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**Local Rock Sample as Catalytic Material for Biodiesel Production via
Transesterification of Used Cooking Oil**

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ABSTRACT

Sufficient energy supply is increasingly becoming an important mechanism for catalyzing the development of a nation. 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 local rock sample can catalyze the upgrading of used groundnut oil into fuel-grade biodiesel at the laboratory scale via transesterification with methanol. The rock-based catalyst was characterized mainly to compose of oxides in the order $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{Fe}_2\text{O}_3$ with traces of Na_2O , K_2O , MnO and P_2O_5 . The overall catalysis was believed to be initiated and aided by support, active sites participation and promotion effect. The optimum properties of 65°C , 6:1 (methanol: oil), moderate stirring and 100 mg catalyst loading were responsible for deriving 98.05% biodiesel yield. All the assessed fuel properties were also within the standard limits approved by ASTM. Thus, this suggests the feasibilities of the process parameters employed.

Keywords: Rock sample; Catalysis; Biodiesel; Properties; Evaluation.

1.0 INTRODUCTION

The production of sustainable fuels for energy generation and other industrial/house hold applications is a critical issue highlighted in the Sustainable Development Goals (SDGs) as well as strategic plans of many countries around the world (Hak et al., 2016; SDG, 2019; Zakari et al., 2022). Although there are acceptable indicators for escalations in the discovery of more reserves of crude oil (both light and heavy), natural gas, coal and associated energy sources, the numerous challenges attributed to the production and utilization of these fossil fuels are responsible for their limited sustainability.

Undoubtedly, the fossil fuels are responsible for the global rise in CO_2 emissions within the last 100 years (Hook and Tang, 2013; Johnson et al., 2019). This factor alone triggered the global warming and associated climate change inconsistencies that have negative effects of low agricultural productivity, un-predictable rainfall margin and extinction of plants and wild species around the planet earth. Despite these, the fossil fuels are not evenly distributed and therefore the

energy-chain is clearly difficult in many developing regions. Above all, the non-renewable features of this category of fuels inferred that the "sustainability clause" defined by energy experts could not be completely achieved (Gustavsson et al., 2017).

One of the important options considered sustainable and economically profitable by scientists and policy makers is the exploration and utilization of biofuels. These substances (i.e. the biofuels) are liquid fuels with possibility for direct usage or as blending components that could cheaply be derived from biomass resources. Like the fossil fuels, the biofuels exhibit good applications as feeds for transportation, heating and electricity generation. The biofuels are many, but bioethanol and biodiesel are the most widely produced and utilized around the world today. In fact, statistical formulations have demonstrated the production of biofuels to be rising by billion of litres (see Figure 1). Therefore, the global energy trend is increasingly consistent with their production and utilization.

Biodiesel is one of these biofuels that can cheaply be prepared even at the laboratory scale with limited thermodynamics, kinetics, economics and environmental difficulties. It proceeds by the reaction of light alcohols (usually methanol or ethanol; see Figure 2) with oils and/or fats via activation with homogeneous, acidic, basic,

oxides, zeolites or other catalytic materials to generate high grade esters (the biodiesel) and glycerol. Biodiesel has advantages of retaining engine stability properties, renewability, cheap preparation options and environmental protection/sustainability (Galadima and Muraza, 2014).

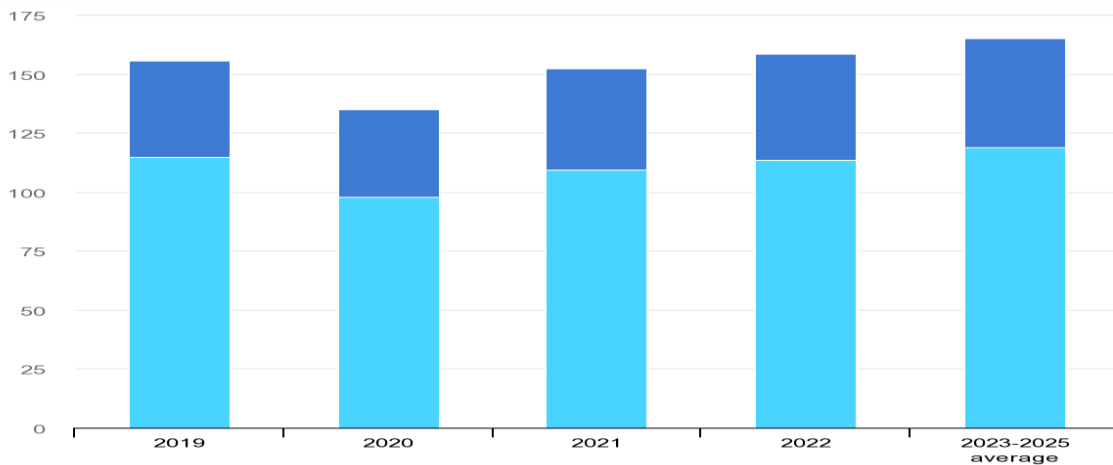


Figure 1. Global production of bioethanol (down bars) and biodiesel (top bars) in billion Litres from biomass resources for the period 2019-2025. Source: IEA (2022).

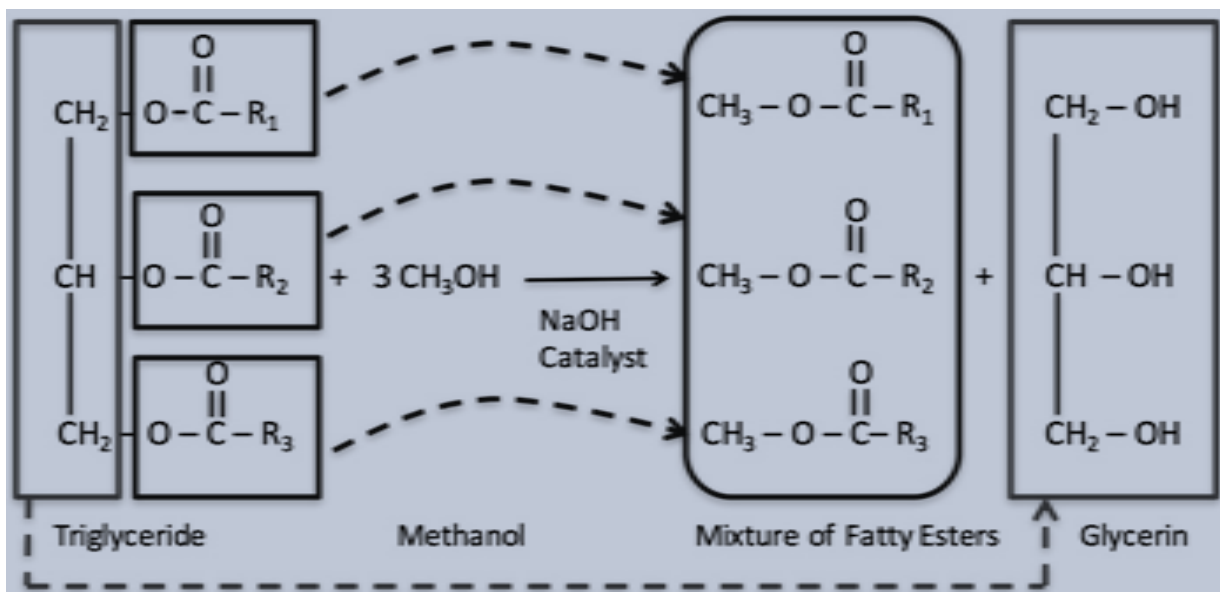


Figure 2. An illustration of the typical reaction for the transformation of oils/fats (i.e. triglycerides) into esters (biodiesel) and glycerol.

1.1 Paper Objectives

Although the process of transesterification is widely practiced around the globe, there are several issues that have not yet been resolved in the literature. These include the formulation of

the most active catalysts with 100% stability for numerous application cycles, achieving 99-100% biodiesel yield, development of high purity glycerol and the inhibition of cracking/decarboxylation side reactions when

heterogeneous systems are employed as catalysts (Galadima and Muraza, 2014; Galadima and Muraza, 2017; Galadima and Muraza, 2020). Another great challenge is the over-dependence on the synthetic catalysts thereby shifting the process costs. Therefore, this investigation targeted the evaluation of local rock sample as catalytic substance for upgrading used groundnut oil into biodiesel fuel. The resulted data were compared with published standard values for the purpose of efficiency and quality evaluation.

2.0 EXPERIMENTAL WORKS

The experimental studies were carried out in line with standard approved procedures as indicated in the following various subsections.

2.1 Sampling and Sample Pre-treatment

Rock samples were surface-collected about 200m away from a local quarry called “Nasidi Quarry” in Kotorkoshi District (12.1409° N, 6.8177° E) of Zamfara state in northern Nigeria using cleaned and dried plastic bottle. Accurately weighed 10g of the sample was crushed into fine powdery substance and sieved to micron sizes. It was kept under laboratory conditions before characterization.

On the other hand, the used groundnut oil was sourced from local soya beans cake (Awara) sellers in the same District using an earlier cleaned and dried plastic bottle. It was repeatedly filtered five times to remove impurities and later stored under laboratory conditions prior to experiments.

2.2 Catalyst Characterization

The pre-treated rock sample was characterized using two non-destructive analytical methods. Initially, N₂ adsorption was performed to establish BET, pore volume and porosity properties using BELCAT equipment at the liquid N₂ temperature (− 196 °C [− 320 °F]). X-ray fluorescence was conducted to establish chemical compositions with the aid of Bruker AXS PORTABLE analytical model.

2.3. Biodiesel Production and Analysis

The laboratory scale transesterification procedure was generally performed in accordance with our earlier validated procedure reported in Anderson

et al. (2009). Typically, an approximately 100 mg of catalyst was accurately weighed and calcined in a flow of dry air (50 mL min⁻¹) from 25 to 40°C for 1 h before maintaining this temperature for 1 h. The sample was then cooled to room temperature in dry nitrogen and immediately transferred to the reaction mixture. The reaction flask was a 250 cm³ 3-necked round bottomed flask fitted with thermometer, reflux condenser and a septum through which sample could be periodically removed by syringe. About 95.0 cm³ (0.1 moles) of the refined waste groundnut oil was added to methanol (99.5% pure, Fischer, 24.30 cm³, 0.6 moles). The mixture was refluxed at 65°C with vigorous stirring and 1 mL samples withdrawn every 10 min and quenched in 1 cm³ of pre-cooled n-pentanol. The resulted biodiesel was analyzed for quality and specifications in line with the American Society for Testing and Materials (ASTM) procedures or the improvised approved standards.

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The results obtained from catalyst characterization are presented in Tables 1 and 2. While the first Table (i.e. Table 1) reported data from XRF studies, Table 2 provided details of the physicochemical properties of the catalyst associated with the N₂ adsorption experiments. Specifically, Table 1 revealed the existence of oxides such as SiO₂, Al₂O₃, CaO, MgO, Fe₂O₃, Na₂O, K₂O, MnO and P₂O₅ with the last four listed oxides constituting only 4.61% of the catalytic rock sample. In fact, the relative abundance of the other oxides followed the trend SiO₂ > Al₂O₃ > CaO > MgO > Fe₂O₃ (see also Figure 3). The SiO₂ stands as the most abundant material in the sample followed by Al₂O₃. It is a well known fact that both SiO₂ and Al₂O₃ were previously employed as very good support materials for active catalysts used in the various biomass upgrading processes including pyrolysis, gasification, reforming reaction, catalytic cracking and many others (Chin et al., 2006; Zhang et al., 2009; Shivhare et al., 2022). The documented excellent surface properties, stability and feasible active metal-support interactions are responsible for these positive properties. They are in fact very favourable in the development of active sites suitable for catalyzing reactions.

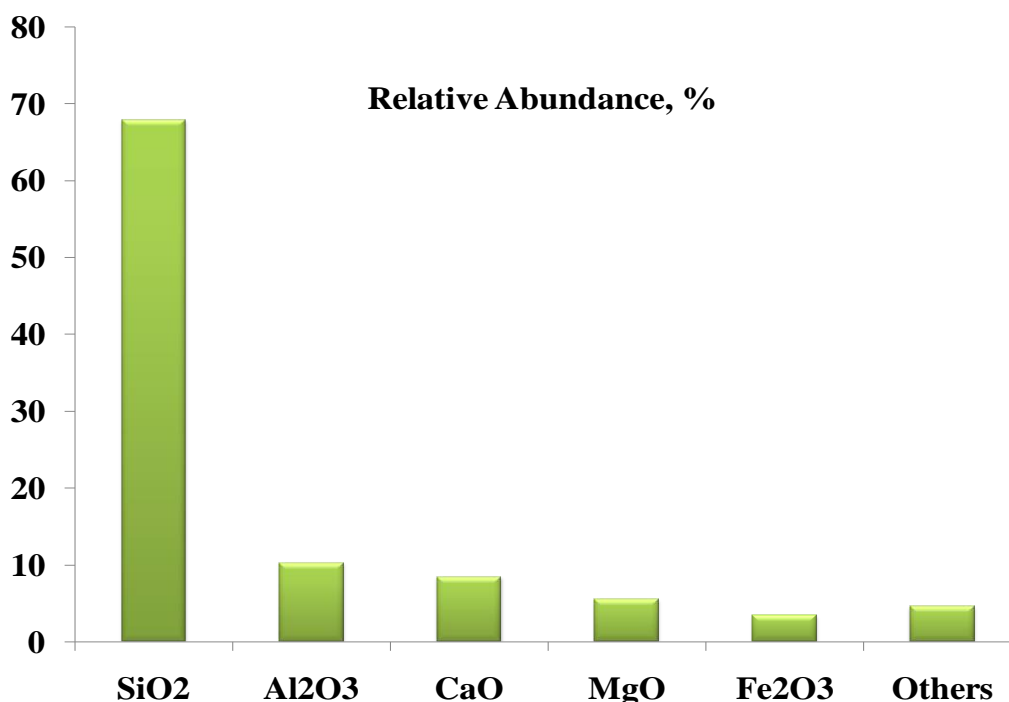


Figure 3. Concentration level (i.e. relative abundance) of the various oxides in the rocky-catalyst.

According to the data reported in Table 2, the catalytic material, although a heterogeneous mixture of many oxides, exhibited good surface area of $124 \text{ m}^2\text{g}^{-1}$ which is adequate enough to allow unhindered adsorption of reactants (i.e. the used groundnut oil and methanol in this case). Similarly, pore diameter range of 6-80 nm accounted for 63.94% of all pores with an associated pore volume of 0.00208 mL/g. The

adsorption properties are consistent with the XRF data by virtue of the fact that the detected oxides can exhibit commingled properties when mixed to form a homogeneous catalyst system. It was remarkably established that the catalyst showed a type II adsorption isotherm as revealed by the porosimetry. This could be an added advantage to the surface properties of the catalyst.

Table 1: Results of X-ray fluorescence (XRF) analysis for the rock sample.

Material	Percentage Composition (%)
SiO ₂	67.82
Al ₂ O ₃	10.26
CaO	8.43
MgO	5.46
Fe ₂ O ₃	3.42
Others including Na ₂ O, K ₂ O, MnO and P ₂ O ₅	4.61
TOTAL	100%

Table 2: Data derived from N₂ adsorption experiments (i.e. via porosimetry).

BET Surface Area $124 \text{ m}^2\text{g}^{-1}$		
Pore Diameter	Percentage (%)	Corresponding Pore Volume (mL/g)
< 6nm	18.75	0.00061
6-80 nm	63.94	0.00208
> 80 nm	17.32	0.00056

3.2 Biodiesel Production

The data derived from the transesterification of used groundnut oil and methanol are provided in Table 3. The yield of monoalkyl esters (i.e. methyl esters, biodiesel) obtained was 98.05%, which is much higher than values range of 88-95% reported in some previous literature (Hoque et al., 2011; Moradi et al., 2012). The formation of these esters proceeds with a stepwise abstraction of $-OH$ from methanol and $R-CO$ from the oil with a net formation of $RCOOCH_3$ (i.e. $RCOOMe$) products (Guo et al., 2022; Munyentwali et al., 2022).

Clearly, the reaction requires active sites that could be acidic/basic in nature to facilitate the process cycle. Among the oxides found in the rock sample CaO , MgO and Fe_2O_3 have previously been demonstrated to exhibit basic active sites suitable for initiation and propagation of the process (Albuquerque et al., 2009; Moogi et al., 2022). Although no dispersion data was provided herein, it could be assumed that the $SiO_2-Al_2O_3$ components of the catalysts were supportive materials that successfully aided the adsorption-desorption of the used groundnut oil and the methanol. Accordingly, the Na_2O , K_2O , MnO and other trace oxides were proposed to have acted as catalyst promoters.

Table 3: Data obtained from activity testing and properties evaluation of the biodiesel produced using the characterized catalyst.

Biodiesel Yield (%)	98.05		
Parameter	ASTM Method	ASTM Limit	This Research
Acid Number (mgKOH/g)	D664	0.50 max	0.10
Oxidation Stability (h)	EN14112	3.0 min	2.8
Methanol Content (%mass)	EN14110	0.2 max	0.05
Water and Sediments (%vol)	D2709	0.05 max	0.015
Sulphated Ash (%mass)	D874	0.02 max	0.005
Carbon Residues (%mass)	D4530	0.05 max	0.03

The high yield of 98.05% obtained was also consistent with the fact that pore properties are very influential in assessing the overall effectiveness of the catalyst. The triglyceride esters in the oil are bulky groups and therefore could experience diffusional problems if the pore properties of the catalyst are poor (Galadima and Muraza, 2018; Galadima and Muraza, 2019). Thus, low yield and evidence of facile cracking could be observed. The pore volume properties with good diameter in the range 6-80 nm associated with the present catalyst therefore acted positively in eliminating diffusional limitations thereby enhancing the formation of high biodiesel yield.

Some key important parameters that are critical with biodiesel production are its resulting properties when compared with standard values

approved by ASTM (Okoronkwo et al., 2009). As demonstrated in Table 3, the various experiments revealed 0.1mgKOH/g, 2.8min, 0.05% mass, 0.015% vol, 0.005% mass and 0.03% mass as observed values for acid number, oxidation stability, methanol content, water and sediments, sulphated ash and carbon residues, respectively. A close comparison of these values with standards reported by ASTM (see Table 3), indicates that they are all within the accepted limits required internationally. Although limitation of access to facilities could not allow for the evaluation of all the standards required by ASTM, the data showed the produced biodiesel to exhibit good potential fuel properties for application as B5, B20 and B100. The acid number could be an indication of the presence of un-neutralized free fatty acids during the transesterification reaction (Ramos et al., 2009;

Stansell et al., 2012). Thus, the very low value of 0.10mgKOH/g obtained consequently showed either the parent used groundnut oil as low in free fatty acids content or that they were strongly transformed by the catalytic action of CaO, MgO and Fe₂O₃ due to their associated basic properties (Albuquerque et al., 2009; Moogi et al., 2022). Parameters such as carbon residues, sulphated ash, oxidation stability and methanol content must be maintained within the required international limits to avoid difficulties of advanced-engine, combustion and stability problems. Therefore, the obtained results were positive in this direction. Water and sediments are known to cause severe destruction to catalytic converter and the overall fuel properties of the biodiesel when their properties are above the standard limits (Ramos et al., 2009). In addition to damage to the catalytic converter, incomplete combustion and reverse ester-hydrolysis could be the net consequence. Thus, the value of 0.015% vol obtained is greatly good when compared with the allowed maximum limit of 0.05% vol. Accordingly, the results could be termed as very positive.

Overall, the combination of the various oxides in the rock sample and the associated in-situ stability established revealed the catalyst as potentially good candidate for biodiesel production from waste oils.

4.0 CONCLUSION

Production of biodiesel requires the suitable combination of catalyst, reactants and other reaction conditions like temperature and the degree of stirring. As clearly demonstrated in this work, the tested rock sample exhibited properties as catalyst for successful transesterification of used groundnut oil and methanol at 65°C. The produced biodiesel also exhibited very good fuel properties that are consistent with international standards approved by ASTM. However, for the interest of overall assessment those parameters not evaluated in the current research should be studied for successful application as B5, B20 and B100 without any doubt of unforeseen difficulty.

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