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Synthesis of Cu-1,4-Benzene Dicarboxylate Metal-Organic Frameworks (Cu-BDC MOFs) from Plastic Waste and Its Application as Catalyst in Biodiesel Production

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Abstract

The increasing of PET plastic waste causes various environmental problems because decomposing it is difficult to compose. This study aims to utilize PET plastic waste as a source of terephthalic acid organic linker in the solvothermal synthesis of Cu-1,4-Benzene Dicarboxylate metal-organic frameworks (Cu-BDC MOFs). Cu-BDC MOFs were characterized using FTIR, XRD, and SEM-EDX. The characterization results showed that the crystals of Cu-BDC MOFs had an irregular cubic morphology with an average crystal size of 67.96 nm. Furthermore, Cu-BDC MOFs were applied as catalysts for the esterification reaction to produce biodiesel from coconut oil. The conversion percentage of free fatty acids in the esterification process was 43.75 %, while in the transesterification process, it was 68.90 %. Analysis using GC-MS showed the presence of 8 peaks, with the largest percentage of areas identified as fatty acid methyl esters. The major components were methyl laurate (31.17 %), methyl myristate (18.77 %), methyl palmitate (12.50 %), methyl caprylate (10.76 %), methyl elaidate (10.07 %), methyl caprate (7.34 %), methyl stearate (5.67 %), and methyl linoleate (2.26 %). The quality of the biodiesel was tested, and the results were as follows: The density parameter was measured at 842.5 kg/m^3, the viscosity measurement showed 2.9572 cSt, and the water content was found to be 0.09 %. Additionally, the acid number parameter was determined to be 0.2799 mg-KOH/g.

Keywords: Cu-BDC MOFs, Biodiesel, Plastic, Catalyst, Esterification, Transesterification, PET, Solvothermal

Introduction

The increase in energy consumption, accompanied by population growth, has raised urgent global concerns about the sustainability of fuel reserves and environmental problems, including climate change. The development systems in both developed and developing countries are based on the use of fossil fuels. The depletion of oil reserves and global warming are the main factors driving the development of renewable energy sources that are more environmentally friendly. Biodiesel is a type of renewable fuel sourced from vegetable oils and animal fats. It is produced by transesterifying triglycerides with methanol and a catalyst. Biodiesel is considered an environmentally friendly renewable fuel because it emits relatively low quantities of CO_2, SOx, and hydrocarbons into the air [1-4]. Biodiesel can be produced by reacting vegetable or animal oils with alcohol, assisted by a catalyst.

Efforts to produce biodiesel that can compete with the price of diesel oil derived from fossil fuels continue to be pursued, one of which involves modifying the catalyst. The use of catalysts in the esterification and transesterification reactions in biodiesel production has a significant impact on the reaction rate. In its development, porous materials have been utilized to facilitate the rapid transport of mass and electrons for energy storage and conversion [5]. One of the catalysts that shows potential for biodiesel production is Metal-Organic Frameworks (MOFs), which are porous materials. MOFs have been intensively studied and developed for various applications, particularly in the field of renewable energy. They are composed of a framework structure built from various metals or metal clusters connected by organic linkers, forming porous coordination polymers. The unique porosity and surface area of MOFs provide active sites that play a crucial role in their catalytic activity [5-8]. Polyethylene terephthalate (PET or PETE) can be used as a raw material for synthesizing MOFs. PET is a synthetic molecule that belongs to the polyester polymer family. It is known for its strength and rigidity [9-10]. The abundance of PET-

based waste makes it a viable source for obtaining organic linkers, such as terephthalic acid (BDC), through the depolymerization process [11,12].

On the other hand, utilizing plastic waste as a source of PET is highly promising due to the ongoing challenge of recycling plastic waste in society. Currently, only ten percent of all plastic produced is processed for recycling, excluding the portion that is incinerated [13-14]. The difficulty in plastic recycling arises from the extensive variability in plastic composition and its widespread distribution across the environment. For instance, it has been observed that 10 percent of the plastic bottles produced to date consist of non-biodegradable PET polymer [15,16]. Downstream products derived from the recycling processes of PET are economically less viable. This condition makes the process (whether through physical or chemical treatment) less attractive compared to using pure and cheaper PET. Additionally, PET recycling still poses various environmental challenges due to the contaminants generated during the process [17,18].

To date, several materials have been successfully produced using commercially available PET as a raw material through depolymerization reactions. The depolymerization process yields organic ligands, such as terephthalic acid, which can be used to construct various Metal-Organic Frameworks (MOFs), including Zn-MOFs [19], Zr-MOFs [20], and Cr-MOFs [21], with high purity. Furthermore, Cu-1,4-benzene dicarboxylate (Cu-BDC) is another type of MOF that has been extensively researched and developed. Cu-BDC MOFs consist of copper metal and the organic linker H_2BDC, which is derived from terephthalic acid. In recent years, various modifications to Cu-BDC have been explored, and they have found applications as catalysts in diverse chemical reactions.

Based on this background, a study on the utilization of PET obtained from plastic waste in the Maluku Islands, Indonesia as a source of the BDC organic linker, which functions as a precursor in Cu-MOF synthesis, has never been conducted. The utilization of the plastic waste is also an effort to assist the Maluku government in reducing the increasing amount of plastic waste in the Maluku Islands every year. Furthermore, a study to explore the use of Cu-BDC MOFs as a catalyst in biodiesel synthesis has not been published to date. Therefore, the synthesis study of organic BDC from PET derived from plastic waste as a precursor in Cu-MOF synthesis and its application as a catalyst in biodiesel synthesis using coconut oil in this research is a novel investigation.

Materials and methods

Materials

The materials to be used are distilled water, PET plastic waste, ethanol (C_2H_5OH) p.a (Merck), sodium hydroxide (NaOH) p.a (Merck), hydrochloric acid (HCl) p.a (Merck), copper sulfate pentahydrate ($CuSO_4.5H_2O$) p.a (Merck), methanol p.a (Smartlab), DMF p.a (Merck), coconut oil, potassium hydroxide (KOH) p.a (Merck), anhydrous sodium sulfate (Na_2SO_4) (Merck). The tools used are a set of glassware (Pyrex), hot plate stirrer (Cimarec 2), analytical Scales (Denver Instrument XP-3000), spatula, stirring Rod, Burette, glass funnel, Stative, filter paper, oven (Shel Lab), microwave reactor (Electrolux), separatory Funnel (Pyrex), FTIR (Nicolet Avatar 360 IR), X-Ray Diffractometer (Bruker D2 Phaser), SEM-EDX (Phenom Desktop ProXL), GC-MS Spectrometer (QP-2010 UltraShimadzu).

Synthesis and characterization of terephthalic acid

The PET plastic is first washed using distilled water and then cut into smaller pieces, approximately 0.5×0.5 cm^2 in size. A solution of NaOH, with a concentration of 100 % (w/v), is added to the PET plastic. The mixture is heated to 100 °C and stirred until it dries, resulting in the formation of a white solid. This solid is then dissolved in 100 mL of distilled water and filtered. The filtrate is combined with 100 mL of 6 N HCl, which leads to the formation of a white precipitate. The mixture is cooled for 30 min in an ice bath. The precipitate is subsequently dried at 100 °C for 6 h to obtain solid terephthalic acid. To characterize the obtained terephthalic acid or benzene-1,4-dicarboxylic acid, FTIR (Fourier Transform Infrared) instruments are used to determine the functional groups present. The results of the FTIR analysis are then compared with reference data for terephthalic acid.

Synthesis and characterization of Cu-BDC MOFs

The solution of pentahydrate copper sulfate and the solution of benzene-1,4-dicarboxylic acid were combined in a Schott Duran bottle and stirred using a stirrer. The mixture was then heated at 85 °C for 24 h. After the heating process, the mixture was allowed to cool down to room temperature and left undisturbed for 2 days. Subsequently, the mixture was filtered to obtain the synthesized Cu-BDC MOFs solids. The obtained Cu-BDC MOFs solid, which appears turquoise in color, was then washed using distilled water and DMF. Afterwards, it was washed again using warm methanol at a temperature of 60 - 65 °C and left at

room temperature for 2 days. Finally, the MOFs solids were dried at 100 °C for 24 h and weighed. Characterization of the Cu-BDC MOFs was carried out using FTIR (Fourier Transform Infrared), XRD (X-Ray Diffraction), and SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-Ray) instruments.

Esterification reaction

The esterification reaction of coconut oil using Cu-BDC MOFs as a catalyst was carried out with a mole ratio of coconut oil to methanol of 1:6. Assuming the molecular weight of coconut oil is 713.31 g/mol, the catalyst used was 1 % of the weight of coconut oil. Prior to the reaction, the catalyst was activated by heating it at a temperature of 100 °C for 1 h. In the next step, the activated catalyst and methanol were added to a modified microwave reactor equipped with a stirrer, and the mixture was stirred for 10 min. Subsequently, the coconut oil was added to the reactor. The reaction mixture was then refluxed at a temperature of 60 - 65 °C for 1 h. After the refluxing period, the mixture was filtered. A separatory funnel was used to separate the mixture into 2 layers. The top layer consisted of methyl esters, while the bottom layer contained the triglyceride phase.

Transesterification reaction

The triglycerides obtained from the esterification stage were further reacted with methanol in a mole ratio of 1:9 (oil:methanol) using a 1 % KOH catalyst. The first step involved the reaction of the KOH catalyst with methanol to form a potassium methoxide solution. In the next stage, the methoxide solution and the triglyceride oil were added to the modified microwave reactor, and the mixture was refluxed at a temperature of 60 - 65 °C for 1 h. After the refluxing period, the mixture was cooled down and then separated using a separatory funnel, resulting in 2 layers. The top layer consisted of methyl ester, which is the biodiesel, while the bottom layer contained a mixture of the catalyst and glycerol. The methyl ester (biodiesel) was washed repeatedly using distilled water at 60 - 65 °C until the water layer became clear. This washing step helps to remove any impurities or remaining catalyst. In the final stage, the washed methyl ester was combined with 1.5 g of anhydrous Na_2SO_4 to remove any remaining water. The mixture was then filtered through a Whatman No. 42 filter paper. The resulting biodiesel was weighed to calculate the conversion percentage based on Eq. (1).

$$\text{Conversion (\%)} = \frac{W_{biodiesel}}{W_{oil}} \times 100\% \quad (1)$$

$W_{biodiesel}$ is the weight of biodiesel produced in the experiment (grams). W_{oil} is the weight of coconut oil used in the experiment (grams). The biodiesel product was characterized by FTIR and GC-MS instruments and tested the physical properties.

Results and discussion

Synthesis of terephthalic acid from pet plastic waste

The dried plastic pieces were depolymerized using the hydrolysis method in a 100 % (w/v) NaOH solution. The hydrolysis method was chosen because water can effectively break down the polyester chains of the plastic, resulting in the formation of ethylene glycol and terephthalic acid, which are the monomers. This method is preferred over glycolysis, as glycolysis only converts PET into BHET or bis (2-hydroxyethyl) terephthalate. The yield of terephthalic acid obtained in this hydrolysis process is nearly 100 %, as sodium terephthalate remains unaffected by oxidation. In the hydrolysis process, NaOH is used as it provides hydroxide ions that act as nucleophiles in the addition process to the carbonyl group, breaking down the polyester chain into oligomers and subsequently into monomers [22]. The estimated mechanism of the PET hydrolysis reaction under alkaline conditions is illustrated in **Figure 1**. Subsequently, the mixture is heated to 100 °C. The elevated temperature in the depolymerization process increases the kinetic energy of the polymer particles, thereby accelerating the rate at which polymers break down into monomers [23].

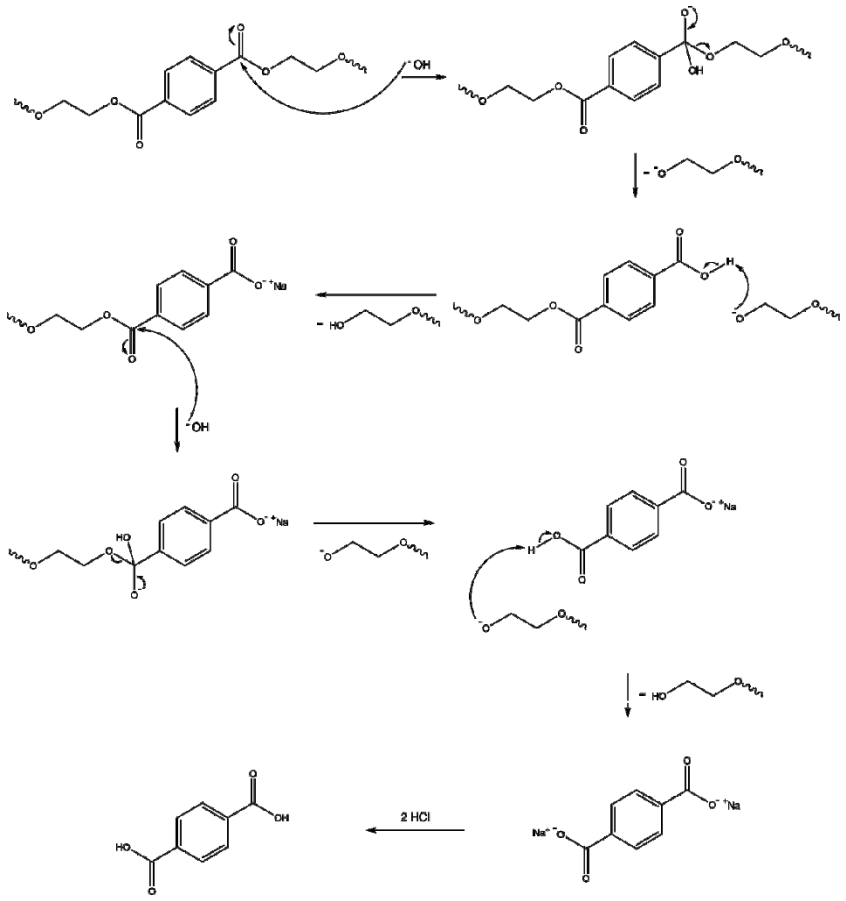


Figure 1 The approximate mechanism of PET hydrolysis reaction in alkaline conditions.

The white precipitate was dissolved in water to separate the sodium terephthalate product from other monomers and oligomers present in the liquid phase. The resulting solution was then filtered to separate any remaining unreacted reactants. The filtrate was treated with a 6 N HCl solution, resulting in the formation of a white solid. This step involved acidification, where the Na^+ ions in the sodium terephthalate product were exchanged with H+ ions upon the addition of HCl. [23]. A solid mass of terephthalic acid was obtained with a PET conversion percentage of 86.64 %. The dry solid product is depicted in **Figure 2**. The conversion percentage achieved falls short of 100 % due to the fact that not all PET plastic pieces undergo complete depolymerization into monomers. Instead, some of them are converted into oligomers or simple polymers [22].

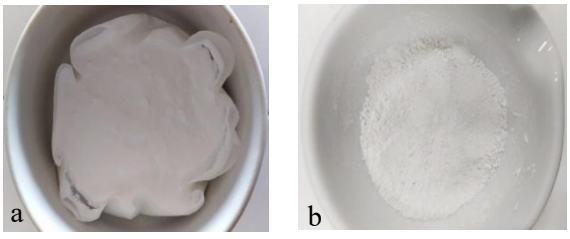


Figure 2 Synthesized terephthalic acid products (a) before drying and (b) after drying.

Characterization of terephthalic acid

The FTIR analysis of the synthesized terephthalic acid solids is depicted in **Figure 3**. The observed absorption bands provide valuable information about the functional groups present in the sample. The absorption band at 3,250 - 2,550 cm^{-1} corresponds to the O-H stretching vibration of the COOH carboxylic acid group. The appearance of an absorption band at 3,066.57 cm^{-1} indicates aromatic C-H stretching vibrations. Additionally, the absorption bands at 2,825.56, 2,667.29 and 2,550.11 cm^{-1} are attributed to

overtones and absorption combinations in the intermolecular environment of carboxylic acids. The absorption band at 1,684.8 cm^{-1} indicates the C=O stretching vibration of the carboxylate group. The presence of aryl (aromatic) groups is supported by the absorption band observed at 1,571.53 - 1,509.2 cm^{-1}, which indicates aromatic C=C stretching vibrations. Furthermore, the absorption band at 1,425.63 cm^{-1} corresponds to the symmetrical stretching vibration of COO- in the carboxylic acid group. This finding is reinforced by the absorption band observed at 1,288.57 cm^{-1}, which indicates a stretching vibration of the C-O bond in the carboxylic acid group [24].

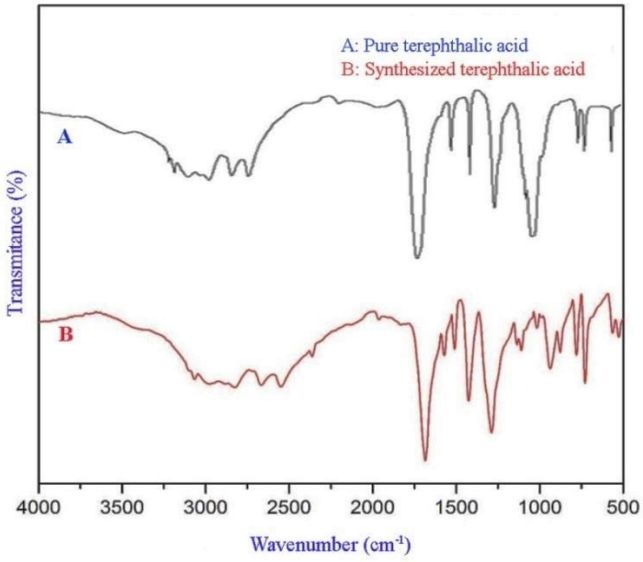


Figure 3 FTIR spectrum of pure terephthalic acid and synthesized terephthalic acid.

The FTIR spectrum of the synthesized terephthalic acid solids was compared to that of pure terephthalic acid. The FTIR spectrum of pure terephthalic acid exhibits a distinct absorption band that corresponds to a specific functional group. Interestingly, this absorption band is also present in the FTIR spectrum of the synthesized product, indicating the presence of terephthalic acid resulting from the hydrolysis of PET plastic waste. The similarity between the absorption bands in the 2 spectra provides strong evidence for the successful formation of terephthalic acid during the hydrolysis process. It confirms that the chemical structure of the synthesized terephthalic acid is consistent with that of pure terephthalic acid. Thus, the comparison of the FTIR spectra supports the conclusion that terephthalic acid has been successfully obtained from the hydrolysis of PET plastic waste.

Synthesis of Cu-BDC MOFs

The synthesis of Cu-BDC MOFs was conducted using the solvothermal method [11], with modifications to the heating treatment [25]. The pentahydrate copper sulfate is dissolved in water to form a blue solution, which is then further dissolved in DMF and ethanol. DMF is chosen as the solvent because it has the ability to dissolve benzene-1,4-dicarboxylic acid. This allows the ligand to be deprotonated more easily, forming O^- groups that can react with Cu^{2+} metal ions [26]. After the solvothermal process, a turquoise solid is formed, while a greenish filtrate is obtained, as shown in **Figure 4**. The mixture is allowed to stand at room temperature to allow the crystallization process to complete. The turquoise solid obtained is Cu-BDC MOFs, while the greenish filtrate is a result of the presence of DMF trapped within the MOFs crystals. This leads to a color change in the filtrate, giving it a greenish hue [27]. The turquoise blue Cu-BDC MOFs solid is washed using distilled water and DMF to eliminate any residual reactants. Subsequently, the obtained solid is further washed using methanol. Methanol is used to remove any remaining DMF and other impurities that might be trapped within the pores of the Cu-BDC MOFs crystals, while preserving their structural integrity [27]. The obtained MOFs solids were in the form of fine powder with a turquoise color, as depicted in **Figure 5**. The reaction mechanism for the synthesis of Cu-BDC MOFs is illustrated in **Figure 8**.

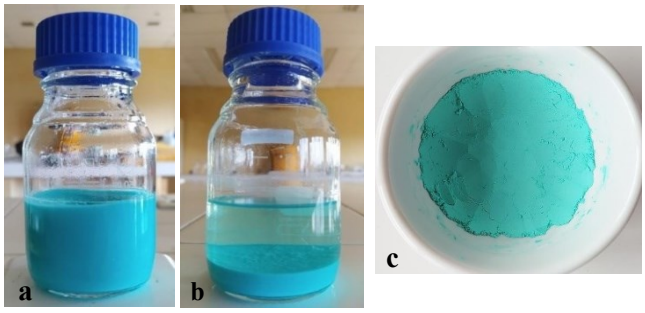


Figure 4 (a) mixture after stirring, (b) after solvothermal treatment, and (c) synthesized Cu-BDC MOFs solids.

Cu-BDC MOFs crystals have a monoclinic crystal system, with a space group C2/m with lattice parameters a = 11.4 Å, b = 14.3 Å, c = 7.8 Å, and β = 108 ° [28]. Visualization of Cu-BDC MOFs crystals based on CCDC-687690 crystallographic data shown in **Figure 6**.

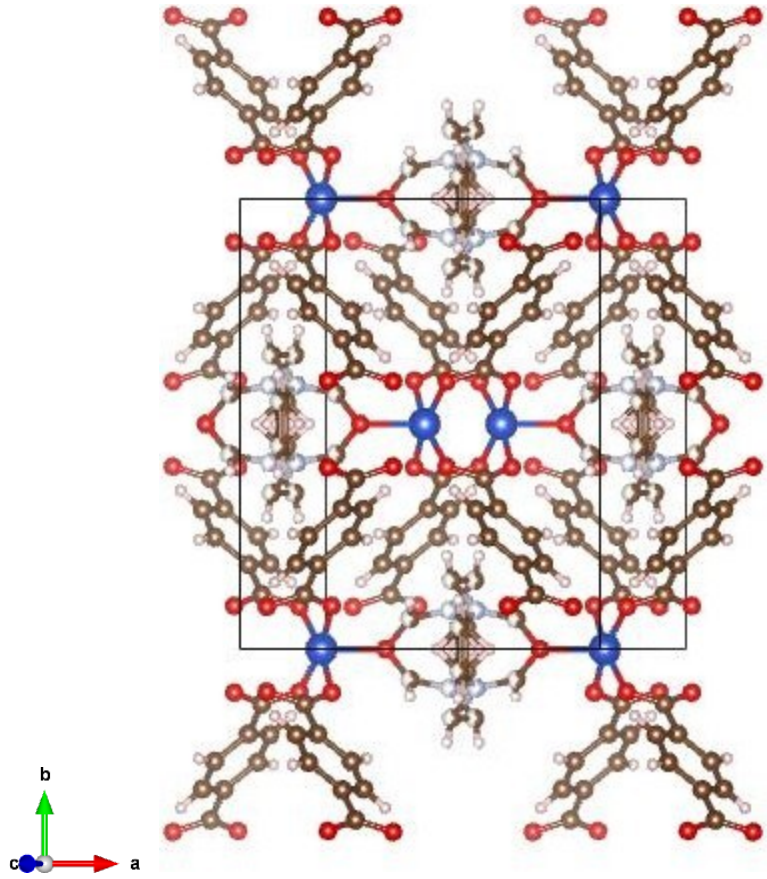


Figure 6 Visualization of Cu-BDC MOFs crystals based on CCDC-687690

Cu-BDC MOFs FTIR analysis results

The absorption band at 3,152.42 cm^{-1} corresponds to the N-H stretching vibration of DMF. This observation is further supported by the absorption at 3,000.842 cm^{-1}, which indicates a C-H stretching vibration. These results indicate that DMF is still present and bound to Cu-BDC. Additionally, the absorption band at 1,673.21 cm^{-1} for Cu-BDC exhibits a lower intensity compared to the absorption band at 1,684.8 cm^{-1} for H_2BDC (**Figure 7**). This difference in intensity can be attributed to the stretching vibration of the C=O group [27].

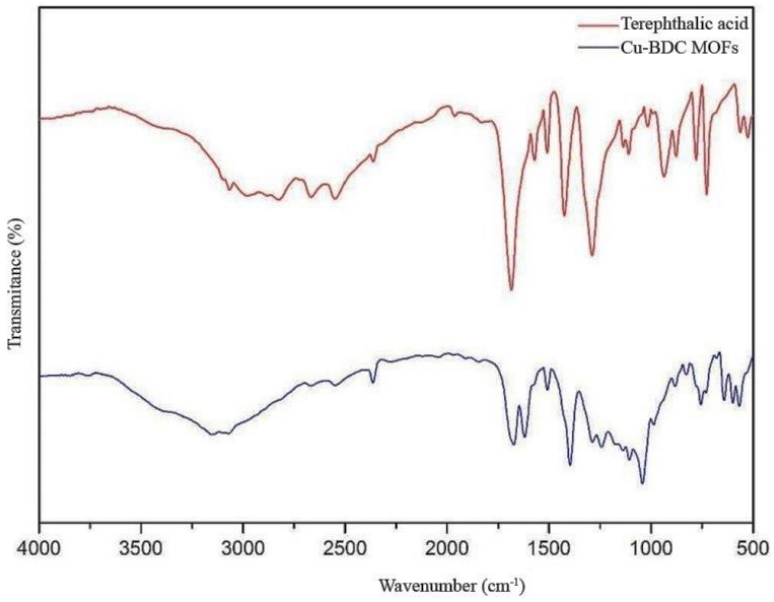


Figure 7 FTIR spectrum of terephthalic acid and Cu-BDC MOFs.

Cu-BDC MOFs XRD analysis result

The characterization results in the form of a diffractogram for Cu-BDC MOFs material are presented in **Figure 9**. The diffractogram of the synthesized Cu-BDC MOFs material reveals several well-defined peaks with sharp intensities. This indicates the high crystallinity of the Cu-BDC MOFs crystals. Moreover, the diffractogram of the synthesized Cu-BDC MOFs material exhibits a prominent peak at 2θ that aligns with the findings of previous studies [30]. In this study, the formation of Cu-BDC MOFs crystals is evidenced by several peaks observed in the diffractogram at 2θ = 10.250 °, 17.241 °, and 24.907 °. To further validate the synthesis, the diffractogram of the synthesized Cu-BDC MOFs material was compared with simulation results obtained from the Cambridge Crystallographic Data Center (CCDC-687690), which provides crystallographic data.

The comparison confirms that the Cu-BDC MOFs crystals possess a space group C2/m, as indicated by the observed peaks at 2θ = 10.250 ° (110), 17.241 ° (021), and 24.907 ° (131). These findings provide strong evidence for the successful synthesis of Cu-BDC MOFs material. The difference in peak intensity observed between the synthesized and simulated diffractograms is attributed to variations in the orientation of the crystallites within the material, as well as the influence of pore filling. The effect of pore filling causes a deviation in the diffraction intensity, resulting in either an increase or decrease, depending on the presence of solvent molecules in the experimental material and the absence of solvent in the simulated material [31]. The crystallographic data of the synthesized Cu-BDC MOFs material are presented in **Table 1**.

Table 1 Crystallographic data of Cu-BDC MOFs.

Diffractogram of Cu-BDC MOFs				
Space group	**2θ (°)**	**hkl index**	**d (Å)**	**Crystal size (nm)**
C2/m (12)	10.25	110	8.62	56.18
	17.24	021	5.14	78.13
	24.91	131	3.57	69.57
		Average crystal size		67.96

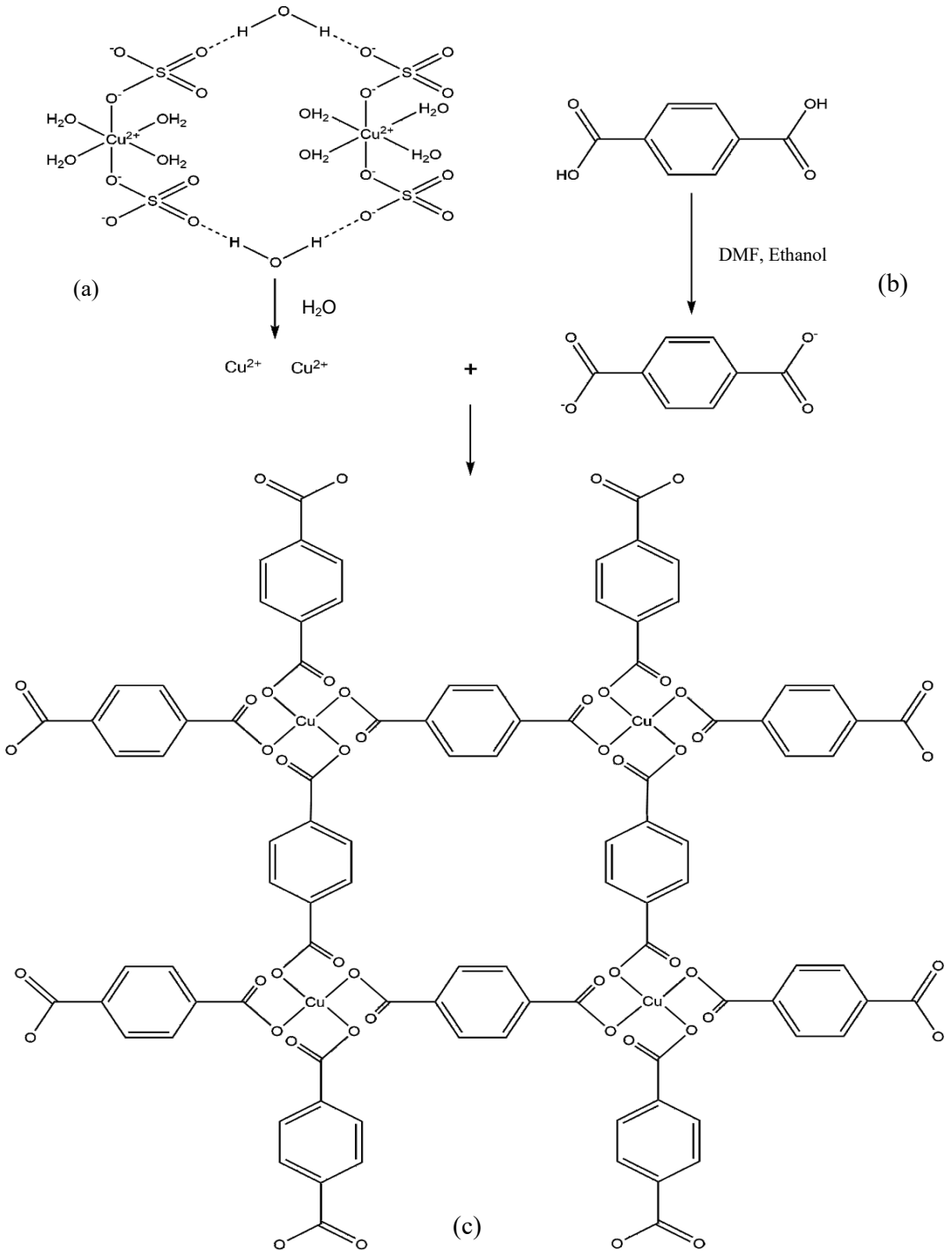


Figure 8 (a) Cu ion dissociation, (b) H2BDC linker deprotonation, and (c) Cu-BDC MOFs.

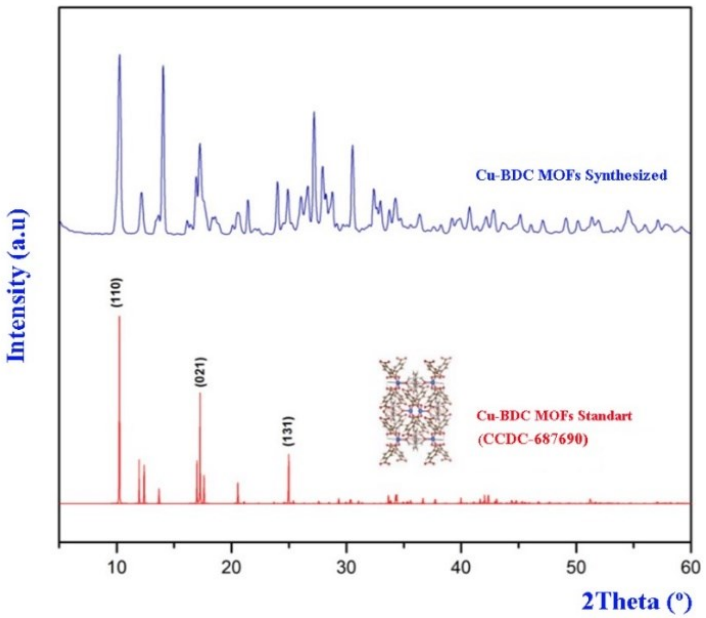
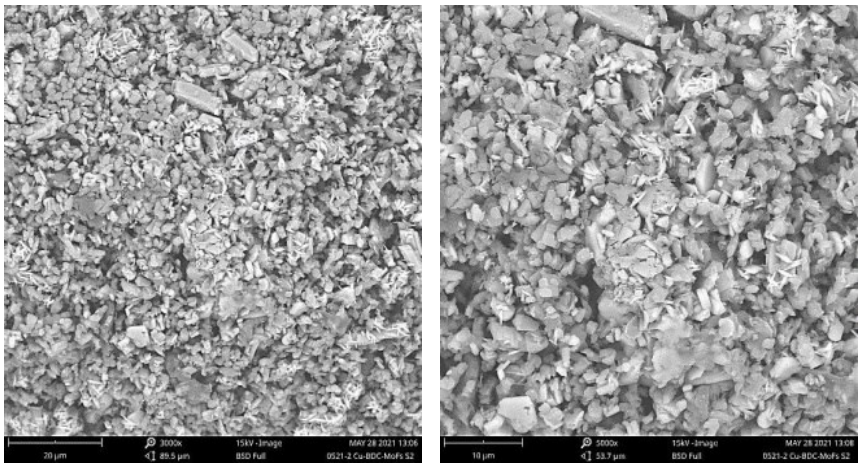


Figure 9 Cu-BDC MOFs diffractogram.

Cu-BDC MOFs SEM-EDX analysis result

The SEM and EDX characterization results, in the form of Cu-BDC MOFs micrographs, are depicted in **Figure 10** and **Figure 11**. Previous research has reported that the Cu-BDC MOFs material does not exhibit a consistent crystal form, including hexahedral shapes [32], cubes [27], stem shapes [29], and rectangular sheets [25]. The SEM micrograph of the synthesized sample reveals the crystal topography of Cu-BDC MOFs, exhibiting clustered structures with irregular shapes. The presence of several particles that aggregate on the surface is attributed to unreacted reactants.



(a) (b)

Figure 10 SEM micrograph of synthesized Cu-BDC MOFs with magnification (a) 3,000x and (b) 5,000x.

When the sample micrographs are magnified, several crystals with significantly larger sizes can be observed. This phenomenon is attributed to the use of N,N-dimethylformamide (DMF) as a solvent, which promotes crystal growth. When DMF is used in a lower ratio, certain crystals tend to grow larger than others, leading to a less uniform crystal distribution. In contrast, the utilization of protic solvents such as water (H_2O) and ethanol in the synthesis process facilitates the coordination of Cu^{2+} ions with H_2BDC ligands. When a protic solvent is used in a higher ratio, the H_2O ligand replaces DMF in coordination with the Cu-BDC complex. This results in a higher number of H_2O molecules bound to Cu-BDC, leading to a non-uniform appearance of the crystals [18].

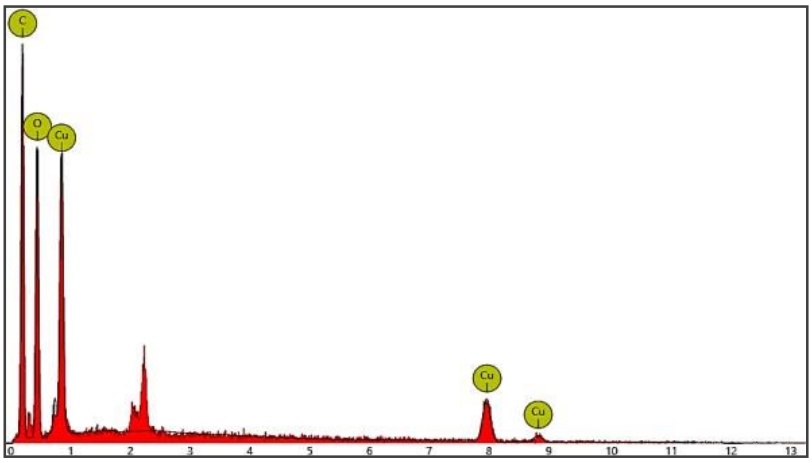


Figure 11 EDX spectrum of synthesized Cu-BDC MOFs.

The EDX analysis was intended to determine the elemental composition of the synthesized Cu-BDC MOFs material. The results of the EDX analysis of the Cu-BDC MOFs material are shown in **Figure 6**. The quantitative EDX analysis results show that the Cu-BDC MOFs material consists of the elements carbon, oxygen, and copper, as shown in **Table 2**. Based on the results of FTIR, XRD, and SEM-EDX analyses, it can be confirmed that the Cu-BDC MOFs material has been successfully synthesized.

Table 2 Results of EDX analysis of Cu-BDC MOFs.

Elements	Weight percentage (%)	Element percentage (%)
Carbon (C)	45.85	64.96
Oxygen (O)	25.81	27.45
Copper (Cu)	28.34	7.59
Total	100	100

Esterification reaction

Esterification is an initial process aimed at reducing the free fatty acid content of oils or triglycerides by converting the free fatty acids from these oils or triglycerides into methyl esters. The catalyst acts as a Lewis acid in the esterification process, using Cu-BDC MOFs. An estimation of the esterification reactionechanism using the Cu-BDC MOFs catalyst is schematically presented in **Figure 12**.

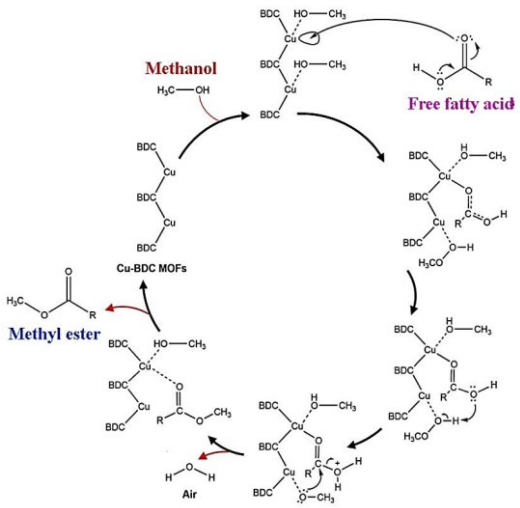


Figure 12 Estimated mechanism of esterification reaction using Cu-BDC MOFs catalyst.

The Cu-BDC MOFs catalyst, comprising up to 1 % of the total oil weight, undergoes a solvent exchange and drying process, followed by thermal activation at 100 °C for 1 h. This treatment aims to eliminate solvent molecules that are still coordinated to the central metal or expose the material to air, thereby enhancing the number of open metal sites (OMS) that serve as Lewis acid sites. The presence of OMS facilitates interactions between the metal sites and reactant molecules, leading to an increase in their catalytic activity [1]. The esterification results of traditional coconut oil demonstrate a conversion percentage of 43.75 %. The notable reduction in the free fatty acid content of coconut oil, from 1.59 to 0.89 %, indicates the catalytic activity of Cu-BDC MOFs. These MOFs act as Lewis acid catalysts in the esterification process of free fatty acids present in coconut oil.

Transesterification reaction

The transesterification process aims to convert triglycerides through reactions with alcohols, resulting in a mixture of fatty acid alkyl esters and glycerol. Based on the obtained results, the conversion percentage of coconut oil into biodiesel using 1 % Cu-BDC MOFs and 1 % KOH catalyst was 68.90 %. This conversion rate can be compared to the research conducted by Jamil *et al.* [25], the Cu-BDC catalyst MOFs and KOH provide a conversion rate of 78.3 % for converting used cooking oil into biodiesel. The results show that the Cu-BDC MOFs synthesized from PET plastic waste also have catalytic performance close to that of pure synthesized Cu-MOFs catalysts. These results confirm that PET plastic waste has the potential to be used as a source of the organic linker in the synthesis of Cu-BDC MOFs materials for catalytic applications.

Characterization of biodiesel

The FTIR spectrum of biodiesel is then compared to the FTIR spectrum of coconut oil, as shown in **Figure 13**. Based on the FTIR spectrum of the synthesized biodiesel, the absorption bands appearing at 2,923.42 and 2,854.27 cm^{-1} correspond to C-H stretching vibrations. The presence of the absorption band at 1,741.40 cm^{-1} indicates the C=O stretching vibration of the ester group.

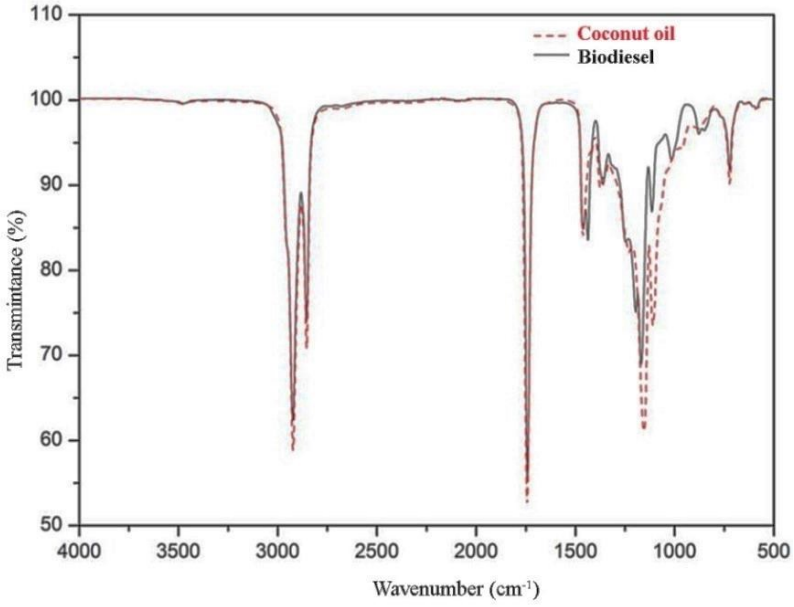


Figure 13 FTIR spectrum of coconut oil and biodiesel.

The appearance of absorption bands at 1,461.44 and 1,436.93 cm^{-1} is associated with the stretching vibration of CH_2. The presence of absorption bands at 1,361.22 cm^{-1} indicates the stretching vibration of $-CH_3$. The presence of ester groups is confirmed by the absorption bands at 1,195.82, 1,168.25 and 1,114.13 cm^{-1}, indicating the stretching vibration of the C-O group. This finding is supported by an absorption band at 1,014 cm^{-1}, which indicates the bending vibration of the C-O bond in the ester group. A comparison of the absorption data between coconut oil and biodiesel is presented in **Table 3**.

Table 3 FTIR spectrum results for traditional coconut oil and biodiesel.

Functional group	Wavenumber (cm^{-1})	
	Coconut oil	Biodiesel
Stretching C-H	2,922.54	2,923.42
Stretching C-H	2,853.78	2,854.27
Stretching C=O	1,743.04	1,741.40
Stretching CH_2	1,461.44	1,461.44; 1,436.93
Stretching CH_3	1,375.77	1,361.22
Stretching C-O	1,155.31	1,195.82; 1,168.25; 1,114.13
Bending C-O	1,109.55	1,014
Bending C-H	722.30	876.57; 722.81

The FTIR spectrum of the synthesized biodiesel was then compared with the FTIR spectrum of traditional coconut oil acids. The results of the FTIR analysis showed that the absorption in the range of 4,000 - 1,500 cm^{-1} for coconut oil and biodiesel corresponded, although with a decrease in the absorption intensity in the synthesized biodiesel. The appearance of new absorption peaks at 1,436.93 cm^{-1} ($-CH_2$), 1,195.82 cm^{-1} (C-O), 1,114.13 cm^{-1} (C-O), and 876.57 cm^{-1} (C-H) in the biodiesel spectrum indicates the conversion of traditional coconut oil into biodiesel.

Biodiesel GC-MS analysis results

Based on its mass spectrum data, GC-MS analysis of biodiesel aims to identify the types of methyl esters that constitute biodiesel. The chromatogram of the synthesized biodiesel is depicted in **Figure 14**. The methyl ester content in biodiesel can be separated based on the polarity of each compound, with shorter carbon chain esters being more polar than those with longer carbon chains. The GC-MS chromatogram of biodiesel revealed the presence of 22 peaks, out of which 20 peaks were identified as fatty acid methyl esters, as shown in **Table 4**.

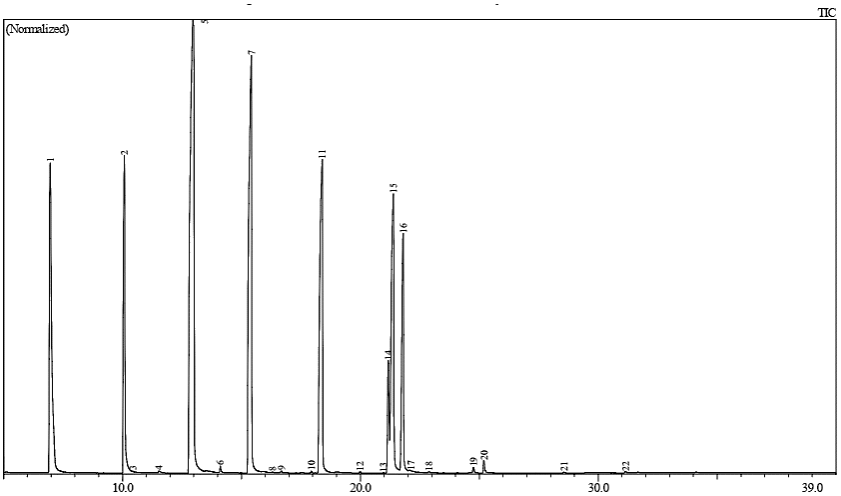


Figure 14 Chromatogram of methyl ester (biodiesel) from traditional coconut oil.

Based on the results of the biodiesel chromatogram, there were 8 peaks with the largest percentage area. The first peak corresponds to methyl caprylate ($C_9H_{18}O_2$) with a percentage area of 11.40 % and m/z = 158. The second peak represents methyl caprate ($C_{11}H_{22}O_2$) with a percentage area of 7.51 % and m/z = 186. The fifth peak corresponds to methyl laurate ($C_{13}H_{26}O_2$) with a percentage area of 28.14 % and m/z = 214. The 7 peak corresponds to methyl myristate ($C_{15}H_{30}O_2$) with a percentage area of 18.12 % and m/z =

242. The eleventh peak represents methyl palmitate ($C_{17}H_{34}O_2$) with a percentage area of 13.45 % and m/z = 270. The 14 peak corresponds to methyl linoleate ($C_{19}H_{34}O_2$) with a percentage area of 2.76 % and m/z = 294. The fifteenth peak represents methyl elaidate ($C_{19}H_{36}O_2$) with a percentage area of 11.10 % and m/z = 264. Finally, the 16 peak corresponds to methyl stearate ($C_{19}H_{38}O_2$) with a percentage area of 6.69 % and m/z = 298. It is worth noting that diesel fuel typically contains carbon atoms ranging from C-12 to C-20 [1,2]. Based on the separated biodiesel fraction, methyl caprylate, methyl caprate, and methyl undecanoate are classified as gasoline fuel (biogasoline) with a total percentage of 18.98 % because they contain less than twelve carbon atoms. Methyl laurate, methyl tridecanoate, methyl myristate, methyl 5-octadecanoate, methyl pentadecanoate, methyl palmitoleate, methyl palmitate, methyl margarate, methyl 5-oxotridecanoate, methyl linoleate, methyl elaidate, methyl stearate, methyl linoleate, methyl 9,11-octadecanoate, methyl 11-eikosanoate, methyl arachidonate, and methyl behenate are classified as diesel fuel (biodiesel) with a total percentage of 80.98 % because they contain more than twelve carbon atoms.

Table 4 Results of the GC-MS analysis of biodiesel.

Peak number	Retention time (minute)	% Peak area	Molecular formula	Compound
1	6.964	11.40	$C_9H_{18}O_2$	Methyl caprylate
2	10.081	7.51	$C_{11}H_{22}O_2$	Methyl caprate
4	11.539	0.07	$C_{12}H_{24}O_2$	Methyl undecanoate
5	12.958	28.14	$C_{13}H_{26}O_2$	Methyl laurate
6	14.110	0.11	$C_{14}H_{28}O_2$	Methyl tridecanoate
7	15.415	18.12	$C_{15}H_{30}O_2$	Methyl myristate
8	16.309	0.01	$C_{19}H_{36}O_2$	Methyl 5-octadecanoate
9	16.678	0.03	$C_{16}H_{32}O_2$	Methyl pentadecanoate
10	17.942	0.03	$C_{17}H_{32}O_2$	Methyl palmitoleate
11	18.396	13.45	$C_{17}H_{34}O_2$	Methyl palmitate
12	19.992	0.03	$C_{18}H_{36}O_2$	Methyl margarate
13	20.967	0.01	$C_{14}H_{26}O_3$	Methyl 5-oxotridecanoate
14	21.176	2.76	$C_{19}H_{34}O_2$	Methyl linoleate
15	21.386	11.10	$C_{19}H_{36}O_2$	Methyl elaidate
16	21.797	6.69	$C_{19}H_{38}O_2$	Methyl stearate
17	22.125	0.06	$C_{19}H_{34}O_2$	Methyl linoleate
18	22.888	0.03	$C_{19}H_{34}O_2$	Methyl 9,11-octadekadienoate
19	24.756	0.12	$C_{21}H_{40}O_2$	Methyl 11-eicosanoate
20	25.195	0.26	$C_{21}H_{42}O_2$	Methyl arachidate
21	28.559	0.03	$C_{23}H_{46}O_2$	Methyl behenate

Results of biodiesel quality analysis

The results of the biodiesel quality analysis are presented in **Table 5**. The density parameter yielded a value of 842.5 kg/m^3, the viscosity measurement for biodiesel showed a value of 2.9572 cSt, and the water content was determined to be 0.09 %. On the other hand, the acid number parameter resulted in a value of 0.2799 mg-KOH/g. The density, viscosity, and acid number parameters meet the American Society for Testing and Materials (ASTM) and Indonesian National Standard (INS). However, the water content parameter test yielded results that exceeded the established standards. This outcome is likely due to the presence of water content during the biodiesel washing process.

Table 5 Results of biodiesel quality analysis.

Test	Unit	Test result	ASTM	INS
Density	kg/m^3	842.5	820 - 860	820 - 860
Viscosity	cSt	2.9572	2 - 4.5	2.3 - 6
Water content	% mass	0.09	0.05 (Max.)	0.05 (Max.)
Acid value	mg-KOH/g	0.2799	0.5 (Max.)	0.8 (Max.)

Conclusions

Cu-BDC MOFs are produced through the hydrolysis of PET waste using a solvothermal mixture of distilled water, ethanol, and DMF at 85 °C for 24 h. The FTIR spectra of the synthesized Cu-BDC MOFs solids exhibit typical absorption peaks for the C=O, C=C, COO-, C-O, and Cu-O functional groups. The results of the XRD analysis demonstrate the presence of characteristic peaks, confirming the formation of Cu-BDC MOFs. The micrograph of the synthesized Cu-BDC MOFs samples, based on SEM analysis, reveals a clustered topography of Cu-BDC MOFs crystals with irregular cubic (hexahedral) shapes. The results of the EDX analysis confirm the presence of C, O, and Cu, which are the major constituents of the Cu-BDC MOFs material. FTIR analysis of biodiesel displays distinctive peaks corresponding to the -C-H, -C=O, $-CH_2$, $-CH_3$, and -C-O functional groups. The GC-MS analysis of biodiesel from coconut oil shows the presence of 8 major peaks, namely methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, methyl linoleate, methyl elaidate, and methyl stearate, with the largest percent area. The conversion percentage of free fatty acids in the esterification process is 43.75 %, while the conversion percentage of traditional coconut oil to biodiesel in the transesterification process is 68.90 %. The quality test results of biodiesel indicate a density parameter of 842.5 kg/m^3, a biodiesel viscosity measurement of 2.9572 cSt, a water content of 0.0898 % and an acid number of 0.2799 mg-KOH/g.

References

[1] IW Sutapa, Sarti, C Putnarubun, AB Kamari and A Bandjar. Biodiesel production using Calophyllum inophyllum L. oil and CaO as catalyst in the microwave assisted reactor. *AIP Conf. Proc.* 2023; **2642**, 040001.

[2] IW Sutapa, DA Kasmanto, Rosmawaty and MF Maahury. Biodiesel cracking process from beef tallow using catalyst bentonite intercalated $NiCl_2$. *AIP Conf. Proc.* 2021; **2360**, 050041.

[3] Z Fang. *Biodiesel - feedstocks, production and applications*. IntechOpen, London, 2012.

[4] N Hamidi and J Nugroho. Single droplet combustion characteristics of petroleum diesel- philippine tung biodiesel blends. *Trends Sci.* 2021; **18**, 1409.

[5] X Liu, L Zhang and J Wang. Design strategies for MOF-derived porous functional materials: Preserving surfaces and nurturing pores. *J. Materiomics* 2021; **7**, 440-59.

[6] MH Yap, KL Fow and GZ Chen. Synthesis and applications of MOF-derived porous nanostructures. *Green Energ. Environ.* 2017; **2**, 218-45.

[7] H Wang, QL Zhu, R Zou and Q Xu. Metal-organic frameworks for energy applications. *Chem* 2017; **2**, 52-80.

[8] P Silva, SMF Vilela, JPC Tomé and FAA Paz. Multifunctional metal-organic frameworks: From academia to industrial applications. *Chem. Soc. Rev.* 2015; **44**, 6774-803.

[9] H Furukawa, KE Cordova, M O'Keeffe and OM Yaghi. The chemistry and applications of metal-organic frameworks. *Science.* 2013; **341**, 1230444.

[10] OK Akeremale, OT Ore, AA Bayode, H Badamasi, JA Olusola and SS Durodola. Synthesis, characterization, and activation of metal organic frameworks (MOFs) for the removal of emerging organic contaminants through the adsorption-oriented process: A review. *Results Chem.* 2023; **5**, 100866.

[11] R Kaur, A Marwaha, VA Chhabra, K Kaushal, KH Kim and SK Tripathi. Facile synthesis of a Cu-based metal-organic framework from plastic waste and its application as a sensor for acetone. *J. Cleaner Prod.* 2020; **263**, 1-10.

[12] EIM Bardoquillo, JMB Firman, DB Montecastro and AM Basilio. Chemical recycling of waste polyethylene terephthalate (PET) bottles via recovery and polymerization of terephthalic acid (TPA) and ethylene glycol (EG). *Mater. Today Proc.* 2023, https://doi.org/10.1016/j.matpr.2023.04.160.
[13] R Kumar, K Sadeghi, J Jang and J Seo. Mechanical, chemical, and bio-recycling of biodegradable plastics: A review. *Sci. Total Environ.* 2023; **882**, 163446.
[14] J Hopewell, R Dvorak and E Kosior. Plastics recycling: Challenges and opportunities. *Phil. Trans. Biol. Sci.* 2009; **364**, 2115-26.
[15] M Kumar, S Bolan, LP Padhye, M Konarova, SY Foong, SS Lam, S Wagland, R Cao, Y Li, N Batalha, M Ahmed, A Pandey, KHM Siddique, H Wang, J Rinklebe and N Bolan. Retrieving back plastic wastes for conversion to value added petrochemicals: Opportunities, challenges and outlooks. *Appl. Energ.* 2023; **345**, 1-20.
[16] R Geyer, JR Jambeck and KL Law. Production, use, and fate of all plastics ever made. *Sci. Adv.* 2017; **3**, 1-5.
[17] W Guo, K Li, Z Fang, T Feng and T Shi. A sustainable recycling process for end-of-life vehicle plastics: A case study on waste bumpers. *Waste Manag.* 2022; **154**, 187-98.
[18] R Ediati, MA Setyani, DO Sulistiono, E Santoso, D Hartanto and MMAB Abdullah. Optimization of the use of mother liquor in the synthesis of HKUST-1 and their performance for removal of chromium (VI) in aqueous solutions. *J. Water Process Eng.* 2021; **39**, 101670.
[19] Manju, PK Roy, A Ramanan and C Rajagopal. Post consumer PET waste as potential feedstock for metal organic frameworks. *Mater. Lett.* 2013; **106**, 390-2.
[20] L Zhou, S Wang, Y Chen and C Serre. Direct synthesis of robust HCP UiO-66(Zr) MOF using poly(ethylene terephthalate) waste as ligand source. *Microporous Mesoporous Mater.* 2019; **290**, 109674.
[21] J Ren, X Dyosiba, NM Musyoka, HW Langmi, BC North, M Mathe and MS Onyango. Green synthesis of chromium-based metal-organic framework (Cr-MOF) from waste polyethylene terephthalate (PET) bottles for hydrogen storage applications. *Int. J. Hydrogen Energ.* 2016; **41**, 18141-6.
[22] M Han. 5 - Depolymerization of PET bottle via methanolysis and hydrolysis. *Recycl. Polyethylene Terephthalate Bottles* 2019, https://doi.org/10.1016/B978-0-12-811361-5.00005-5.
[23] A Barredo, A Asueta, I Amundarain, J Leivar, RM Fernández, S Arnaiz, E Epelde, RL Fonseca and JIG Ortiz. Chemical recycling of monolayer PET tray waste by alkaline hydrolysis. *J. Environ. Chem. Eng.* 2023; **11**, 109823.
[24] SA Ravichandran, VP Rajan, PV Aravind, A Seenivasan, DG Prakash and K Ramakrishnan. Characterization of terephthalic acid monomer recycled from post-consumer PET polymer bottles. *Macromol. Symp.* 2016; **361**, 30-3.
[25] U Jamil, AH Khoja, R Liaquat, SR Naqvi, WNNW Omar and NAS Amin. Copper and calcium-based metal organic framework (MOF) catalyst for biodiesel production from waste cooking oil: A process optimization study. *Energ. Convers. Manag.* 2020; **215**, 112934.
[26] X Yan, S Komarneni, Z Zhang and Z Yan. Extremely enhanced CO_2 uptake by HKUST-1 metal-organic framework via a simple chemical treatment. *Microporous Mesoporous Mater.* 2014; **183**, 69-73.
[27] VD Doan, TL Do, TMT Ho, VT Le and HT Nguyen. Utilization of waste plastic pet bottles to prepare copper-1,4-benzenedicarboxylate metal-organic framework for methylene blue removal. *Separ. Sci. Tech.* 2020; **55**, 444-55.
[28] YA Patil and GS Shankarling. Deep eutectic solvent-mediated, energy-efficient synthesis of copper terephthalate metal-organic framework and its application in degradation of an azo dye. *Chem. Eng. J. Adv.* 2020; **3**, 100032.
[29] SJ Singh, SR Kale, MB Gawande, A Velhinho and RV Jayaram. A synthesis of copper based metal-organic framework for o-acetylation of alcohols. *Catal. Comm.* 2014; **44**, 24-8.
[30] T Rodenas, I Luz, G Prieto, B Seoane, H Miro, A Corma, F Kapteijn, FXLI Xamena and J Gascon. Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nat. Mater.* 2015; **14**, 48-55.
[31] MY Chao, WH Zhang and JP Lang. Co_2 and Co_3 mixed cluster secondary building unit approach toward a three-dimensional metal-organic framework with permanent porosity. *Molecules* 2018; **23**, 755.
[32] R Huang, D Zheng, B Yang and B Wang. Preparation and simultaneous sorption of CTMAB-HTCC bentonite towards phenol and Cd(II). *Desalination Water Treat.* 2011; **44**, 276-83.