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5**Journal of Environmental Chemical Engineering 7 (2019)** 103277 **Contents lists available at ScienceDirect Journal of Environmental Chemical Engineering journal homepage: www.elsevier.com/locate/jece** Short communication **The** synthesis **of**

biodiesel using copper based metal-organic framework as a catalyst T Tresia Pangestua,1, Yosafat Kurniawana,1, Felycia Edi Soetaredjoa,b,, Shella Permatasari Santosoa,b, Wenny Irawatya, Maria Yulianaa, Sandy Budi Hartonoa, 11**Suryadi Ismadjia,** b,□ **a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

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ARTICLE INFO ABSTRACT Keywords: Metal-organic framework Copper complex Tricarboxylic acid Trimesic acid Biodiesel Transesterification The metal-organic framework (MOF) used as a heterogeneous catalyst for biodiesel production has been pro- duced from the coordination of benzene-1,3,5-tricarboxylic acid (BTc) and divalent copper (Cu). A straight- forward solvothermal method with ethanol-water solvent was employed for the production of MOF, and rod-like CuBTc-MOF particles with a unit cell length of 37.12 nm were obtained. Brunauer–Emmett–Teller (BET) sorp- tion-isotherm characterization revealed that CuBTc holds

16**a surface area of** 1085.72 **m2/g and a total pore volume of** 1.68 **cm3/g. The** high thermal stability **of**

CuBTc, with a degradation temperature of 303 °C, was confirmed through thermogravimetric analysis (TGA). Other characterizations were also carried out to characterize the CuBTc. Specifically, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and X-ray dif- fraction (XRD) analysis. The produced CuBTc-MOF is applied to produce biodiesel from palm oil. The compo- sition in biodiesel was quantified using gas chromatography (GC) analysis. The optimal FAME yield in biodiesel of 91% was obtained from transesterification using 0.04 g CuBTc and methanol to oil volume ratio of 5:1. Recycled CuBTc- MOF was also capable of producing biodiesel with high FAME yield, which is 86%. The ob- tained result signifies the potential catalytic activity of CuBTc-MOF in the production of biodiesel. 1. Introduction The depletion of petroleum reserves and global warming are the main factors to develop renewable and more environmentally friendly energy. The blending of biodiesel with engine fuel has been widely carried out; this practice is especially to reduce the use of non-renew- able fossil fuels. Biodiesel is mainly produced by transesterification of triglyceride in biomass-oil (such as vegetable oil and animal fat) with methanol. Biodiesel is considered an environmentally friendly fuel be- cause it produces lower levels of CO2, SOx, and hydrocarbon emissions [1]. The use of the catalyst in transesterification is significantly affected the reaction rate; the use of catalyst may favor the formation of product over by-product. Over the practices, the use of heterogeneous catalysts is more preferred than a homogeneous catalyst. In the use of homo- geneous catalysts, a challenging separation-purification process is re- quired to separate product from catalyst and excess reactant [2]. The use of heterogeneous catalysts offers more advantages over homogeneous catalysts, such as recyclable, ease separation-purification process, high glycerol purity, and not corrosive. The use of hetero- geneous catalysts also helps to reduce the total production cost [3]. Furthermore, the presence of water in homogeneous catalysts (either as a solvent and/or attached water) give a depression effect to the cata- lytic activity of the catalyst; this effect is minimized in the use of het- erogeneous catalysts

[4]. Heterogeneous catalysts can be alkaline or acidic; the acidic catalyst is used in this study. The advantage of acidic heterogeneous catalyst is that the formation of soap as byproducts is minimized or nil. In this study, the MOF is prepared by combining a bio-derived carboxylic acid ligand, namely

> 10**benzene-1,3,5-tricarboxylic acid** (BTc), with Lewis **acid** metal, namely copper **(Cu).**

BTc, also known as trimesic acid, offers a beneficial structure as a MOF starting material; it has three carboxylic groups which can form a coordination complex with metal ions. As reported by Giammar and Dzombak (1998), the carboxylic groups of BTc have a pKa value of 3.01, 3.71, and 4.49, respectively. BTc ligand □ Corresponding authors at:

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Fig. 1. (a) Cu ions and dissociated BTc molecules in aqueous solution. (b) Schematic structure of CuBTc-MOF in water; and (c) with the presence of ethanol. The molecules/particles in the reaction scheme are partially presented, and water molecules are removed for simplification purposes. forms a complex with copper (CuBTc) which has a complex formation constant of 2.67 [5]. Reconstruction of species distribution diagram (Supplementary Data Figure S1) from these constants shows that the CuBTc complex is formed in all range of pH (acidic to alkali) [5], this indicates the possibility of the complex formation. Many studies have shown the synthesized of CuBTc MOF and its use in various applications, such as being used as an ion exchanger, ad- sorption agent, reduction agent, and antioxidant agent [6–11]. How- ever, there are still no studies investigating the potential of CuBTc-MOF to catalyze biodiesel production thus far. The CuBTc used in this study is synthesized through a simple method solvothermal method, and the prepared MOF is used as a heterogeneous acid catalyst in the transes- terification of palm oil and methanol to produce biodiesel. The effect of catalyst mass, the volume ratio of methanol to oil, and recyclability of MOF as a heterogeneous catalyst is examined. 2.

> 2**Methods 2.1. Materials The** chemicals **used in this study**

are copper (II) sulfate pentahydrate (CAS:7758-99-8, 99.995%purity), benzene-1,3,5-tricarboxylic acid (CAS:554-95-0),

14**ethanol (CAS:64-17-5, 99.8%purity),**

14**methanol (CAS:67-56-1, ≥99.8%purity),** N-hexane **(CAS:**

110-54-3, ≥95% purity). All chemicals were obtained from Sigma Aldrich. The palm cooking oil was obtained from a local supermarket in Surabaya, East Java, Indonesia. All

2**chemicals are used as received without** any **further purification. 2.2. Preparation of**

CuBTc-MOF Copper sulfate pentahydrate (1.6101 g) was dissolved in 62.5 mL reverse osmosis water. The copper solution was then added to 1.00 g BTc in 62.5 mL of 50% (v/v) ethanol. The mixture was continuously stirred for 1 h before transferred into a sealed autoclave. The mixture was then for 18 h at 110 °C. The mixture was then cooled slowly to room temperature. The solid MOF formed was separated from the su- pernatant by using centrifugation. MOF was washed 5 times with 50% (v/v) ethanol to remove unreacted reactants. Subsequently, MOF was dried in an oven at 100 °C for 12 h. The scheme of preparation of CuBTc-MOF is presented in Supplementary Data Figure S2. 2.3. Characterization of CuBTc-MOF The diffraction pattern of CuBTc was analyzed using an X-ray Diffractometer Phillips X'pert with Cu-Kα radiation (λ = 1.5406 Å) at Fig. 2. Characterization of CuBTc-MOF: (a) XRD pattern, (b) SEM image and (c) N2 adsorption-desorption isotherm. Fig. 3. FTIR spectrum of CuBTc-MOF. 40 kV and 30 mA. The surface morphology of was analyzed

10**using a JEOL JSM-6500F Field Emission Scanning Electron Microscope.**

N2 sorption was obtained using a Quantachrome at a temperature of −195.6 °C. The

7**surface area of** Cu-BTC **was determined using** the multiple-point **Brunauer–Emmett–Teller (BET) equation**

at p/po range of 0.05–0.3, and total pore volume was determined at saturation point at p/po = 0.997. Thermal stability was analyzed using a TGA system (model SDT 2960 & Thermal Analyst 2000, TA Instruments). The sur- face functional groups were analyzed using FTIR with KBr background; the spectrum was recorded in the range of 400–4000 cm−1. 2.4. Production of biodiesel The transesterification reactions of palm oil using CuBTc as the catalyst was carried out as follows: palm oil (5 g), methanol (50 mL), and MOF (0.04 g) were mixed in a three-neck flask. The mixture was heated at 60

13**°C for** 4 **h. The** biodiesel **was separated from the mixture** (glycerol **and**

unreacted reactants) by dissolving in 75 mL n-hexane. The biodiesel layer was heated at 65 °C to vaporize n-hexane. The used MOF was collected through simple filtration and

13**washed with n-hexane to remove oil**

residue before reused for another transesterification ex- periment. Fig. 4. TGA curve of Cu-BTC MOF. 2.5. Characterization of biodiesel Analysis of

7**fatty acid methyl esters (FAME)** content in biodiesel **was conducted using** a **Gas-Chromatography (GC),** equipped **with**

SLB-IL 111 column (30 m × 0.25 m × 0.20 µm). Helium gas was used as the mobile phase with a flow velocity of 30 cm/s. The injected sample volume was 1 µL, with a splitting ratio of 50:1. The oven

9**temperature was maintained at** 180 °C. **The injection port and detector temperature were set at 250 °C and 260 °C, respectively.**

15**3. Results and discussion 3.1.** The **formation** mechanism **of**

CuBTc-MOF CuBTc-MOF was synthesized by reacting divalent Cu with BTc li- gand in 50% ethanol solution. Schematically the formation of CuBTc- MOF is presented in Fig. 1. The divalent copper present as positively charged ions in the solution [5,12]. Meanwhile, BTc ligand, which has low acid dissociation constants, tend to be negatively charged due to deprotonation of H+ ions from its carboxyl groups (Fig. 1a). The pre- sence of water functions as a mobile phase which brings Cu and BTc close to each other; the interaction then occurs due to the charge dif- ference between Cu and BTc (Fig. 1b). The presence of ethanol mole- cules helps stabilize CuBTc-MOF network by binding to the Cu central Fig. 5. Transesterification of triglycerides into biodiesel and glycerol by using CuBTc-MOF catalyst. The molecules/particles in the reaction scheme are partially presented, and water molecules are removed for simplification purposes. Table 1 Fatty acid methyl esters composition of the biodiesel product. FAME Composition, % C12:0 (Lauric

4**acid methyl ester)** C14 **:0** (Myristic **acid methyl ester) C16:** 0 (Palmitic **acid methyl ester) C18:0 (Stearic acid methyl ester) C18:** 1n9c **(Oleic acid methyl ester) C18:** 2n6c **(Linoleic acid methyl ester)**

2.12 ± 0.10 1.84 ± 0.06 42.8 ± 0.50 3.91 ± 1.23 38.25 ± 0.81 6.47 ± 1.25 atom (Fig. 1c) [13–15]. The ethanol molecules are removed when CuBTc-MOF is dried to obtain dry particles. 3.2. Characterization of CuBTc-

MOF As shown in Fig. 3(a), XRD analysis on CuBTc shows a flat baseline; this indicates a high crystalline structure with only a few amorphous regions. The intensive peaks with a tight region were observed at 2? of 9.20°, 11.48°, 13.33°, 13.85°, 16.10°, 16.74°, 17.32°, 18.63°, 19.26°, 21.12°, 22.64°, 24.99°, and 25.91°. The characteristic XRD peaks of CuBTc show similarities with the published data [16]. The average crystallite unit cell size (D) is determined from the XRD pattern using the Scherrer equation; it is obtained that CuBTc has D = 37.12 nm. The morphology of CuBTc is observed by using SEM. As shown in Fig. 2b, the synthesized Cu-BTc has a rod-like shape. The shape of CuBTc is strongly influenced by the polarity of the solvent, and the size of counter ions from the metal salt [15,17]. Sahiner et al. (2014) re- ported that CuBTc synthesized in the presence of water molecules may have a rod-like shape. Furthermore, the morphology of CuBTc is af- fected by reaction condition, such as temperature. At a moderate tem- perature (100–110 °C), CuBTc tend to has a rod-like structure; while at a higher temperature, the shape altered to a round shape

15**[13]. The N2 adsorption-desorption isotherms of the**

Cu-BTC MOF was analyzed at a temperature of −195.6 °C. The Brunauer–Emmett–Teller (BET) surface area was calculated at a relative pressure from 0.05 to 0.30; it is obtained that CuBTc has a BET surface area of 1085.72 m2/g. The total pore volume was determined at the highest relative pressure, which gave the value of 1.68 cm3/g. These results confirmed that the Cu-BTC MOF had the micro-/meso-/macroporous structure [18]. The synthesized Cu-BTC MOF exhibits the type I adsorption-desorption isotherm with monolayer adsorption and follows the type-H4 hysteresis in the partial pressure range from 0.2 to 1.0 (P/P0), as shown in Fig. 3(c) [19]. Nitrogen adsorption of MOF usually occurs at low re- lative pressure where P/P0 < 0.1 and an increase in adsorption occur at the range pressure of 0.2–1.0 (P/P0) [20]. The surface functional groups of CuBTc was confirmed through the FTIR analysis. As shown in Fig. 3, CuBTc possesses broad bands at 3163.04, 3105.18, and 3068.53 cm−1 which corresponding to C–H stretch vibrations originate from the aromatic structure of the BTC linker. A sharp peak at 2925.81 cm−1 was corresponding to C–H alkane stretching vibration, while a strong peak at 1710.14 cm−1 was due to C=O stretching vibration. The medium-weak peaks at 1390.58, 1569.95 and 1710.14 cm−1 were due to C=C stretching vibrations originating from the aromatic structure. The sharp peaks at 1116.71, 1186.14 and 1249.79 cm−1 were due to C–O stretching vibrations. The peaks at 543.89 and 578.60 cm−1 indicate the Cu–O vibrations, which suggest the formation of the CuBTc-MOF [21]. Thermal gravimetric analysis was conducted at a temperature range of 32.8–800 °C prior to determine the thermal stability of CuBTc. From Fig. 4, it can be seen that a weight loss (~8 wt%) begins in the tem- perature range of 32.8–134 °C, which is due to the evaporation of free moisture. The CuBTc is thermally stable

17**in the temperature range of** 134–303 **°C; it**

is evident that the structure of MOF is quite stable since weight loss of MOF is not significant. After 303 °C, the second stage Fig. 6. Influence of (a) catalyst and (b) methanol amount in biodiesel (FAME) yield. Reaction conditions (a) 10:2 MeOH:oil volume ratio; (b) 0.04 g CuBTc. weight loss occurs, which signify by a drastic decrease in weight up to 43 wt%. This phenomenon indicates the damage of the BTc linker. The constant weight was observed at a temperature greater than 387 °C, indicating that entire BTc linker was degraded and only CuO and Cu2O residue remained [16]. 3.3. Biodiesel production mechanism by using CuBTc catalyst CuBTc-MOF was used as the Lewis acid catalyst in the transester- ification of triglycerides into biodiesel. The transesterification me- chanism steps are schematically presented in Fig. 5. As a Lewis acid catalyst, CuBTc provides unsaturated open sites that readily coordinate with methanol and triglycerides. Theoretically, the transesterification is assisted by several forces, including interface dipole [22,23], electron delocalization [24], and nucleophilic attack [25,26]. The explanation of the steps in detail is as follows: Step 1: Methanol molecules establish coordination with the central Cu atoms of the CuBTc particles. Coordination is induced by the pre- sence of surface metal dipoles which promote interface dipole-dipole interaction. Step 2: Triglyceride molecule attach to the central Cu atom of the CuBTc particle. The interaction is promoted by delocalization of elec- tron, which forms a resonance between two oxygen atoms of the tri- glyceride. Step 3: Methanol and triglyceride have positions that are close to each other so that their interaction can occur facilely. The nucleophilic oxygen atom from methanol hydroxyl group then attacks the electro- philic carbon at the triglyceride ester group thus transesterification occurs. The nucleophilic attack produces glycerol by-product. Step 4: The produced biodiesel detached from the CuBTc through electron delocalization at the oxygen atoms; thus, the main product of biodiesel is obtained. The produced biodiesel was then analyzed for its composition by using gas chromatography analysis. It is shown that there are six FAMEs contained in biodiesel product, which showed by six major chromato- graphy peaks between 2.37 and 3.97 min (Table 1). The identified compounds are lauric acid methyl ester (C13H26O2), myristic acid methyl ester (C15H30O2), palmitic acid methyl ester Fig. 7. The influence of (a) reaction time, and (b) reaction temperature on the yield of biodiesel (FAME). (C17H34O2), stearic acid methyl ester (C19H38O2), oleic acid methyl ester (C19H36O2) and linoleic acid methyl ester (C19H34O2). The pal- mitic and oleic methyl ester was the highest contained in FAME, where the yields were 42.8% and 38.25%, respectively. The total content of FAME is 95.39%. 3.4. Recyclability and the effect of the amount of CuBTc, methanol, reaction time, and reaction temperature in biodiesel production Recyclability is an attractive factor in the use of catalysts. Used CuBTc-MOF is regenerated by removing the oil residue using fresh n- hexane. The ability of recycled CuBTc-MOF in the transesterification process is investigated. As shown in Fig. 6(a), the transesterification process by using 0.04 g of fresh CuBTc is able to yield 91% of FAME; while, the recycled CuBTc can yield 86% of FAME. This result proves that the CuBTc catalytic activity only slightly decreases, but the bio- diesel yield still high even though it has undergone a regeneration process. The amount of CuBTc MOF used in transesterification gives significant influence to the FAME yield. The increase of the

12**amount of catalyst provides** more active **sites** for **the** transesterification **reaction**

of triglyceride and methanol, leading to an increase in the yield of FAME. It can be seen from Fig. 6(a) that the optimum FAME yield was reached by using 0.04 g of fresh or recycled CuBTc. The higher amount of CuBTc used causes a decrease in FAME yield. The use of CuBTc greater than 0.04 g does not favor the transesterification process due to the disper- sion of active centers and retard the molecular interactions between the reactants and active sites (partial coverage), and it decreases the reac- tion between triglycerides and methanol to produce FAME [27]. The maximum yield of FAME (91% using fresh CuBTc) obtained in this study is higher than the reported research using some common cata- lysts, namely NaOH as a homogeneous catalyst [11]. The use of CuBTc as a catalyst in transesterification provides more advantages, such as higher yield of FAME, a straightforward separation process, and lower production cost. The amount of methanol used in transesterification is usually given in excess amounts so that the reaction shifts toward the product side [25,28,29]. Although the yield of biodiesel may increase as methanol Yield/conversion after regereneration, % References Yield/conversion, % Operating condition Comparison the catalityc activity of several MOFs for biodiesel production. Modification Table 2 MOF [1] [27] [31] [32] [33] This study increased, the exaggerating amount of methanol also causes an increase in glycerol production.

This may provoke a back reaction to the re- actant side since transesterification is a reversible reaction. As depicted in Fig. 6(b), the FAME yield increases with increasing of MeOH to oil volume ratio from 2:1 to 5:1; the FAME yield then decreases as the ratio further increased to 10:1. This result suggests that excessive methanol usage does not favor transesterification. Moreover, an excessive amount of methanol gives several disadvantages such as high production cost and also cause higher solubility of glycerol in methyl ester that could – 82.1 (re-used 6 times) 73.6 (re-used 6 times) 82.49 (re-used 3 times) 97.8 (re-used 5 times) complicate the separation of biodiesel and glycerol [30]. The effect of reaction time and temperature on the FAME yield during the production of biodiesel using CuBTc as the catalyst is given in Fig. 7. The effect of reaction time on the yield of biodiesel was studied at 86.0 the temperature of 60 °C and the amount of BTc 0.04 g.

12**The yield of biodiesel increased with the increase** of **reaction time**

(1–4 h) as seen in 64 for UiO-66, and 99 for UiO-66-NH2 Fig. 7(a). Longer reaction time provide more time for the reactants to diffuse into the internal interior of the catalyst (where the reaction take place), and for the catalyst itself, it provides more time to adsorp the reactants and desorp the product of the reaction. Therefore, the longer the reaction time, more and more reactants could diffuse into the cat- alyst molecules, resulting in a higher conversion of the reactants and the yield of the FAME product. After 4 h, a further increase in reaction time gave no significant influence on the yield of FAME; this phe- nomenon indicates that 4 h is best reaction time to produce biodiesel 38 to 97 C̊, 0.5 and 0.6 h, catalyst 0.5 to 18% weight 91.0 74.8 96.19 98.02 91.0 using CuBTC as the catalyst. The influence of the reaction temperature on the yield of FAME is depicted in Fig. 7(b). The temperature gave a positive effect on the yield of FAME. The transesterification reaction between triglycerides and methanol is an endothermic and reversible process. The increase in temperature increases the reaction rate constant and will shift the re- Amine tagged and grafted by Salen-Zr(IV) complex 40, 60, and 67 C̊, 6 h, catalyst: 4% weight action into the products side. The mass transfer barrier between the 80 - 240 C̊, 2 h, catalyst: 4% weight catalyst and reactants decrease with the increase of temperature, and as 65 C̊, 30 min, catalyst: 6% weight a result, the adsorption rate of reactants into the surface of the catalyst becomes faster leading to the faster diffusion of the reactants into the pore of catalyst. This phenomenon will increase the yield of FAME. At temperature 65 °C, the yield of FAME around 90.4%. Since the increase of reaction temperature from 60 to 65 °C only increase the yield around 0.4%, and for energy consideration, the temperature of 60 °C was chosen as the optimum temperature for the biodiesel production using 78 C̊, 8 h 60 C̊, 4 h CuBTc as a catalyst. A comparison of the FAME yield/conversion produced using CuBTc as a catalyst with other studies using MOFs and its modified forms as Immobilization of thiol-functionalized ionic liquid catalysts are given in Table 2. In general, CuBTc has comparable cat- Kegging type heteropoly acid functionalization alytic activity with those MOFs catalysts which available in the litera- ture. Even without modification, CuBTc gave excellent catalytic cap- ability, a yield of FAME above 90% is the evidence. 4. Conclusions The CuBTc-MOF was successfully synthesized using a facile sol- vothermal method with 50 v% ethanol solvent. The CuBTc-MOF par- ticles have a rod-like shape, a large BET surface area, and good thermal UiO-66 and UiO-66-NH2 Zirconium stability. The N2 sorption isotherm shows that CuBTc possesses type I sorption isotherm with an H4 hysteresis. The CuBTc-MOF shows great SrO catalytic activity in the transesterification process to produce biodiesel – (FAME); it is functioned as a Lewis acid catalyst. The optimum yield of FAME was reached with the use of 0.04 g CuBTc and MeOH: oil volume ratio of 5:1. The CuBTc also able to recycle without losing the catalytic activity.

17**MIL-101(Cr) MIL-101(Cr) MIL-100(Fe)**

ZIF-8 CuBTc Conflicts of interest The authors declare no conflict of interest. Acknowledgments

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6**is highly appreciated.** **Appendix A. Supplementary data Supplementary data associated with this article can be found, in the online version, at** https **://doi.org/10.1016/j.**

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(2019) 103277 T. Pangestu, **et al. Journal of Environmental Chemical Engineering 7 (2019)** 103277 T. Pangestu, **et al. Journal of Environmental Chemical Engineering 7 (2019)** 103277 **2 3 4 5 6**

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