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5 Efficient One-Step Conversion of a Low-Grade Vegetable Oil to Biodiesel over a Zinc Carboxylate Metal−Organic Framework

2 Valentino Bervia Lunardi,⊥ Fransiska Gunawan,⊥ Felycia Edi Soetaredjo, Shella Permatasari Santoso,* Chun-Hu Chen, Maria Yuliana, Alfin Kurniawan, Jenni Lie, Artik Elisa Angkawijaya, and Suryadi Ismadji

ABSTRACT: In this study, a metal−organic framework, namely, Zn3(

1 BTC)2 (BTC = 1,3,5-benzenetricaboxylic acid), **was solvothermally synthesized and**

employed

23**as a catalyst for biodiesel production from** degummed vegetable **oil via** a one-step **transesterification** and esterification reaction. **The**

resulting Zn3(BTC)2 particles exhibit a well-defined triclinic structure with an average size of about 1.2 μm, high specific surface area of 1176 m2/g, and thermal stability up to 300 °C. The response surface methodology−Box−Behnken design (RSM− BBD) was employed to identify the optimal reaction conditions and to model the biodiesel yield in relation to three important parameters, namely, the

17**methanol/oil molar ratio** (4:**1**−8:1), **temperature** (45−65 °**C**), and **time (1**

.5−4.5 h). Under the optimized reaction conditions (i.e., 6:1 methanol/oil molar ratio, 65 °C, 4.5 h), the maximum biodiesel yield reached 89.89% in a 1 wt % catalyst, which agreed very well with the quadratic polynomial model's prediction (89.96%). The intrinsic catalytic activity of Zn3(BTC)2, expressed as the turnover frequency, was found to be superior to that of other MOF catalysts applied in the transesterification and esterification reactions. The reusability study showed that the as-synthesized Zn3(BTC)2 catalyst exhibited good stability upon three consecutive reuses without a noticeable decrease in the methyl ester yield (∼4%) and any appreciable metal leaching (<5%). Furthermore, a preliminary technoeconomic analysis showed that the total direct operating cost for the kilogram-scale production of Zn3(BTC)2 is estimated to be US$50, which may sound economically attractive.

1. INTRODUCTION Biomass-derived energy sources are considered a promising solution to the global energy crisis resulting from the overconsumption and continuous depletion of finite fossil fuel reserves. In this context, biodiesel has drawn wide attention as a green and sustainable alternative to petroleum- derived diesel fuels owing to its similar properties, inherent lubricity, and lower net emissions of carbon monoxide (CO), particulate matter (PM), and unburned hydrocarbons. The high oxygen content of biodiesel can also contribute to reducing soot formation, leading subsequently to a cleaner and more efficient combustion.[1,2] Apart from the less polluting exhaust emissions, the rapid escalation in biodiesel con- sumption and production worldwide may build up the atmospheric concentrations of CO_2 and other greenhouse gases. Plant cultivation in biodiesel feedstocks can help establish a sustainable and net-zero carbon-neutral cycle through the Calvin−Benson−Bassham photosynthetic cycle.[3] Moreover, plant biomass utilization provides additional benefits such as renewability, nontoxicity, and biodegrad- ability.[4−6] While such an energy crop plantation scenario presents a promising opportunity for the sustainability of biodiesel production, one can reasonably expect adverse ©

socioeconomic and biodiversity impacts as a result of the considerable land use and land-use changes. In addition, the use of edible crops for biodiesel feedstock may raise a contentious issue of food vs fuel, specifically in underdeveloped and developing regions. Therefore, the biodiesel industries' policy measures and implementation are vital in tackling the above issues and achieving a wider social acceptance. While

research and development of biodiesel have been continuously pursued during the last two decades, the economic viability of the process remains a significant barrier to widespread commercialization.[7] In this context, the utilization of nonedible low-cost feedstock oils and the

[21]**development of highly** active, economic, **and** easily **recyclable catalysts**

represent two major strategies

[21]**to make the** biodiesel **production process** more **economically**

attractive. The latter strategy has become the main focus of the biodiesel research Received: August 10, 2020 Accepted: January 4, 2021 Published: January 14, 2021 Figure 1. Characterizations of the $Zn_3(BTC)_2$. (a) FTIR spectra of the H_3BTC linker and as-synthesized $Zn_3(BTC)_2$. (b) Powder XRD patterns of the as-

[43]**synthesized Zn3(BTC)2** along **with** the simulated diffraction **pattern** from **CCDC**

-664416. The Bragg reflections denoted with asterisks (*) and octothorpe (#) indicate the crystal lattice of $Zn_3(BTC)_2$ and impurity phases, respectively. (c) Nitrogen adsorption−desorption isotherms of $Zn_3(BTC)_2$ at 77 K. The solid and hollow circles represent the adsorption and desorption branches of the isotherm, respectively. (d) Thermogravimetric weight loss of $Zn_3(BTC)_2$ recorded under a N_2 atmosphere. (e) SEM images of polydisperse $Zn_3(BTC)_2$ particles and (f) the particle size distribution histogram obtained by measuring more than 60 randomly selected particles on the SEM image using the Fiji-ImageJ software. The red line in the histogram represents the best-fit log-normal distribution ($R^2 = 0.96$) obtained using the SigmaPlot software. community toward improving product yield, which in turn reduces the total manufacturing costs. Homogeneous catalytic systems based on alkali metal hydroxides (e.g., NaOH or KOH) or related alkoxides suffer from the intricate and costly separation and recycling of the catalyst after the reaction. Moreover, the practical utility of homogeneous alkaline catalysts is complicated by the stringent demand for expensive refined lipid feedstocks in the process. On the other hand, heterogeneous catalysts allow for the easy recovery and reuse for multiple reaction cycles, as well as possess a comparatively high activity to homogeneous catalysts. Various solid acid and base catalysts with tunable structural and surface functionalities have been extensively developed, and many of them show promising activity for improving the biodiesel production yield.[4,8] Heterogeneous solid base catalysts generally afford faster reaction rates and therefore higher biodiesel yields compared with the acid counterparts under milder reaction conditions. However, they are sensitive to free fatty acids (FFAs; max. 2 wt %) and water content (<0.06 wt % or 600 ppm tolerable level) in the starting feedstock,[9−11] which can promote saponification and hydrolysis side reactions and decrease both the catalyst activity and the ester yield. Hence, the solid acid catalysts remain the preferred choice when dealing with low-quality or nonedible vegetable oils containing significant quantities of FFAs and water. Metal−organic frameworks (MOFs) have emerged as an attractive and versatile porous crystalline material in the realm of

[9]**heterogeneous catalysis**, thanks **to their unprecedented** attributes, **such as** exceptionally **high** internal **surface areas**

, tailorable nanoscale porosity, enormous structural and chemical diversity, good thermal stability, and modular synthetic design.[12] The open metal sites (OMS; also referred to as

40coordinatively unsaturated metal centers) in the MOF structure are known to behave as the

adsorption

9and Lewis acidic sites, thus playing a central role in modulating the

catalytic activity and selectivity for various reactions. To date, numerous studies have demonstrated the outstanding perform- ance of MOF catalysts to achieve both high conversion efficiency and selectivity in a variety of industrially relevant reactions; however, less attention has been paid to the transesterification and esterification reactions. With respect to the biodiesel production, only a few types of MOFs have been investigated, such as iron and copper benzenetricarbox- ylate (Fe-BTC and Cu-BTC), MIL-53(Fe), UiO-66, and Cr(III) and Co(II) terephthalate,7,8,13,14 While these MOF catalysts can afford fatty acid alkyl esters in good to excellent yields (85−98%), the conversion is accomplished by either esterification using well-defined fatty acid substrates (e.g., oleic acid)13,14 or a two-step trans/esterification of pre-esterified oil,7 while the model reaction featuring a one-step trans/ esterification remains unexplored. In this study, the catalytic performance of a three- dimensional (3D) Zn(II)-based carboxylate MOF (hereafter denoted as Zn3(BTC)2) is examined for direct conversion

1of degummed palm oil (DPO) to biodiesel

via the simultaneous transesterification and esterification in methanol. The one-step process of transesterification and esterification provides an economic advantage and improves the efficiency of biodiesel production.15 Based on the intensive review of available literature, the Zn3(BTC)2 MOF has been applied to various organic transformation reactions, such as the alkylation of toluene with benzyl bromide, cycloaddition of carbon dioxide to cyclic carbonates, synthesis of benzimidazole derivatives, and Knoevenagel condensation.16−19

12To the best of our knowledge, this study is the first to report the catalytic activity of

Zn3(BTC)2 for the

9transesterification and esterification of a low-grade vegetable oil

(DPO)

9to produce fatty acid methyl esters (FAMEs) or biodiesel. The second objective of

this study is to pinpoint the optimal conditions for maximizing the conversion efficiency of Zn3(BTC)2-catalyzed biodiesel production by the response surface methodology (RSM). The preliminary cost analysis of the MOF synthesis on a kilogram scale is also provided to assess the economic potential of Zn3(

. 2. RESULTS AND DISCUSSION 2.1. Structure and Characterization of the Zn3(BTC)2 Catalyst. The 3D porous Zn3(BTC)2 MOF is constructed from the coordination interaction between the tritopic linker H3BTC and Zn2+ ions in a multidentate fashion.20 In the fdoerpmroattoionnateodf toZnf3o(rBmTCa)n2,egtahtievelHy3cBhTaCrgedlinBkTerCs3−arsepefcuiellsy. The polar aprotic DMF molecules act as a mobile phase that assists the interactions between Zn2+ ions and the deproto- nated BTC3− ligands. Meanwhile, the Zn metal centers are six- coordinated with two carboxyl oxygen atoms in two independent BTC3− ligands and four oxygen atoms belonging to water molecules to form an octahedral coordination geometry. The resultant octahedral coordination environment with an extensive hydrogen bonding among water eventually leads to the formation of a stable crystalline framework between the carboxylate groups of BTC3− and Zn2+ ion.20,21 interactions between triangular BTC3− bridging ligands and The formation of Zn3(BTC)2 from the coordination Zn2+ ions is investigated using FTIR spectroscopy. As shown in Figure 1a, the H3BTC linkers exhibit a strong, broad OH stretching band corresponding to the carboxylic groups at 3364 cm−1.22 The broad absorption features between 3000 and 2600

, respectively. After the C?O and C−O vibrational modes of the carboxylic groups bands of H3BTC at 3000−2500 cm−1 vanish, while the OH coordination reaction with Zn2+ ions, the broad absorption band blueshifts and becomes more intense and broader. This OH band can be assigned to the asymmetric and symmetric vibrations of the coordinated water molecules in the Zn3(BTC)2 structure.23 The absorption bands associated wavenumbers of 1665 and 1414 cm−1, respectively, than those with the carbonyl groups also appear at lower and higher observed for the H3BTC linker. These shifts suggest the and coordination of the carboxylic groups with Zn2+ ions.24 complex formation of Zn3(BTC)2 through the deprotonation −COOH groups around 1700 cm−1 also implies the complete The absence of the absorption band corresponding to the the binding of Zn2+ ions.20 Moreover, the presence of the Zn− deprotonation of the H3BTC linkers after metal binding upon O stretching vibrations corresponding to the octahedral at 756 cm−1.23 coordinated zinc center is confirmed by the absorption band The powder XRD pattern of the as-synthesized Zn3(BTC)2 is presented in Figure 1b, while the details of the Bravais lattice parameter are given in Table S1. Compared with the simulated XRD pattern of Zn3(BTC)2 obtained from the Cambridge Crystallographic Data Centre (CCDC no. 664416), the as- synthesized sample exhibits quite distinctly different crystalline features, particularly for the Bragg reflections observed at higher 2θ angles of 15−40°. The relatively weak yet well-resolved reflections at higher Bragg angles may represent the impurity phases with smaller crystallite domains. The most intense (102) reflection located at 2θ = 10.44° in the experimental XRD pattern, however, well matches the simulated one (2θ = 10.37°). In addition, the two reflections that appear at 2θ = 9.33 and 12.71° are also the typical crystal features of Zn3(BTC)2.23 This result thus suggests that the resultant product may contain multiphases, especially for the peaks at low Bragg angles of 9.39, 10.44, and 10.78°. The unit cell dimensions (Table S2) from the obtained XRD pattern show the triclinic crystal geometry of Zn3(BTC)2. The average crystallite size (D) obtained from the Scherer equation for the strongest (102) reflection was 8.5 nm. The N2

typical IUPAC Type I(a)/II hybrid characteristic with well-defined steps at low and high relative pressures (Figure 1c). The significant uptake of N2 in the low relative filling of narrow micropores in the MOF structure.

The second pressure region (P/P0 < 0.05) can be attributed to the volume of the isotherms may reflect the multilayer adsorption of N2 on steep uptake observed at

5**high relative** pressures (**P**/P0 > **0.95) the large** mesopores **and**

the external surface (i.e., macropores) of the samples,25 thus characterizing the hierarchical architecture of porosity of Zn3(BTC)2. The

5**presence of large mesopores and macropores** inside **the MOF** material **can**

facilitate the mass transport of large-sized reactant molecules into the catalytically active Lewis acid Zn2+ sites and desorption of products from the porous framework. The Zg−n13, (rBeTspCe)ct2ivweelyr.eCfoomunpdarteod btoe t1h1e7m5.e8s1opmo2rogu−s1Zann-dBT0C.81McOmF3

21**BET surface area** (SBET) **and** total **pore volume** (VT) **of** (SBET = 12−50 **m2 g**

−1) reported in the Wang et al. work,23 the much higher SBET of the Zn3(BTC)2 particles synthesized in this work can be ascribed to the existence of a micro/ macroporous structure. In this regard, the high surface area of Table 1. ANOVA Results for the FAME Yield Response at an Optimal Zn3(BTC)2 Loading of 1 Wt % factora SSb coef. estimated (α) DFc MSd F value P valuee model 1036.73 79.80 9 115.19 68.79 <0.0001* Linear ef fect X1 156.65 4.42 1 X2 559.49 9.15 1 X3 162.73 4.22 1 Interaction ef fect X1X2 11.87 −1.86 1 X1X3 23.14 2.24 1 X2X3 4.49 −1.14 1 Quadratic ef fect 156.65 93.54 559.49 334.10 162.73 97.17 11.87 7.09 23.14 13.82 4.49 2.68 <0.0001* <0.0001* <0.0001* 0.0374* 0.0099* 0.1525NS X12 0.7665 0.4642 1 0.7665 0.4577 0.5239NS X22 236.24 −9.11 1 236.24 141.07 <0.0001* X32 16.26 −2.26 1 16.26 9.71 0.0207* residual 10.05 6 1.67 lack of fit 10.05 5 2.01 0.7218NS

39**pure error 0.0000** 1 **0.0000 corrected total**

1046.78 15

35**std. dev**. mean **R2 adj. R2 pred. R2 precision**

1.29 75.05 0.9904 0.9760 0.9113 29.6294 aX1 = reaction

17**time (h); X2 = methanol/oil molar ratio; X3** = reaction **temperature (°C**

). bSS =

32**sum of squares**. cDF = **degree of freedom**. dMS = **mean squares**

. e* = statistically significant; NS = not significant. the Zn3(BTC)2 particles with a significant micropore contribution (~60% of the SBET, Table S3) would benefit the catalytic reaction by affording abundant OMSs, which allow the reactant molecules (i.e., triglycerides/free fatty acids and methanol) to interact more

frequently with these active sites and promote the conversion efficiency toward the reaction product. The TGA curve of Zn3(BTC)2 reveals a two-step thermal degradation process, as shown in Figure 1d. A mass loss (8.7%) observed below 100 °C could

13**be attributed to the evaporation of the adsorbed** moisture and **the**

elimination of the lattice water molecules in the framework structure. The TGA curve shows a negligible

36**weight loss between 100 and** 270 °**C**, which denotes **the** absence **of**

any coordinated DMF molecules after the activation process; the elimination of the DMF molecules occurs in the temperature range of 100−170 °C under a N2 atmosphere.[26] The as-synthesized MOF possesses good thermal stability with no appreciable weight loss (<2 wt %) up to 300 °C. This result unambiguously confirms that the Zn3(BTC)2 MOF is thermally stable and does not lose its crystalline order or undergo structural collapse during the transesterification reaction at low temperatures (45−65 °C). The representative examples of MOF materials possessing good thermal stability and applied to the transesterification and esterification reactions can be found in Table S4. Upon increasing the temperature above 300 °C, a rapid weight loss (~40%) was observed, which reflects the collapse of the framework structure of Zn3(BTC)2 due to the decomposition of organic linkers. The weight loss profile reaches a plateau at temperatures between 400 and 600 °C, yielding a residual crystalline ZnO around 40 wt %. Beyond 600 °C, neither weight loss nor phase transition of the ZnO particles was observed,

6**which is in good agreement with previous** reports.[20,27] **The SEM** image **of**

the Zn3(BTC)2 particles shows a nonisometric and triclinic morphology with relatively broad size distributions from 0.3 to 3.5 μm (Figure 1e,f). The observed discrepancy between the crystallite and particle sizes measured from the XRD and SEM image may suggest that the resultant products are polycrystalline. The morphology of the Zn3(BTC)2 particles is also somewhat different from that reported earlier for a similar method.[28] A possible explanation for this morphological difference is due to the variation of the solvothermal synthetic conditions in the Zn3(BTC)2 system, such as the solvent type, metal salt, precursor molar ratio, temperature, reaction time, and others. Compared to the rod morphology reported by Wang et al.,[23] the addition of triethylamine as a co-solvent was not included in the present approach. Feng et al. also reported the rod-shaped Zn3(BTC)2 particles through a solvothermal method using ethanol− water.[28] Hao et al. demonstrated that the pore size and framework topology of Zn3(BTC)2 can be modulated by the solvent molecular size.[29] The results of the SEM observation are in agreement with the powder XRD pattern. 2.2. Effect of the Catalyst Loading on the FAME Yield. The optimization of the catalyst loading is pivotal not only to maximize the reaction yield but also to minimize the production cost. Thus, the dependence of the catalyst loading on the yield of FAMEs was examined through

39**a one-factor-at- a-time (OFAT**) optimization method. **The**

OFAT approach was selected due to its simplicity and with the consideration of excluding the catalyst loading factor from the intrinsic reaction parameters. As shown in Figure S1, a volcano-like relationship between the catalyst loading and FAME yield was observed, where the maximum conversion of 84.4% was accomplished at a catalyst load of 1 wt %. At a 0.5 wt % Zn3(BTC)2 catalyst loading, the simultaneous conversion of triglycerides and free fatty acids into FAMEs reaches about 80%. As the catalyst loading increased to the optimal value, the FAME yield slightly rose from 80 to 84.4%, which can be explained by the

increased availability of the Lewis acid sites of Zn3(BTC)2, thus favoring the conversion of the reactant. The FAME conversion gradually declined upon increasing the catalyst concentration beyond 1 wt %. This phenomenon may be attributed to the decrease of the

30**dispersion of active centers** that hinder **the molecular interactions between the reactants**

Figure 2. The 3D surface mesh plots with contour lines underneath illustrating the binary

19**interaction effects of the** independent reaction **parameters on the ester yield**

: (a) temperature (X3) and

27**methanol/oil molar ratio** (X2), (b) **methanol/oil molar ratio** (X2) and **time** (X1), **and**

(c) time (X1) and temperature (X3). and active sites.30 The blank reaction test without a catalyst under the same conditions shows no appreciable formation of FAMEs, affording only ~3% yield. This result confirms the indispensable role of catalysts in accelerating the trans- esterification reaction rate by decreasing the free energy barrier ($\Delta G\ddagger$). 2.3.

16**Optimization and Modeling** Studies **of Biodiesel Production**

. The

16**analysis of variance (ANOVA)** results showing **the** effects **of** linear, **quadratic**

, and interaction terms of the three investigated reaction parameters (i.e., reaction time (X1), methanol/oil molar ratio (X2), and reaction temperature (X3)) on the FAME yield are summarized in Table 1. The statistical significance of the coefficient of each model term was examined through the Fisher's exact (F value) and probability (P value) tests, where P values less than 0.05 are considered statistically significant. Our preliminary analysis based on the P value, goodness of fit (R^2), and lack of fit suggested that the quadratic polynomial model is the most suitable for describing the response values compared to the linear and cubic functions.

3**Based on this significance testing, the quadratic** polynomial **model (eq 1) was found to be appropriate and statistically acceptable at the 95% confidence level (P value < 0.0001) with an insignificant lack of fit (P value > 0.05) for predicting** FAME **yields. Moreover, the predicted results agree well with those obtained from the experiments (see Table** 1), **with the satisfactorily adjusted coefficient of determination (adj**. R2) **of 0**.976. **This value implies that** 97.6% **of the** FAME **yield response variability could be described well by the model**

. Figure S2 also shows that

18**all the data points** lie **close to the** 45° reference **line**

. The predicted R2 value of 0.91 may reflect that the obtained model adequately approximates the response values under the experimental range studied without overfitting. Furthermore, the

2**very low value of the coefficient of variation (CV** = 1.72%) **and**

the considerably high adequate precision (i.e., signal-to- noise ratio > 4) point out that the model provides an accurate fit of the observed response and can navigate the design space.[31,32] The ANOVA test results reveal that

2**all the linear, quadratic, and interaction** parameters **are** statistically **significant**

in the implemented model with P values lower than 0.05 (highlighted with an asterisk (*) in Table 1), except for the quadratic X12 (P = 0.5239) and interactive X2X3 effects (P = 0.1525). The

27**linear effect of** the **methanol/oil molar ratio** (X2) emerges as **the most**

important contributor to increasing FAME yields (P < 0.0001 and F value = 334.1) among the other linear effects, namely, reaction temperature (F value = 97.17) and time (F value = 93.54). The same trend was also observed for the square terms of reaction parameters, where X22 (F value = 141.07) > X32 (F value = 9.71) > X12 (F value = 0.46). The optimal polynomial regression model after discarding the insignificant model terms (i.e., X12 and X2X3) are expressed in eq 1 with respect to the coded variables. FAME yield (%) = 79.80 + 4.42X1 + 9.15X2 + 4.22X3 − 1.86X1X2 + 2.24X1X3 − 9.11X2 2 − 2.26X3 2 (1) In eq 1, the positive and negative signs of the model terms represent the synergistic and antagonistic behavior, respec- X3) have positive coefficients, suggesting that an increase of the tively. It can be seen that all the main effects (i.e., X1, X2, and reaction time, methanol/oil molar ratio, and temperature leads to higher reaction yields in the biodiesel production catalyzed confirms the more significant role of the methanol/oil molar by Zn3(BTC)2. A more positive value of X2 factor (α2 = 9.15) ratio in maximizing the FAME conversion rather than the reaction time (α1 = 4.42) and temperature (α3 = 4.22), which will be discussed in more detail in the next section. The positive coefficient of X1X3 (α13 = 2.24) suggests the mutualistic effects

37**between the reaction time and temperature** in facilitating **the** conversion rate and **yield**

of FAMEs. On the contrary, the negative signs for the X1X2, X22, and X32 significant model terms demonstrate the antagonistic effect of the square terms of the methanol/oil molar ratio and reaction temperature on the DPO conversion to biodiesel. 2.4. Parametric Study of the Biodiesel Production.

20**2.4.1. Effect of** the **Methanol/Oil Molar Ratio**. Based on **the** ANOVA results, the **methanol/oil molar ratio**

has the strongest influence on the FAME production in the presence of Zn3(BTC)2. To further verify the significant influence of this factor, the interactions

20**between the methanol/oil molar ratio and** temperature (X2X3) or **time**

(X2X1) in promoting FAME conversion are investigated, as portrayed in Figure 2a,b. As

13**can be seen from the response surface plots, the**

curvature tends to be elliptical in shape, which indicates a significant interaction between each axis variable to the FAME response yield.33 The increase in the molar ratio of methanol to DPO from 4:1 to 6:1 positively affects the FAME production. This can be simply explained by the fact (and in accord with Le Chatelier's principle) that an excess amount of alcohol is required to drive the chemical equilibrium toward the product side. However, further increasing the methanol/oil molar ratio from 6:1 to 8:1 results in lower FAME yields. In this regard, the presence of excess methanol may encapsulate some active sites of the catalyst, leading to the hindered dipole interactions between the catalytically active sites with TG and FFA.34 Moreover, the excessive methanol loading can promote the emulsification of the reaction mixture due to a recombination of FAMEs and glycerol to produce monoglycerides,35,36 thus hindering the separation process of the product. Also, a large excess of methanol can improve the

38**solubility of glycerol in the FAME**- rich **phase**, which **could**

adversely affect the purity and yield of the final biodiesel product. Thus, optimizing the methanol/oil molar ratio in the transesterification process is crucial not only for maintaining the high conversion efficiency of FAMEs and product quality but also for minimizing the operating cost for unreacted methanol recovery. 2.4.2.

33**Effects of the Reaction Temperature and Time. The**

37**interaction effect between the reaction** temperature **and** time (X3X1) **on FAME**

productivity is presented in Figure 2c. From the 3D response surface plot,

19**it can be** observed **that the reaction** temperature and **time play a** less significant **role in** modulating **the** FAME conversion efficiency **compared** to **the**

methanol/oil molar ratio. The transesterification and ester- ification reactions are both endothermic and reversible, and thus, an increase in temperature provides more energy to the reaction mixture that shifts the chemical equilibrium in favor of the FAME formation. The elevated reaction temperatures also help to decrease the mass-transfer limitation between the methanol and oil phases, leading to the enhanced adsorption and diffusion of reactant molecules toward the catalytically active sites.37 Meanwhile, a prolonged reaction time improves the FAME production, allowing a greater number of reactant molecules to be consumed and converted to FAMEs over the catalyst surface. However,

33**a further increase in the reaction temperature and time**

beyond their optimum conditions has negligible effects on the ester yield and may incur additional cost and energy requirements of the process.8 2.5. FAME Compositions and Fuel Properties of the DPO-Derived Biodiesel. Based on the above statistical optimization study, the maximum yield of biodiesel obtained from the

1**one-step transesterification and esterification reactions of DPO over** Zn_3(**BTC)2**

was achieved at a

29**methanol/oil molar ratio of 6:1, temperature of 65 °C, and reaction time of** 4.5 h. **The** percent **yield of**

biodiesel obtained from the second-order polynomial model prediction (eq 1) under these optimized reaction conditions was found to be 89.96%, which agrees remarkably well with the experimental value of 89.89% (see Table 4, entry 12). The total mass fractions of the FAME species in the product were 95 wt %, with predominantly palmitic and oleic acid methyl esters present (see Figure S3 for details on the FAME concentration profiles and the corresponding GC−FID chromatogram). The

38**fuel properties of the** DPO-derived biodiesel **are presented in Table**

2, which conform to the quality standard requirements specified in ASTM D6751 and the Indonesian National Standard (SNI 7182-2015), thereby suggesting the potential use of the as-produced biodiesel as either a neat fuel or petroleum diesel blends. 2.6. Catalyst Reusability and Catalytic Performance Comparison of Zn_3(BTC)2. Reusability

13**is an important** aspect **to consider when evaluating** the robustness **of**

a heterogeneous solid catalyst and its commercial potential, particularly from Table 2. Fuel Properties of the Biodiesel Obtained from DPO along with a Comparison to the ASTM D6751 and SNI 7182-2015 Standard Specifications fuel specifications acid value cetane number cloud point density at 40 °C flashpoint kinematic viscosity at 40 °C moisture content unit mg KOH/g °C kg/m3 °C mm2/s ppm ASTM D6751a 0.50 max 47 min report NS 100−170 1.9−6.0 NS SNIb 0.50 max 51 min 18 max 850− 890 100 min 2.3−6.0 500 max DPO biodiesel 0.36 58.7 min −11 885 148 5.44 291 aASTM: American Society for Testing and Materials; NS = not specified. bSNI: Indonesian National Standard. economic and practical viewpoints. In this regard, the catalytic stability of Zn_3(BTC)2 was assessed for

1**up to five** reaction **cycles under** optimal **reaction conditions**

. As depicted in Figure 3a, the FAME yields were maintained at 85−90% over three consecutive runs but then gradually decreased

. Such a decline in the catalytic activity could be attributed to the partial blocking of active catalytic sites by the surface adsorbed oil residue and byproduct (glycerol) molecules or the decreased Lewis acidic OMSs present in the MOF from the leaching event. To confirm the correlation between the activity decrease and metal leaching, we carried out flame atomic absorption spectroscopic (FAAS) measurements of FAME- and glycerol- rich layers at the end of each catalytic cycle. The results indicate that no appreciable leaching of the Zn metal (<5% with respect to the initial content in the catalyst) into the reaction mixture occurred during the first three reuse experiments. In comparison, a more pronounced Zn leaching takes place in the

(see Figure S4). We also compare the catalytic performance of Zn3(BTC)2

through the trans/esterification routes with other MOF materials reported in the literature.[8,38−40] To provide a valid comparison and to better reflect the intrinsic activity of the as- prepared MOF catalyst, the

comparative performance evaluation. Determining the identity and number of active sites can be difficult in the MOF composite catalysts; thus, the moles of the catalyst were used instead

TOF values.[42] As schaotawlynticin aFctigivuirtye 3wbi,ththea ZTnO3(FBTvCalu)2e eoxhfib1i8ts.2 a hh−i1g,h winhtircihnsiics comparable and/or exceeds that of the MOF materials reported by others.[38−40] For example, the intrinsic catalytic aCZcroti((vlTiIlt)OyMFanO=dF1s(3t1a.5)bi(hlTi−ty1O)Foinf=Zth2ne.03(tBhra−Tn1Cs)e)as2ntedarirNfiecHastu2i-poMenrlioLofr-1pt0loa1n(ttChoori)sl-eSanaold-f

lower catalyst loading and methanol/oil molar ratio. The as- prepared catalyst also exhibits an intrinsic activity comparable ttohethBartøonfstFeed3Oio4n@icNlHiq2u-MidILD-8A8ILB(F(Te)OMFO=F1f7u.n5cthio−n1)alifzoerd tbhye Figure 3. (a) Recyclability of the Zn3(BTC)2 catalyst for the simultaneous transesterification−esterification of DPO

.,

22**methanol/oil molar ratio = 6:1; temperature** = 65 °C; **time = 4**.5 h

) along with its catalytic performance compared to the other MOF materials previously reported for FAME production, such as DAIL-Fe3O4@NH2-

1**MIL- 88B(Fe**), NH2-**MIL-101(Cr)-Sal-Zr, Co(II) MOF 1, and Cu-BTC. The**

recovery and reuse experiments of the MOF catalysts in the present work and cited studies were performed according to the procedure described in Section 4.4, with slight variations in the separation process and drying conditions. Note that the catalytic activity of the representative MOF materials over several cycles in the 3D bar chart was redrawn and presented based on the corresponding literature data. (b) Comparison of the intrinsic activity (TOF) of the as-synthesized Zn3(BTC)2 and other MOF catalysts in the trans-esterification and esterification reactions, along with the achieved conversion yield.

26**esterification of oleic acid with methanol**

, while also affording milder and more economical

28**reaction conditions, such as** lower **methanol/oil molar ratio**, temperature, **and catalyst loading**

. Moreover, it is important to remark that the solvothermal preparation of Zn3(BTC)2 MOF is quite simple and involves less expensive precursor chemicals (including an organic linker) than the abovementioned MOF materials, thus presenting an economic benefit. Taken together, these results suggest the great potential of the Zn3(BTC)2 MOF with abundant active sites as an efficient, high-activity, and robust catalyst

1**for the one-step transesterification and esterification reactions**

. 2.7. Proposed

1**Mechanism for the One-Step** Trans- **esterification**−Esterification Reaction **of DPO. The**

proposed

1**mechanism for the one-step transesterification− esterification** reaction **of DPO**

to FAMEs is illustrated in Figure 4. In this kind of reaction, the preactivated Zn3(BTC)2 with open and unsaturated metal centers acts as a mediator that facilitates the convergence of methanol and DPO,

resulting in biodiesel conversion.43,44 These active sites can facilitate the adsorption of reactant species (i.e., triglycerides and methanol) by forming coordination reactions via the interface dipole,45,46 electron delocalization,47 or nucleophilic attack.48 The reaction mechanism steps are explained in details as follows: Step 1: The TG (RCOOR′ as monoglycerides) and FFA (RCOOH) species present in the DPO bind to the central hexa-coordinated zinc atom via their carbonyl oxygen atom, resulting in the formation of carbocation intermediates. The formation of Zn−O bonding could be ascribed to the presence of the dipole on the metal surfaces and the protonation of oleic acid (taken as representative of FFA). At the same time, methanol molecules may also bind to the unsaturated metal sites. Then, a nucleophilic attack occurs between the two neighboring molecules. Steps 2: In the esterification reaction pathway, FAME (RCOOCH3) conversion occurs along with water molecules. proton (H+) transfer to the ester group (R′O) to produce Meanwhile, the transesterification of monoglycerides involves a glycerol (R′OH) through the delocalization of the oxygen atom. Step 3: The resulting FAME molecules are desorbed

> 30**from the** catalyst **through** the **electron delocalization at the oxygen**

atom, where FAMEs as the main product are collected, and the catalyst can be reused for the next catalytic run after regeneration treatment. 2.8. Cost Analysis of the Zn3(BTC)2 Synthesis. The biodiesel production economics depend predominantly on the direct operating cost (DOC), which reflects the costs of raw materials (i.e., feedstock oil, alcoholic reaction solvent, and catalyst) and the operating labors. According to the previous cost analysis study by You et al.,49 the catalyst cost represents the second most significant proportion of the DOC after the cost of the feedstock oil. Accordingly, a great economic advantage in the commercial-scale biodiesel production, aside from utilizing low-grade fatty feedstocks, can also be realized using efficient, low-cost, and reusable solid catalysts. In this section, we examined the economics and energy cost of the kilogram-scale solvothermal synthesis of the Zn3(BTC)2 catalyst

> 24**based on** the **reaction conditions and process steps demonstrated at** the **laboratory scale**

(see Section 4.3). The metal salt and organic linker precursors, reaction solvent, and necessary capital equipment

> 24**in each** process **step (i.e., synthesis, filtration**, activation, **and drying**

) are presented in Table 3 along with their price quotes in US dollars, unless otherwise noted. The cost evaluation results demonstrate that the production cost of the Zn3(BTC)2 catalyst is about US$51

> 12**per kg, which is** found **to** be considerably **cheaper than** those of **commercial**

acidic ion-exchange resin catalysts, such as

> 1**Amberlyst 15 (∼US $100** per **kg), Amberlyst 36 (∼US$120** per **kg), and Purolite D5081/CT175 (∼US$120** per **kg**

). Moreover, compared with the production costs of representative MOFs reported in Figure 3a, the synthesis of Zn3(BTC)2 is intrinsically more affordable by considering (i) the less expensive bridging organic

ligands (the linker price can be found in Table S5), (ii) milder solvothermal reaction conditions, and (iii) fewer synthesis steps. A technoeconomic analysis of the solvothermal MOF synthesis reported by DeSantis and coworkers has identified that the linker costs are the second largest contributor to the MOF production costs after the organic solvents.[50] Although the production cost of $Zn_3(BTC)_2$ is expected to be higher than those of heterogeneous solid base Figure 4. Proposed

1mechanism for the one-step transesterification and esterification reactions of DPO over the Zn_3**(BTC)2 MOF catalyst**

. Table 3. Detailed DOC for the Solvothermal Synthesis of $Zn_3(BTC)_2$

12on the Kilogram Scale DOC specification price (US\$ kg−1) amount (kg)b total (US

\$) chemicalsa 1. $ZnSO_4·7H_2O$ 99.9% 5.6 2.0 11.2 2. H3BTC min 99% 20.0 0.9 18.0 3. DMF min 99.9% 0.9 18 16.2 4. methanol min 99.9% 0.35 4.0 1.4 5. H_2O 18.2 MΩ 0.1 14.0 1.4 Utility electricity 0.1 US\$ per kWh 20.0 kWh 2.0 Total DOC 50.2 aH3BTC = 1,3,5-benzenetricarboxylate; DMF = N,N-dimethylformamide. bThe estimated total amount of DMF solvent for the synthesis and washing steps. Methanol was used for the washing and activation steps. catalysts, such as the alkaline earth metal oxides (CaO and MgO), the feasibility of using substantially cheaper low-quality or waste feedstock oils can lead to the lower overall cost of biodiesel production. A detailed economic cost analysis of the large-capacity biodiesel production is beyond the scope of this study, and the interested readers can refer to a comprehensive study by You et al.[49] 3.

10CONCLUSIONS In summary, we have demonstrated the catalytic utility **of**

a Zn(II)-based carboxylate MOF ($Zn_3(BTC)_2$) for the simulta- neous transesterification and esterification of a low-grade vegetable oil (DPO) to biodiesel. The influential

18reaction parameters, including the methanol/oil molar **ratio**, temper- ature, **and time**

, are optimized through the RSM−BBD method. A one-way ANOVA test points out a more significant role of the methanol/

16oil molar ratio over both **temperature and time to** achieve **the**

maximum FAME conversion. Moreover, the reusability of the $Zn_3(BTC)_2$ catalyst is also successfully demonstrated across five consecutive runs with only a marginal decrease in the FAME conversion. In addition, the following points represent the important results of this study: • The solvothermally synthesized $Zn_3(BTC)_2$ MOF exhibits a triclinic crystal structure with a hierarchical macro/microporous structure and Lewis acidic OMSs. • The maximum biodiesel yield (89.9%) with a 95% DPO- to-FAME conversion

9was achieved under the optimum **reaction conditions of**

a

a 1 wt % catalyst. • The DPO-derived biodiesel properties satisfy the standard fuel specification requirements of ASTM6751 and SNI 7182-2015. • The total DOC of the Zn3(BTC)2 catalyst

than those of previously reported MOF materials and the benchmark acid resin catalysts. 4. EXPERIMENTS ≥99.95% trace metal basis), H3BTC (C6H3(CO2H)3, 98% 4.1. Materials. Zinc sulfate heptahydrate (ZnSO4·7H2O, purity), methanol (CH3OH, anhydrous, ≥99.8% purity), n- hexane (HPLC grade, ≥95% purity), N,N-dimethylformamide (DMF, ACS reagent, ≥99.8% purity), and the FAME reference Table 4. RSM−BBD Experimental Design Showing the Coded and Actual Values of the Reaction Parameters in the Transesterification of DPO Using the Zn3(BTC)2 Catalyst coded parametersa response % FAME yield (Y) run time, h (

) 1 0 (3) 0 (6) 2 1 (4.5) 0 (6) 3 −1 (1.5) −1 (4) 4 −1 (1.5) −1 (4) 5 0 (3) 0 (6) 6 0 (3) 0 (6) 7 1 (4.5) −1 (4) 8 1 (4.5) −1 (4) 9 −1 (1.5) 0 (6) 10 0 (3) 0 (6) 11 0 (3) 0 (6) 12 1 (4.5) 0 (6) 13 −1 (1.5) 1 (8) 14 0 (3) 1 (8) 15 0 (3) 1 (8) 16 1 (4.5) 1 (8) 17 0 (3) 0 (6) aThe actual values of the coded parameters are given in parentheses. temperature, °C (X3) 1 (65) 0 (55) −1 (45) 1 (65) 0 (55) 0 (55) −1 (45) 1 (65) 0 (55) −1 (45) 1 (65) 1 (65) 0 (55) −1 (45) 1 (65) 0 (55) 0 (55) experimental predicted 60.20 59.58 64.02 63.34 63.98 64.21 68.60 69.20 72.80 73.76 73.93 74.12 69.89 70.24 83.41 84.21 79.62 78.17 76.77 75.45 84.33 83.27 89.96 89.89 77.12 77.75 73.77 74.51 80.33 80.67 83.28 82.87 73.24 73.11 standard mixture (Supelco 37-component FAME mix, 47885- U)

. Crude palm oil (CPO) was supplied by

(Bintang Era Sinar Tama, PT). 4.2. Degumming Pretreatment of CPO. CPO was degummed using a conventional dry method with phosphoric acid according to the procedure described elsewhere.51 The acid value (AV) and saponification value (SV) of DPO

AOCS official methods Cd-3d-63 and Cd-3- 25. The average molecular weight of DPO was determined from the AV and SV using the equation described by Akusu et al.[52] and found to be 780.1 g mol−1. The fatty acid composition of DPO (Table S6) was determined using gas chromatog- raphy−flame ionization detector (GC−FID) analysis (GC- 2014, Shimadzu, Japan) as described by Ong et al.[53] The labeling of fatty acid peaks in the chromatogram was performed by comparing their retention times with those of authentic standards. 4.3. Solvothermal Synthesis of Zn3(BTC)2. The one-pot solvothermal synthesis of Zn3(BTC)2 was carried out following a previously reported procedure with minor modifications.[23] Briefly, ZnSO4·7H2O (2.16 g, 7.51 mmol)

36**and H3BTC (1.05 g**, 5.0 mmol) **were dissolved in**

30 mL of the DMF/H2O (1/1; v/ v) mixture and then magnetically stirred at 200 rpm for an hour at room temperature. Subsequently, the

31**mixture was transferred to a Teflon-lined stainless steel autoclave and heated** isothermally **at** 85 **°C for 24 h**

.

35**Afterward, the** autoclave **was** gradually **cooled to room temperature. The**

resultant white powder (∼1.2 g; 76% molar yield based on Zn)

6**was collected** by **vacuum filtration followed by washing with** fresh DMF **and**

anhydrous methanol to remove the unreacted starting material. The obtained Zn3(BTC)2 was activated using methanol reflux for 4 h followed by drying in an oven at 150 °C for 12 h. 4.4. Biodiesel Production. The catalytic activity of Zn3(BTC)2 was assessed for the simultaneous transesterifica- tion and esterification reactions of DPO in a batch mode. The methanol/oil molar ratios were varied from 4:1 to 6:1 to 8:1, while the catalyst loading was adjusted to 0.5, 1.0, 3.0, and 5.0 wt % relative to the DPO. The mixtures were then heated to the desired temperatures (i.e., 45, 55, and 65 °C) using an electric heating mantle and held isothermally for 1.5, 3, and 4.5 h with continuous magnetic stirring at 500 rpm. After the reaction, the flask was quenched in an ice-water bath. The resulting products composed of the upper fatty acid methyl esters (FAMEs)-rich and lower glycerol-rich phases were separated by centrifugation at 4900 rpm for 5 min. The FAME compositional analysis was carried out by the GC−FID method described in our previous study.[53] The yield of FAMEs was determined based on the following equation: FAME yield (%) = weight of biodiesel (g) weight of DPO (g) × FAME content FAME content = 100 × i ΣA − AIS y × ji CIS × j VIS y k AIS z { k m z { (2) (3) The FAME content was calculated as the sum of the integrated peak areas of all individual FAMEs identified in the samples (ΣA) according to eq 3.[54] The notations AIS, CIS, and VIS denote the peak area, concentration, and volume of the methyl heptadecanoate (C17:0) solution as the internal standard, respectively. The spent catalyst powder was further collected by centrifugation and purified

16**by multiple washing with n-hexane to remove**

any residual oil left on the catalyst surface. The recovered catalyst was dried under vacuum at 60 °C for 12 h and then used in the subsequent reaction cycles for the reusability test. 4.5. Material Characterizations. Characterizations of the as-synthesized Zn3(BTC)2 were carried out using field- emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), nitro- gen (

> 5**N2) adsorption−desorption isotherms, and Fourier** transform **infrared (FTIR) spectroscopy**

. SEM images were collected using an FEI Inspect F50 at an accelerating voltage of 10 kV. XRD patterns were acquired using a

> 5**Bruker D2 Phaser** X-ray **diffractometer equipped with a Cu Kα radiation source (λ = 0.15406 nm) in the 2θ range of** 10−**50° at a scan** speed **of 0**

.1°/s.

> 32**N2 adsorption−desorption** measurements **were** con- ducted **at −196 °C using a**

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> 6**analyzer. Prior to** the **sorption measurements, the sample was degassed** at 200 °C **under vacuum for 12 h. The**

> 43**thermal stability of the** catalyst **was** examined **using a** Perkin-Elmer **TGA**

8000 analyzer

> 10**from 30 to 600 °C with a** heating **ramp of 10 °C/ min under**

a N2 flow at 20 mL/min. FTIR spectra were collected in transmission mode using a Shimadzu 8400S spectrometer in the wavenumber range of 4000−500 cm−1 with a KBr pellet method. 4.6. Design of Experiments and Mathematical Modeling.

> 26**RSM based on the Box−Behnken design** (BBD) **was** adopted **to investigate the effects of**

the reaction parameters and their interactions toward optimizing a particular response. The mathematical modeling and statistical analysis were performed using the Design-Expert version 12 software (Stat-Ease Inc., Minneapolis, MN, USA). Three reaction parameters affecting the production of FAMEs were investigated, namely, time (coded as X1), methanol/oil molar ratio (coded as X2), and temperature (coded as X3). The experimental design was constructed using 17 runs with three levels for each parameter, including three replications at the center point, as presented in Table 4. The experimental data were then

analyzed using a second-order polynomial response surface model as follows: K K K K Y = αo + ∑ αiXi + ∑ αiiXi2 + ∑ ∑ αijXiXj + e i=1

18i=1 i=1 j=i+1

(4) where Y is the target response (i.e., % FAME yield), Xi is the coded levels of independent variables, αo

14is the regression constant, αi is the linear term corresponding to the input factor Xi, αij corresponds to the interaction term between the input factors Xi and Xj, αii is the quadratic term of input factor Xi, and e is the experimental error value of Y. The

term K represents the total number of experimental variables involved in the optimization of the response. ∎

11ASSOCIATED CONTENT *sı Supporting Information The Supporting Information is available free of charge at

https://pubs.acs.org/doi/10.1021/acsomega.0c03826. • Bravais lattice parameter of Zn3(BTC)2 (Table S1), unit cell parameters of Zn3(BTC)2 (Table S2), textural properties of the Zn3(BTC)2 (Table S3), representative MOF catalysts applied in the transesterification and esterification reactions (Table S4), cost details of the organic linkers used in the synthesis of representative MOFs (Table S5), fatty acid composition of DPO obtained from GC−FID analysis (Table S6), OFAT analysis of the Zn3(BTC)2 catalyst loading (Figure S1), plot of actual vs predicted FAME yield response (Figure S2), GC−FID chromatogram and mass fraction of FAME species in DPO-derived biodiesel (Figure S3), leaching profiles of zinc metal post-usage of Zn3(BTC)2 (Figure S4) (PDF) ∎ AUTHOR INFORMATION Corresponding Authors Shella Permatasari Santoso Department of Chemical − Engineering, Widya Mandala Surabaya Catholic University, Surabaya 60114, Indonesia; orcid.org/0000-0003-4698- 583X; Phone: +62 31 3891264; Email: shella_p5@ yahoo.com; Fax: +62 31 3891267

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