIA reports (EIA, 2023). While solar energy, natural gas, coal and related fuels were predicted to greatly contribute in providing sustainable energy supply, there are indications that the biomass resources will also have positive impacts in addressing the energy challenges (Ahmed et al., 2018). The biomass resources are abundant and susceptible for conversion into energy and energy-related resources via direct combustion, chemical and/or thermochemical conversion methodologies (Adam et al., 2011).

Among the derivable biomass-based fuels, biodiesel is increasingly becoming an attractive fuel for the energy industry. It can be produced by direct reaction of simple alcohols (i.e. usually C₁ – C₃ OH bearing compounds) with fats/oils at optimal conditions of temperature (60-65°C), reactants ratio (1:6), active catalysts (acidic or basic) and affordable degree of stirring. When carefully produced and purified, the biodiesel can have fuel properties suitable for direct application in diesel engines. Recent statistical evidences showed the global biodiesel market to be increasingly attractive. For instance, in the year 2022, the market size was USD 47479.2 million, but predicted to hit USD 55965.8 million within six (6) years (i.e. by the end of 2028) (Koizumi et al., 2023; Marcuta et al., 2023). This statistical valuation accounted for at least 2.78% CAGR.

A key lesson from the above predictions is that researches with the view of developing sustainable and advanced strategies for biodiesel production are required. Within the last three to four decades, several reaction methodologies have been explored by researchers and industries around the world (Galadima et al., 2022a). Specifically, efforts were devoted toward formulating catalytic systems that are beneficially cheap, recoverable, reusable and chemically stable under variable reaction conditions (including those attributed to used cooking oils and free fatty acids). Following the phase-out of most homogenous acids and bases due to their associated environmental and stability difficulties, several categories of solid acids and bases are being tested for the

transesterification (i.e. biodiesel production) application (Galadima et al., 2022b).

While zeolites and metal-promoted systems are defined by favouring cracking reactions and decay due to pore-blockages, low yield of the mono-alkyl esters (i.e. biodiesel) remained another challenge with some other heterogeneous acids and bases screened (Galadima et al., 2021; Rezki et al., 2024; Soodesh et al., 2024; Tsubota et al., 2024).

1.1. Research Objectives

There is no iota of doubts, different literature reports revealed a great shift exploration of heterogeneous acids and bases as catalytic systems for the transesterification reaction. One beneficial issue targeted is the development of cheap and chemically sustainable catalyst from low-cost feedstock. In this direction, the current research evaluated the prospects of different activated charcoal systems as catalysts for upgrading groundnut oil with a C₁-alcohol (methanol). The resulted biodiesel was also screened for its fuel properties in line with the standard ASTM procedures.

2.0 EXPERIMENTAL APPROACH

2.1 Source of Feedstock

The groundnut oil used in the study was a cooking-grade feed directly purchased from house-hold based producers at the Low-cost housing estate of Gusau in Zamfara state, Nigeria (12.1628°N, 6.6745°E). It was used as received to allow for screening of catalysts resistance to fundamental impurities. On the other hand, the co-reactant (i.e. methanol) was a laboratory grade BDH England product (percentage purity of 99.8%).

The charcoal employed was a neem-based product manufactured locally by compression in a briquette mould followed by 48h sun drying. 1kg of the sample was obtained from Sabon Gida Community (9.9243°N, 9.8087°E) near Kotorkoshi in Zamfara State. It was further crushed, grinded to particle sizes of 350-371nm and stored in cleaned plastic bottles prior to further experiments.

2.2 Catalyst Modification

The grinded charcoal particles were modified through separate application of chromium oxide (Cr₂O₃: BDH-grade, 98%), acid and base modifiers under different designed conditions.

For the Cr₂O₃ modification, 9.0g of a charcoal sample (previously treated with 0.5m H₂SO₄ and air-dried) was impregnated by wetness method with 1.0g Cr₂O₃. The filtered material was air-dried for 3h.

For the acid-alone modification, 10.0g of the charcoal material was soaked in 100 cm³ of 0.5m H₂SO₄ and vigorously stirred for 0.5h. The resulted mixture was homogenized for 24h, filtered and air-dried for 2h. The basic modification of the charcoal on the other hand was performed using a similar procedure but by replacing 0.5M H₂SO₄ with 100cm³ of 0.5M NaOH (BDH, laboratory grade, 98% purity). The resulted catalyst systems were coded as illustrated in Table 1.

Table 1: Showing the various codes assigned to the charcoal-based catalysts

S/No.	Material	Code
1.	Powdered Neem Charcoal	NC
2.	Chromium Oxide	Cr ₂ O ₃
3.	Chromium Oxide Modified Charcoal	Cr-C
4.	H ₂ SO ₄ Modified Charcoal	H-C
5.	NaOH Modified Charcoal	Na-C

2.3 Transesterification and Fuel Quality Assessment

Accurately weighed 0.3g of a catalyst was added to a glass reactor earlier charged with 20cm³ and 100cm³ of groundnut oil and methanol, respectively. The resulted mixture was subjected to the reaction conditions of 400 rpm constant stirring, 60°C temperature and 1 L reaction time. The reaction products were gravity-separated with the aid of separating funnel.

The recovered methyl esters (i.e. biodiesel) were assessed for yield and fuel-quality properties in line with the procedures adopted in ASTM.

3.0 RESULTS AND DISCUSSION

3.1 Active Sites in Charcoal Based Catalysts

The presence of active sites in any catalytic material suitable for biodiesel production is necessary to allow for adsorption, sequential transformation at the transition states as well as final formation of reaction products. Many literature studies demonstrated that charcoal or carbon in its pure form has little or no catalytic activity due to non-existence of catalytically active sites (Zhao et al., 2021; Sunil et al., 2023). However, the charcoal material can provide adequate surface area for the adsorption of the reactant molecules.

This feature alone is very influential in promoting catalytic performance because large-uninterrupted surfaces are good candidates for generation of active sites via feasible modifications. To develop the active sites, powdered charcoal material must be modified with

metals such as Pt, Pd, Ni, Co, etc., acidic or basic substances (Sultana et al., 2021; Neisan et al., 2023).

In the present study, the introduction of Cr_2O_3 material onto the charcoal via impregnation can have positive effect on catalytically active sites generation. Similarly, both H_2SO_4 and NaOH modifiers can produce acidic and basic sites, respectively. Consequently, the performance of these sites in transesterification process is dependent on their strength and relative concentrations.

3.2 Effect of Catalyst on Biodiesel Yield

The activities of the various catalysts were measured in terms of percentage yield of the methyl esters and the results are presented in Table 2.

Table 2: The yields of methyl esters produced using different catalyst systems.

S/No.	Catalyst	Methyl esters (i.e. Biodiesel yield), %
1.	Blank test	No reaction
2.	NC	49.45
3.	Cr_2O_3	59.30
4.	Cr-C	71.50
5.	H-C	95.70
6.	Na-C	90.70

According to these results, reaction conducted without the incorporation of any catalyst material failed to transform the reactants (i.e. alcohol and groundnut oil) into any reaction products. Therefore, the stirring effect was not adequate to catalyse the transesterification process under the conditions employed. However, both NC and Cr_2O_3 materials were apparently active and produced 49.45% and 59.30% as respective methyl esters yields.

It could be deduced mechanistically that Cr_2O_3 exhibited active acidic sites, being an acidic oxide that favoured the abstraction of $-\text{OH}$ species from methanol, cleavages of triglyceride esters in groundnut oil into RCOO derivatives and the consequent coupling reactions to form RCOOCH_3 and glycerol at the termination stages of the transesterification process (Vuurum et al., 1993; Alqarni et al., 2021). This proposed mechanism is consistent with the effect of active acidic sites in Cr_2O_3 in attacking basic centres in compounds during hydro conversion processes of biomass and oxygenate compounds. However, the moderate yield of 59.30% infers that the active sites in Cr_2O_3 are relatively of medium strengths. More importantly, these sites

remained active after three cycles of repeated application. The NC material on the other hand produced 49.45% yield of methyl esters that reduced to 45% after three reaction cycles. Apparently, an activity decay of 4.45% was observed.

The latter was attributed to partial surface coverage of the neem-charcoal by the reactant species that were not completely removed during catalyst recovery and regeneration. The reaction over the NC system was generally believed to proceed via temperature-activated chemisorption of CH_3OH and triglyceride esters. However, the effect was low compared to that observed with active sites in the Cr_2O_3 material.

The role of modification of the NC on the yield of methyl esters is provided in Figure 1. Modification with 0.5M H_2SO_4 produced the highest yield of methyl esters (i.e. 95.70%). This can be attributed to the generation of acidic sites on the NC material that are adequate in number and strength. The Na-C catalyst formed following modification with 0.5M NaOH also raised the methyl esters yield from 49.45% for pure NC to 90.7% for the modified catalyst (i.e. Na-C). Therefore, it could be argued that basic sites were developed on the NC material, but with activity lower than that found with the H-C catalyst under constant reaction conditions.

Impregnation of Cr_2O_3 onto the NC material raised the methyl esters yield from 59.30% to 71.5%, which can also be considered as a positive effect. Generally, the activity of the modified catalysts followed the trend $\text{H-C} > \text{Na-C} > \text{Cr-C}$, revealing the incorporation of mineral acid (i.e. 0.5M H_2SO_4) as the best approach.

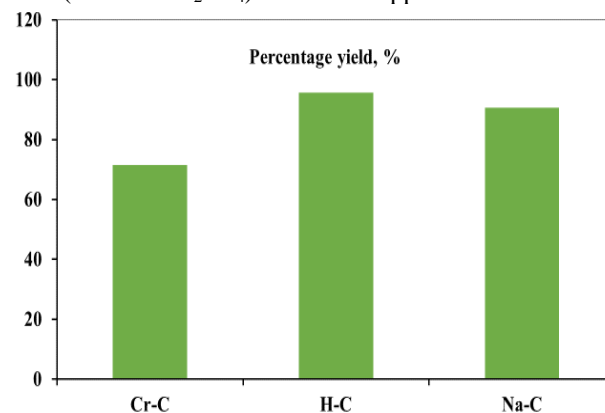


Figure 1. Biodiesel production potentials of the modified catalysts expressed as yields.

3.3 Biodiesel Quality Assessment

Methyl esters suitable for direct application as B100, B20 or any other biodiesel grades must satisfy certain approved international specifications in line with the ASTM standards. Meeting these guidelines is unavoidable to hinder low fuel-efficiency, engine

damages and ensure very good heating value (Atadashi et al., 2010; Modi et al., 2024). Table 3 provides the results of five (5) parameters assessed for the various methyl esters produced with different catalysts. Methanol was employed as a co-reactant for the transesterification reaction and its excess concentration can be found in the biodiesel. According to the ASTM guidelines, the methanol concentration should not exceed a maximum of 0.2% by mass. Data derived from this study revealed methanol concentrations in the range of 0.04% to 0.05%, which clearly agreed with the ceiling approved internationally.

Table 3: Results of quality evaluation of the produced methyl esters (i.e. biodiesel).

Parameter	ASTM Method	Cr-C	H-C	Na-C	ASTM Standard
Methanol content (mass %, max)	EN14110	0.05	0.04	0.04	0.2
	D2709	0.01	0.015	0.013	0.05
Water and Sediments (% volume, max)	D664	0.30	0.32	0.16	0.5
	D6584	0.10	0.10	0.15	0.240
Acid Number (mgKOH/g, max)	D445	3.0	3.2	3.5	1.9-6.0
Total glycerin (mass%, max)					
Kinematic Viscosity (mm ² /s, 40°C)					

Non-allowed volumes of water and sediments in biodiesel products have been considered as responsible for engine damages including corrosion and combustion inconsistencies. Therefore, the maximum allowed limit according to the ASTM standards is 0.05% by volume. As apparent from Table 3, the values obtained are 0.01%, 0.015% and 0.013%, respectively for Cr-C, H-C and Na-C. Although all the values are within the approved range, the highest concentration of water sediments found with H-C based methyl esters could be attributed to hydrolysis process associated with acidic nature of the catalyst.

Figures 2 and 3 depicted respective comparison of acid number (mgKOH/g) and total glycerin between the approved international standards and those observed with

the produced methyl esters. Interestingly, all the values are within the acceptable limits.

The approved range for kinematic viscosity is 1.9 – 6.0 mm²/s and all the methyl esters analyzed exhibited values in the range of 3.0 – 3.5 mm²/s.

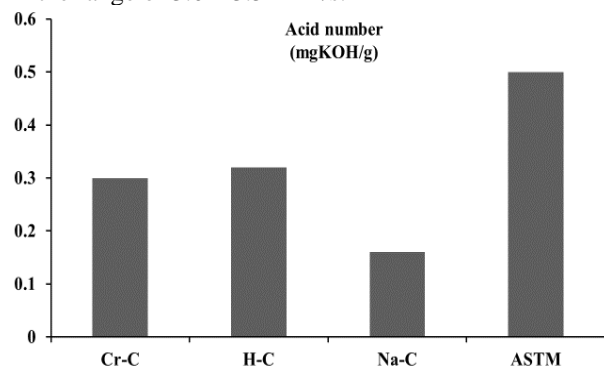


Figure 2. A depiction of the acid number (mgKOH/g) for the various biodiesel fuels synthesized compared with the approved standard for B100.

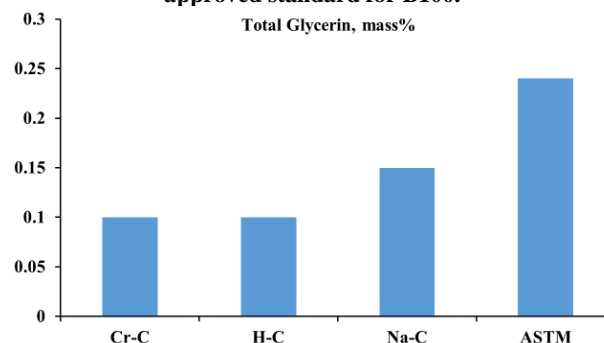


Figure 3. A depiction of the total glycerin (mass%) for the various biodiesel fuels synthesized compared with the approved standard for B100.

4.0 CONCLUSION

Charcoal derived from mechanical treatment of neem-based wood was successfully modified and evaluated to establish different catalysts (i.e. Cr-C, H-C, and Na-C) for upgrading a virgin groundnut oil via transesterification. Apparently, the unmodified charcoal catalyst was inactive and therefore a poor transesterification candidate. On the other hand, treatment with Cr₂O₃, H₂SO₄ and NaOH separately yielded active catalytic systems due to substantial generation of active sites with associated different strengths. One important noticeable feature was the possible creation of adequate surface for reactants adsorption-desorption over the developed catalysts. Specifically, the catalyst H-C formed from H₂SO₄ modification of charcoal was very active and yielded up to 95.70% methyl esters (i.e. biodiesel) and was stable for several reaction cycles. On the other hand, although strongly active, the Cr₂O₃ modified catalyst (i.e. Cr-C)

produced the lowest biodiesel content of 71.50%. Thus, it could be established from the overall results that liquid modifiers (i.e. H_2SO_4 and $NaOH$) provided more actives due to enhanced interactions with the fundamental charcoal. Interestingly, irrespective of the catalyst modifier, the produced biodiesel exhibited properties that are completely consistent with approved international specifications.

5.0 ACKNOWLEDGEMENT

The authors are immensely grateful to Tertiary Education Trust Fund (TETFUND, Nigeria) for funding support to Federal University Gusau under the Institutional Based Research (IBR) scheme batches 7 & 8 (Project No: TETF/DR&D/UNI/GUSAU/IBR/2024/VOL.I).

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