SSRG International Journal of Applied Chemistry
ISSN: 2393 – 9133 / https://doi.org/10.14445/23939133/IJAC-V11I1P101

Volume 11 Issue 1, 1-6, Jan-Apr 2024

Original Article

Production of Biodiesel from Waste Cooking Oil using A Zinc-Based Metal-Organic Framework (Zn-MOF) As Catalyst

Okpara Sergeant Bull[1*], Sunday Monsuru Adewale[1], Eyu Okpa[1]

[1]*Department of Chemistry, Rivers State University, Port Harcourt, Nigeria.*

[*]*Corresponding Author : bull.okpara@ust.edu.ng*

Received: 16 October 2023 Revised: 25 November 2023 Accepted: 11 January 2024 Published: 24 January 2024

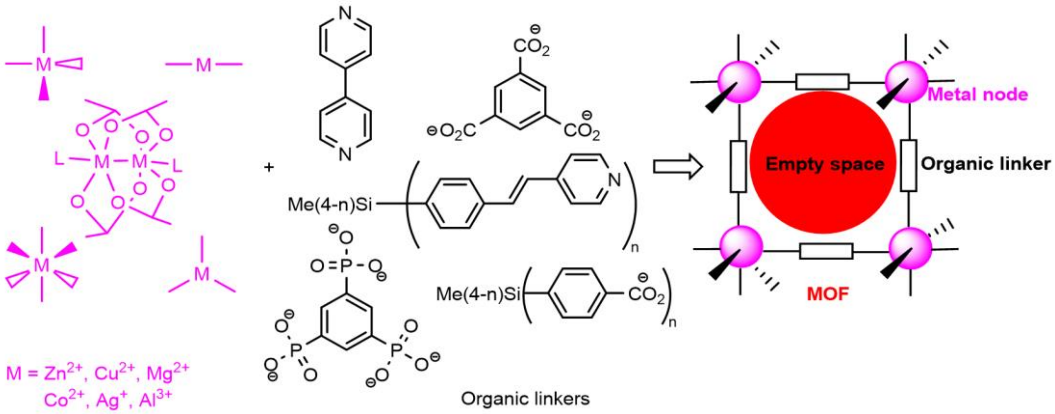
Abstract *- Due to fossil fuel diminishing reserves, global warming, and high petroleum prices, there is a need to generate alternative, sustainable, renewable, and biodegradable biodiesel. In this paper, a zinc-based Metal-Organic Framework (Zn-MOF) was solvothermally synthesized, characterized and then used as a catalyst in place of the traditionally used toxic acids and bases as catalysts in biodiesel production. The Zn-MOF was synthesized using zinc nitrate hexahydrate, $(ZnNO_3)_2.6H_2O$ as the source of metal ion (a Lewis acid), while benzene-1,4-dicarboxylic acid (BDCA) served as a ligand (a Lewis base). A mixture of dimethylacetamide (DMA) and H_2O (1:1 ratio) functioned as solvent. In a clean and dry beaker, 0.297 g (0.999 mmol) of $Zn(NO_3)_2.6H_2O$ was completely dissolved in 2 ml of distilled water. In another clean and dry beaker, 0.166 g (0.999 mmol) of BDCA was dissolved in 2 mL of DMA. Then, both solutions were mixed together and then transferred into a Teflon-lined autoclave. The Teflon-lined autoclave containing the mixture was put in an oven and heated at 150 °C for 24 h. After this period, the Zn-MOF was formed as colourless plate crystalline solids. The Zn-MOF remain unmelted even beyond 360 °C. Furthermore, the Zn-MOF was characterized by FTIR and powder X-ray diffraction. The FTIR shows the incorporation of the ligand into the Zn-MOF. The melting point and the powder X-ray diffraction results agree with the properties of MOFs in the literature. After that, the Zn-MOF was used as a catalyst in the transesterification of treated Waste Cooking Oil (WCO) for biodiesel production. The biodiesel was obtained by transesterification process at a temperature of 60 °C using a 1:5 molar ratio of oil to methanol. The biodiesel yield was 96%. The biodiesel diesel produced was physicochemically characterized. The analysis results revealed that the experimentally obtained values for viscosity, density, flashpoint, cloud point and pour point were 4.1 cSt, 821 kg/m³, 170 °C, below 0 °C and 2 °C, respectively. These values, when compared with standards (ASTM), were in agreement. The Zn-MOF recovered and recycled five times without degradation. Hence, it can be said that Zn-MOF is a good catalyst in the transesterification process of biodiesel production and can, therefore, replace the traditionally used toxic acids and bases.*

Keywords *- Metal-Organic Frameworks (MOFs), Zn-MOF, Solvothermal, Waste Cooking Oil (WCO), Transesterification, Biodiesel, Catalysis.*

1. Introduction

1.1. Metal-Organic Frameworks

Metal–Organic Frameworks (MOFs) are crystalline porous materials formed by self-assembling central metal ions or clusters with bidentate or multidentate organic ligands via coordination bonds [1]. A typical example of a MOF preparation with metal ions and ligands is Scheme 1 [2].



Scheme 1. A typical example of a MOF preparation is with metal ions and ligands [2]

As a result of the nature and properties of MOFs, they have a plethora of potential applications, such as gas storage [3], gas separations, chemical sensing, ion exchange, drug delivery, and catalysis [4]. Because of their large surface area to volume ratio, they can be used as catalysts for chemical reactions.[5] However, there are still challenges in that there is a dearth of literature for studies investigating the potential of Zn-MOF to catalyze waste cooking oil for biodiesel production. Fossil fuels demand domestic and industrial energy generation, which causes problems such as global warming, melting of ice caps, loss of coral reefs, and many more negative effects on the environment, mankind, and livestock [6-8]. One way to solve problems associated with excessive utilization of fossil fuels for industrial and domestic applications is to limit their use in favour of renewable energy sources such as solar power, wind power and biofuels (bioethanol and biodiesel). Biodiesel is famous for being a sustainable alternative to fossil fuels [9]. Its low Sulphur content, renewability, non-toxicity, biodegradability, carbon-neutrality and fewer hazardous gas emission makes biodiesel outstanding. Biodiesel may be prepared by chemical and thermal methods such as transesterification, pyrolysis, and microemulsion [10]. Transesterification and pyrolysis are two of the most popular methods for producing biodiesel. However, the transesterification-based biodiesel synthesis is more attractive. Biodiesel is a fatty acid alkyl ester prepared by transesterifying triglycerides in the presence of alcohol using a homogeneous or heterogeneous catalyst given off glycerol as a by-product. The generated biodiesel mostly consists of various fatty acids depending on its composition [11]. Although homogeneous catalysts have their merits, much attention is currently geared towards the chemical synthesis of heterogeneous catalysts for biodiesel production. They can be tuned per specific requirements and easily recover, thus enhancing reusability. Biomass-derived heterogeneous catalysts have risen to the forefront of biodiesel production because of their sustainable, economical and eco-friendly nature. Furthermore, nano and bifunctional catalysts have emerged as a powerful catalysts largely due to their high surface area and potential to convert free fatty acids and triglycerides to biodiesel, respectively. Most biodiesels reported in the literature are based on edible oils. Biodiesel produced from edible oils is currently more expensive than conventional petroleum-based fuels; in addition, edible vegetable oils have a vital role in the body of mankind. Edible vegetable oils are one of the most important sources of energy. They are essential to maintain the balance of lipids, cholesterol and lipoproteins that circulate in the blood. They provide vitamins A, D, E and K. They highlight some characteristics of foods, such as taste, aroma and texture. If the trend continues, then there will scarcity of food in the very near future. One way, to avert this is to go for non-edible oils or the used of waste cooking oils. In this study, we report the production of relatively cheap biodiesel via transesterification waste cooking oils that are usually discarded into drainages instead of edible oils and methanol using Zn-MOF as catalyst which helps to reduce cost.

2. Waste Cooking Oil (WCO)

Reducing the feedstock cost is necessary for biodiesel's long-term commercial viability. One way to reduce the cost of this fuel is to use less expensive feedstocks, including WCOs and vegetable oils that are non-edible and/or require low harvesting costs [12]. WCO, which is much less expensive than edible vegetable oils, is a promising alternative to edible vegetable oil.[9, 12-14] Although some portions of WCOs are used for the production of soaps, a larger chunk of cooking oil waste is usually disposed of in municipal drainage systems, rivers, and landfills. Thus, WCO has become a significant disposal problem in many parts of the world. This environmentally-threatening problem could be turned into both economic and environmental benefits by proper utilization and management of WCO as a feedstock for biodiesel production.[15, 16]WCO can be grouped into two classes depending on the percentage of Free Fatty Acid (FFA) content. If the FFA content is >15%, it is referred to as 'brown grease'. However, if the FFA content is < 15%, it is referred to as 'yellow grease'. Globally, more than 1 billion tons of WCO is generated per annum. Around the EU countries, it is estimated that around 0.7–1 MT of WCO were obtained per annum. For every 80,000 tons of WCO collected, about 65,000 tons are collected from the UK alone, and these basically emanate from commercial restaurants and food processing industries. Table 1 shows the estimated WCO of some EU countries [4].

Table 1. Estimated waste cooking oil collected in a year[4]

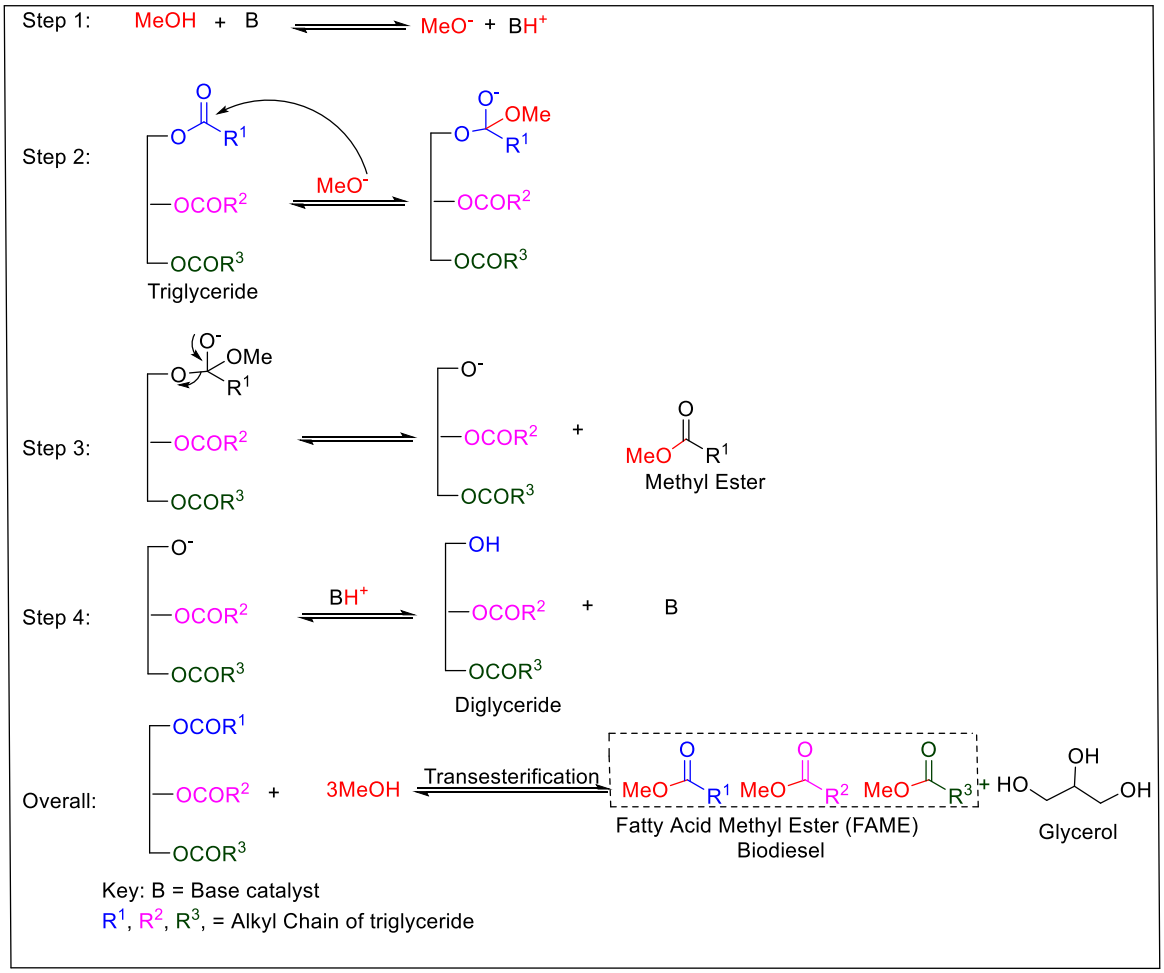
Country	M^3/annum
The Netherlands	89,311
Italy	79,980
Portugal	31,724
Spain	305,910
Germany	283,250
Hungary	6,232
Norway	1,133

3. Transesterificaion Reaction

Biodiesel is produced by the transesterification reaction of feedstocks like edible, non-edible or waste oil with methanol in the presence of an acid or base catalyst. The use of the catalyst in transesterification significantly affects the reaction rate; the use of a catalyst may favour product formation over by-product. In practice, using heterogeneous catalysts is preferred over a homogeneous catalyst. In the use of homogeneous catalysts, a challenging separation-purification process is required to separate the product from the catalyst and excess reactant.

The use of heterogeneous catalysts offers more advantages over homogeneous catalysts, such as being recyclable, easing the separation-purification process, having high glycerol purity, and not being corrosive. The use of heterogeneous catalysts also helps to reduce the total production cost.

Furthermore, the presence of water in homogeneous catalysts (either as a solvent and/or attached water) gives a depression effect to the catalytic activity of the catalyst; this effect is minimized by using heterogeneous catalysts. A typical pathway for the making of fatty acid methyl ester (Fame), also called biodiesel and glycerol (a by-product), is shown in Scheme 2. The scheme generally involves three reversible reaction steps:[11] (i) conversion of triglyceride to diglyceride, (ii) further conversion of diglyceride to monoglyceride, and (iii) conversion of monoglyceride to glycerol. In each conversion step, a methyl ester is formed. This implies that if every triglyceride (oil) molecule reacted, three ester molecules are formed alongside one glycerol molecule.



Scheme 2. Base-catalyzed reaction for the conversion of triglyceride (oil) to biodiesel and glycerol [11]

4. Materials and Methods

Chemicals and Reagents: All chemicals, reagents and solvents used in this work were commercially purchased from Sigma Aldrich and used as received unless otherwise stated.

4.1. Synthesis of the Zinc-Based Metal-Organic Framework (Zn-MOF)

MOF was synthesized using 0.297 g (0.998 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ (metal source) and 0.166 g (0.999 mmol) benzene-1,4-dicarboxylic acid (linker). The $Zn(NO_3)_2{\cdot}6H_2O$ was completely dissolved in 2 mL of deionized water, while the linker was dissolved in 2 mL of dimethylacetamide (DMA). The two solutions were combined and stirred for complete dissolution and then which was transferred to a Teflon-lined stainless-steel autoclave (35 mL), tightly sealed and heated in a programmable oven at 150 °C for 24 h and allowed to cool for 6 h. At the end of this period, the light colourless crystalline solid formed, which was separated from the mother liquor and washed with DMA three times.

4.2. Sample Collection and Preparation

Waste cooking oil was collected from a food vendor at Orazi, Port Harcourt. The WCO was filtered to remove solid residue and purified using warm water in a separatory funnel trice to remove water and other impurities [17, 18].

4.3. Transesterificaion Process

The ratio used was 1:5, that is, 50 mL of oil and, 250 mL of methanol and 0.5 g of the Zn-MOF as a catalyst. The Zn-MOF was put in a beaker containing the methanol. (Note: The MOF crystals do not dissolve in methanol). Then, the oil was added. There were three phases: the methanol at the upper phase, the oil at the bottom, and the Zn-MOF between the interface of the methanol and the oil.

The mixture was poured into a conical flask heated to 60 °C and stirred for 4 hours using a magnetic stirrer bar.

The biodiesel did not form after 4 hours, and the mixture was kept in a cupboard for about two weeks. When checked, the biodiesel was formed. The biodiesel produced was at the top, and glycerol and the MOF were at the bottom. Warmed distilled water was added to the separatory funnel to remove impurities and trace methanol that did not react. The glycerol, water and other impurities were collected from the bottom of the separatory funnel. The biodiesel was collected for analysis. The Zn-MOF was recovered and reused for five more cycles with a notable degradation.

5. Results and Discussion

5.1. Characterization of the MOF (Light Microscope)

After the synthesis of the MOF, it was taken to an electronic microscope to check the shape of the crystals that had formed. The crystals were in block form, as shown in Figure 1.

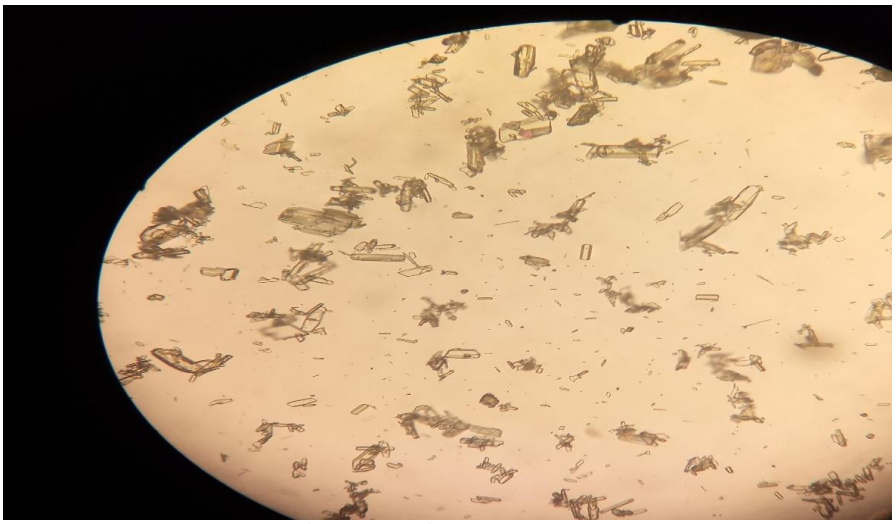


Fig. 1 Image of the crystals formed under a light microscope

The crystalline as well as the purity of the bulk Zinc-based MOF was confirmed by powder X-ray diffraction shown in Figure 2.

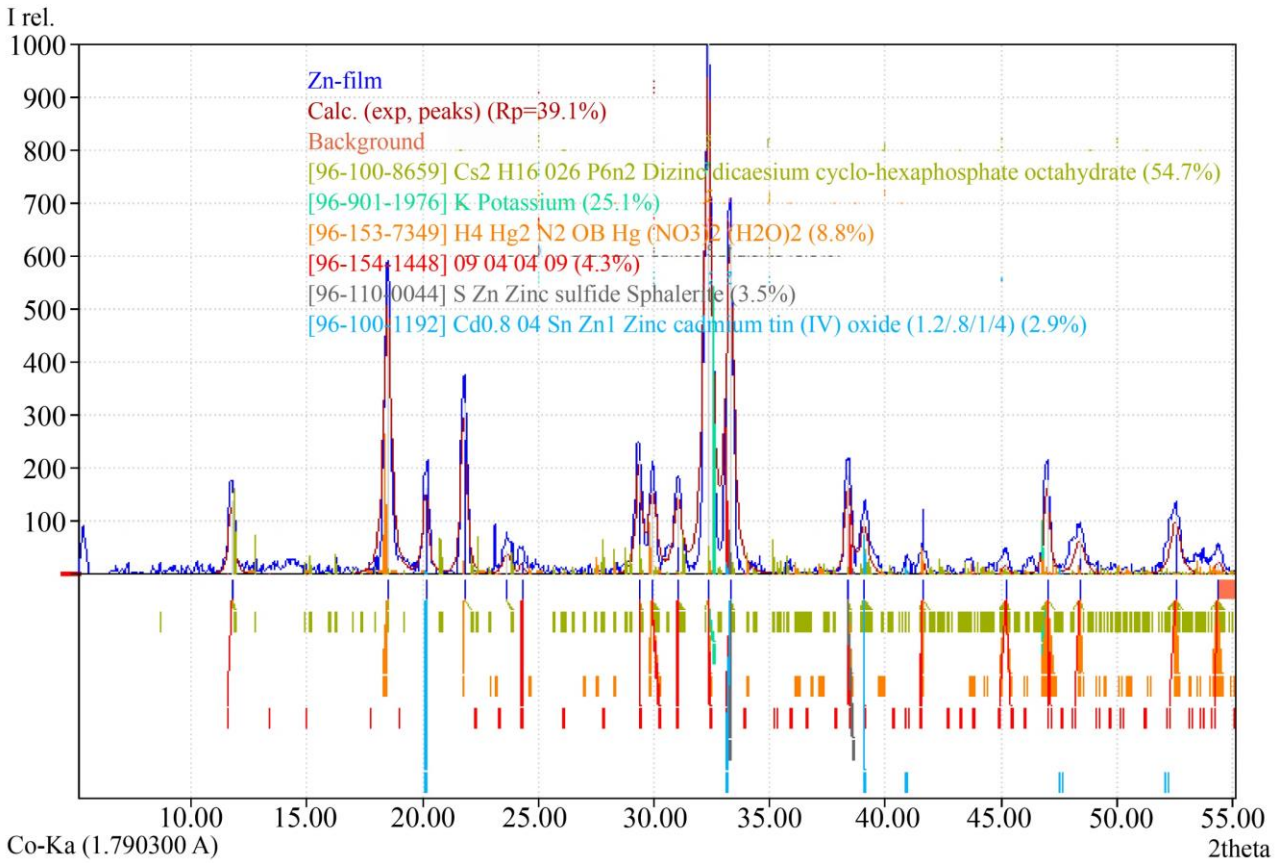


Fig. 2 Powder X-ray Diffraction of the bulk Zn-MOF sample

Table 2. Physicochemical properties of biodiesel produced using Zn-MOF as the catalyst

Biodiesel Parameter	Experimental Value	ASTM Standard
Density	821 Kg/m³	820---845 Kg/m³
viscosity	4.1 cSt	1.9---6.0cSt
Flash Point	170 °C	60---190 °C
Pour Point	Below 0 °C	-5---10 °C
Cloud Point	2 °C	-3---15 °C
Percentage Yield	96 %	

In addition, the melting point of the Zn-MOF was checked. The thermometer used has the highest calibration point of 360 °C, and the crystals temperature on reaching 360 °C remained unmelted, i.e. the temperature of the Zn-MOF crystals is above 360 °C.

5.2. Quantitative Observation of Result

Volume Yield = volume of product

Volume of oil used = 50 mL

Volume of biodiesel produced = 48 mL

$$\% \text{ Yield} = \frac{Mass\ of\ Biodiesel\ produced}{Mass\ of\ oil\ Used} \times 100$$

Percentage of biodiesel yield = 96%

5.3. Physiochemical Properties of the Produced Biodiesel

The methyl ester obtained from waste cooking oil, methanol and MOF was analysed for biodiesel-related properties and compared with ASTM standard, as shown in Table 2.

6. Discussion

The Zn-MOF was viewed under the light microscope, and the crystals formed were seen (Fig.1). The crystallinity and purity of Zn-MOF are in agreement with the literature [1]. The peaks are sharp and range from 12 to 55.2 theta

The results from Table 2 show that the percentage yield of the biodiesel was 96%. This is a very high yield, meaning that the Zn-MOF is a good catalyst when used for biodiesel production [19]. Furthermore, the results of the physicochemical parameters, as shown in Table 2, revealed that the experimentally obtained values for viscosity, density, flashpoint, cloud point, and pour point were 4.1 cSt, 821 Kg/m, 170 °C, 2 °C and below 0 °C respectively. When these values were compared with standard (ASTM), they were in agreement with the standards since their values did not exceed the permissible or acceptable values of 1.9-6.0 cSt, 820-845 Kg/m³, 60-190 ° C, -3-5 °C and -5-10 °C respectively [1,9,12].

7. Conclusion

A zinc-based Metal-Organic Framework (Zn-MOF) has been solvothermally synthesized using benzene-1,4-dicarboxylic acid (BDCA) as a Lewis base. The synthesised Zn-MOF appeared as colourless bladelike crystals. These crystals have a melting point above 360 °C, which agrees with other MOFs in the literature [1]. The Zn-MOF have been used for the catalysis of waste cooking oil to produce biodiesel with a 96% conversion yield. The Zn-MOF was recovered and used for five more cycles. Thus, the Zn-MOF should replace the traditional toxic acids and bases used for transesterification reactions.

References

[1] O.S. Bull, "Solvothermal Synthesis and Characterization of a New 3D Potassium Metal-Organic Framework (MOF) Structure," *Journal of Chemical Society of Nigeria*, vol. 45, no. 1, pp. 126-134, 2020. [Google Scholar] [Publisher Link]

[2] Okpara Sergeant Bull et al., "A Review on Metal- Organic Frameworks (MOFS), Synthesis, Activation, Characterisation, and Application," *Oriental Journal of Chemistry*, vol. 38, no. 3, pp. 490-516, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[3] Thazhe Kootteri Prasad, and Myunghyun Paik Suh, "Control of Interpenetration and Gas-Sorption Properties of Metal-Organic Frameworks by a Simple Change in Ligand Design," *Chemistry – A European Journal*, vol. 18, no. 28, pp. 8673-8680, 2012. [CrossRef] [Google Scholar] [Publisher Link]

[4] Colin McKinstry et al., "Scalable Continuous Production of High Quality HKUST-1 via Conventional and Microwave Heating," *Chemical Engineering Journal*, vol. 325, pp. 570-577, 2017. [CrossRef] [Google Scholar] [Publisher Link]

[5] Jinhee Bae et al., "Multiple Coordination Exchanges for Room-Temperature Activation of Open-Metal Sites in Metal-Organic Frameworks," *ACS Applied Materials and Interfaces*, vol. 9, no. 29, pp. 24743-24752, 2017. [CrossRef] [Google Scholar] [Publisher Link]

[6] O.S. Bull, I. Bull, and G.K. Amadi, "Global Warming and Technologies for Carbon Capture and Storage," *Journal of Applied Sciences and Environmental Management*, vol. 24, no. 9, pp. 1671-1686, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[7] Naeem Abas Kalair, Ali Kalair, and Nasrullah Khan, "Review of Fossil Fuels and Future Energy Technologies," *Futures*, vol. 69, pp. 31-49, 2015. [CrossRef] [Google Scholar] [Publisher Link]

[8] Christian Azar et al., "Carbon Capture and Storage From Fossil Fuels and Biomass-Costs and Potential Role in Stabilizing the Atmosphere," *Climatic Change*, vol. 74, pp. 47-79, 2006. [CrossRef] [Google Scholar] [Publisher Link]

[9] O.S. Bull, and D. Mc George, "Assessment of Fuel Properties of Biodiesel Obtained From African Pear (Dacryodeseludis) Seeds Oil," *International Journal of Advanced Research in Science*, vol. 2, no. 10, pp. 894-898, 2015. [Google Scholar]

[10] Hideki Fukuda, Akihiko Kondo, and Hideo Noda, "Biodiesel Fuel Production by Transesterification of Oils," *Journal of Bioscience and Bioengineering*, vol. 92, no. 5, pp. 405-416, 2001. [CrossRef] [Google Scholar] [Publisher Link]

[11] Bishwajit Changmai, "Widely Used Catalysts in Biodiesel Production: A Review," *Royal Society of Chemistry Advance*, vol. 10, no. 68, pp. 41625-41679, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[12] O.S Bull, and C.C Obunwo, "Bio-Diesel Production from Oil of Orange (Citrus Sinensis) Peels as Feedstock," *Journal of Applied Sciences and Environmental Management*, vol. 18, no. 3, pp. 371-374, 2014. [Google Scholar] [Publisher Link]

[13] Vincent Ishmael Egbulefu Ajiwe, and A.E. Obika, "African Pear Seed Oil: Potential Alternative Source to Diesel Oil," *Energy and Fuels*, vol. 14, no. 1, pp. 112-116, 1999. [CrossRef] [Google Scholar] [Publisher Link]

[14] G. Sujaykumar et al., "Comparative Study of Waste Cooking Oil and Cashew Nut Shell Oil Bio Fuel Blends with Diesel," *Energy and Power*, vol. 7, no. 3, pp. 65-69, 2017. [Google Scholar] [Publisher Link]

[15] Andrew P. Nelson et al., "Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal Organic Framework Materials," *Journal of the American Chemical Society*, vol. 131, no. 2, pp. 458-460, 2009. [CrossRef] [Google Scholar] [Publisher Link]

[16] Vivi Sisca et al., "Biodiesel Production from Waste Cooking Oil Using Catalyst Calcium Oxide Derived of Limestone Lintau Buo," *Archives of Pharmacy Practice*, vol. 11, no. 3 pp. 8-14, 2020. [Google Scholar] [Publisher Link]

[17] Omojola Awogbemi, Daramy Vandi Von Kallon, and Victor Sunday Aigbodion, "Trends in the Development and Utilization of Agricultural Wastes as Heterogeneous Catalyst for Biodiesel Production," *Journal of the Energy Institute*, vol. 98, pp. 244-258, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[18] Tresia Pangestu et al., "The Synthesis of Biodiesel Using Copper Based Metal-Organic Framework as a Catalyst," *Journal of Environmental Chemical Engineering*, vol. 7, no. 4, pp. 103277-103281, 2019. [CrossRef] [Google Scholar] [Publisher Link]

[19] C.O. Odu, C.C. Obunwo, and O.S. Bull, "Solvothermal Synthesis and Characterization of Terephthalic Acid- Based Metal-Organic Frameworks and Their Catalytic Application in Biodiesel Production," *Journal Of Chemical Society Of Nigeria*, vol. 48, no. 3, pp. 474-486, 2023. [CrossRef] [Google Scholar] [Publisher Link]