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paper text:

2**Iron (II) impregnated double-shelled hollow mesoporous silica as acid-base bifunctional catalyst for the conversion of low-quality oil to methyl esters**

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abstract To promote the use of low-quality oils in producing biodiesel, a bifunctional acid-base catalyst

2**Fe/DS- HMS-NH2** is **fabricated using** the **two-step condensation technique**

. The obtained

2**Fe/DS-HMS-NH2** is of **a** doubled **shell structure**

in spherical shape with a uniform size of 156 nm. Its hollow core (with a diameter of

9**86 nm) and two spatial shells with different active** sites enables **the esterification and** trans- esterification **reactions to be** accomplished **in** a **one**-pot **synthesis. The**

influences of four independent reaction variables

16 on the yield of fatty acid methyl esters YF **was**

studied, including catalyst loading mc, reaction time t, reaction temperature T, and the methanol to degummed palm oil mass ratio rm/o. The highest yield was obtained at 85.36% (w/w) when mc ¼ 6% (w/w), t ¼ 4.5 h, T ¼ 60 C, and rm/o ¼ 6:1. The Fe/DS-HMS-NH2 shows a good recyclability with YF > 80% (w/w) up to three reaction cycles. © 2021 Elsevier Ltd. All rights reserved. 1. Introduction The global fuel demand is growing rapidly as it undergoes an extensive urbanization. Our heavy reliance on fossil fuel brings the risk of unstable market price and reduced fuel availability. The gas emission from fossil fuel combustion also causes environmental concerns. Therefore, developing an alternative fuel that is biode- gradable, sustainable and with a low carbon emission is the most significant energy and environmental challenge for us in the coming decades [1,2]. Since 2006, the Indonesian government has been committed to reducing carbon emissions by replacing fossil Abbreviations: FFA, Free fatty acids; FAME, Fatty acid methyl esters; DPO, Degummed palm oil; CPO, Crude palm oil; SS-HMS-NH2, Single-

2 shelled hollow mesoporous silica; DS-HMS-NH2

,

2 Double-shelled hollow mesoporous silica; Fe/DS- HMS-NH2

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2 Iron (II) impregnated double-shelled hollow mesoporous silica

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7 1 These authors contributed equally to this work

fuels with biodiesel [3]. It is also declared that the

7 use of biodiesel in diesel blend will be increased **from B20 to B30**

starting from 2020 [4], with a strategy to boost the domestic use of palm oil and lower down energy imports. Usually, biodiesel is obtained through the conventional transesterification process of refined oil [5]. However, the technologies of utilizing non-refined oil, specifically the low- quality oil, have currently attracted extensive interests and are being developed. Various types of low-quality oil

3 have been studied **to produce high-quality biodiesel using sundry of** technical **routes**, including **the**

4**two steps acidic esterification followed by** basic **transesterification**

[6],

4**noncatalytic transesterification using** alcohol **under subcritical** [7] **and supercritical conditions**

[8], enzymatic transesterification [9] and solid-catalyzed trans- esterification [10]. Among the available routes, the use of hetero- geneous (solid) catalysts has been attracting a growing interest in recent years, as it has the advantage of easier separation, tolerance to impurities (i.e., FFA, water and other minor compounds), and good reusability [11] which means minimal waste and toxic water production [12] and environmentally friendly [13]. Boey

4**et al**. (2011) **and** Lam **et al**. (2010) **also stated that**

heterogeneous cata- lysts lower the product contamination level, and reduce the corrosion problem [14,15]. Various solid catalysts and their modi- fications have been reported, such as zirconia [16], silica impreg- nated with zinc stearate (ZS/Si) [17], heterogeneous KF/ZnO catalyst [18], heterogeneous Zn/I2 catalyst [12]. However, despite their insensitivity to impurities, these catalysts solely act as the mono functional catalysts, depending on their acidity nature and have the following disadvantages during the

2**conversion of low-quality oil to**

biodiesel: (1) the reaction carried out in the presence of an acidic heterogeneous catalyst is slow, and at the same time, requires large amount of alcohol [19], meanwhile (2) the basic heterogeneous catalysts usually result in a lower biodiesel yield and purity, since this type of catalyst leaves the FFA unreacted during the reaction. In this paper, we prepared and characterized a new class of heterogeneous catalyst, the double- shelled hollow mesoporous silica impregnated with divalent iron metal (

12**Fe/DS-HMS-NH2**), to be used **as** an **acid-base bifunctional catalyst** in **the** production **of** biodiesel from a **low-quality oil**

. This catalyst enables a simple process of converting low-quality oil to biodiesel by combining the two processes of esterification and transesterification into a single- stage process. This is achieved by having double active surface layers that facilitate the two reactions to run simultaneously. The primary (inner) shell is designed to promote the transesterification reaction by adding eNH2 as the basic site, while the outer layer is impregnated with the divalent iron (Fe (II)), which is selected as the impregnated metals due to its nature as a strong Lewis acid, and its ability to change the oxidation level and activate the substance during the process [20]. The

2**synthesis, characterization and catalytic activity of**

the Fe/ DS-HMS-NH2 will be investigated in this paper. Its performance

2**as an acid-base bifunctional catalyst for biodiesel**

preparation will be examined at various conditions, including catalyst loading mc (%,

14**w/ w**), reaction **temperature T (C), reaction time t (h**), and **the**

mass

20**ratio of methanol to oil** rm/o. **In**

this present research, degummed palm oil (DPO) is selected as the lipid material. With similar content of FFA and moisture as the crude palm oil (CPO), DPO is also clas- sified as a low-quality oil, along with industrial fats, oils and greases, and other crude/waste lipids. Therefore, it is considered as a suitable raw material to determine the catalytic ability of Fe/DS- HMS-NH2 in converting both FFA and triglycerides in DPO into biodiesel. We will also show that the Fe/DS-HMS-NH2 can be re- generated and reused, which is regarded as an important feature for heterogeneous catalysts as it will reduce the cost for production and pollutant discharges [21,22]. The recyclability of the catalyst will be investigated at the operating condition giving the highest yield of fatty acid methyl esters (FAME) YF. 2. Materials and methods 2.1. Materials

11**CPO was** collected **from the local** manufacturer **in Indonesia. Prior** to **use, CPO was degummed using** 1% (**w/w**) **phosphoric acid** (PA, 85% **purity**

) at a temperature of 80e90 C for 30 min to reduce the phosphorus content.

11**Several important characteristics of** the degummed **CPO** (i.**e**

., DPO), namely free fatty acid content, acid value, saponification value, and moisture

11**content were analyzed in accordance with the standard** method **of AOCS Ca 5a-40, Cd**

3d-63, Cd 3d-25, and Ca 2e-84, respectively. 3-aminopropyl-triethoxysilane (APTES) was purchased from Fisher Scientific (Pittsburgh, USA), while other chemicals required for the fabrication of Fe/DS-HMS, namely iron (II) sulfate hepta- hydrate (FeSO4$7H2O, 99.99% purity), tetraethylorthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), ethanol (98% purity), methanol (99,9% purity), hydrochloric acid (HCl, 37% pu- rity), ammonium hydroxide solution (NH4OH, 25% purity), and n- hexane (95% purity) were obtained

1**from Merck** (Merck, **Germany**). The **FAMEs standard (47885 U**) containing **37 components FAME mix was** procured **from Supelco (Bellefonte, PA, USA**). Ultra-high purity **nitrogen gas (>99**.0% **purity) was purchased from Aneka Gas**

. 2.2. Preparation of DS-HMS-NH2 In a typical synthesis, 0.14 g of CTAB, 20 ml of ethanol,

13**50 ml of deionized water and** 1 **ml of**

NH4OH solution were simultaneously introduced into a glass beaker and mixed for 15 min

8**at room temperature. Then** 1 **ml of TEOS**

was slowly

17**added into the above solution and kept stirring for**

24 h. The precipitates were collected through centrifugation at 4500 rpm for 30 min, triplicate ethanol washing, and drying at 120 C overnight. After the calcination at 550 C for 6 h, the single shelled hollow mesoporous silica (SS- HMS-NH2) was obtained. The outer shell of the particle was fabricated using a multilevel scheme based on SS-HMS-NH2. In a typical synthesis, 0.5 g CTAB,

8**18 ml deionized water, and 50 ml of ethanol**

were introduced into a beaker glass. Meanwhile, 0.063 g of SS-HMS-NH2 was added into a mixture of 4 ml deionized water and 8.5 ml of 25% (w/w) NH4OH solution. The above two solutions were then combined and stirred for 15 min at 250 rpm, after which

8**100 ml TEOS and 21 ml APTES were**

slowly added into it and the mixture was kept stirring for 24 h to allow the condensation reaction of silica. Finally, the solid product was collected by centrifugation at 4500 rpm for 15 min, which was then repeatedly washed with 60 ml of ethanol and 4 ml of HCl, and oven-dried at 120 C. The dried product was calcined at 550 C for 6 h to obtain

2**double-shelled hollow mesoporous silica (DS-HMS-NH2**

). 2.3. Iron (II) impregnation onto DS-HMS-NH2 surface The impregnation of divalent iron onto the DS-HMS-NH2 surface was achieved as follows to fabricate Fe/DS-HMS-NH2 catalysts. In a typical synthesis, 0.1 g DS-HMS-NH2 was mixed with 50 ml of deionized water under sonication for 30 min at room temperature. Meanwhile, two separate solutions were prepared: (1) 5 mg of FeSO4$7H2O

13**was dissolved in 50 ml of deionized water, and**

(2)

170.2 g of CTAB was dissolved in 10 ml

ethanol. Solution (1) and (2) were then added into the DS-HMS-NH2 solution and stirred for 12 h at ambient conditions. The Fe/DS-HMS-NH2 precipitates were sepa- rated by a centrifugation at 4500 rpm for 15 min, and then dried at 120 C for 12 h and calcined at 550 C for 5 h to obtain the Fe/DS- HMS-NH2 powder. 2.4. Catalytic activity of Fe/DS-HMS-NH2 at various reaction conditions The in-situ esterification/transesterification reactions from DPO to FAME were carried out in a glass flask equipped with a reflux condenser and external heater under constant magnetic stirring (250 rpm) at various conditions. Specifically, the influence of four reaction parameters were investigated due to their relevance to industrial applications: catalyst loading mc (%,

14w/w), reaction temperature T (C), reaction time t (h), and the

mass ratio of methanol to DPO rm/o. To determine the amount of Fe/DS-HMS-NH2 catalyst that produces the maximum FAME yield YF, a few reactions were carried out with different amounts of Fe/DS-HMS-NH2 (mc ¼ 2%, 4%, 6%, 8%, w/w) at the following condition: T ¼ 60 C, t ¼ 4.5 h and rm/o ¼ 10:1. Once the optimum catalyst loading is obtained, the catalytic activity of Fe/DS-HMS-NH2 was investigated within an experimental matrix defined by T ¼ 40 C, 50 C, 60 C, t ¼ 0.5 h, 2.5 h, 4.5 h, and rm/o ¼ 2:1, 6:1, 10:1. The experimental runs were designed in a random order using face centered-central composite design (CCF-CCD) as listed in Table 3. All the experi- mental runs were conducted with the same procedure. After the reaction completed, Fe/DS-HMS-NH2 catalyst was recovered by centrifugation at 4500 rpm for 15 min, and

19calcination at 550 C for 5 h. The

liquid product was subjected to a two-stage liquid-liquid extraction using methanol and n-hexane sequen- tially for purification. Then the FAME-rich phase was separated from the by-products (i.e., glycerol, excess methanol, soap, and the other unwanted materials) and evaporated under vacuum to obtain the final FAME product. As an evaluation of the catalytic activity of Fe/DS-HMS-NH2,

16the yield of FAME was calculated by the following equation

: YFð%; w = wÞ ¼ mmFspF 100 (1) where mF

6is the mass of the final FAME product (g), pF is the

FAME purity (%, w/w) obtained from equation (2) shown in the next section, and mS is the total mass of the DPO (g). 2.5. Characterization of Fe/DS-HMS-NH2 catalyst and FAME The characterization of Fe/DS-HMS-NH2 was conducted

15using field-emission scanning electron microscopy with energy disper- sive X-Ray spectroscopy (FESEM

/EDX), transmission electron mi- croscopy (TEM), nitrogen sorption, and thermogravimetric analysis (TGA). The FESEM/EDX images were taken on a JEOL JSM-6500 F (Jeol Ltd., Japan) running at 15 kV with a working distance of 12.4 mm, while TEM was carried out on JEOL JEM-2100 with an accelerating voltage of 200 kV. Nitrogen sorption analysis was conducted at 77 K on a Micrometrics ASAP 2010 Sorption Analyzer. The sample was degassed at 423 K prior to analysis. To determine the thermal stability and volatile component fraction of the Fe/DS- HMS-NH2 catalyst, a TGA analysis was performed

3**using TG/DTA Diamond instrument (Perkin-Elmer, Japan**

). The final FAME product characteristics, including its kinematic viscosity (at 40 C), flashpoint, cetane number, acid value and calorific value were determined according to the standard methods of ASTM D445, ASTM D93, ASTM D613, ASTM D664, and ASTM D240, respectively. The purity of FAME (pF)

1**in the** final **product was analyzed using** a **gas** chromatograph (**Shimadzu GC-2014**) equip- ped **with a split**/splitless **injector** and a **flame ionization detector (FID**

). The stationary phase used for separation was the narrow bore non-polar

4**DB-WAX column (30 m 0.25 mm ID 0.25** mm **film thickness, Agilent Technology, CA**

), and the

6**temperature profile for the analysis was in accordance with the study conducted by** Har- ijaya **et al. (2019**

) [23].

3**Methyl heptadecanoate** (MH) **was used as an internal standard**

, while an

4**external FAME reference (47885 U, containing 37 components FAME standard mix) was used** to obtain **the**

FAME compositional profile. pF is calculated by the following equation: Table 1 Textural properties of Fe/DS-HMS-NH2. Material SBET (cm2/g) Pore volume (cm3/g) Pore size (nm) Fe/DS-HMS-NH2 782.84 0.64 2.43 Table 2 Characteristics of DPO. Parameter Value FFA (%, w/w) Moisture Content (%, w/w) Saponification Value (mg KOH/g DPO) Acid Value (mg KOH/g DPO) Molecular weight (g/mol) 5.54 0.20 234.08 12.04 756.62 Table 3 Experimental matrix at the optimum catalyst loading mc ¼ 6% (w/w). Run Input Parameters YF (%, w/w) T (C) t (h) rm/o 1 60 2 40 3 40 4 50 5 50 6 40 7 40 8 50 9 60 10 50 11 50 12 50 13 50 14 60 15 50 16 60 17 50 18 50 19 60 20 40 4.5 10:1 0.5 10:1 2.5 6:1 4.5 6:1 2.5 10:1 0.5 2:1 4.5 10:1 2.5 2:1 4.5 2:1

2.5 6:1 2.5 6:1 2.5 6:1 0.5 6:1 4.5 6:1 2.5 6:1 0.5 10:1 2.5 6:1 2.5 6:1 0.5 2:1 4.5 2:1 85.24 ± 1.19 40.27 ± 0.58 55.09 ± 0.76 75.15 ± 0.65 60.07 ± 0.44 35.19 ± 0.92 70.22 ± 1.01 67.03 ± 0.51 80.11 ± 0.68 65.16 ± 0.47 66.96 ± 0.73 65.87 ± 0.79 65.01 ± 0.37 85.36 ± 0.62 63.21 ± 0.42 70.01 ± 0.56 63.20 ± 0.69 67.18 ± 0.45 69.09 ± 0.53 59.11 ± 0.78 P pF ð%; w = wÞ ¼ AF AMH VMHCMH ? AMH mF 100 (2) where SAF is the total peak area of FAME, AMH

4**is the corresponding area of** methyl heptadecanoate (**MH) peak**, VMH **is the volume of MH solution (ml**), CMH **is the actual concentration of MH solution (g/ml), and** mF **is the actual** mass **of the** final **FAME** product (**g**

). 2.6. Recyclability of Fe/DS-HMS-NH2 Fe/DS-HMS-NH2 was repeatedly used

3**for the transesterification process at the** operating **condition** where **the maximum yield of** FAME was obtained. **The**

recyclability of Fe/DS-HMS-NH2 was determined by the number of repetitions until when the yield became lower than 80% (w/w). The purity and yield of FAME were analyzed according to the procedures in section 2.4-2.5. All ex- periments were carried out in triplicates to verify the results. 3. Result and discussions 3.1. The mechanism scheme of Fe/DS-HMS-NH2 fabrication The

2**Fe/DS-HMS-NH2** was synthesized by **a two-step** co- **condensation technique**

. The mechanism scheme in Fig. 1 illus- trates the fabrication route: (1) firstly, TEOS and CTAB undergo a co- condensation reaction along with the ammonium solution; (2) then CTAB, the soft template of the core, is removed by calcination, and the SS-HMS-NH2 is thus formed; (3) TEOS, APTES, and CTAB un- dergo another co-condensation reaction on the outer surface of the SS-HMS-NH2 spheres; (4) DS-HMS-NH2 nanosphere is obtained by removing CTAB and APTES in calcination; (5) the divalent iron (Fe Fig. 1. The mechanism scheme of Fe/DS-HMS-NH2 fabrication. (II)) was incorporated onto the surface of DS-HMS-NH2 by a traditional wet impregnation technique, and the Fe/DS-HMS-NH2 nanosphere is obtained. 3.2. Characterization of Fe/DS-HMS-NH2 catalysts Fig. 2a, ced present the SEM and TEM images of the Fe/DS-HMS- NH2 catalyst synthesized by the co-condensation technique. The catalyst is spherical with a uniform size at ca. 156 nm (Fig. 2a). Notably, Fe/DS-HMS-NH2 is composed of two shell layers, indicated by the darker color of the inner shell in Fig. 2c and d. Its hollow-core structure is clearly presented with the diameter of 86 nm (Fig. 2d). The shell thicknesses of the inner and outer layer of Fe/DS-HMS- NH2, are 22 nm and 13 nm, respectively. The impregnation of Fe (II) Fig. 2. (a) SEM image, (b) Elemental composition, (c)e(d) TEM images at various magnifications, (c) BJH pore size distribution curve, (e)

8**Nitrogen adsorption-desorption isotherm** with **BJH pore size distribution**

curve (inset), (f) Thermogravimetric profile of the Fe/DS-HMS-NH2 catalyst. on the surface of the silica layer was successful, evidenced from the EDX result showing a percentage of 2.87% (Fig. 2b).

8**Based on the** fabrication procedure, **it was reasonable to consider that the** Fe (II) **sites and basic amino sites were** spatially **isolated and located in different shells**

. The textural properties of Fe/DS-HMS-NH2 analyzed by the ni- trogen sorption are presented in Table 1 and Fig. 2e. The nitrogen adsorption and desorption isotherm of the catalyst exhibits a typical type-IV isotherm, indicating the presence of a mesoporous structure with worm-like capillary pores molded by the CTAB mi- celles. The

> 19**pore size of the** mesoporous structure is **found to be 2**.43 **nm**

(Fig. 2e (inset)). A steep

> 13**increase of** the **nitrogen adsorption** amount **at p/p0** close **to**

unity also suggests that there are macro- pores structure within the particle, corresponding to the hollow core. Similar adsorption and desorption profile also pointed out that the pores are highly accessible. The specific surface area SBET obtained in this study was 782.84 m2/g, lower than the value 1100e1350 m2/g for a similar double shelled hollow mesoporous silica [22]. Such a discrepancy was likely due to the reason that it was strongly influenced by the shell thickness. Zhou et al. (2014) reported that when the thickness of hollow mesoporous silica nanoparticles (HMSN) increases from 46 nm to 82 nm, the surface area of HMSN particles was declined from 986 m2/g to 614 m2/g [24]. Zhou et al. (2014) and Cao et al. (2011) also observed that an increase in the particle mass due to the addition of TEOS and CTAB in the synthesis of the second shell lowers the surface area, since the amount of TEOS during the fabrication

> 15**is directly proportional to the thickness of the**

shell [24,25]. Meanwhile, the pore volume of Fe/DS-HMS-NH2 (0.64 cm3/g) was found to be slightly higher than that reported by You et al. (2018) (0.61 cm3/g) [22]. Based on its textural analysis, Fe/DS-HMS-NH2 possesses comparable specific surface area and pore volume with those of existing heterogeneous catalysts (i.e., HMS-Al@MS-NH2 [22], char-based catalyst [26], g- alumina industrial-grade catalyst [27], and copper-based metal- organic framework [28]), which usually range from 200 to 1300 cm2/g and 0.18e1.68 cm3/g respectively. To demonstrate the feasibility of Fe/DS-HMS-NH2 for the re- actions at an elevated temperature, its thermal stability was investigated. The TGA profile in Fig. 2f shows a 20% decrease in weight up to the temperature of 100 C, attributed to the removal of free moisture content. Further heating up to 800 C does not significantly decrease the mass of Fe/DS-HMS-NH2, suggesting that the catalyst is stable at high temperatures [29]. Therefore, our Fe/ DS-HMS-NH2 can be considered

> 21**as a** promising **heterogeneous catalyst for the** in-situ esterification/**transesterification**

reaction. 3.3. The catalytic activity of Fe/DS-HMS-NH2 in the in-situ esterification/transesterification of DPO The

> 3**characteristics of** DPO **as the raw material for biodiesel preparation**

are presented in Table 2.

5As homogenous catalysts are sensitive to impurities, the conversion of DPO to

FAME for biodiesel production usually requires two reaction steps, namely acid- catalyzed

3esterification to lower the FFA content by converting them into

FAME, and basic

5catalyzed transesterification to convert the acyl glycerides into FAME. However, heterogeneous catalysts can have good tolerance towards the FFA and water content in the lipid materials

[10]; for Fe/DS-HMS-NH2, its

9two spatial shells with different active sites can facilitate the above two reactions

in a one- pot process, and

5therefore efficient conversion from DPO to FAME is achieved in a single step. Fig. 3 presents the FAME yield obtained at various

Fe/DS-HMS- NH2 loadings at the condition of T ¼ 60 C, t ¼ 4.5 h and rm/o ¼ 10:1. The results indicate that the yield of FAME is proportional to the number of active sites offered by the Fe/DS-HMS-NH2 [30,31]; Fig. 3. The yield of FAME at various Fe/DS-HMS-NH2 loadings with the reaction con- dition of T ¼ 60 C, t ¼ 4.5 h and rm/o ¼ 10:1. therefore YF increases with mc when the latter is within 6% (w/w). This agrees well with previous work on biodiesel production using different solid catalysts, e.g., pomacea sp. shell-based CaO [30], sulfonated biochar [31], and KI/mesoporous silica [32]. A maximum yield 85.24% (w/w) is obtained when the catalyst loading mc 6% ¼ (w/w). Further increase of the Fe/DS-HMS-NH2 results in a reduced yield of FAME, which is probably due to the

5aggregation and inconsistent dispersity of the catalyst in the reaction system

of an enhanced viscosity [33,34]. Cai

6et al. (2018) and Samart et al. (2010) also mentioned that excess

catalyst may also disturbed the mixing between the reactants, due to stronger adsorption of the reactants to the catalyst [35,36]. At a constant catalyst loading mc 6% (w/w), Fig. 4 and Table 3 ¼ present the FAME

yield YF at various

6reaction time t, temperature T, and mass ratio of methanol to

DPO rm/o. The maximum YF 85.36% ¼ (w/w) (with a purity of 97.89% (w/w)) is obtained at the condition of T 60 C, t 4.5 h, rm/o 6:1. Based on the experimental results, ¼ ¼ ¼ the reaction time t was the most significant factor, followed by rm/o and T, which is supported by

7the Pareto chart of the standardized effect in Fig. 5 showing

that t, rm/o, and the two-way interaction between t and T are the three significant parameters

1in the reaction system. The effect of reaction temperature on the

production of bio- diesel using Fe/DS-HMS-NH2 is shown in Fig. 4a and b. An increased reaction temperature contributes to a higher yield, with the maximum achieved at 60 C, which is related to the

6fact that both esterification and transesterification reaction are endothermic and reversible

[38,39]. At a higher reaction temperature, the kinetic energy and mobility of reactant molecules increase, promoting the collisions between the molecules and Fe/DS-HMS-NH2 particles which then

10increases the reaction rate constant and shift the re- action towards the

product [38,40]. Moreover, the mass transfer of the reactant molecules through the boundary layer of Fe/DS-HMS- NH2 is also accelerated at an elevated temperature, resulting in the

10faster diffusion of the reactants into the pore of catalyst

; hence, improving the FAME yield. Specifically, Fig. 4a and c shows a significant

5increase of the FAME yield by extending the duration of the biodiesel synthesis from

0.5 h to 4.5 h, at a

4constant temperature or mass ratio of methanol to

DPO.

10**Longer reaction time** provides sufficient **time for the reactants to** reach **the** active sites **of**

Fe/DS-HMS-NH2 through adsorption and diffusion, and convert DPO into FAME [41]. Mean- while, prolonged

5**duration of reaction also gives the catalyst** more **time to adsorb the** reactant **and desorb the** reaction **product** [28]. Fig. 4. **The**

FAME yield YF (%, w/w)

6**at various (a) T and t, (b) T and** rm/o, and (**c) t and** rm/o. **Fig**

.

75. **Pareto chart of the standardized effect** for **the**

biodiesel preparation with Fe/DS- HMS-NH2, using YF

6**as the response at a 95% confidence** interval **where A ¼ T, B ¼ t, C**

¼ rm/o.

3**Wei et al. (2009) also mentioned that adsorption and desorption of reactants from the catalyst is the rate-determining step in the overall reaction** [42]. **Therefore**

, allowing longer contact between the reactant molecules and the catalyst ensures high conversions of FFA and acyl glycerides to FAME. Stoichiometrically, 3 mol of methanol are required to react with 1 mol of triglycerides in the transesterification reaction, while 1 mol of methanol is needed to react with 1 mol of free fatty acids in the esterification reaction [43,44]. Both reactions are known to be reversible; thus, the amount of methanol in the two reactions is usually provided

1**in excess to shift the reaction** equilibrium **to the** product **side**

. As seen from Fig. 4b and c, having excess methanol from rm/o ¼ 2:1 to rm/o ¼ 6:1 contributes to a higher FAME yield, while further addition up to rm/o ¼ 10:1 has no improvement. While most studies agree that excess methanol is desirable to allow

4**more frequent** interactions **between the lipid and methanol triggering the formation of FAME**, Pangestu **et al**. (2019) found **that excess methanol**

may also accelerate the production of glycerol despite the higher yield of FAME [28]. As the esterification and trans- esterification are both reversible, a higher concentration of glycerol in the reaction system may induce a reverse reaction to the reactant side, creating an equilibrium between the products and reactants [28]. Hayyan et al. (2011) also reported that an excessive

1amount of methanol causes higher solubility of glycerol in

the FAME phase that could lead to a complicated separation between biodiesel and glycerol [45]. Moreover, from the techno-economic viewpoint, the higher mass ratio of methanol to DPO also increases the material and processing cost [23,45]. Therefore, it can be concluded that the optimum level is rm/o ¼ 6:1.

10A comparison of the FAME yield produced using

Fe/DS-HMS- NH2 with other existing catalysts is given in Table 4. It is notable that although the value of YF is higher when the refined feedstock is used as the reactant, the

20reaction time and the mass **ratio of methanol to oil** used in **this**

study are lower. Moreover, among the studies

9using low-quality oil as raw lipid **material**

, Fe/DS-HMS-NH2 shows

9a higher catalytic activity compared with **the** other **catalysts**

reported by Omar and Amin (2011), and Bala et al. (2017). This shows that Fe/DS-HMS-NH2, as a bifunctional catalyst, is able to enhance the yield of biodiesel at a comparable operating condition, which is due to its ability to convert not only triglycerides but also FFA into FAME in a one-pot system. The analysis result of the final FAME product shows that the conversion of FFA after reaction reaches 95.6%. The fuel properties of the final FAME product are presented in Table 5. The measurement results indicate that the product resulted in this study has

3comparable combustion and flow properties with those of **the**

commercial biodiesel. The calorific value (45.143 MJ/ kg) is also within the range required in the common petrodiesel (42e46 MJ/kg). Meanwhile, its compositional profile is obtained by comparing the methyl ester peaks

4in the chromatogram with those in **the external FAME standard (47885 U, containing 37 components FAME standard mix**). The 12 **identified peaks**

are 3.05% myristoleic acid Table 4 The comparison of catalytic activity of several heterogeneous catalysts for biodiesel production. Catalyst Reactants Operating condition Yield (%) References Mesoporous zinc-doped silica Alumina-supported KI Sr/ZrO2 Phosphotungstic acid-loaded KIT-5 Fe/DS-HMS-NH2 Cyanoacetate ester Refined soybean oil Waste cooking oil Waste cooking oil DPO T ¼ 60 C, t ¼ 24 h, rm/o ¼ 10:1, mc ¼ 7% (w/w) t ¼ 8 h, rm/o ¼ 15:1, mc ¼ 2.5% (w/w) T ¼ 115.5 C, t ¼ 169 min, rm/o ¼ 29:1 (mol/mol), mc ¼ 2.7% (w/w) T ¼ 70 C, t ¼ 4 h, rm/o ¼ 2:1 (v/v), mc ¼ 26.5% (w/w) T ¼ 60 C, t ¼ 4.5 h, rm/o ¼ 6:1 (v/v), mc ¼ 6% (w/w) 94.0 96.0 79.7 83 85.36 [17] [37] [16] [21] This study Table 5 Fuel properties of the final FAME product. Properties Methods Unit Final FAME product ASTM D6751 Kinematic viscosity (at 40 C) Flashpoint Cetane number Acid value Calorific value ASTM D445 ASTM D93 ASTM D613 ASTM D664 ASTM D240 mm2/s C e mg KOH/g MJ/kg 2.64 1.9e6.0 164.2 93 min 55.7 47 min 0.24 0.5 max 45.143 e

1methyl ester (C14:1), 2.37% cis-10-pentadecanoic acid methyl ester (C15:1), 35.78% palmitic acid methyl ester (C16:0

), 8.13% palmito- leic

1acid methyl ester (C16:1), 8.36% stearic acid methyl ester (C18:0), 32.57% oleic acid methyl ester (C18:1n9c), 3.05% elaidic acid methyl ester (C18:1n9t), 1.17% cis-8,11,14-eicosatrienoic acid methyl ester (C20:3n6), 2.48% arachidonic acid methyl ester (C20:4n6), 0

.52%

1cis-5,8,11,14,17-eicosapentaenoic acid methyl ester (C20:5n3), 1.07% erucic acid methyl ester (C22:1n9), 1.45% cis- 13,16-docosadienoic acid methyl ester (C22:2

). 3.4. Recyclability of Fe/DS-HMS-NH2 An important feature of using heterogeneous catalysts for bio-diesel preparation is its recyclability. In order to determine the recyclability of Fe/DS-HMS-NH2, several reaction cycles were con- ducted in series using the operating condition of mc ¼ 6% (w/w), T ¼ 60 C, t ¼ 4.5 h, rm/o ¼ 6:1. Fe/DS-HMS-NH2

3was recovered following the method described in section 2.4, while fresh

meth- anol and DPO were used in every cycle. The catalytic ability of the recycled Fe/DS-HMS-NH2 for in-situ esterification/trans- esterification process is presented in Fig. 6. The result indicates that recycled Fe/DS-HMS-NH2 can maintain a high yield of FAME above 80% (w/w) until the third cycle, close to the yield of fresh catalyst 85.36% (w/w). The purity of FAME for the first three cycles are 97.89%, 97.66% and 98.01% (w/w) respectively, higher than the Fig. 6. Recyclability of Fe/DS-HMS-NH2 in the in-situ esterification/transesterification of DPO. commercial purity (96.5%, w/w). These results indicate that the catalytic activity of Fe/DS-HMS-NH2 is maintained at a high level after regeneration. A significant drop in catalytic ability is observed from the forth cycle in Fig. 6; similar performance has been re- ported for some other heterogeneous catalysts where three cycles seem to be an average number in term of their recyclability [46,47]. The catalytic deactivation of Fe/DS-HMS-NH2 is generally due to the pore blockage

3**caused by the contact between** active **sites on the catalyst surface and the deactivation-induced components**

, namely

5**free glycerol, acyl glycerides, and biodiesel**. Moreover, **the** high **content**

of FFA in DPO

21**also plays an important role in the** deacti- vation **of**

Fe/DS-HMS-NH2 catalyst because

3**FFA tends to neutralize** the **basic sites in the**

inner shell of Fe/DS-HMS-NH2 [48],

3**resulting in the generation of** amine-**carboxylate that** induces **the**

formation of emulsion. 3.5. The reaction mechanism of the in-situ esterification/ transesterification of DPO using Fe/DS-HMS-NH2 In the preparation of biodiesel from DPO,

12**Fe/DS-HMS-NH2** acts **as** both **acid** and **base** catalysts to facilitate **the** esterification **of**

FFA and the transesterification of acyl glycerides. The main steps for the reaction mechanism catalyzed by Fe/DS-HMS-NH2 are the forma- tion of nucleophilic alkoxides, the nucleophilic attack on the elec- trophilic part of the carbonyl group of the triglycerides, and electron delocalization [49,50] as depicted in Fig. 7. The detailed description is as follows: Step 1: Acyl glycerides, FFA and methanol enter the surface of catalyst through the adsorption process to reach the outer shell impregnated by the divalent iron. In this step, FFA undergoes the electron delocalization to form a carbocation and a carbanion, where the latter binds to the iron embedded on the catalyst. Step 2: The reaction continues as the methoxide anion of methanol attacks the carbocation, whereas the hydronium cation attaches to the hydroxyl group of FFA to form water. Step 3: Through the electron delocalization of the carbon atom, the water is released from the complex with FAME and the iron- embedded catalyst, followed by the release of FAME from the catalyst. Step 4: The reaction continues when the acyl glycerides and methanol diffuse further to the amine-functionalized inner shell. The oxygen atom in the carbonyl group of acyl glycerides readily binds to the amine active sites. Fig. 7. The reaction mechanism of the in-situ esterification/transesterification of DPO using Fe/DS-HMS-NH2. Step 5: Subsequently, the methoxide anion of the methanol attacks the carbon atom in the carbonyl group of acyl glycerides, while the protonated H binds to the alkoxy group (RO-) of the þ acyl glycerides to form a complex of amine-functionalized catalyst with FAME and glycerol. Step 6: Again, through the delocalization of oxygen in the complex, the glycerol and amine-functionalized catalyst are successively released from the complex. Step 7: All three products, including FAME, glycerol, and water are then desorbed to the surface of the

Fe/DS-HMS-NH2 catalyst. 4. Conclusions Fe/DS-HMS-NH2 is synthesized through the two-step condensation technique and successfully employed as a heterogeneous catalyst for preparing biodiesel from DPO, a lipid source with sig- nificant FFA and moisture content. The obtained Fe/DS-HMS-NH2 has a uniform spherical shape with a particle size of 156 nm and hollow diameter of 86 nm. It is composed of two spatial silica

12**shells with different active sites, and**

their thickness are 22 nm for the inner shell and 13 nm for the outer shell.

2**Fe/DS-HMS-NH2 has a specific surface area of 782.84 m2/g with a pore volume of 0.64 cm3/ g**

, comparable with the existing solid catalysts. In the in-situ esterification/transesterification process using the Fe/DS-HMS-NH2 catalyst, reaction time t is the variable with most significant influ- ence

10**on the yield of FAME** YF, followed by **the reaction** temperature T **and**

the mass ratio of methanol to DPO rm/o. The maximum YF is 85.36% (w/w), obtained

3**at the following conditions**: T ¼ **60 C**, t ¼ **4**.5 **h**

, and rm/o ¼ 6:1, with a catalyst loading of 6% (w/w). Notably, Fe/DS-HMS-NH2 catalyst shows a good recyclability, with the yield staying above 80% for three

9**reaction cycles. Therefore, Fe**/ DS-HMS-NH2 **is a promising heterogeneous catalyst**

to obtain bio- diesel from DPO or other lipid materials

2**with high FFA and water content**. Further **study** on (1) **the** extension **of**

the catalyst lifetime by creating a technique suitable for its regeneration, and also (2) the design of a plausible route between the current research and its industrial application should be the main focus for future research expansion.

7**CRediT authorship contribution statement** Stefanus Kevin Suryajaya: **Conceptualization, Methodology, Investigation, Software, Writing - original draft**. Yohanes Ricky Mulyono: **Conceptualization, Methodology, Investigation**, Soft- ware, **Writing - original draft. Shella Permatasari Santoso: Conceptualization, Data curation, Supervision**. Maria Yuliana: Conceptualization, **Resources, Visualization**

, Writing - review & editing, Supervision. Alfin Kurniawan: Investigation, Resources. Aning Ayucitra: Investigation, Validation. Yueting Sun: Writing - review & editing. Sandy Budi Hartono: Software, Validation. Felycia Edi Soetaredjo: Resources, Visualization. Suryadi Ismadji: Resources, Validation. Declaration of competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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