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SOLVOTHERMAL SYNTHESIS AND CHARACTERIZATION OF TEREPHTHALIC ACID-BASED METAL-ORGANIC FRAMEWORKS AND THEIR CATALYTIC APPLICATION IN BIODIESEL PRODUCTION

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ABSTRACT

Metal-Organic Frameworks (MOFs) are a class of porous crystalline materials, consisting of metal ions or nodes linked with organic ligands. The study was aimed at solvothermal synthesis and characterization of terephthalic acid-based Metal-Organic Frameworks and their catalytic application in biodiesel production. Three MOFs of Cu-, Fe-, and Cr-based were solvothermally synthesized, characterized and applied as catalysts in biodiesel production using ethanol and oil extracted from Yellow Oleander seeds. The MOFs were synthesized using terephthalic acid as the linker and copper (II), iron (III) and chromium (III) nitrates as metal ion sources. Each of the synthesized MOFs showed high melting point exceeding 360 ^{o}C. Microscopic view and powder X- ray diffraction analysis indicated Cu-MOF to be crystalline with numerous sharp peaks while those for Fe- and Cr-MOFs were amorphous. A comparison of the FT-IR spectra of the ligand and those of the MOFs confirmed the presence of the ligand in the synthesized MOFs. In the absence of a catalyst, the transesterification was not achieved. However, in the presence of the more crystalline Cu-MOF as catalyst resulted to high yield (83.33%) and in a shorter time compared to the less crystalline Fe- (33.33%) and Cr- (25.00%) MOFs. Thus, catalytic ability of the MOFs were in the order: Cu-MOF > Fe-MOF > Cr-MOF. Hence MOFs especially Cu-MOFs can be applied as catalyst in biodiesel production. Further studies and characterization (single X-ray diffraction) should be done for proper elucidation of the crystal structure of the MOFs.

Key words: Solvothermal synthesis, Metal Organic Framework, Terephthalic acid

INTRODUCTION

The name Metal-Organic Frameworks (MOFs) was coined in 1995 [1]. MOFs study came into being through coordination chemistry and solid-state inorganic chemistry and are synthesized usually by solvothermal or hydrothermal methods where the MOF crystals are developed from a hot solution [2, 3, and 4]. Thus, they are crystalline porous materials [5] made-up of metal ions or nodes with vacant orbital that can accommodate lone pair(s) of electrons merged or put together with organic bridging ligands or linkers that contain nitrogen or oxygen donors such as carboxylates, nitriles and azoles [6].

Some typical molecular structures of ligands used for the making of MOFs materials are exhibited in Fig 1.1 [7]

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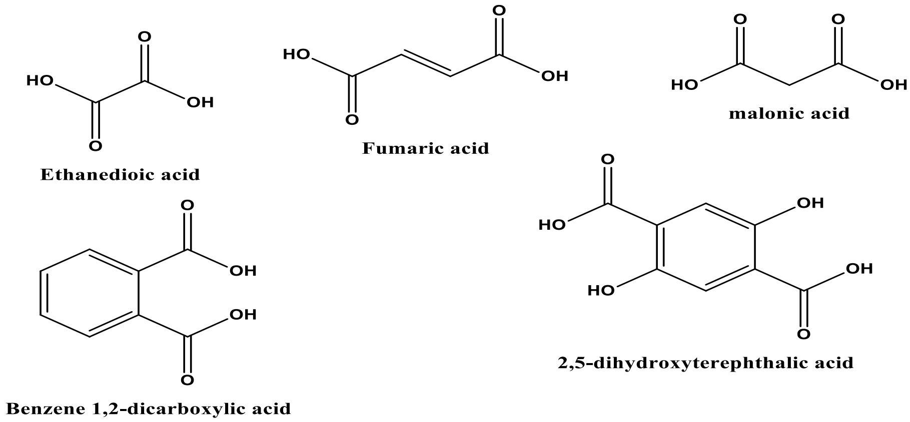

Fig 1.1. Structural Representation of Some Organic Ligands [7]

Preparation of a variety of MOFs with differing architectural geometry and features are possible with a combination of either transition metal ions (including lanthanides metal ions) and organic linkers or main group elements and organic linkers [8].

MOFs are famous for having moderate surface areas, more sites that makes it possible to be applied as catalyst in biodiesel production replacing the conventional acid-based catalyst in biodiesel production [9].

Following the increasing rate of pollution of the Earth atmosphere due to combustion of fossil fuel, as well as the growing cost of petroleum hydrocarbon, the need for renewable, sustainable, greener fuel that will replace fossil fuel for domestic and industrial uses in the near future arises. Thus, solar energy, wind power, hydroelectric power, fuel cells as well as bio-fuels are some of the alternatives that can serve as renewable, sustainable sources of energy [10].

According to Demirabas, [11] biodiesels could be seen as an immensely good and likely alternative source of energy in the near future because they are derived from renewable resources, sustainable and environmentally friendly.

MATERIALS AND METHODS

Synthesis of the MOFs

In a clean beaker the ligand (terephthalic acid) was dissolved using dimethyl acetamide (DMA) and in another separate beaker, distilled water was use to dissolve the metal salt. The ratio of DMA /water was 1:1. The two solutions were mixed and stirred using a magnetic stirrer. The mixture was then carefully transferred into a Teflon-line autoclave which was firmly sealed

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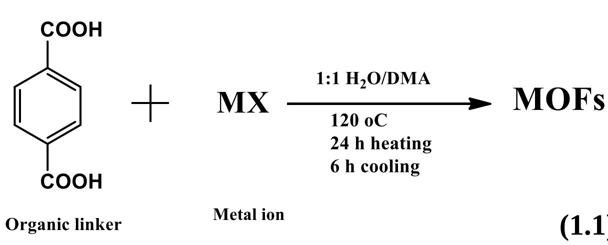
and placed into a muffle furnace for 24 h at 120 ^{O}C and allowed to cool.

For copper- based terephthalic acid MOF, 1.20 mmol (0.20 g) of terephthalic acid and 0.83 mmol (0.2 g) of copper (II) nitrate were used while for iron-based terephthalic acid MOF, 1.81 mmol (0.3 g) of terephthalic acid and 0.5 mmol (0.2 g) iron (III) nitrates were used similarly, for chromium-based terephthalic acid MOF, 1.81 mmol (0.3g) of terephthalic acid and 0.50 mmol (0.2g) of the chromium (III) nitrates were used

The crystalline products (materials) formed were collected and allowed to air dry after which the melting points were determined or carried out using a Gallenkamp melting point apparatus, further characterization such as crystallinity were carried out using X- ray diffractometer terra-575 model of X-ray, the functional groups present were determined using Agilent Technologies FT-IR spectrophotometer cary 630.

Equation 1.1 depicts the general method of the syntheses of MOFs



(1.1)

MX= $(Cu(NO_3)_2 . 3H_2O$, $Fe(NO_3)_3 . 9H_2O$, $Cr(NO_3)_3 . 9H_2O$

Extraction of Oil from Yellow Oleander Seed

the seeds were obtained from Ubeta, Ahoada-West Local Government Area Rivers State. After air drying and blending of the seed two methods were used in extracting the oil. (i) Solvent free and (ii) With solvent. Following the air drying and crushing of the seeds, ½ was placed in a clean white handkerchief and pressed and oil from the crushed seeds pass through the handkerchief the remainder was soaked in n- hexane for 5 days after which the extract was filtered and allowed to stand in the open for a week for complete volatilization of the n- hexane and constant weight of the Oil.

Transesterification Process using NaOH and The MOFs As Catalyst

The ratio used was 1:3, that is 30.0 ml of the oil and 90.0 ml of ethanol followed by 0.5 g of the produced MOF material (as catalyst) as well as the inorganic sodium hydroxide catalyst. Though poorly soluble in water and in alcohol, the MOFs as well as the sodium hydroxide were carefully mixed with ethanol in a separate clean beaker before transferring into its individual conical flask containing the oil that has been heated slightly and stirred for 1 h at 60 ^{o}C using a magnetic stirrer. the mixtures were subsequently left in a cupboard for 24 h for complete reaction and formation of product(s).

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Biodiesel Analysis

The flash point, viscosity, pour point as well as the cloud point of the produced biodiesel were measured.

RESULTS AND DISCUSSION

Characterization

1. **Melting point determination**

   The melting points of the synthesized MOFs were evaluated and it was observed to be high exceeding 360 °C

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2. **X- ray Diffraction (XRD) Analysis**

   The result of the characterization of the MOF materials (XRD) analysis are presented in figures 1.2, 1.3 and 1.4 respectively. Figure 1.2 shows peak for copper-based MOF. There are lots of sharp peaks starting from 10 2θ which could be attributed to its crystalline nature. Figures 1.3 and 1.4 are those for iron and chromium respectively, the peaks are broad at 10 2θ with few sharp peaks at 20 2θ and 30 2θ.

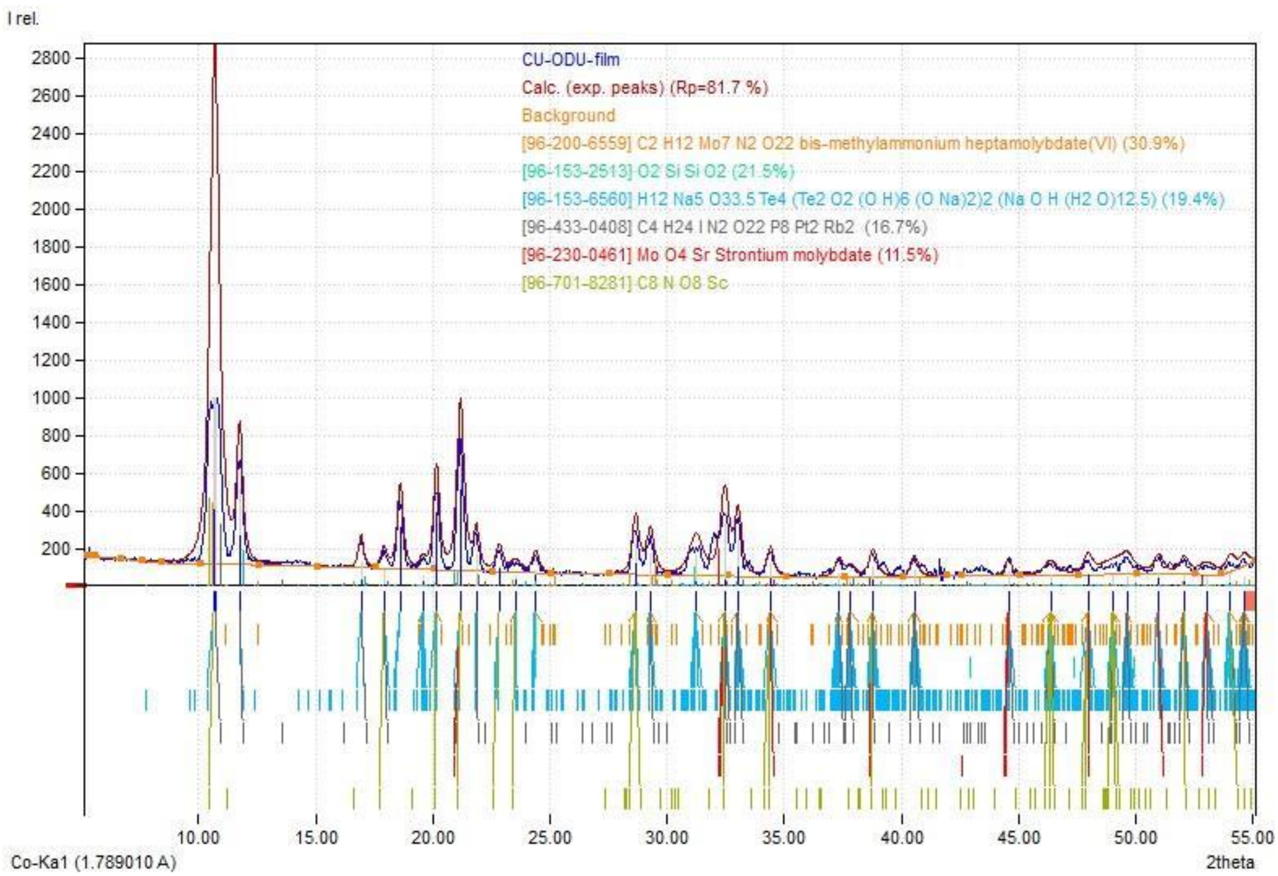

Figure 1.2 XRD Pattern of the Cu-MOF

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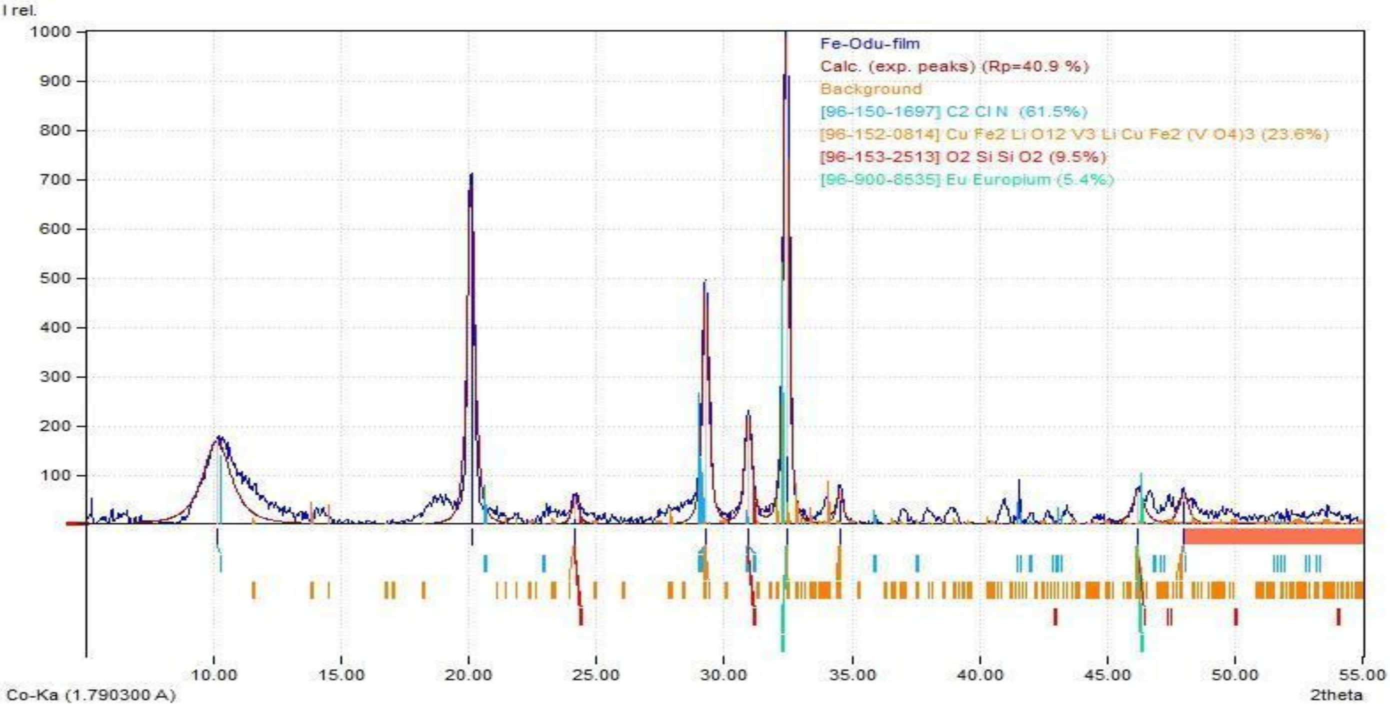

Figure 1.3 XRD Pattern of Fe-Based MOF

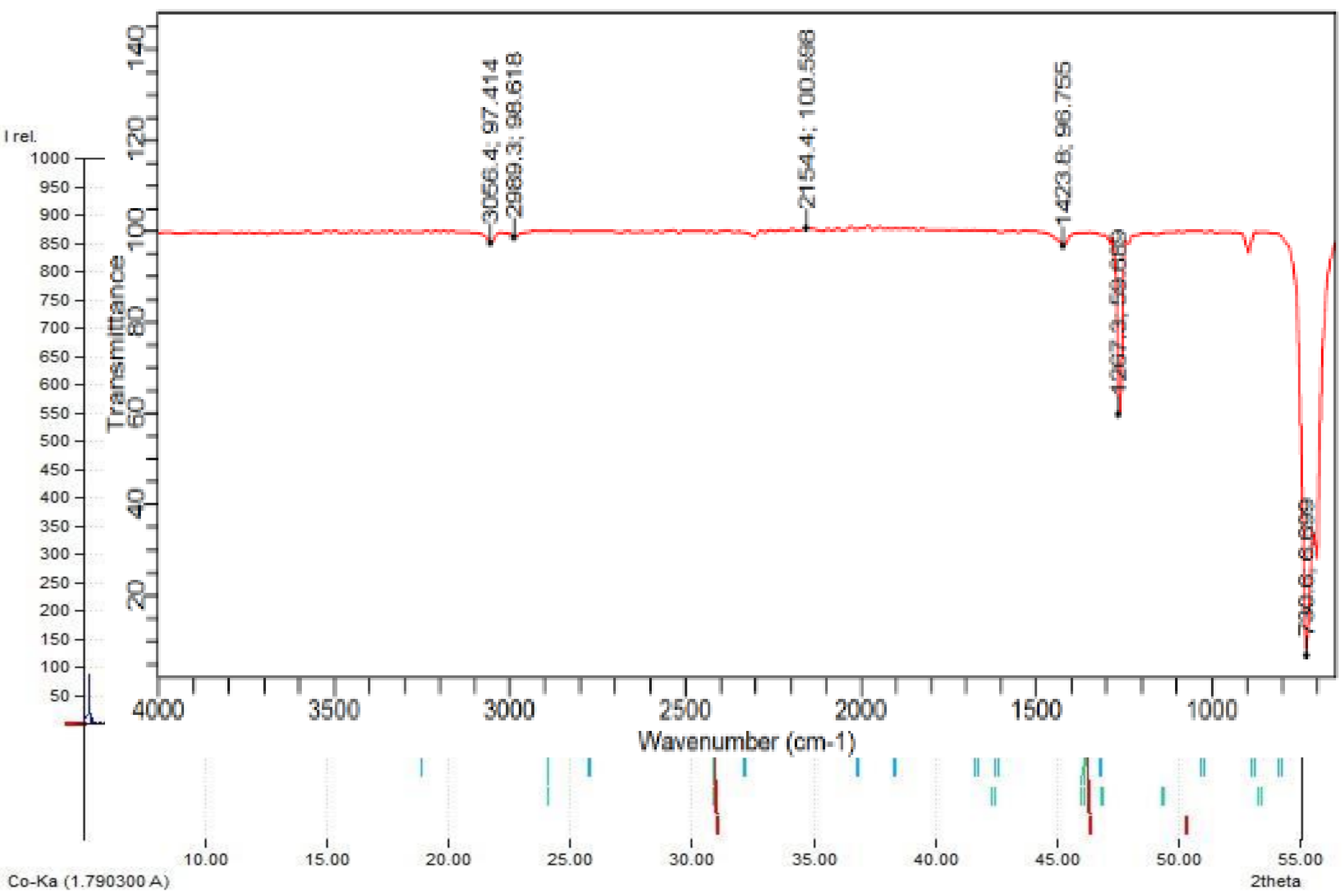

Figure 1.4 XRD pattern of Cr-Based MOF

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IR Analysis

Figures 1.5, 1.6, 1.7 and 1.8 respectively shows the FT- IR spectrum of Cu-, Fe-, Cr-MOFs as well as that of the pure ligand.

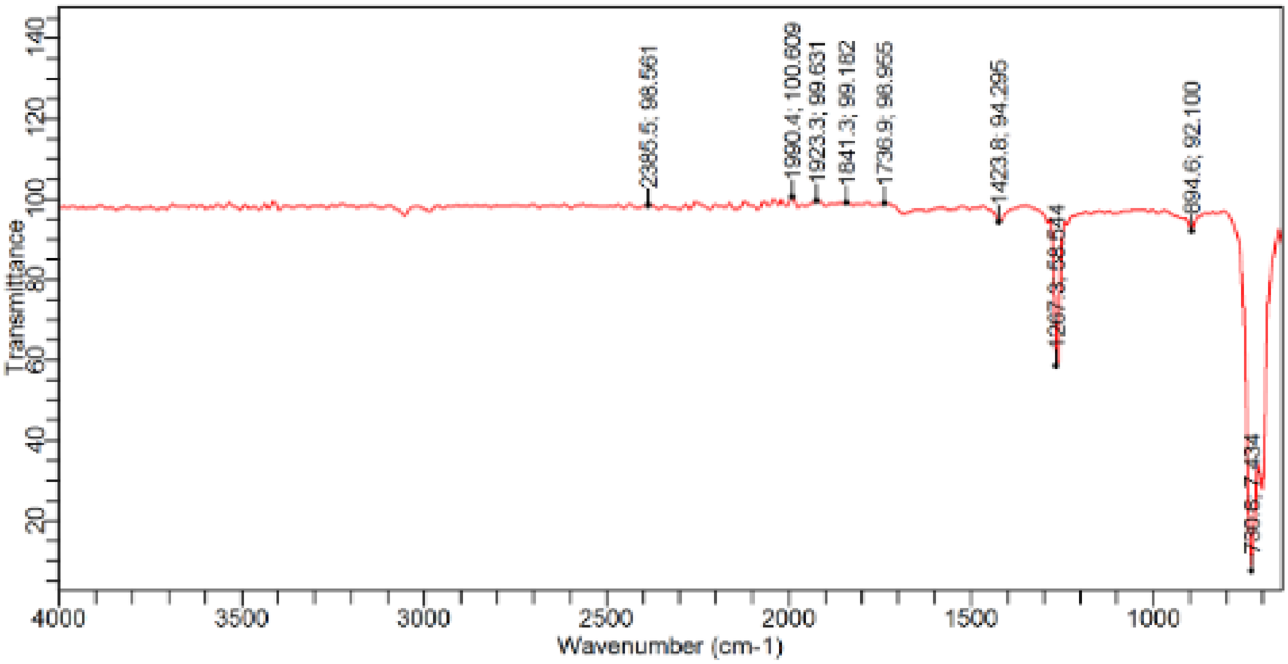

Figure 1.5 FT- IR Spectrum of Fe-Based MOF

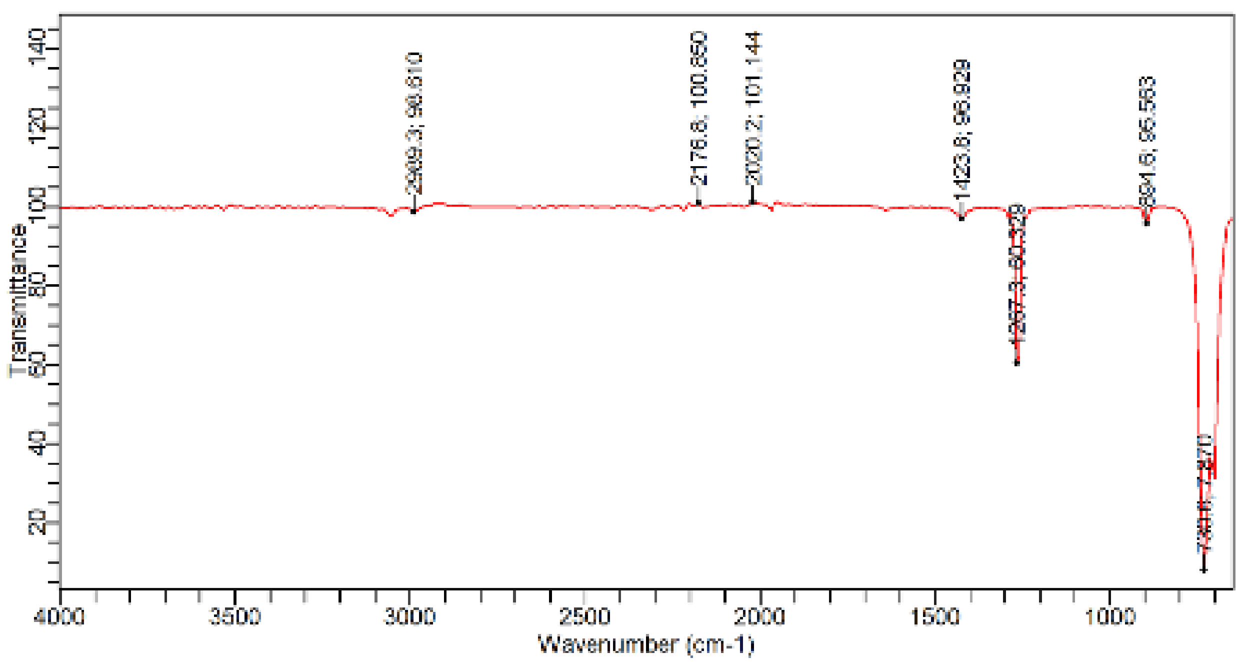

Figure 1 .6 FT- IR Spectrum of Cr-Based MOF

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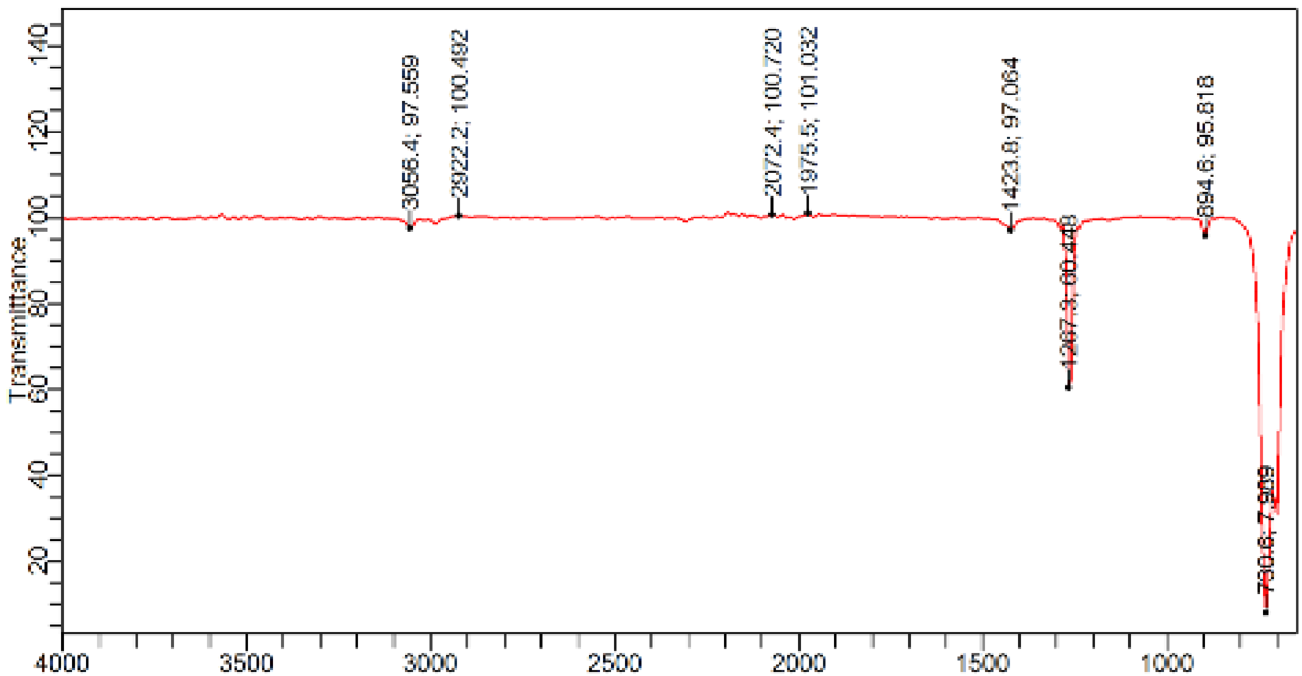

Figure 1.7 FT- IR Spectrum of the Pure Ligand

Result on Biodiesel Produced

Table 1.1: Percentage Yield of Biodiesel Produced

S/No.	MOF	Percentage yield (%)
1	NaOH	87.50
2	Cu-MOF	83.33
3	Fe-MOF	33.33
4	Cr-MOF	25.00

Table 1.1 shows the percentage yield of the produced biodiesel catalyzed by NaOH as well as the Cu, Fe and Cr-MOFs.

Physicochemical properties of the Produced Biodiesel

The methyl esters (Biodiesel) obtained from the oil of the non-edible yellow oleander seed via the transesterification process catalyzed by the inorganic sodium hydroxide and the synthesized MOFs were analyzed for Biodiesel related

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properties and compared with ASTM standard as shown on table 1.2

Table 1.2: Physicochemical Properties of Biodiesel Produced

Biodiesel Parameter	Experimental Values				ASTM Standard
	NaOH Catalyst	Cu-MOF	Fe-MOF	Cr-MOF	
Density (g/cm^3)	0.840	0.820	0.830	0.834	0.820 – 0.845
Viscosity (cSt)	4.5	4.3	4.4	4.4	1.9 – 6.0
Flash point (^{o}C)	100	80	90	100	60- 190
Pour point (^{o}C)	Below 0	Below 0	Below 0	Below 0	-5 – 10
Cloud point (^{o}C)	Below 0	8	Below 0	Below 0	-3 – 15
Volume (ml)	105	100	40	30	Ns
Percentage yield (%)	87.50	83.33	33.33	25.00	Ns

Ns = Not stated

DISCUSSION

MOFs materials are known to have high melting points and are thermally stable [12] which agrees with the high melting points exceeding 360 ^{o}C observed. The numerous sharp peaks observed in the powder X- ray diffraction pattern of the Cu-based MOF indicates its high crystallinity; broad peaks usually indicate non- crystallinity or amorphous [5]. Powder X-ray Diffraction is sometime used for the characterization of MOFs, mostly when the crystals are extremely small or when there is difficulty obtaining single-crystal X-ray diffraction for proper identification of the crystal structure. The powder X-ray diffraction patterns could be used to tell how crystalline the MOFs (since sharp diffraction peaks are indicates how crystalline the bulk MOFs material is) and could be used to establish unit cell parameters and determination of the bulk crystallinity after de-solvation. Powder patterns can thus be used to predict the single crystal structure and compared

with that of the experimental powder patterns or through the use of computational modelling [6] to ascertain the true crystal structure of the MOFs materials.

The IR of the product (Fig 1.6) shows an OH stretch at 3056 cm^{-1}, a CO asymmetric stretch at 1631cm^{-1}, CO symmetric stretch at 1511 cm^{-1} and aromatic C=C peak at 1423 cm^{-1}. A comparison of the spectra of the ligand (Fig 1.7) and that of the products confirmed the presence of the ligand in the product implying the incorporation of the ligand in the synthesized MOF.

Without the catalyst, the transesterification and subsequent production of biodiesel was not

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achieved which agrees with the fact that the reaction will be feasible when a catalyst is present [9]. Thus, using NaOH as catalyst as well as the more crystalline copper-based MOF resulted in high yield of products (87.50% and 83.33% respectively) and in a shorter time compared to when the less crystalline or amorphous Fe-based (33.33%) and Cr-based (25%) MOFs were used which could be attributed to the crystalline nature or surface area of the later [9].

Conclusion

In this study, three MOFs (that is copper, iron and Chromium metal- based MOFs) were synthesized and characterized. The result was in close agreement with previous studies. Also, the synthesized MOFs were used as catalyst for the production of Biodiesel, using ethanol and oil extracted from yellow oleander seed.

The produced biodiesel was compared with ASTM standards and were in close agreement. Also, the catalytic ability of the three synthesized MOFs were compared and it was observed to be in the order: Cu-based MOF > Fe-based > Cr-based MOF. Hence biodiesel that is economically and environmentally viable can be produced using the oil from yellow oleander seed and MOFs especially those of the more crystalline Cu-based MOF which gave higher yield as catalyst replacing the corrosive acid-base catalyst via the transesterification process. It is therefore recommended that Further study and characterization should be done especially single X-ray diffraction for proper identification and elucidation of the crystal structure of the synthesized MOFs.

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