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Received: 1 April 2021 Revised: 5 July 2021 Accepted: 6 July 2021 DOI: 10.1002/er.7064 RESEARCH ARTICLE

5Double-shelled hollow mesoporous silica incorporated copper (II) (Cu/DS-HMS-NH2) as a catalyst to promote in-situ esterification/transesterification of low-quality palm oil

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: mariayuliana@ukwms.ac.id Funding information Widya Mandala Surabaya Catholic University, Grant/Award Number: 2263/ WM01/N/2020; National Taiwan University of Science and Technology; National Sun Yat-Sen University Summary To encourage the utilization of low-quality palm oil with high free fatty acid and moisture content (>0.1 wt%), a novel catalyst with

1**two spatial shells** and **different active sites**

,

5**double-shelled hollow mesoporous silica incorporated copper (II) (Cu/DS-HMS**

-

1**NH2), is fabricated** via **the two**-stage hydrolysis and **condensation technique. The**

influence of four parameters (eg, catalyst loading, temperature,

1**reaction time, and the mass ratio of methanol to** degummed palm **oil**

(DPO)) on the yield of fatty acid methyl ester (FAME) are monitored and optimized

4**using a combination of response surface methodology (RSM) and**

1**face centered-central composite** experimental **design (CCF-CCD**

). The optimized FAME yield is predicted at 86.63 wt% and experimentally obtained at 87.14 ± 0.11 wt% (FAME

4**purity of 98**.45 ± **0**.67 **wt**%) under **the following** optimum **condition**

: 55.3 C, 5 h,

12**methanol to** DPO **mass ratio of 5**.3:**1**

, and 5 wt% catalyst loading. The experimental and

2**predicted values are** proportional and **in direct agreement with an error of 0**.51%. **The** goodness **of fit**

analysis also indicates conformity between the mathematical model and the experimental results. The reusability study shows that Cu/DS-HMS-NH2 is stable until the fifth run, evident from the yield of FAME which stays above 80%. These results prove the potential utility of Cu/DS-HMS-NH2

19**for the** direct **conversion of low-quality** vegetable **oils to biodiesel**

without any pre-treatment.

1**KEYWORDS bifunctional catalyst, biodiesel**, double-shelled, **mesoporous silica**

, optimization study Abbreviations: CPO, crude palm oil; DPO, degummed palm oil; FAME, fatty acid methyl esters; FFA, free fatty acids; MSN, mesoporous silica nanoparticles; S-

1**HMS-NH2, single-shelled hollow mesoporous silica**

. Antonius Nova Rahadi and Jeremia Jonathan Martinus

1**contributed equally to this work**. 1 | INTRODUCTION **The** ever-increasing dependency on fossil fuel as an energy source may endanger its sustainability. At the same time, the long-term use of this fuel also raises an environmental concern because it's flue gas emission Int J Energy Res. 2021;1–18. wileyonlinelibrary.com/journal/er ©

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contains various greenhouse gases (ie, CO2, CH4, N2O, and O3).1 The development of sustainable and environ- mentally benign alternative fuels is, therefore, urgently required. Among the available alternative fuels, biodiesel is known to be environmentally friendly as it possesses a high oxygen content, which can increase the fuel com- bustion rate, and reduce carbon monoxide production.2,3 Currently, the mass production of biodiesel uses the con- ventional base catalysts, such as sodium methylate and potassium hydroxide, since they provide a high reaction rate and satisfactory yields. However, these homogenous catalysts require several additional post-separation steps (eg, acid washing, separation, and refining) for biodiesel purification, exhibit poor tolerance to contaminants (free fatty acids [FFA] and moisture),4 and are not reusable.5 Hence, the use of this type of catalyst limits the selection of feedstock materials and increases the overall production cost. On the other hand, heterogeneous catalysts offer sev- eral advantages over their homogeneous counterparts due to their reusability, insensitivity to impurities in the feedstock, and easier separation from the reaction prod- uct.6 Many studies have reported the synthesis of biodie- sel using heterogeneous acid or base solid catalysts for producing biodiesel,6,7 such as metal-organic frame- works8,9 and functionalized mesoporous silicas.5,10 A wide variety of solid catalyst, for example, alkaline- modified zirconia,11 polyoxometalate (POM)-

5**based sulfonated ionic** liquid immobilized-**UiO-66-2COOH**

,12 Amberlyst?15 and its modified form,13

5**carbon nanotube- based solid sulfonic acids**

,14 sulfated niobium oxide,15 and solid superacid catalyst (SO42+/ZrO2-TiO2/La3+),16 has been studied. However, despite their insensitivity to impurities and ability to perform simultaneous reactions, these catalysts require extreme reaction conditions, with the

16**temperature range between** 100 **and** 250 **C**. Amberlyst?15 **and**

POM-

16**based sulfonated ionic** liquid immobilized-**UiO-66-2COOH**

also require a long reaction time (up to 9 h)13 and high catalyst loading (up to 10 wt%),12 respectively. In recent years, mesoporous silica nanoparticles (MSN) have gained extensive attention in many applica- tions, due to their low cost, facile synthesis, ease of sur- face modification, considerable pore capacity, various particle frameworks, and tunable textural properties.17-19 García-Sancho et al (2011)20 reported the use of niobium- containing MCM-41

8**to produce biodiesel from edible** sunflower **oil**, while Xie **et al**

(2015)7 studied the perfor- mance of

23**SBA-15 immobilized with 1,3-dicyclohexyl- 2-octylguanidine**

, to prepare commercial soybean oil-based FAME. While both MCM-41 and SBA15 possess excellent textural properties, for example, high surface area and good porosity, it requires complicated synthesis procedures to design two spatial shells with different active sites within a particle of the two materials, as both have rod-like structure. This hinders the impregnation of two active components on the surface of MSN, and therefore, limits its use

1**in the** synthesis **of biodiesel from low-quality** oils. In **this** study, we design **a**

1**new class of catalyst, the** copper-incorporated **double-shelled hollow mesoporous silica**

(Cu/DS-HMS-NH2), with distinct functionalities that can facilitate both esterification and trans- esterification reactions simultaneously in one simple pro- cess with mild reaction conditions. While the inner layer is purposedly

1**designed to promote the transesterification reaction by adding -NH2 as the basic site** in **the**

fabrica- tion,

1**while the outer layer is impregnated with**

copper (Cu (II)) to induce the esterification reaction. The copper metal is mainly used as an active site for the ester- ification reaction due to its availability and high reactiv- ity to various types of reactions. The incorporation of copper to the DS-HMS-NH2 surface also increases the thermal stability of the catalyst and improves the esterifi- cation efficiency in converting the FFA to fatty acid methyl ester (FAME).8,21 Therefore, it is certainly of great interest to study the catalytic performance of Cu/DS- HMS-NH2, as this bifunctional catalyst improves the chance of low-quality oil to be widely utilized

6**as the raw material for biodiesel production**

, and at the same time, offers an ability to

22**promote the** concurrent **esterification/ transesterification** reaction **in a one-pot** synthesis. The utilization of low-quality oils for biodiesel pro- duction has attracted public attention, as it may sustain the supply chain of the food sector. Various feedstocks, for example, animal fats,22,23 waste cooking oil,24 leather tanning waste,25 and jatropha (Jatropha curcas L.) oil,26 have been developed to prepare commercial-grade biodie- sel. The present research tests the catalytic ability of Cu/DS-HMS-NH2 to produce biodiesel from degummed palm oil (DPO) in several operating variations (catalyst loading (wt%), temperature (C), the mass ratio of metha- nol to DPO, and reaction time (h)). With the high amount of FFA and moisture, DPO is regarded as a low- quality oil;

1**therefore, it is considered as a suitable raw material to determine the** viability **of** Cu/**DS-HMS-NH2**

22**for the conversion of** both **FFA and triglycerides** in DPO **into biodiesel**

. The selection of DPO is also to avoid food shortages, simplify the process and lower the operational cost. The process evaluation and optimization are deter- mined using a response surface methodology (RSM) approach combined with face centered-central composite experimental design (CCF-CCD). The reusability of Cu/DS-HMS-NH2 is then investigated at the optimum operating condition. Moreover, the catalytic

1**reaction mechanism of the in-situ esterification/transesterification** during the conversion **of DPO** to biodiesel **using** Cu/**DS- HMS-NH2**

is also discussed. 2 | MATERIALS AND METHODS 2.1 | Materials All chemicals used in this study were of reagent grade and purchased from Sigma-Aldrich (Germany). There- fore, they were used without further purification. Mean- while, the raw lipid material, crude palm oil (CPO), was obtained from PT. Batara Elok Semesta Terpadu, a local palm oil manufacturer in Indonesia. Prior use, CPO was subjected to the degumming process: CPO and phospho- ric acid (PA) with a ratio of 100:1 (v/v) were mixed and heated to 80 C, where the temperature of the system was maintained isothermally for 15 min. The mixture was then cooled down to room temperature and subse- quently subjected to centrifugation at 4900

13**rpm for 10 min to remove the** gum soluble in **the**

PA-rich phase. To ensure the remnants of gum in CPO were completely removed, a 2-portion of hot water was added to one- portion of CPO. The mixture was vigorously mixed using a high-speed agitation system before subjected to another centrifugation process (4900 rpm, 10 min) to obtain the DPO. Both CPO and DPO were analyzed for their FFA,

1**acid value, saponification value, and moisture content**

using the

1**standard method of AOCS Ca 5a-40, Cd 3d-63, Cd 3d-25, and Ca 2e-84, respectively**

. The fatty acid pro- file in DPO was also observed using

3**GC-2014 (Shimadzu Ltd., Japan**) equipped with **Restek Rtx-65TG**

(

21**30 m 0.25 mm** ID **0**.10 **μm film thickness**, Restek) and a **flame ionization detector (FID). The average** molar **weight of**

CPO and DPO (MPO) was calculated by Equa- tion (1), where SV and AV are corresponding to the saponification value (mg KOH/g oil) and acid value (mg KOH/g oil) of the oil. MPO ¼ 56:ð1SV ?10A0V0Þ 3 : ð1Þ 2.2 | Synthesis of Cu/DS-

1**HMS-NH2** The **single-shelled hollow mesoporous silica** (S-**HMS- NH2**

) was prepared

9**in accordance with the** procedures **reported by** Wang **et al** (2015),27 where **a** mixture **of**

CTAB (0.14 g), ethanol (20 mL), deionized water (50 mL), and ammonia solution 25% (1 mL) was intro- duced into a beaker and stirred for 15 min at room tem- perature. One milliliter of tetraethyl orthosilicate (

1**TEOS) was** then **slowly added** to **the** mixture **and kept stirring for 24** h. **The**

pH during the synthesis was monitored at 10-11. The white precipitates were separated via centrifu- gation

1**at 4500 rpm for 30 min, ethanol washing, and** dry- ing **at 120 C overnight. The**

resulting dried solid

1**was calcined at 550 C for 6 h to obtain**

S-HMS-NH2. Meanwhile, the fabrication of the second shell was conducted using the modified methods of You et al (2018)28:0.5 g CTAB was dissolved in

15**18 mL deionized water and 50 mL ethanol. Then, 4 mL deionized water**

, 0.063 g S-HMS-NH2, and 8.5 mL 25% ammonia solution were added into the solution. A 100 μL

15**of TEOS and 21** μL **of APTES were** subsequently **added to** the above solution at room temperature to induce the condensation of silica. The reaction system was maintained homoge- nous for 24 h under continuous agitation; the same pH range (pH = 10-11) was observed. After the reaction was completed, the mixture

13**was centrifuged at 4500 rpm for 10 min to** obtain **the**

solid phase,

1**which was repeatedly washed with ethanol**

. The sample was dried at 100 C overnight to remove the solvent. To eliminate the surfac- tant from mesoporous material, the sample

1**was calcined at 550 C for 6 h to obtain**

1**DS-HMS-NH2** particles. **The impregnation of**

Cu (II) to DS-HMS-NH2 particles was carried out using the traditional wet impregnation method studied by Zaidi and Pant (2008)29 with few mod- ifications. A 0.1 g DS-HMS-NH2 was dissolved into 0.001 M CuSO4 solution and reacted for 12 h at constant pH (5.0). The solid phase was

1**separated by centrifugation at 4500 rpm for** 10 **min**

, oven-

26**dried for 12 h at 100 C, and calcined for 5 h at** 550 **C to**

yield Cu/DS-HMS-NH2 parti- cles with 1 wt% of impregnated Cu (II). 2.3 | Experimental design and process optimization The biodiesel synthesis through an in-situ esterification/ transesterification reaction between methanol and DPO using the heterogeneous catalyst of Cu/DS-HMS-NH2 was conducted in various conditions, namely reaction temperature, time, and the mass ratio of DPO to metha- nol. These experiments were conducted at a constant cat- alyst loading that gives the highest amount of FAME yield. These independent factors were selected based on their relevance to the process efficiency and economic applicability. A

3**design of experiment (DOE**), combined **with the**

standard design tools, face-centered central com- posite design (CCF-CCD), and RSM, 3**was employed to determine the optimum operating** condition **for the** synthesis **of biodiesel** with **the**

FAME yield selected as the response. The three optimized variables were divided into the following coded level: low (?1), middle (0), and high (+1), as presented in Table 1. The designed matrix between the encoded variables, the predicted and experimental responses are presented in Table 2. Triplicated experiments were carried out for every set of the input parameter to generate a good response reproducibility. Seven experimental data at the center point (0,0,0) were presented individually for every run. The responses were fitted into a second-order poly- nomial

2**model, developed using** a 3-**way analysis of** vari- ance (**ANOVA**

) with a

2**95% confidence level. The goodness-of-fit** of **the** mathematical **model was** evaluated **by** various parameters, including **the**

coefficient of deter- mination (R2), the

2**lack-of-fit sum of squares**

, coefficient of variations (C.V.), and adequate precision. The surface plots between the two inter-correlated variables were developed using the regressed experimental results by maintaining

3**one variable constant in the middle** point **while** changing **the other two variables. The correlation between the predicted response (yield** of FAME, wt%) **and the independent** variables **are expressed by Equation** (2), **where Y is the predicted** FAME **yield**

(wt%);

10**k0, ki, kii, kij are the** regression coeffi- cients **for the intercept, linear, quadratic, and interactions of the** independent **variables, respectively**; Xi **and Xj are the** coded factors (**A, B, C**

). X3 X3 X3X3 Y ¼ k0 þ kiXi þ i¼1 i¼1 kiiX2i þ kijX iX j: ð2Þ i¼1 j¼1 Reaction parameter Temperature (

1**C) Reaction time (h) Mass ratio of methanol to DPO**

Coded factor A B C Factor level ?1 0 45 55 1 3 2:1 4:1 +1 65 5 6:1 T A B L E

21 **The coded parameters** with **their** actual **values in the design**

of the experiment Run 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 Input parameters A B ?1 ?1 ?1 ?1 ?1 0 ?1 1 ?1 1 0 ?1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1 ?1 1 ?1 1 0 1 1 1 1 Responses (yield of FAME, wt%) C Experimental (n = 3) Predicted ?1 52.94 52.87 1 59.68 59.39 0 73.48 73.52 ?1 76.85 76.65 1 80.46 80.97 0 65.82 66.97 ?1 72.85 73.81 0 80.49 79.95 0 79.81 79.95 0 81.42 79.95 0 80.86 79.95 0 79.27 79.95 0 78.85 79.95 0 80.85 79.95 0 85.68 85.49 ?1 58.75 58.00 1 68.95 68.91 0 75.77 76.69 ?1 73.42 73.47 1 82.35 82.17 T A B L E 2 The experimental design based on CCF-CCD, presented along with the experimental dan predicted responses 2.4 | The synthesis

1**of biodiesel using** Cu/**DS-HMS-NH2**

as a heterogeneous catalyst The

27**reaction was carried out in a flask, equipped with a** heating mantle, and **reflux condenser, under atmospheric pressure**

. Methanol and DPO were initially introduced into the flask in various mass ratios (2:1, 4:1, and 6:1). The mixture was stirred and

7**heated to the desired** tem- perature (**45, 55, and 65 C**

) before the addition of Cu/DS- HMS-NH2 to the system (1, 3, 5, and 7 wt% of the DPO). The system was maintained homogenous under constant agitation (250 rpm) throughout the reaction (1, 3, and 5 h). Once the reaction reached completion, Cu/DS- HMS-NH2 was removed from the mixture by filtration to obtain the two-layered product, which was subsequently subjected to an overnight liquid-liquid separation using n-hexane. The light phase

2**contains n-hexane and FAMEs, while the** heavy phase **was** rich in **glycerol**, excess **methanol, and other** by-products. **The bottom** layer **was**

repeatedly washed by

2**n-hexane to** ensure **that all** FAME has **been extracted. The** obtained **FAME**-rich phase **was**

then subjected to a solvent removal using an IKA RV 10B vacuum evaporator to obtain a purified final product. The yield of FAME can be expressed by the fol- lowing equation: Yield of FAME ð%Þ ¼ PFAME mBD 100%, ð3Þ mDPO where PFAME (%) is the purity of FAME obtained from Equation (4), mBD (g)

25**is the mass of the final** biodiesel **product** obtained from **the** in-situ esterification/trans- esterification reaction process, and mDPO (g) is the mass of DPO used in the reaction. 2.5 | Characterization The catalyst characterization includes

19**scanning electron microscopy (SEM), transmission electron microscopy (TEM**), energy-dispersive **X-ray spectroscopy**

(EDX),

1**nitrogen sorption, and thermogravimetric analysis (TGA**) to respectively determine **the**

morphology; pore and double-shelled structure; elemental composition; textural properties; and thermal stability of Cu/DS-HMS-NH2. SEM and

1**EDX images were taken on a JEOL JSM-6500 F (Jeol Ltd., Japan) running at 15.**0 **kV**

accelerating voltage and 12.2-12.5 mm working distance. TEM images were acquired using

1**JEOL JEM**-3010 **with an accelerating** volt- age **of 200 kV**. The **nitrogen sorption analysis was** carried out **at 77 K on a Micrometrics ASAP 2010 Sorption**

Ana- lyzer. Before analysis, the samples were outgassed at 150 C for 4 h under vacuum. The adsorption-desorption of nitrogen isotherm is run at a pressure range (p/p) of zero to unity. To analyze the catalyst stability at high temperatures, TGA analysis was employed on a

6**TG/DTA Diamond instrument (Perkin-Elmer, Japan). A**

certain mass of the sample was placed in a platinum pan and heated from the ambient temperature

6**to 900 C with a** heating **rate of 10 C/min to monitor the** thermal stability **of the catalyst**

. Nitrogen gas was purged

25**into the system at** the **rate of** 20 **mL**/min throughout **the**

entire analysis to maintain the system oxygen-free. To verify the formation of FAME from the DPO, the functional groups of DPO and FAME were analyzed using Shimadzu FTIR 8400 s in the wavenumber range of 4000-400 cm?1. Then, the purity and compositional anal- ysis of FAME were conducted using Shimadzu GC-2014 (Shimadzu, Japan), according to the method reported by Santosa et al (2019).23 The FAME purity in the sample Pwas calculated following Equation (4) below, where AFAME is the total area of FAME peaks, AMH

11**is the peak area of methyl heptadecanoate** (MH), **V** MH **is the volume of** MH **solution added to the sample (ml**), CMH **is the** actual **concentration of** MH **solution (g/ml), and** mBD **is the** sample weight **of**

the final biodiesel prod- uct (g). FAMPEPurity ðPFAME,wt%Þ ¼ AFAME ? AMH V MHCMH ð4Þ AMH mBD 100%: 2.6 | Reusability study The reusability study was performed by repeatedly using Cu/

1**DS-HMS-NH2** for **the preparation of biodiesel**

at the optimum reaction condition. After each reaction cycle, Cu/

1**DS-HMS-NH2 was recovered by centrifugation** (4500 **rpm**, 15 **min) and calcination**

(550 C, 5 h) to be subsequently reused. Meanwhile, fresh DPO and metha- nol were used in every cycle. The repetition was con- ducted until the FAME

1**yield became lower than 80** wt%. **The purity and yield of FAME were** measured using **the** procedure **in** Sections **2.4**

and 2.5. 3 | RESULTS

1**AND DISCUSSIONS 3.1** | Characterization **of** Cu/**DS- HMS-NH2**

As presented in

1**Figure 1, the** synthesis route **of** Cu/**DS- HMS-NH2**

can be divided into several steps as follows: (1) the ellipsoidal micelles of CTAB are formed with an F I G U R E 1 Fabrication route of Cu/DS-HMS-NH2 [Colour figure can be viewed at wileyonlinelibrary.com] inner core consisting of the hydrophobic tail, (2) during the addition of TEOS, the micelles enlarge, and result in the transformation of micelle shape from ellipsoidal to spherical, (3) TEOS has then undergone hydrolysis and condensation reaction along with the ammonium solu- tion to form a silica shell around the micelles, (4) the CTAB micelles are removed from the core using calcina- tion to form HMS-NH2, (5) to synthesize the outer shell and create the DS-HMS-NH2, TEOS, APTES, and CTAB are subjected for another hydrolysis and condensation reaction, (6) Again, both CTAB and APTES are removed from the DS-HMS-NH2 nanospheres by calcination at high temperature, and (7) Cu (II) are impregnated on the

1**surface of DS-HMS-NH2** using **wet impregnation** tech- nique to produce Cu/

1**DS-HMS-NH2. The** morphological structure **of the**

fabricated catalyst (Cu/DS-HMS-NH2) powder is analyzed using SEM and TEM analysis (Figure 2). Figure 2A,B captures the respec- tive surface morphology of

1**DS-HMS-NH2** and Cu/**DS- HMS-NH2**

particles. Due to the spontaneous formation through co-condensation during the synthesis, both parti- cles are found to be spherical in shape, uniform in size (at ~150 nm), and have a neat surface structure.27 Spheri- cal particle shape was also reported by You et al (2018)28

1**for a similar double-shelled hollow mesoporous silica**

. As seen from the corresponding figures, there is a clear dif- ference between

1**DS-HMS-NH2** and Cu/**DS-HMS-NH2**

, particularly in their surface roughness. It is apparent from Figure 2B that Cu/

1**DS-HMS-NH2** possesses **a** rough **surface** topography because **of**

the impregnation of cop- per nanoparticles, which shapes including rods, cubes, and tetrahedrons. The TEM images (Figure 2C-F) confirm the formation of the double-shell, where the inner shell has a higher silica density than the outer one, indicated by the darker color gradation. Figure 2D shows that both the inner and outer shells of DS-HMS-NH2 have a similar thickness, approximately 16-19 nm. It also verifies that DS-HMS-NH2 has a diameter of 150 nm, with a hollow core size of 81 nm. Meanwhile, Figure 2F shows that the Cu/DS-HMS-NH2 possesses a diameter of 157 nm, slightly larger than the not-impregnated parti- cles, indicating that copper incorporation onto the sur- face adds some layer, with approximately 7 nm in thickness. The copper impregnation is further verified by the results of the EDX analysis (Figure 2G). It can be seen from the elemental composition that there is 1.22 wt% of impregnated copper on the particle surface, which meets the expected copper content in the Cu/DS-HMS-NH2 cat- alyst. The other elemental content includes (1) 30.5 wt% silica and 52.39 wt% oxygen which are the main elements constructing silica nanoparticles, (2) 15.78 wt% carbon which comes from the undegraded TEOS and/or surfac- tant, and (3) trace amount of calcium (0.11 wt%). The adsorption-desorption isotherm of Cu/DS-HMS- NH2 (Figure 3A) implies that this catalyst possesses a typi- cal type-IV mesoporous isotherm,30,31 indicating the pres- ence of mesoporous capillary pores within the particles, with the mean pore diameter of 2.43 nm. Khatun et al (2017)32 reported similar adsorption-desorption profile for the mesoporous particle, where only a gradual increase in nitrogen adsorption occurs in the p/po range from 0.1 to 0.9, while a sharp increase was observed in the range of p/p0 between 0-0.1 and 0.9-1.0. Another study mentioned that a steep increase

1**at p/p0 close to unity also suggests**

FIGURE 2

6**A, SEM image of** DS- HMS-NH2; **B, SEM image of**

Cu/DS-HMS- NH2; C, and D, TEM image of DS-HMS- NH2, E, and F, TEM images Cu/DS-HMS- NH2; and G, EDX image of Cu/DS-HMS- NH2 [

18**Colour figure can be viewed at wileyonlinelibrary.com**] that there **are** macropores interior **in**

the particle, which indicates the same sorption tendency and behavior corresponds to the hollow structure.33 An identical hyster- between the two, emphasizing that this catalyst possesses esis loop between the adsorption and desorption curves high accessibility.10 The textural properties of Cu/DS- FIGURE

243 **A, N2 adsorption/desorption isotherm and B**, TGA profile **of**

Cu/DS-HMS-NH2 HMS-NH2 (

7**surface area, SBET, and pore volume**

, Vp) are monitored at 733.24

7**m2/g and 0**.54 **cm3/g**

. This result shows that the catalyst possesses comparable, if not higher, textural properties to the existing heterogeneous catalysts used for biodiesel production which generally

1**range from 200** to **1300 cm2/g** for the SBET, **and**

from 0.18 to 1.68 cm3/g for the Vp.8,28,34,35 Figure 3B presents the degree of thermal stability of the catalyst which is determined through TGA analysis. The figure shows that a weight loss of 23 wt% occurs in the temperature range of 0 to 100 C. This is likely due to the dehydration and removal of the hydroxyl groups from the surface of the particles. At a temperature higher than 100 C, the catalyst particles do not experience significant weight loss, implying that surfactants and the other organic compounds have been removed in the previous calcination process36; thus, it can be concluded that Cu/DS-HMS-NH2 has good thermal stability. 3.2 | The

3**effect of the reaction parameters on the yield** of FAME in **the**

biodiesel preparation using Cu/DS- HMS-NH2 Table 3 summarizes the characteristics of CPO and DPO used in biodiesel production using Cu/DS-HMS-NH2. Notably, DPO possesses high FFA content (5.54 wt%), rendering the lipid material a low-quality oil. Figure 4 shows the influence of the catalyst loading on the yield of FAME. Based on the figure, it can be seen that the in-situ esterification/transesterification is significantly affected by the amount of catalyst used. Escalating the Cu/DS- HMS-NH2

6**loading from 1 wt% to** 5 **wt% greatly** improves **the yield** of FAME **by**

more than 10 folds. However, a T A B L E 3 Characteristics of CPO and DPO Parameter CPO FFA (wt%) 5.68 Acid value mggDKPOOH 12.13 Moisture (wt%) 0.51 Fat content (wt%) 93.18 Saponification value mggDKPOOH 232.23 ? Molar weight mol g 764.65

8**Fatty acid** profile (**wt%) - Lauric acid (C12:0**) Myristic **acid (C14:0) Palmitic acid (C16:0) Stearic acid (C18:0) Oleic acid (C18:1) Linoleic acid (C18:2**) Linolenic **acid(C18:3**) Arachidic **acid**

(C20:0) DPO 5.54 12.04 0.57 93.65 234.08 756.62 0.9 1.4 43.7 3.4 38.3 11.2 0.7 0.4 further catalyst addition to 7 wt% slightly reduces the FAME yield. Previous studies agree that the catalyst amount above 7.5 wt% is inefficient and instead, reduces the yield.5,37-39 This is because the higher the content of solid catalyst added to the reaction system, the higher the mixture viscosity, leading to an inconsistent dispersity. Gurunathan and Ravi (2015)1 added that a high amount of catalyst inhibited the interaction of reactant with the active sites of the catalyst due to aggregation; therefore, lowers the FAME yield. Figure 5A(1-3) presents the effect of two inter- connected variables on the experimental FAME yield, in F I G U R E 4 The effect of Cu/DS-HMS-NH2 loading (wt%) on the yield of FAME (wt%) (reaction time = 5 h, temperature = 65 C, and mass ratio of methanol to DPO = 6:1) 3D surface plots. The effect of reaction time on the yield of FAME is depicted in Figures 5A(1,2). Looking at the data curve, it is apparent that reaction time gave a signifi- cant

2**influence on the yield of FAME**. An increase in **the** duration **of**

reaction from 1 to 5 h sharply escalates the response. Longer reaction time gives the reactants higher opportunities to come into contact with the active sites of Cu/DS-HMS-NH2.40 It also allows the adsorption and

1**diffusion of the reactants** to reach **the** internal pores **of** the **catalyst**

, where the actual reactions took place. In terms of the catalyst, extending the reaction time also provides the

1**catalyst more time to adsorb the reactant and desorb the product**

.8 Moreover, as the sorption of reactant from the catalyst is the reaction governing step,41

1**allowing longer contact between** both reactants **and catalyst** assures **high** conversion **of**

DPO to FAME. The

1**effect of reaction temperature on the**

other two variables is depicted in Figure 5A(1,3).

1**Both esterification and transesterification** reactions **are endothermic and reversible**

process.42,43 Therefore, it can be seen that when the temperature is increased from 45 C to 55 C, a significant increase is observed in the yield of FAME. Heating the reaction system accelerates the mobility of the reactant molecules and catalyst particles, leading to intensive particle collision in the system. This phenome- non increases the

3**reaction rate constant and shifts the** reaction **to the right (product side**).43-46 **From another viewpoint**, an increase in **temperature** also enhances **the**

mass transfer and diffusivity

1**of the reactant molecules** to **the** pore **of** Cu/**DS-HMS-NH2**

; therefore, heightening the yield of FAME. A further increase to the temperature of 65 C, on the other hand, lowers the yield of FAME. Madhuvilakku and Piraman (2013) and Yin et al (2016)47,48 stated that this tendency occurs due to the loss of methanol in the reaction system caused by evapora- tion, which induces the reverse reaction towards the reactants.

3**A similar trend is also observed for the**

24**influence of methanol to** DPO mass **ratio on the** FAME **yield**

. As seen from Figure 5A(2,3), increasing the level of

7**methanol to DPO** mass ratio **from** 2:**1 to** 4:**1** escalates **the FAME**

yield, while further addition of methanol in the system, reaching the

7**methanol to** DPO **mass ratio of** 6:**1**

, gives an antagonistic effect to the yield. This result is in accor- dance with the study proposed by Gunawan et al (2014)49 where the excess methanol is

6**favorable to the** reaction, **only to a certain extent**

. Pangestu et al (2019)8 added that even though the yield of FAME may increase along with the amount of methanol, it may as well rapidly improve glycerol production. This phenomenon may subsequently provoke

3**a reverse reaction to the reactant side**, lowering **the**

FAME yield. Furthermore, a

1**higher mass ratio of methanol to DPO** will only increase **the** production **cost**

, reducing the operating efficiency.23 3.3 | Process optimization RSM is statistically

3**employed to determine the optimum operating conditions for the production of**

FAME using Cu/DS-HMS-NH2, by simultaneously integrating the three important parameters, for example,

1**reaction time, temperature, and** the **mass ratio of methanol to DPO**

.

4**Table 2 presents the** correlation **between the** input variables **and their corresponding**

response (FAME yield, wt%). The average SE estimate between the actual and predicted response is obtained at 0.01% (n = 20), indicating sufficient data accuracy. A similar trend as the experimental data is also observed from the predicted plots, as depicted in Figure 5B(1-3). The statistical analysis

16**to determine the** significance **of the** three **independent variables on the**

yield of FAME is conducted using ANOVA, with the α value set at 0.05 to minimize the analysis error; and the results are pres- ented in Table 4. All linear terms and the interaction between

1**reaction temperature and the mass ratio of methanol to DPO**

are observed to have a positive effect on the FAME yield, while in contrast, the quadratic coef- ficients and the other two interactions give an antagonis- tic effect to the yield of FAME. It can be seen from Table 4 that all terms, except the interaction between reaction time

1**and the mass ratio of methanol to DPO** (BC), show prominence **to the**

FAME yield (P value <0.05). Based on the perturbation plot pres- ented in Figure 6A, reaction time (B) is regarded as the most dominant contributor, where the plotline rises the steepest compared to the other variables. It is successively F I G U R E 5 The

2**yield of FAME** (wt%) **based on** the **A, experimental results** and **B**

, predicted results, due to the

3**interaction between** (1) **reaction time** (h) **and temperature**

(C), (2)

1**reaction time (h), and the mass ratio of methanol to DPO**

, and (3) temperature (C) and the mass

2**ratio of methanol to** DPO [**Colour figure can be viewed at wileyonlinelibrary.com**

] followed by the methanol to DPO mass ratio (C) and reac- tion temperature (A). The coefficients for the three inde- pendent variables (A, B, C) obtained from this plot are 1.58, 9.26, and 3.80, respectively. This coefficient value indi- cates the sensitivity of the variable. For instance, the coeffi- cient value of reaction time (B, 9.26) pointed out that this variable contributes to the response with the average value of 9.26% when the reaction time is increased by one level. The results obtained from the perturbation plot were also supported by the generated Pareto chart (Figure 6B). As seen from the figure, the significance order of all the linear, quadratic and two-way interaction terms can be sorted into the following sequence: reaction time (B) >

1**mass ratio of methanol to DPO**

(C) > quadratic temperature (A2) > temperature/time (AB) > quadratic reaction time (B2) > temperature (A) > quadratic mass ratio of methanol to DPO (C2) > temperature/mass ratio of methanol to DPO (AC). These parameters contribute to the suitability of the mathematical regression model. By inserting all the signifi- cant coefficient values to Equation (5), the

20**mathematical model can be expressed as follows: Y**

¼ 79:95 þ 1:58 A þ 9:26 B þ 3:80 C ? 4:84 A2 ? 3:72 B2 ? 2:33 C2 ? 2:08 AB þ 1:10 AC ð5Þ where Y is the yield of FAME (wt%), and

4**A, B, C are the** encoded **level of** input **variables (?1**

, 0, 1). T A B L E 4 The estimated regression coefficient and

2**their significance for the calculation of** FAME **yield**, generated by ANOVA **Term**

Constant A B C A2 B2 C2 AB AC BC Coef SE Coef 79.947 0.336 1.583 0.315 9.262 0.315 3.805 0.344 ?4.842 0.648 ?3.717 0.648 ?2.333 0.746 ?2.078 0.352 1.097 0.352 ?0.550 0.352 T-value 238.14 5.03 29.45 11.07 ?7.48 ?5.74 ?3.13 ?5.91 3.12 ?1.56 P-value 0.000 0.001 0.000 0.000 0.000 0.000 0.011 0.000 0.011 0.149 The goodness-of-fit analysis for the regressed equa- tion is summarized in Table 5. Based on the ANOVA, the regressed mathematical model shows significance, indi- cating that the model can be used for predicting the yield of FAME. The low value of SD (0.9947) further points out that most of the experimental data approaching the sta- tistical average.50 Figure 6C also observes a well-behaved residual vs predicted plot, indicating that the linear corre- lation is reasonable. The horizontal band around the zero-line formed by the residuals, without any value stood out from the basic random pattern also suggests that the variances of the error terms are equal and there are no outliers. The

2**lack-of-fit test** shows that **the P-value of the model is 0**

.3625, emphasizing that the derived equation is well-fitted to the actual data and the discrep- ancy of the model shows no significance. The value of R- squared for the model is found to be 0.9934, implying that 99.34% of

10**the experimental** data **can be** adequately **interpreted by Equation**

(5).

3**A good agreement between the predicted and experimental** response **of** FAME **yield**

is also observed from the

2**value of adjusted and predicted R-squared which** are also **close to unity (0**.9875 **and 0**.9656, **respectively**

). This result indicates that the model is sufficient to support the prediction of new responses within the tested range. Furthermore, two other parameters, for example, the coefficient of variation and adequate precision, are also monitored through the ANOVA. Table 5 presents that the values of C.V. and adequate precision are obtained at 1.34% and 46.3751, respectively. While C.V. is used to express the model reproducibility and has a maximum value of 10%, the

17**adequate precision** shows **the signal-to-noise ratio**

, which can be used to compare the

17**range of the predicted values at the design points to the average prediction error**

, with the optimal value of >4.0. Based on the obtained value of C.V. (1.34%) and adequate precision (46.3751), it can be concluded that the level of data clarity is high and the experimental values are sufficient; indicating that the regressed model can be used to represent all the inde- pendent variance assumption. Meanwhile, the optimum operating condition for the

1**in-situ esterification/transesterification** reaction **using** Cu/**DS-HMS-NH2**

is obtained using Minitab (version 18.1) (Figure 7): temperature of 55.3 C (coded level of 0.0303), the reaction time of 5 h (coded level of 1)

12**and methanol to** DPO **mass ratio of 5**.3:**1**

(coded level of 0.6970). The

12**predicted FAME yield under this** optimum **condition**

is monitored at 86.63%

2**with model desirability of 1.00. Three replicated experiments were** performed **using these** optimum **variables to** confirm **the** plausibility **of the**

developed mathematical model. The experimental FAME yield

2**obtained at the optimum** operating **condi- tion**

4**is found at** 87.14 ± **0**.11 **wt% with the** FAME **purity of 98**.45 ± **0**.67 **wt**

%.

3**With the error between the** experi- mental **and predicted values of only 0**.51%, we **can** con- clude **that** adequate accuracy in **the**

determination of FAME

3**yield using the operating parameters within the tested levels** can be achieved via the established equa- tion. The optimum yield of FAME also shows that Cu/DS-HMS-NH2 is comparable to the existing catalysts published in the literature. Xie and Wan (2019)12 stud- ied that the oil conversion of 95.8 wt% was achieved only after a 6 h reaction at a temperature of 110 C using the POM-

23**based sulfonated ionic** liquid immobilized- **UiO-66-2COOH metal-organic**

framework, while da Conceiç~ao et al (2016)15 presented the use of extreme temperature and catalyst loading (250 C and 30 wt%) to attain 99.2 wt% FAME yield using sulfated niobium oxide. High

9**reaction temperature** (200 **C) and catalyst loading (7**.5 **wt**

%) was also reported by García-Sancho et al (2011)20 to obtain a 95 wt% biodiesel conversion using niobium-impregnated MCM-41 catalyst. More- over, Omar and Amin (2011)11 mentioned that the transesterification of waste cooking oil in the presence of alkaline-modified zirconia catalyst requires a temper- ature of 115.5 C to achieve less than 80 wt% FAME yield. Therefore, the mild temperature (55 C), moderate catalyst loading (5 wt%), and comparable reaction time (5 h) obtained from this optimization study are highly favorable since the three parameters are directly related to the process efficiency in the industries. Table 6 presents the characteristics of the final FAME product. The results show that its fuel properties are fol- lowing the standard of ASTM D6751. The measured heating

1**value (45**.72 **MJ/kg) is also within the range** observed **in the common petrodiesel**

fuel (42-46 MJ/ kg).51 We observe a similar profile in the FTIR spectra of F I G U R E 6 A, Perturbation plot and B, Pareto chart

4**showing the significance order of various reaction variables**

, where A = temperature (C), B = reaction time (h), C = mass ratio of methanol to DPO; and C, the residual vs predicted plot [Colour figure can be viewed at wileyonlinelibrary.com] DPO and FAME (Figure 8). Several functional groups, for example, the bending vibrations of –CH, –CH2, –CH3 (1395, 1187, and 760 cm?1 for DPO and 1395, 1181, and 754 cm?1 for FAME), their respective stretching bands (3024, 2953, and 2876 cm?1 for DPO and 3030, 2929, and 2858 cm?1 for FAME), carbonyl (C=O, 1786 cm?1 for DPO and 1756 cm?1 for FAME), C–O stretching band (1140 cm?1 for DPO and 1134 cm?1 for FAME) are moni- tored in both spectra. Fadhil (2021)52 also reported simi- lar spectra for bio-oil from the non-edible feedstock, indicating that oils and fats generally consist of the same functional groups. However, the FTIR spectra of FAME show a new signal at 1465 cm?1 which indicates the pres- ence of the ester group with its deformation vibration. This implies that FAME is formed during the simulta- neous esterification/transesterification reaction. More- over, using the external standard pack (47 885 U, containing 37 components FAME standard mix), 11 FAME peaks, including C11:0, C14:1, C15:1, C16:0, C16:2, C18:0, C18:1n9c, C18:1n9t, C18:2, C18:3, C20:0, and C20:3n6, are identified. 3.4 | Reusability study of Cu/DS-HMS-NH2

1To determine the reusability of Cu/DS-HMS-NH2, several reaction cycles were conducted in series using the

T A B L E 5 The ANOVA results

20for the fitted regression model Source Sum of squares DF

Model 1497.29 9 A 25.06 1 B 857.85 1 C 121.19 1 A2 55.30 1 B2 32.59 1 C2 9.67 1 AB 34.53 1 AC 9.64 1 BC 2.42 1 Residuals 9.89 10 Lack of fit 4.63 4 Pure error 5.27 6 Total 1507.18 19 R-squared (R2) 0.9934 Adjusted R2 Adequate precision 46.3751 Coefficient of variation (C.V., %) Mean square 166.37 25.06 857.85 121.19 55.30 32.59 9.67 34.53 9.64 2.42 0.9893 1.16 0.8778 0.9875 1.34 F-value 168.16 25.33 867.09 122.50 55.89 32.94 9.78 34.90 9.74 2.45 1.32 Predicted R2 SD P-value <0.0001 0.0005 <0.0001 <0.0001 <0.0001 0.0002 0.0108 0.0001 0.0109 0.1489 0.3625 0.9656 0.9947 Remarks Significant Significant Significant Significant Significant Significant Significant Significant Not significant Not significant F I G U R E 7

3Response optimization plot of the three independent variables

for the

1in-situ esterification/transesterification reaction using Cu/DS-HMS-NH2 [Colour figure

can be viewed at wileyonlinelibrary.com] following optimum condition: temperature = 55.3 C, reac- Figure 9 presents the catalytic ability of the reused Cu/DS- tion time = 5 h, and methanol to DPO mass ratio = 5.3:1. HMS-NH2. Notable from the figure, this catalyst can T A B L E 6 The characteristics of the resulting FAME product Properties Methods Kinematic viscosity (at 40 C) ASTM D445 Flashpoint ASTM D93 Cetane number ASTM D613 FAME content (purity) EN 14103 Acid value ASTM D664 Monoglycerides content ASTM D6584 Diglycerides content EN14105 Triglycerides content EN14105 Calorific value ASTM D240 Unit mm2/s C - wt% mg KOH/g wt% wt% wt% MJ/kg Final FAME product 3.54 168.4 53.2 98.45 0.27 0.32 0.09 0.09 45.72 ASTM D6751 1.9-6.0 93 min 47 min - 0.5 max 0.4 max - - - F I G U R E 8 The FTIR spectra of DPO and FAME [

2Colour figure can be viewed at wileyonlinelibrary.com

] F I G U R E 9 The

1catalytic activity of Cu/DS-HMS-NH2 during the

reusability study maintain the

1yield of FAME above 80 wt% until the fifth cycle, before significantly drop to

72.18 wt% at the sixth cycle. Similar catalytic

1performance has been reported for some other solid catalysts, where 5 cycles seem to be the average number in terms of their reusability.12,53 The

FAME purity for the first five is measured at 97.16 wt%, 97.72 wt%, 98.02 wt%, 97.77 wt%, and 96.94 wt%, respec- tively; higher than the required ester content in the com- mercial biodiesel (minimum at 96.5 wt%). The

1deactivation of Cu/DS-HMS-NH2 is attributed to the blockage of the

cat- alyst pores by the components present in the reaction sys- tem, for example,

1glycerol, acyl glycerides, and biodiesel.33 Besides, the FFA content in DPO also

contributes to the neutralization of the

1basic sites in the inner shell of Cu/DS- HMS-NH2

catalyst,54 thereby promoting the production of the amine-carboxylate compound and subsequently, gener- ating

1emulsion. 3.5 | The catalytic reaction mechanism for the in-situ esterification/transesterification

Figure 10 presents the catalytic

1reaction mechanism for the in-situ esterification/ transesterification reaction using Cu/DS-HMS-NH2. As shown in the

figure, the outer layer of the catalyst is impregnated by copper (a strong Lewis acid) which was intended to convert FFA to FAME through an esterification process, while the inner shell was functionalized with amine (–NH2) as the basic sites to further convert the acyl glycerides to FAME through the process of transesterification. The

1in-situ esterification/transesterification mecha- nism using the Cu/DS-HMS-NH2 catalyst

can be described as follows: all reactant molecules, including

1**acyl glycerides, FFA, and methanol** migrate onto **the** boundary layer **of** the **catalyst** and diffuse **through the**

layer onto the outer shell of the catalyst, which is impregnated by the copper. In this layer, the pi carbonyl bond in FFA resonates and undergoes electron F I G U R E 1 0 The

1**in-situ esterification/transesterification** reaction mechanism **using** Cu/**DS-HMS-NH2**

[

18**Colour figure can be viewed at wileyonlinelibrary.com**] delocalization **to** form carbocation **and**

carbanion,55,56 which are highly reactive. The pi carbonyl bond has a weak molecular interaction due to the distance between the electron in the carbanion and the positively charged atomic nucleus (carbocation).57 As a result, the copper impregnated on the Cu/DS-HMS-NH2 catalysts acts as a proton donor and binds the carbanion to form a complex by holding the excess electron density; therefore, stabilize the charge and promote the next reaction step to occur. The chemical interaction in the outer shell continues when the lone pair in the hydroxyl group of methanol, which possesses the electronegative properties, binds to the carbocation, resulting in the release of the hydrogen atom in the hydroxyl group of methanol, further driving the atom to move to the hydroxyl group of FFA. Due to the addition of the attached hydrogen atom, another elec- tron delocalization occurs to adjust the distribution of electrons in the hydroxyl group of FFA. Subsequently, the hydrogen atom attached

1**to the hydroxyl group of FFA** is released **to form**

H2O, followed by the release of the copper complex bond to form the final product in the form of FAME. Meanwhile, the acyl glycerides diffuse further to the basic sites contained in the inner shell of the catalyst to engage in a transesterification reaction. Initially, metha- nol undergoes a deprotonation reaction to give the hydro- gen atom to the amine group of the catalyst. This reaction results in two products, namely NH3+-embedded catalyst and the alkoxy (RO-) group of methanol. Then, in one of its pi-carbonyl bonds, the acyl glycerides encounter an

1**electron delocalization to form carbocation and carbanion. The**

alkoxy (RO-) group of methanol is then bound to the carbocation. A further electron reso- nance occurs to produce a complex of FAME and glyc- erol. To create a stable compound, the positively charged NH3 in the catalyst donates the hydrogen proton to the + complex of FAME and glycerol to release glycerol from one of the chains58 and at the same time, produce FAME as well. Once the reaction is completed, the three prod- ucts (FAME, H2O, and glycerol) from the in-situ esterifi- cation/transesterification reaction are subsequently desorbed to the surface of the catalyst. 4 | CONCLUSION Cu/DS-HMS-NH2 is successfully fabricated and employed

2**to promote the** in-situ **esterification/transesterification reaction**

, for the synthesis of FAME from DPO with

2**high FFA and moisture content. The** particle size **of**

the Cu/DS-HMS-NH2 catalyst is uniform at 157 nm with a hollow core size of 81 nm. This catalyst consists of 2 layers with a similar thickness of 16-19 nm. The textural properties of Cu/DS-HMS-NH2 are also comparable to the existing heterogeneous catalyst, with SBET of 733.24 m2g?1, and Vp of 0.54 cm3g?1. The maximum FAME yield at 87.14 ± 0.11

4**wt% with the purity of 98**.45 ± **0**.67 **wt**

% was obtained using Cu/DS-HMS-NH2 under the following optimum condition: 55.3 C, 5 h,

12**methanol to** DPO **mass ratio of 5**.3:**1**

, and 5 wt% catalyst loading, indicating the high

1**catalytic activity of** Cu/**DS-HMS-NH2. The** result **of**

the statistical ANOVA shows that the reac- tion time gives the

1**most significant influence on the yield of FAME, followed** successively **by the**

1**mass ratio of methanol to DPO** and temperature. **The** predicted **and**

experimental results have a direct proportional output, as shown by the

4**goodness of fit analysis**. Based **on the**

reus- ability study, the catalyst produces

4**a high yield of** FAME (>80 **wt%) until the**

fifth cycle. Therefore, Cu/

1**DS-HMS- NH2 can be considered as a promising** solid **catalyst** to prepare biodiesel from low-quality oils. ACKNOWLEDGEMENTS The authors

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14**data that support the findings of this study are avail- able from the corresponding author upon reasonable request**

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