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9**Efficient conversion of leather tanning waste to biodiesel using crab shell-based catalyst: WASTE-TO-ENERGY approach**

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ARTICLE INFO ABSTRACT Keywords: Leather tannery waste Crab shell Biodiesel Waste-derived fuel Reusability Optimization study To promote the use of waste-originated resources in biodiesel production, this study proposes the utilization of leather tanning waste (LTW) and crab-shell (CS) waste as the respective lipid source and catalyst material. The obtained CS-based calcium oxide (CaO) has comparable textural properties with those of existing waste-based catalysts and shows high catalytic activity

6**for the conversion of** LTW **to biodiesel. The optimum** yield of **fatty acid**

ethyl esters (FAEE) is predicted at 97.9 wt%, while it is experimentally observed at 98.7 ± 0.4 wt% (

5**purity of 98**.6 ± **0**.4 **wt**%) using **the following** operating **condition**

: reaction time t = 3.58 h, catalyst amount mc = 3.87

2**wt%, and** a **molar ratio of ethanol to LTW** meo = 12:**1. The**

CS-based CaO shows good reusability with

2FAEE yield staying above 90 wt% for four cycles. The

fuel properties of

1LTW-based biodiesel meet ASTM D6751 and ASTM D975-08

standards, with the ethyl ester ranging from C14 to C20. 1. Introduction Worldwide interest in the use of waste to fulfill the energy demand is currently growing in a very rapid manner. Many types of research related to waste-to-energy have been conducted to improve the trans- esterification yield, find the simplest and low-cost technique as well as fabricate waste-based catalysts. Known as an archipelago country, the aquaculture industries are one of the biggest and most important sectors in Indonesia. Approximately 30,000 tons of crab are produced annually, where its meat only accounts for only around 35 wt% of the total crab mass. This leaves almost 20,000 tons of solid waste discharged each year [1]. While in the developed countries, waste disposal is costly, crab shells (CS) in Indonesia are often directly discharged to the environment. CS exhibits potential value due to its valuable chemical contents, namely protein (20–40 wt%), calcium carbonate (20–50 wt%), and chitin (15–40 wt%) [2]. Being the largest component in CS, calcium carbonate finds extensive applications in pharmaceutical, agricultural, material development, and catalysis. Many studies have been conducted to develop calcium-based solid catalyst, with calcium oxide (CaO) as the main focus due to its advantages of substantial catalytic activity, high basicity, non-toxicity [3,4], good availability, and low cost [5]. In addition, the conversion of calcium carbonate to CaO can be achieved using a relatively simple method, that is, by thermal decomposition via calcination at high temperatures to liberate carbon dioxide from the raw materials [6]. Currently, transesterification of lipid to biodiesel is employed mainly using a homogenous catalyst, due to its phase homogeneity and shorter reaction time [5,7]. However, this type of catalyst cannot

12be reused and requires additional washing and separation steps, hence inducing attention in the use of the heterogeneous solid catalyst for the

biodiesel preparation process. Despite its comparable catalytic activity and Abbreviations: ANOVA, Analysis of variance; CaO, Calcium oxideCS Crab shell; DOE, Design of experiment; FA, Fatty acid; FAEE, Fatty acid ethyl esters; FFA, Free fatty acid; FID, Flame ionized detection; LTW, Leather tanning waste;

3MLFD, Multilevel factorial design; RSM, Response surface methodology

; SEE, Standard error of estimate; TGA, Thermogravimetric analysis. * Corresponding author. E-mail addresses: maria_yuliana_liauw@yahoo.com, mariayuliana@ukwms.ac.id (M. Yuliana).

9https://doi.org/10.1016/j.biombioe.2021.106155

Received 8 January 2021; Received in revised form 16 May 2021; Accepted 6 June 2021 0961-9534/ simpler use in the transesterification process, many heterogeneous cat- alysts are not viable for industrial usage since most of the catalysts are expensive and require complicated preparation efforts [8,9]. Therefore, synthesizing simple yet highly active catalysts for biodiesel preparation is important. Due to this very reason, an increasing number of studies on the neat, supported, loaded, and mixed CaO has been widely investi- gated [3,6]. The high catalytic activity of CaO might be attributed to the presence of oxygen attached to its surface, which acts as a strong basic conjugate [10]. These basic sites abstract a proton from the organic compounds and initiate the basic catalysis reaction [6]. The catalytic activity of CaO-based catalyst in the transesterification has been con- ducted using various natural-based raw materials as follows: mussel shells [11,12], eggshells [13], waste capiz shells [8,9], cockle shells [12], Pomacea sp. shells [14] and river snail shells [15]. Extensive uti- lization of waste-based catalysts is expected to reduce the material cost as well as to conduct a good waste management practice. To date, the development of waste-based solid catalyst mainly fo- cuses on the conversion of refined oils, rather than waste lipid materials, to biodiesel. The selection of refined oils as the raw materials is generally due to its low free fatty acid (FFA) and moisture content; therefore, it is easier to process and gives a more stable yield. However, the mass uti- lization of this type of lipid will disrupt the food supply chain. Yuliana et al. [16] mentioned that non-edible oils, specifically fat, oil, and grease (

1**FOG) and animal** fats, **are currently the best** options **for biodiesel feedstock compared to** edible ones **due to** their low **price**. Moreover, the **valorization**

of the waste-based lipid will significantly lessen the amount of the waste, and at the same time, turn them into a valuable asset. Therefore, this study combines the use of CS-based catalysts and leather tanning waste (LTW) as a lipid source to produce biodiesel. With 80 wt% of the rawhide is discharged as waste during the commercial tanning process of leather [17,18], the annual production of LTW in Indonesia reaches 100,000 tons [19,20]. LTW contains a sub- stantial amount of crude fat (>60 wt%) [18] that can be converted to biodiesel; which renders it an abundant raw material to prepare bio- diesel. A number of valorization approaches have been previously con- ducted to prepare biodiesel from LTW, namely using supercritical methanol [20], Cs2O-loaded Fe3O4 nanoparticles [21], solid-state fermentation using silica-immobilized micro bacteria soaked in inor- ganic nutrients (e.g., MgSO4, FeSO4, CoCl2, MnCl2, CaCl2, and (NH4)6Mo7O24) [22], and conventional basic catalyst (e.g., potassium methoxide [23], sodium and potassium hydroxide [24,25], and meth- anolic tetramethylammonium hydroxide [26]). While the first three techniques require a high amount of energy and complicated processing steps, the last technique using basic catalysts often faces many chal- lenges

1**due to the presence of** high **water and FFA content**

. These two components promote the hydrolysis and saponification reactions during the traditional conversion [16], which leads to a difficult separation and lower yield. Therefore, with the above-mentioned advantages of simple preparation, low cost, and insensitivity to contaminants during use, CS-based CaO can be considered highly potential to prepare biodiesel with commercial yield and specification from LTW in one-pot trans- esterification. Besides, due to the nature of the two waste materials, a waste-to-energy approach can be achieved via the utilization of CS and LTW as the starting catalyst and biodiesel feedstocks, respectively. The influence of

1**three independent processing variables** (catalyst loading mc, **reaction time t, and the molar ratio of ethanol to LTW**

meo)

6**on the** yield **of fatty acid** ethyl **esters** (FAEE) is studied. **The optimization** approach is conducted

5**using a combination of response surface** meth- odology (**RSM) and**

1**multilevel factorial design (MLFD) to** obtain **the**

optimized reaction parameters, which can be implemented in industrial practice. Among many statistical and mathematical approaches, MLFD is selected because it (1) incorporates all interactions of the three vari- ables at all levels, and (2) offers more flexibility in assessing these in- teractions when the number of degrees of freedom is sufficient [27]. Moreover, the use of the factorial design also increases the statistical sensitivity and generalizability without decreasing precision [28]; therefore, it is superior compared to the other methods. This study also uses ethanol as the alcohol source to maintain the phase homogeneity in the reaction system which leads to an increase in reaction rate [29,30]. The reusability of the CS-based CaO is also monitored at the optimum operating condition. 2. Materials and methods 2.1. Materials Both raw waste materials, CS and LTW, were collected from a local supplier in Surabaya, Indonesia. While CS was obtained from a local fish market, LTW was provided by a leather tannery in Indonesia. The pre- treatment of CS was conducted using the following procedures [8]: CS was first rinsed to remove the impurities. The cleansed CS was pulver- ized to a powder and

12**subjected to** the **calcination** process **at 900 ◦C for** 2 **h. The**

calcined CS was further ground to a powder with a particle size of smaller than 25 μm. The obtained powder was then stored in a vacuum container before use. At the same time,

1**LTW was washed with water to remove unwanted dirt and impurities**

, followed by heating at 120 C to ◦ remove retaining moisture. LTW was then purified using a membrane filter. All solvents and chemicals used for biodiesel preparation and anal- ysis were purchased from Merck (Germany) and of analytical grade; therefore, does not require any further purification. The gases required for gas chromatography analysis, namely nitrogen and helium (>

6**99.9%) were** procured from **Aneka Gas Industry Pty. Ltd., Surabaya**

. The composition of the biodiesel product was identified using the FAEE certified reference (10008188) obtained

2**from Cayman Chemicals (MI, USA), while methyl heptadecanoate**, which acts **as** the **internal standard** to calculate **the** purity **of FAEE**

, was purchased from Sigma-Aldrich (Germany). 2.2. The properties determination of CS-based CaO and LTW The surface topography and morphology images of CS-

2**based CaO were captured by FESEM**

JEOL JSM-6500F (Jeol Ltd., Japan), with the respective voltage and working distance of 10 kV and 8.0 mm. Mean- while, the textural properties of CS-based CaO, such as its specific sur- face area and pore volume, were obtained using

3**Micromeritics ASAP 2010 Sorption Analyzer at 77 K. The XRD** diffractogram **of**

the catalyst was acquired in 2θ = 15◦–90

3**using an X'PERT Panalytical Pro X-Ray ◦ diffractometer (Philips-FEI**, Netherlands). **The wavelength of** mono- chromatic **Cu Kα1 radiation (λ**

) is set at

3**0.154 nm**. The **voltage** and **tube current**

is adjusted at 40 kV and 30 mA, respectively. To measure its thermal stability, 6 mg of CS-based CaO powder were placed in a plat- inum pan and subjected to a PerkinElmer TG/DTA Diamond (Perki- nElmer, Japan). The oven temperature was then increased from 30 ◦C to 900 ◦C at a rate of 10 ◦C/min under a continuous nitrogen purge (ve- locity of nitrogen purge = 20 ml/min) to monitor the degradation profile of the CS-based CaO. Meanwhile, the crude fat, FFA, and moisture content in LTW were determined following

1**AOAC 991.36, ASTM D5555-95, and**

AOCS Ca 2e- 84, respectively. LTW is also further analyzed for its fatty acid (FA) profile

5**using GC-2014 (Shimadzu Ltd., Japan**

), following the method of ISO 12966.

1**Restek Rtx-65TG (30 m 0.25 mm ID x 0.10 μm film**

×

6**Table 1 The** encoded reaction **parameters and their corresponding values**

.

1**Variables Encoded factor Factor level 1 2 3 4 5**

16**Catalyst loading** (mc, **wt**%) A **1 2 3 4 5**

1 2 3 Reaction time (t, h)

1**Molar ratio of ethanol to LTW**

(meo) B C 2 6:1 3 9:1 4 12:1 thickness, Restek, USA) was selected as the separation column to iden- tify the FA profile in LTW. 2.3. Biodiesel preparation using LTW and CS-based CaO Ethanol as the alcohol source and LTW at meo = 6:1, 9:1, and 12:1 was added into a three-neck flask, fully installed along

2**with a condenser**, magnetic **stirrer, and** heater. **A** specified **amount of** CS-**based CaO**

(mc = 1, 2, 3, 4, 5 wt%) was introduced into the system. The reaction system was then heated to 60 C and maintained isothermally throughout the ◦ process with constant agitation

2**at 700 rpm for** various t (**2, 3, 4 h). After the reaction** was **completed, the** catalyst **was**

separated from the liquid product mixture by centrifugation and regenerated through a cycle of repeated washing and calcination at 900 ◦C. The product mixture was settled to obtain two layers, the top layer consisting FAEE and other minor components, and the bottom layer which is the mixture of glyc- erol, excess ethanol, and other undesirable by-products. The separated FAEE-rich phase was then subjected to vacuum evaporation

2**to obtain the biodiesel product**. Using **the**

optimized reaction condition obtained in section 2.5, a repetition of transesterification

2**using the same catalyst** was performed **until the yield** of FAEE reached **below 90 wt**% to measure **the** reusability **of**

the CS-

2**based CaO. All** runs **were** conducted **in triplicates**

. 2.4. Compositional analysis of LTW-based biodiesel

1**using GC-FID The** FAEEs composition **in the LTW-based biodiesel**

was identified by

4**Shimadzu GC-2014, with** the **split/splitless** injection **and** the **flame** ionized detection (**FID**) mode. **The stationary** silica **phase used** in the chromatography **separation** is **the narrow bore** type of **DB-WAX** capillary **column (30 m × 0.25 mm ID**

1**x 0.25 μm film thickness, Agilent** Tech- nology, **CA**

). Before analysis,

2**100 mg of biodiesel product was dissolved in 2 ml of** methyl heptadecanoate **solution** (10 μg/**ml**

) which acts as an internal standard. The mixture was then injected at

1**a split ratio of 1:50** into **the** GC column which **temperature**

has been initially adjusted at 50 C before injection. The temperature profile of the instrument and the ◦ carrier gas (helium, 99.9%) purge flowrate for the compositional > analysis follows the study performed by Santosa et al. [31]. The chromatogram of the FAEE certified reference (10008188) was used against that of the biodiesel product to identify the FAEE peaks. The FAEE purity and yield were computed using equations (1) and (2). ( ) (∑ A) FAEE Purity Fp, wt% = FAEE − AIS VISCIS AIS × mFAEE × 100% (1) ∑

6**where A** FAEE **is the area sum of** FAEE **peaks**

, AIS

10**is the area of methyl heptadecanoate** peak, VIS **is the** volume **of methyl heptadecanoate** so- lution (**ml**), CIS **is the** concentration **of methyl heptadecanoate solution** (g/**ml**), m is **the** actual **mass of the** FAEE **sample**

used in the GC-FID analysis (g). Table 2 The DOE matrix based on MLFD. Run Input variables A B C Response (FAEE yield, wt%) Experimentala Predicted (YFAEE)a Standard deviationb 1 4 2 1 3 3 4 5 5 4 6 4 7 2 8 2 9 5 10 1 11 3 12 1 13 4 14 3 15 3 16 1 17 1 18 3 19 1 20 1 21 1 22 4 23 5 24 5 25 3 26 2 27 4 28 3 29 2 30 5 31 3 32 2 33 2 34 2 35 2 36 3 37 5 38 5 39 2 40 4 41 4 42 5 43 4 44 1 45 5 3 3 3 1 1 2 1 3 1 3 2 2 3 1 3 3 2 3 2 2 2 2 1 2 1 2 3 1 3 3 3 3 3 2 3 2 2 3 2 1 1 3 3 1 3 2 1 2 2 1 1 1 3 2 1 1 1 3 2 2 1 3 3 2 1 2 2 3 2 1 2 3 1 1 2 1 2 2 1 1 2 1 3 3 2 3 1 1 3 1 95.8 97.4 63.8 66.9 85.1 87.1 92.2 90.2 91.4 92.8 93.5 96.1 83.1 82.9 91.2 86.7 93.3 93.5 63.9 65.9 93.4 92.8 59.1 58.1 90.2 91.6 94.6 92.2 95.6 95.4 68.2 71.3 67.6 69.5 94.3 94.2 65.9 67.9 63.6 63.2 57.6 60.2 92.3 94.8 92.3 92.0 92.2 89.3 92.9 90.7 71.2 73.5 95.3 96.4 82.5 85.0 80.2 77.7 92.0 92.8 87.9 88.6 88.6 85.2 75.6 76.0 89.2 84.4 82.8 80.3 94.8 94.1 91.2 87.8 91.6 91.3 86.3 82.7 87.4 89.7 89.5 94.4 92.1 92.6 94.5 97.2 58.9 55.3 93.1 90.6 1.11 2.20 1.44 1.42 0.96 1.86 0.14 3.16 0.16 1.42 0.45 0.72 0.98 1.70 0.14 2.22 1.32 0.11 1.40 0.26 1.81 1.75 0.24 2.03 1.55 1.62 0.79 1.75 1.74 0.55 0.50 2.43 0.26 3.42 1.75 0.47 2.42 0.19 2.55 1.65 3.45 0.36 1.90 2.54 1.75

1a The average standard error of estimate (SEE) between the two corresponding responses is 1.24%. b The deviation between the two corresponding responses for each run

. (FAEE Yield (wt%) = mFAEE x Fp × 100%) mLTW (2) where mFAEE is the final FAEE mass obtained (g), mLTW

18is the initial mass of LTW (g) and Fp is the FAEE purity obtained from equation (1). 2.5. Design of

experiment and determination of optimum point using RSM The statistical analysis using the combination of RSM and MLFD as the design of experiment (DOE) was performed for the determination of the optimum transesterification parameters to obtain the maximum Fig. 1. (a)–(b) FESEM images, (c) TGA analysis, (d) XRD pattern of CS-based CaO.

15Table 3 The textural properties of CS and CS

-based CaO. Materials Specific surface area (SBET, m2/g) Pore volume (Vp, cm3/g) CS 0.91 0.022 CS-based CaO 12.47 0.081 yield of FAEE as the response. The input variables, namely mc (wt%), t (h), and meo (mol/mol) were chosen as the critical parameters due to their relevance to the industrial applicability since these parameters greatly affect the processing efficiency and operational cost. While both t and meo are separated

1into three levels: low (1), middle (2), and high (3), mc is classified into five levels with

an ascending order to accurately observe the influence of the parameter on the yield of FAEE (wt%).

5Table 1 presents the encoded parameters and their actual values. The

DOE matrix, shown in Table 2, lists the correlation between the reaction parameters for each run with their corresponding experimental and predicted responses (FAEE yield, wt%). To attain good data repro- ducibility and accuracy, the

3experimental runs were carried out in triplicates and randomized order

.

6Analysis of variance (ANOVA) is employed by using Minitab (ver. 18.1) with a confidence level of 95% to generate the

fitted equation, to describe the behavior of the three operating variables on the yield of FAEE. The

5goodness-of-fit analysis on the generated mathematical model is also evaluated

using the R-squared value. The following equation (3) shows the

1correlation between the pre- dicted response (FAEE yield, wt%) and the

input variables, where YFAEE is the predicted FAEE yield (wt%);

3k0, ki, kii, kij are the coefficients for the intercept, linear, quadratic, and two-way interactions of the input variables, respectively; Xi and Xj are the encoded reaction variables (A, B, C). While the value of i lies between 1 and

3 for t and meo, it ranges from 1 to 5 for mc. = + ∑3 + ∑3 kiiX2i + ∑3∑3 YFAEE k0 ki Xi kijXiXj (3) i=1 i=1 i=1 j=1

23. Results and discussions 3.1. Characterization of CS-based CaO

Fig. 1 (a) and (b) present the surface topographies of CS-based CaO. It is notable that the catalyst particle is irregular in shape and has a rough surface with a honeycomb-like structure (Fig. 1 (a)). The calci- nation reaction at 900 C removes a substantial amount of bound water ◦ from the catalyst pores, hence creating high porosity [11]. However, it is also evident from the FESEM images that catalyst particles are aggre- gated, resulting in non-uniform particle size. Valverde et al. [32] stated that the presence of carbon in the CS-based CaO will induce the for- mation of CO2 during the calcination. This CO2 gas will then react with the CaO product to produce calcium carbonate, the primary cause of particle aggregation. The textural properties of CS and CS-based CaO analyzed by nitrogen sorption are provided in Table 3. The CS-based CaO has superior prop- erties than those of raw CS. Yoosuk et al. [33] stated that the removal of impurities and moisture during the high-temperature calcination plays a critical role in improving the porosity and textural properties of the CS-based CaO. As the surface area and pore volume of catalyst have a Table 4 The chemical properties of LTW. Parameters Result Moisture, wt% FFA, wt% Total

2crude fat, wt% Molecular mass, g/mol

FA composition,

2wt% C14:0 C16:0 C16:1 C17:0 C18:0 C18:1 C18:2 C18:3 C20:0

11.45 18.89 69.66 798.5 4.30 28.70 2.60 0.70 13.40 43.50 4.90 1.80 0.10 proportional influence on its catalytic activity, it is expected that CS-based CaO has a comparable, if not superior, catalytic activity compared to the existing CaO catalyst. To demonstrate the thermal stability of the CS-based CaO, a ther- mogravimetric analysis (TGA) was carried out, and its profile is presented in Fig. 1 (c). The figure shows a 5 wt% decrease when the temperature is elevated from 595 ◦C to 650 ◦C which corresponds to the evaporation of chemically-bound moisture [34], decomposition, and transition of calcite (CaCO3) to CaO

[11]. As the complete decomposi- tion of $CaCO_3$ can be achieved at the temperature of around 700 C; the ◦ selection of

15**calcination temperature at 900 C is** deemed suitable **to** ◦ ensure **the** complete phase transition **of**

calcite and its derivatives to CaO [34,35], which leads to the formation of a porous structure. Hu et al. [11] also reported that the catalytic activity of a catalyst escalates along with the activation [11]. The XRD image (

2**Fig. 1 (d**)) shows that **the diffraction pattern of** CS-**based**

CaO follows the characteristic fingerprint of CaO (JCPDS file no. 82–1691) as the primary component and calcite (JCPDS file no. 47–1743) as the minor substance. 3.2. Transesterification parameter study The chemical properties of LTW are presented in Table 4, with pal- mitic

2**acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1**) as **the**

three principal fatty acids constituting LTW.

4**As homogenous catalysts are sensitive to** FFA and **impurities, the** conventional **conversion of** LTW **to**

FAEE requires at least a two-stage process: (1) acid-catalyzed esteri- fication to generate FAEE from the FFA content in LTW, and (2) base- Fig. 2. (a) The experimental and (b) the predicted FAEE yield (wt%), based on their interaction between (1) catalyst loading mc (wt%) and

2**reaction time** t (**h**), (2) **catalyst loading** mc (**wt%) and molar ratio of ethanol to LTW**

meo, (3)

1**reaction time t** (h) **and the molar ratio of ethanol to LTW** meo. **Table** 5 **The**

three-way ANOVA study of the tested variables.

5**Term Coef SE Coef T-Value P-Value Constant**

92.76 A 13.433 B 3.507 C 1.713 A2 − 13.432 B 2 − 2.127 C2 − 0.347 (A)(B) − 2.190 (A)(C) − 0.613 (B)(C) − 0.105 R-squared (R2) Adjusted R-squared (Adj-R2) Predicted R-squared (Pred-R2) 1.01 92.25 0.561 23.95 0.486 7.22 0.486 3.53 0.948 − 14.17 0.841 − 2.53 0.841 − 0.41 0.687 − 3.19 0.687 − 0.89 0.595 − 0.18 0.9607 0.9506 0.9317 0.000 0.000 0.000 0.001 0.000 0.016 Non-significant 0.003 Non-significant Non-significant

4**catalyzed transesterification to convert the acyl glycerides into** FAEE. **However, heterogeneous catalysts** show **good tolerance towards the FFA and water content in the lipid materials**

,

4**therefore efficient conversion from** LTW **to** FAEE can be **achieved in a single step. Fig**. 2 **presents the yield** of FAEE **obtained at various**

mc, t, and meo. The experimental results indicate that the catalyst amount, specifically the

4**number of active sites offered by**

CS-based CaO, is proportional to the yield of FAEE (Fig. 2 (a.1) - (a.2)). Its value increases with mc when mc is within 3 wt%. A stagnant FAEE yield at mc > 3 wt% is monitored, extending the duration of reaction from t = 2 h to t = 4 h. Prolonged t provides sufficient opportunities for the catalyst to be dispersed and come into proper contact with the reactants, and ensures the reaction to reach the equilibrium [21]; therefore, increasing the

1**conversion of acyl glycerides and FFA into FAEE**

. From another viewpoint, lengthening the

4**duration of** the **reaction also gives the catalyst** enough **time to adsorb the** reactants **and desorb the** resulting **product**

[39]. The influence of meo is depicted in Fig. 2 (a.2) – (a.3). As seen from the figure, having excess ethanol from meo 6:1 to meo 12:1 con- = = tributes to a slightly higher FAEE yield, and its prominence is incomparable to the effect of mc. It is known that excess alcohol in the reaction system triggers intensive contact between reactants and catalysts, hence, accelerating the reaction rate. However, this is only beneficial to a certain degree because the excess alcohol hinders the phase separation and decreases the apparent FAEE yield [40]. 3.3. Process optimization To determine the optimum operating condition, RSM combined with MLFD is statistically employed by simultaneously integrating three critical parameters (mc, t, meo).

5**Table 2 presents the** relation **between the** responses **and their corresponding**

input variables. Using the least square analysis, the experimental responses are

17**found to fit into a second-order** polynomial **model as**

follows: YFAEE(FAEE yield, wt%) = 13.23 + 29.67(A) + 15.51(B) + 4.23(C) − 3.358 A2 − 2.127 B2 − 0.347 C2 − 1.095(A)(B) − 0.307(A)(C) − 0.105(B)(C) ( ) ( ) ( ) (4) which is probably contributed by (1)

4the aggregation and inconsistent dispersity of the catalyst in the reaction system

[36], and (2) the enhanced viscosity of the LTW, ethanol, and catalyst mixture [37]. Wei et al. [38] also reported that the reaction rate governing step is the sorption of reactants from the catalyst; therefore, while the number of active sites is important, further addition of catalyst higher than a certain extent does not give a significant increase of the yield of FAEE. Fig. 2 (a.1) and (a.3) show a mild increase of the FAEE yield by where YFAEE is the predicted FAEE yield (wt%) which is presented in Table 2;

5A, B, C are the coded level of reaction variables (1

, 2, 3, 4, 5 for A and 1, 2, 3 for B and C). The mathematical equation indicates that all linear variables (A, B, C) give a favorable effect on the yield of biodiesel, and conversely, the other variables (A2, B2, C2, (A)(B), (A)(C), (B)(C)) reduce the response. The statistical ANOVA results presented in Table 5 shows that all terms, except that of C2, (A)(C), and (B)(C), are prominent to the reaction (p-value < 0.05), with the significance order of A > A2 > Fig. 3. The Pareto chart of the standardized effect showing the significance order of various reaction variables.

1Fig. 4. The optimization plot of the reaction variables

. Fig. 5. The catalytic activity of reused CS-based CaO. B > C > (A)(B) > B2 as shown in Fig. 3. The goodness-of-fit analysis for the fitted equation (equation (4)) is measured by using the R-squared (R2), where the R2 value for the model

3is obtained at 0.9607, pointing that 96.07% of the actual experimental data can be interpreted by equation (4). The values of the adjusted and predicted R2 are

also respectively monitored at 0.9506 and 0.9317, indicating that the predicted and experimental FAEE yields are in good agreement. Table 2 shows that the average

1standard error of estimate (SEE) between the two corresponding responses

is observed at 1.24% (n = 45), indicating sufficient data accuracy. Fig. 2 (b.1) – (b.3) further prove that both experimental and predicted plots share a similar response profile.

3Therefore, the mathematical model is considered adequate to predict the response for all input variables

within the tested range. The optimized reaction condition is generated using Minitab (ver. 18.1) and predicted at mc 3.87 wt%, t 3.58 h, and meo 12:1. The = = = computed response at this condition is obtained at 97.9 wt%, with desirability = 1.0 (Fig. 4).

5To confirm the plausibility of the mathe- matical model

, triplicate experiments are carried out at the optimum condition. The average FAEE yield

5is found at 98.7 0.4 wt%, with the ± purity of 98.6 0.4 wt%. The

established model is deemed reliable and ± accurate for all operating conditions within the tested range, as the error between the predicted and experimental results is only 0.85%. A Table 6 The performance of various

2techniques for the production of biodiesel from waste

-originated materials. Lipid material Catalyst type Operating condition Biodiesel yield (wt Catalyst Reference %) reusability Vegetable oil wastewater sludge Waste cooking oil Tallow fats LTW LTW N/A (Subcritical methanol) Zn-doped waste-egg shells CaO KOH N/Aa (Supercritical ethanol) CS-based CaO T = 215 ◦C, P = 6.5 MPa, mmob = 5:1, t = 12 h T = 65 ◦C, mc = 5 wt%, mmob = 20:1, t = 4 h T = 60 ◦C, mc = 0.8 wt%, mmob = 6:1, t = 2 h T = 374.6 ◦C, P = 15 MPa, meo = 40.02:1, t = 47.4 min T = 60 ◦C, mc = 3.87 wt%, meo = 12:1, t = 3.58 h 92.7 96.7 90.8 98.9 98.7 - 2 - - 4 [41] [42] [43] [16] This work a Not available. b mmo stands

17for molar ratio of methanol to oil

. Table 7 The

2properties of LTW-based biodiesel. Properties Methods LTW- ASTM based D6751 biodiesel

Diesel fuel (ASTM D975-08)

14Kinematic viscosity (at 40 C), mm2/s ◦ Density (at 15 ◦C, kg/ m3) Flash point, ◦C Cloud point

Cetane number Water and sediment, vol%

20Acid value, mg KOH/ g Iodine value, g I2/ 100 g Ester content, wt% Linolenic acid ethyl ester content

, wt% Polyunsaturated ethyl ester content, wt% Total glycerine, wt% Free glycerine, wt% Sulfur, ppm Phosphorus, ppm Carbon residue, wt% Oxidation stability, h Calorific value, MJ/ kg ASTM D445 ASTM D1298 ASTM D93 ASTM D2500 ASTM D613 ASTM D2709 ASTM D664 AOCS Cd 1-25 EN 14103 EN 14103 EN 15779 2.1 865 167 10.2 53 0.01 0.22 52.9 98.7 1.2 6.1 ASTM D6584 ASTM D6584 ASTM D5453 0.16 0.01 3.67 ASTM D4951 ASTM D4530 EN 14112 ASTM D240 0.21 0.002 12.7 44.67 1.9–6.0 - 93

13min - 47 min 0.05 max 0.50 max - - - - 0.24 max 0.02 max 15 max

(S15) 500 max (S500) 10

13max 0.05 max 3 min

- 1D: 1.3–2.4 2D: 1.9–4.1 - 1D: 38 min 2D: 52 min - 46 min 0.05 max - - - - - - - 1D and 2D: 15 max (S15) 500 max (S500) - 1D: 0.15 max 2D: 0.35 max - - relatively short reaction time (t 3.58 h) and low catalyst amount (mc = = 3.87 wt%) is highly beneficial in practice, as these variables directly influence the production efficiency. The reusability of CS-based CaO is presented in Fig. 5, where the results show that the regenerated CS-based CaO can maintain a high yield of FAEE (>90

5wt%) until the fourth run before significantly decline to 89.4 wt% in the fifth cycle

. The FAEE yields for the first four cycles are 98.7 wt%, 98.2 wt%, 96.6 wt%, 96.0 wt%, with the respective purity of 98.6 wt%, 98.9 wt%, 97.3 wt, 98.2 wt%. The deactivation of CS-based CaO is probably due to the clogged pores, caused by the deposition of deactivation-induced molecules, e.g., free

5glycerol, acyl glycerides, and biodiesel. The FFA content

may as well deactivate the basic sites of CS- based CaO through neutralization [5] to form calcium carboxylate.

16A comparative study of the biodiesel production from waste-originated materials using

various methods is presented in Table 6. In general, the conversion of LTW to biodiesel using CS-based CaO shows compa- rable performance with the other preparation processes, indicated by its high product yield (higher than 90 wt%) and reusability number. 3.4. Characteristics of

1LTW-based biodiesel Table 7 presents the fuel properties of LTW-based biodiesel

gener- ated using CS-

2based CaO as a catalyst. The

measurements indicate that the properties of the resulting biodiesel product

1are in accordance with the standard of ASTM D6751 and ASTM D975-08

. A high flash point, which is the result of the sufficient post-separation step, shows that the product can be treated, stored, and transported safely. Its calorific value, 44.67 MJ/kg, is within the range of that of petroleum diesel fuel (42–46 MJ/kg) [44]. The chemical compositional analysis of the LTW-based FAEE using GC-FID shows that there are ten distinguished peaks in the chromatogram: myristic

19**acid ethyl ester** (C14:**0**), myristoleic **acid ethyl ester** (C14:**1**), palmitic **acid ethyl ester** (C16:0), palmitoleic **acid ethyl ester** (C16:**1**

), heptadecanoic

8**ethyl ester (C17:0), stearic acid ethyl ester (C18:0), oleic acid ethyl ester (C18:1), linoleic acid ethyl ester (C18:2**), α-**linolenic acid ethyl ester (C18:3), arachidic acid ethyl ester (C20:0**

). 4. Conclusions Successful conversion of LTW to biodiesel is achieved using a CS- based CaO, with the highest FAEE yield of 98.7 0.4 wt% (

5**purity of ± 98**.6 **0**.4 **wt**%) obtained at **the following** reaction **condition**

: mc 3.87 ± = wt%, t = 3.58 h, and meo = 12:1. The CS-based CaO shows good reus- ability; the FAEE yield stays above 90 wt% for four reaction cycles.

1**The fuel properties of LTW-based**

FAEE comply with

1**ASTM D6751 and ASTM D975-08. The** valorization **of**

CS and LTW will prominently allow better environmental destination for these wastes and meanwhile offers an environmentally benign route to produce high value-added renewable energy.

11**Acknowledgment This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.**

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