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Biomass and Bioenergy

EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH

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Abstract:	To promote the use of waste-originated resources in producing biodiesel, 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 catalyst has comparable textural properties with those of existing waste-based catalyst and shows high catalytic activity for the conversion of LTW to biodiesel. The optimum yield of FAEE is predicted at 97.87 wt%, while it is experimentally observed at 98.72 ± 0.36 wt% (purity of 98.57 ± 0.41 wt%) using the following operating condition: reaction time t = 3.58 h, catalyst amount mc = 3.87 wt%, and a molar ratio of ethanol to LTW meo = 12:1. The CS-based catalyst shows good recyclability with FAEE yield staying above 90 wt% for four cycles. The fuel properties of LTW-based biodiesel meet ASTM D6751 and ASTM D975-08 standards, with the ethyl ester ranging from C14 to C20.
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January 9, 2021

Professor Patricia Thornley
Editor
Biomass & Bioenergy

Dear Professor Thornley,

On behalf of my co-author, I am writing to submit the manuscript for publication consideration in *Biomass & Bioenergy*. The details of the manuscript are as follows:

Title of Manuscript: **EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH**

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Keywords: *leather tannery waste; crab shell; biodiesel; waste-derived fuel; recyclability; optimization study*

Rationale of the manuscript:

This manuscript provides an innovative solution to the pressing waste and energy challenges, specifically in Indonesia. We propose a waste-to-energy approach to utilize two wastes, crab shell (CS) and leather tanning waste (LTW), in the synthesis of biodiesel (FAEE) in a single step. The catalytic activity and reusability of CS-based catalyst are discussed in the manuscript. The process optimization is also presented. We believe that our findings are consistent with the journal scope and able to give a significant contribution to the scientific advancement, particularly in the field of waste utilization, environmental science and waste-derived fuel.

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Thank you for your consideration. I am looking forward to hearing from your positive response.

Sincerely yours,

Maria Yuliana

- Waste-to-energy approach is successfully employed using LTW and CS to produce FAEE
- The catalytic effect of CS-based catalyst is comparable to the other solid catalyst
- 98.72 ± 0.36 wt% of FAEE yield was achieved from LTW using CS-based catalyst
- The optimum operating condition: t = 3.58 h, m_c = 3.87 wt%, and m_{eo} = 12:1
- CS-based catalyst has a good recyclability (FAEE yield > 90wt%) up to the 4^{th} run

EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH

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ABSTRACT

To promote the use of waste-originated resources in producing biodiesel, 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 catalyst has comparable textural properties with those of existing waste-based catalyst and shows high catalytic activity for the conversion of LTW to biodiesel. The optimum yield of FAEE is predicted at 97.87 wt%, while it is experimentally observed at 98.72 ± 0.36 wt% (purity of 98.57 ± 0.41 wt%) using the following operating condition: reaction time t = 3.58 h, catalyst amount m_c = 3.87 wt%, and a molar ratio of ethanol to LTW m_{eo} = 12:1. The CS-based catalyst shows good recyclability with FAEE yield staying above 90 wt% for four cycles. The fuel properties of LTW-based biodiesel meet ASTM D6751 and ASTM D975-08 standards, with the ethyl ester ranging from C14 to C20.

Keywords: leather tannery waste; crab shell; biodiesel; waste-derived fuel; recyclability; optimization study

1. INTRODUCTION[1]

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 transesterification yield, find the simplest and low-cost technique as well as to fabricate waste-based catalyst. 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% of the total crab mass. This leaves almost 20,000 tons of solid waste discharged each year [1]. While in the developed countries, the waste disposal is costly, crab shells (CS) in Indonesia are often directly discharged to the environment.

CS exhibit potential value due to its valuable chemical contents, namely protein (20 – 40 %, w/w), calcium carbonate (20 – 50 %, w/w), and chitin (15 – 40 %, w/w) [2], that can be utilized in many applications. 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 [3–6] in various chemical forms. Of the compounds, calcium oxide (CaO)-based catalyst seems to have the highest ability, indicated by the increasing research on this type of catalyst in the form of neat,

[1] **Abbreviation**

CS	Crab shell
LTW	Leather tanning waste
FAEE	Fatty Acid Ethyl esters
FFA	Free fatty acid
CaO	Calcium oxide

supported, loaded and mixed CaO [4,5,7]. The conversion of calcium carbonate to calcium oxide is commonly achieved by thermal decomposition via calcination at high temperature to liberate carbon dioxide from the raw materials [7].

Currently, transesterification of lipid to biodiesel is employed mainly using a homogenous catalyst, due to its phase homogeneity and shorter reaction time. However, this type of catalyst cannot be reused and requires additional washing and separation steps, hence inducing the attention in the use of the heterogeneous solid catalyst in the biodiesel preparation process. Despite its comparable catalytic activity and simpler use in the transesterification process, many heterogeneous catalysts are not viable for industrial usage since most of the catalysts are expensive and require complicated preparation efforts. Therefore, synthesizing simple yet highly active catalysts for biodiesel preparation is important. Due to this very reason, CaO is widely researched. 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 [8]. These basic sites abstract a proton from the organic compounds and initiate the basic catalysis reaction [7]. The catalytic activity of CaO-based catalyst in the transesterification has been conducted using various natural-based raw materials as follows: mussel shells [9,10], eggshells [11], waste capiz shells [12,13], cockle shells [10], Pomacea sp. shells [14] and river snail shells [15]. Extensive utilization 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 focuses 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 and moisture content; therefore, it is easier to process and gives a more stable yield. This study combines the use of CS-based catalysts and leather tanning waste (LTW) as a lipid source to produce biodiesel. LTW is selected as the lipid feedstock because its production reaches 100,000 tons annually

[16–18], with the crude fat content higher than 60% [16]. Several valorization approaches have been conducted to prepare biodiesel from LTW, namely using methanol at supercritical condition [18], magnetic Cs_2O@nanoparticles [19], solid-state fermentation using soak liquor micro bacteria [20] and conventional basic catalyst [21].

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 biodiesel feedstock. Our research focuses on the potential use of CS-based catalysts to prepare biodiesel with commercial yield and specification from LTW in one-pot transesterification. The optimization approach is conducted using response surface methodology (RSM) to obtain the optimized processing variables (catalyst loading m_c, reaction time t, and the molar ratio of ethanol to LTW m_{eo}) which can be implemented in the industrial practice. Ethanol is selected as the alcohol to maintain the phase homogeneity in the reaction system which leads to an increase in reaction rate [22,23]. The recyclability of the CS-based catalyst 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 [12]: CS was first rinsed to remove the impurities. The cleansed CS was pulverized to a powder and 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, 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 analysis 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 (> 99.9%) were procured from Aneka Gas Industry Pty. Ltd., Surabaya. The composition of the biodiesel product was identified using the fatty acid ethyl esters (FAEE) certified reference (10008188) obtained from Cayman Chemicals (MI, USA), while methyl heptadecanoate which acts as the internal standard (IS) to calculate the purity of FAEE was purchased from Sigma-Aldrich (Germany).

2.2 The properties determination of CS based-catalyst and LTW

The surface topography and morphology images of CS-based catalysts were captured by FESEM JEOL JSM-6500F (Jeol Ltd., Japan), with the respective voltage and working distance of 10 kV and 8.0 mm. Meanwhile, the textural properties of CS-based catalysts, such as its specific surface area and pore volume, were obtained using Micromeritics ASAP 2010 Sorption Analyzer at 77 K. The XRD diffractogram of the catalyst was acquired in $2\theta = 15° - 90°$ using an X'PERT Panalytical Pro X-Ray diffractometer (Philips-FEI, Netherlands). The wavelength of monochromatic Cu $K\alpha_1$ radiation (λ) is set at 0.154 nm. The voltage and tube current is adjusted at 40 kV and 30 mA, respectively. To measure its thermal stability, six milligrams of CS-based catalyst powder was placed in a platinum pan and subjected to a Perkin Elmer TG/DTA Diamond (Perkin Elmer, 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 (velocity of nitrogen purge = 20 ml/min) to monitor the degradation profile of the CS-based catalyst.

Table 1 summarized the chemical properties of LTW. The crude fat, FFA, and moisture content in LTW were determined following AOAC 991.36, ASTM D5555-95, and AOCS Ca 2e-84, respectively. LTW is also further analyzed for its fatty acid (FA) profile using GC-2014

(Shimadzu Ltd., Japan), following the method of ISO 12966. Restek Rtx-65TG (30 m x 0.25 mm ID x 0.10 µm film thickness, Restek, USA) was selected as the separation column to identify the profile of fatty acids in LTW.

Table 1. The chemical properties of LTW

Parameters	**Result**
Moisture, wt%	11.45
FFA, wt%	18.89
Total crude fat, wt%	69.66
Molecular mass, g/mol	798.5
FA composition, wt%	
C14:0	4.30
C16:0	28.70
C16:1	2.60
C17:0	0.70
C18:0	13.40
C18:1	43.50
C18:2	4.90
C18:3	1.80
C20:0	0.10

2.3 Biodiesel preparation using LTW and CS-based catalyst

Ethanol as the alcohol source and LTW at m_{eo} = 6:1, 9:1, and 12:1 was added into a three-neck flask, fully installed along with a condenser, magnetic stirrer, and heater. A specified amount of CS-based catalyst (m_c = 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 at 700 rpm for various t (2, 3, 4 h). After the reaction was completed, the CS-based 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 glycerol, excess methanol, and other undesirable by-products. The separated FAEE-rich phase was then subjected to vacuum evaporation to obtain the biodiesel product.

Using the optimized reaction condition obtained in section 2.5, a repetition of transesterification using the same catalyst was performed until the yield of FAEE reached below 90% to measure the recyclability of CS-based catalyst. All runs were conducted in triplicates.

2.4.Compositional analysis of LTW-based biodiesel using GC-FID

The FAEEs composition in the LTW-based biodiesel was identified by 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 x 0.25 mm ID x 0.25 µm film thickness, Agilent Technology, CA). Before analysis, 100-mg of biodiesel product was dissolved in 2 ml of methyl heptadecanoate solution (10 µg/ml) which acts as IS. The mixture was then injected at 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. (2019) [24].

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 equation (2) and (3).

$$\text{FAEE Purity } (F_p, \%) = \left(\frac{\sum A_{FAEE} - A_{\text{IS}}}{A_{\text{IS}}} \times \frac{V_{\text{IS}} C_{\text{IS}}}{m_{\text{FAEE}}} \right) \times 100\% \quad (2)$$

Where $\sum A_{FAEE}$ is the area sum of FAEE peaks, A_{IS} is the area of methyl heptadecanoate peak, V_{IS} is the volume of methyl heptadecanoate solution (ml), C_{IS} 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).

$$\text{FAEE Yield (wt \%)} = \left(\frac{m_{\text{FAEE}}}{m_{\text{LTW}}} x\ F_p\right) \times 100\% \quad (3)$$

Where m_{FAEE} is the final FAEE mass obtained (g), m_{LTW} is the initial mass of LTW (g) and F_p is the FAEE purity obtained from equation (2).

2.5. Design of experiment and determination of optimum point using RSM

The statistical analysis using the combination of RSM and the multilevel factorial design (MLFD) as the design of experiment (DOE) was performed for the determination of the optimum transesterification parameters to obtained the maximum yield of FAEE as the response. The input variables, namely m_c (wt%), t (h), and m_{eo} (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 m_{eo} are separated into three levels: low (1), middle (2), and high (3), m_c is classified into five levels with an ascending order to accurately observe the influence of the parameter on the yield of FAEE (wt%). Table 2 presents the encoded parameters and their actual values.

Table 2. The encoded reaction parameters and their corresponding values

Variables	**Encoded factor**	**Factor level**				
		1	**2**	**3**	**4**	**5**
Catalyst loading (m_c, wt%)	*A*	1	2	3	4	5
		1		**2**		**3**
Reaction time (t, h)	*B*	2		3		4
Molar ratio of ethanol to LTW (m_{eo})	*C*	6:1		9:1		12:1

The DOE matrix, shown in Table 3, lists the correlation between the reaction parameters for each run with their corresponding experimental and predicted responses (FAEE yield, wt%). To attain a good data reproducibility and accuracy, the experimental runs were carried out in triplicates and randomly performed order. Analysis 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 goodness-of-fit analysis on the generated mathematical model is also evaluated using the R-squared value.

The following equation (4) shows the correlation between the predicted response (FAEE yield, wt%) and the input variables, where Y_{FAEE} is the predicted FAEE yield (wt%); k_0, k_i, k_{ii}, k_{ij} are the coefficients for the intercept, linear, quadratic, and two-way interactions of the input variables, respectively; X_i and X_j are the encoded reaction variables (*A*, *B*, *C*). While the value of *i* lies between 1 and 3 for *t* and m_{eo}, it ranges from 1 to 5 for m_c.

$$Y_{FAEE} = k_0 + \sum_{i=1}^{3} k_i X_i + \sum_{i=1}^{3} k_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} k_{ij} X_i X_j \quad (4)$$

Table 3. The DOE matrix based on MLFD

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

[a] 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.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of CS-based catalyst

Figure 1 (a) and (b) present the surface topographies of CS-based catalyst. It is notable that the catalyst particle is irregular in shape and has a rough surface with a honeycomb-like structure (Figure 1 (a)). The calcination reaction at 900°C removes a substantial amount of bound water from the catalyst pores, hence creating high porosity [9]. However, it is also evident from the FESEM images that catalyst particles are aggregated, resulting in non-uniform particle size. Valverde et al. (2015) stated that the presence of carbon in the CS-based catalyst will induce the formation of CO_2 during the calcination. This CO_2 gas will then react with the CaO product to produce calcium carbonate, the primary cause of the particle aggregation [25].

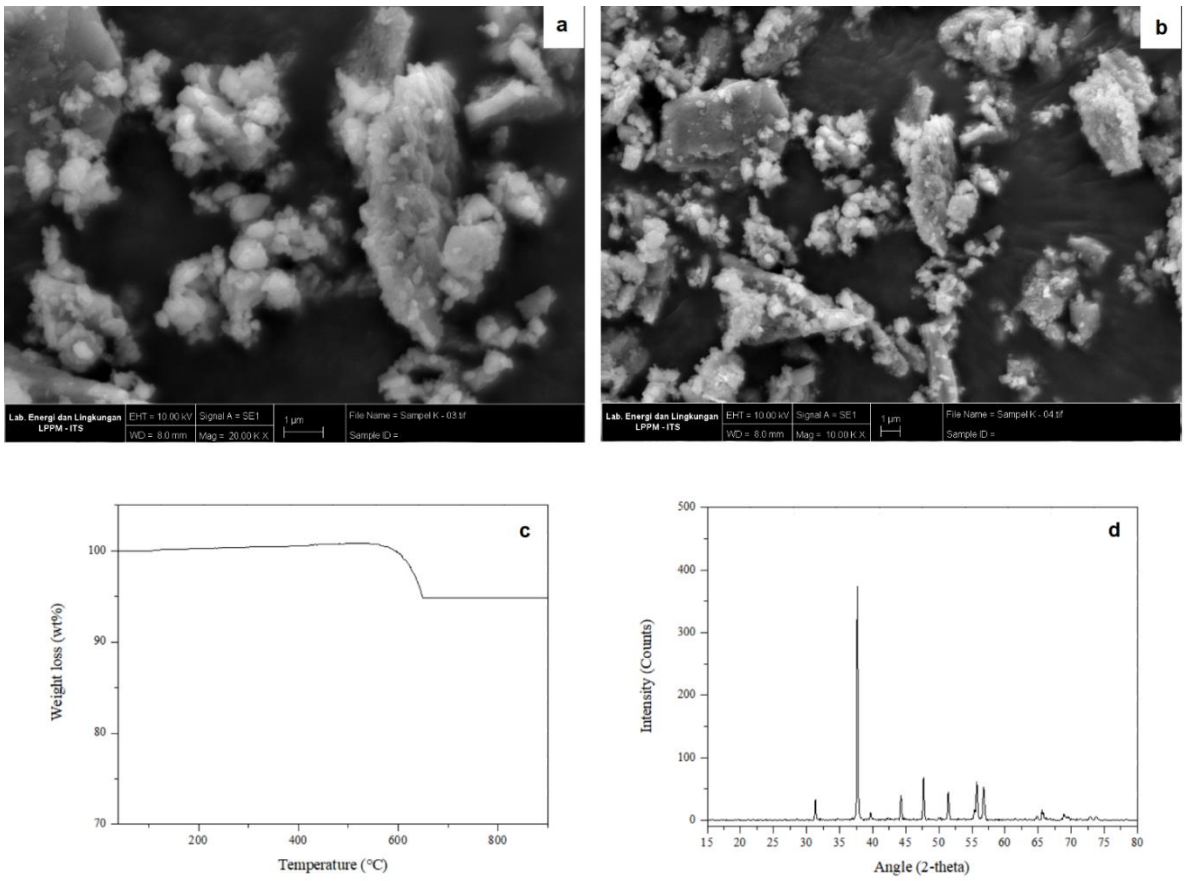

Figure 1. (a) – (b) FESEM images, (c) Thermogravimetric analysis, (d) XRD pattern of CS-based catalyst

The textural properties of CS and CS-based catalyst analyzed by nitrogen sorption are provided in Table 4. The CS-based catalyst has superior properties than those of raw CS. Yoosuk et al. (2010) 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 catalyst [26]. As the surface area and pore volume of catalyst have a proportional influence on its catalytic activity, it is expected that CS-based catalyst has a comparable, if not superior, catalytic activity compared to the existing CaO catalyst.

Table 4. The textural properties of CS and CS-based catalyst

Materials	Specific surface area (S_{BET}, m^2/g)	Pore volume (V_p, cm^3/g)
CS	0.91	0.022
CS-based catalyst	12.47	0.081

To demonstrate the thermal stability of the CS-based catalyst, a thermogravimetric analysis (TGA) was carried out, and its profile is presented in Figure 1 (c). The figure shows a 5% decrease in mass when the temperature is elevated from 595°C to 650°C which corresponds to the evaporation of chemically-bound moisture [27], decomposition and transition of calcite ($CaCO_3$) to CaO [9]. As the complete decomposition of $CaCO_3$ can be achieved in the temperature of around 700°C; the selection of calcination temperature at 900°C is deemed suitable to ensure the complete phase transition of calcite and its derivatives to CaO [27,28], which leads to the formation of a porous structure. Hu et al. (2011) also reported that the catalytic activity of a catalyst escalates along with the activation [9]. The XRD image (Figure 1 (d)) shows that the diffraction pattern of CS-based catalyst 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 1, with palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1) as the three principal fatty acids constituting LTW.

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 esterification to generate FAEE from the FFA content in LTW, and (2) base-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, therefore efficient conversion from LTW to FAEE can be achieved in a single step.

Figure 2 presents the yield of FAEE obtained at various m_c, t, and m_{eo}. The experimental results indicate that the catalyst amount, specifically the number of active sites offered by CS-based catalyst, is proportional to the yield of FAME (Figure 2 (a.1)-(a.2)). Its value increases with m_c when m_c is within 3 wt%. This is in agreement with the previous works on the preparation of biodiesel using different catalysts [14,29,30]. A stagnant FAEE yield at m_c > 3 wt% is probably contributed by the aggregation and inconsistent dispersity of the catalyst in the reaction system, due to its enhanced viscosity [31–35]. Wei et al. (2009) also reported that the reaction rate governing step is the sorption of reactants from the catalyst [36]; therefore, while the number of active sites is important, further addition of catalyst higher than a certain extent does not give a significant increase the yield of FAEE.

Figure 2 (a.1) and (a.3) show a mild increase of the FAEE yield by extending the duration of reaction from t = 2 h to t = 4 h. Prolonged t provides sufficient opportunities for the LTW and ethanol to reach the active sites of the catalyst, and ensures proper contact among them [37]; therefore, increasing the conversion of acyl glycerides and FFA into FAEE. From another viewpoint, lengthening the duration of reaction also gives the catalyst enough time to adsorb the reactants and desorb the resulting product [38].

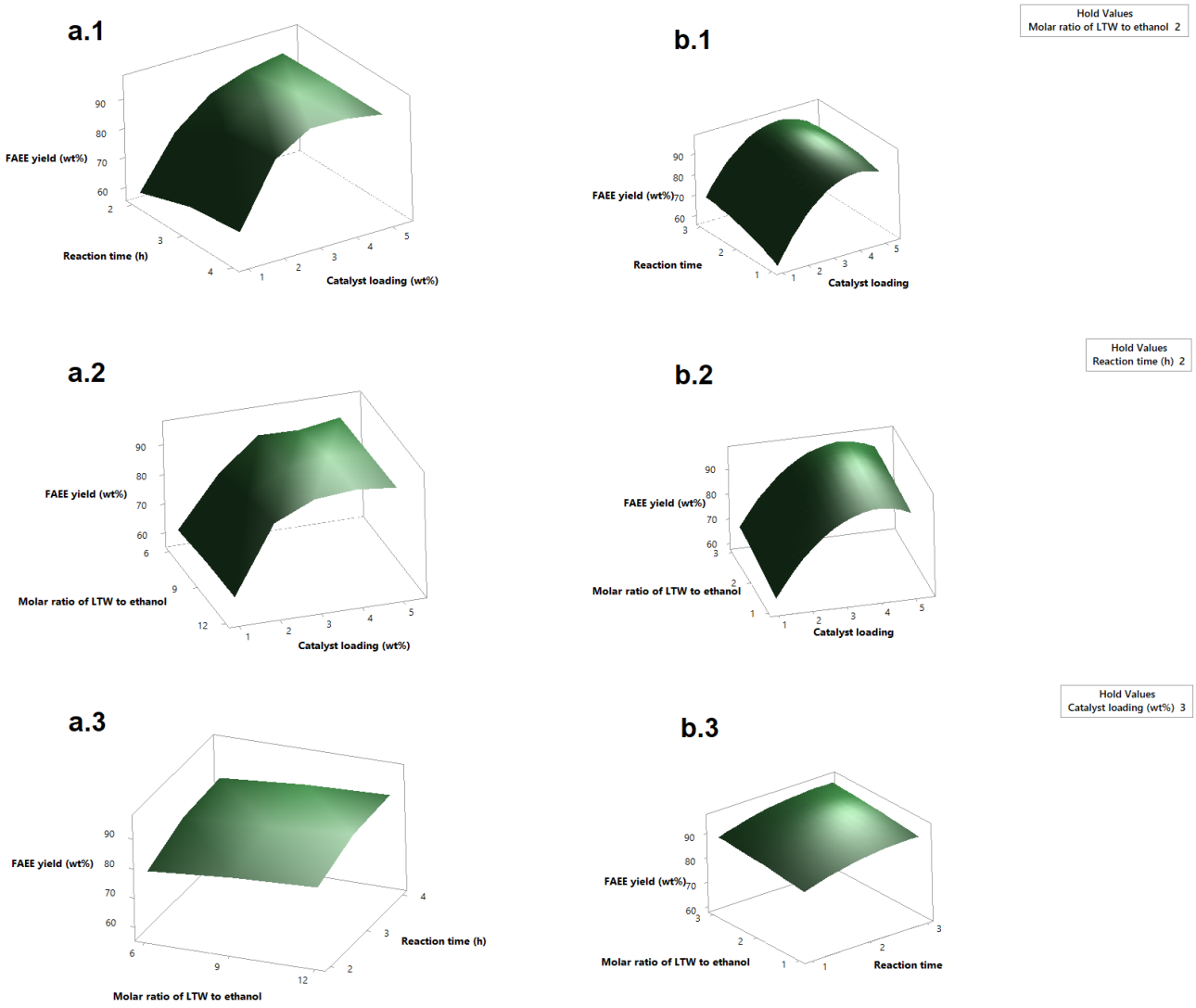

Figure 2. (a) The experimental and (b) the predicted FAEE yield (wt%), based on their interaction between (1) catalyst loading m_c (wt%) and reaction time t (h), (2) catalyst loading m_c (wt%) and molar ratio of ethanol to LTW m_{eo}, (3) reaction time t (h) and the molar ratio of ethanol to LTW m_{eo}

The influence of m_{eo} is depicted in Figure 2 (a.2) – (a.3). As seen from the figure, having excess methanol from m_{eo} = 6:1 to m_{eo} = 12:1 contributes to a higher FAEE yield, even though its prominence is incomparable to the effect of m_c. Excess alcohol in the reaction system triggers intensive contact between reactants and catalyst, hence, accelerating the reaction rate. A similar phenomenon has been reported by Klinghoffer et al. (2012) where excess alcohol is beneficial in increasing the yield of FAEE only to a certain degree and reaches a plateau afterward [39].

3.3 Process Optimization

To determine the optimum operating condition, RSM combined with MLFD is statistically employed by simultaneously integrating three critical parameters (m_c, t, m_{eo}). Table 3 presents the relation between the responses and their corresponding input variables. Using the least square analysis, the experimental responses are found to fit into a second-order polynomial model as follows:

$$Y_{FAEE}(FAEE\ yield, wt\%) = 13.23 + 29.67(A) + 15.51(B) + 4.23(C) - 3.358(A^2) - 2.127(B^2) - 0.347(C^2) - 1.095(A)(B) - 0.307(A)(C) - 0.105(B)(C) \quad (5)$$

where Y_{FAEE} is the predicted FAEE yield (wt%) which is presented in Table 3; A, 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 (A^2, B^2, C^2, (A)(B), (A)(C), (B)(C)) reduce the response. The statistical ANOVA results presented in Table 5 shows that all terms, except that of C^2, (A)(C), and (B)(C), are prominent to the reaction (p-value < 0.05), with the significance order of $A > A^2 > B > C >$ (A)(B) > B^2 as shown in Figure 3.

Table 5. The three-way ANOVA study of the tested variables

Term	Coef	SE Coef	T-Value	P-Value
Constant	92.76	1.01	92.25	0.000
A	13.433	0.561	23.95	0.000
B	3.507	0.486	7.22	0.000
C	1.713	0.486	3.53	0.001
A^2	-13.432	0.948	-14.17	0.000
B^2	-2.127	0.841	-2.53	0.016
C^2	-0.347	0.841	-0.41	0.683
(A)(B)	-2.190	0.687	-3.19	0.003
(A)(C)	-0.613	0.687	-0.89	0.378
(B)(C)	-0.105	0.595	-0.18	0.861
R-squared (R^2)			0.9607	
Adjusted R-squared (Adj-R^2)			0.9506	
Predicted R-squared (Pred-R^2)			0.9317	

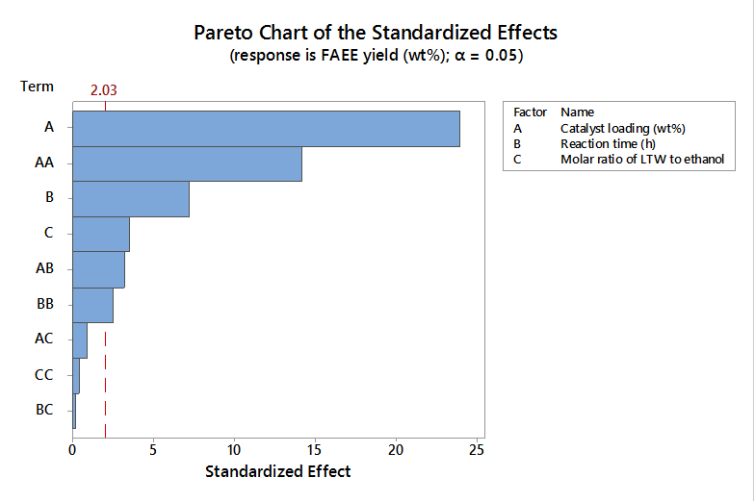

Figure 3. The Pareto chart of the standardized effect showing the significance order of various reaction variables

The goodness-of-fit analysis for the fitted equation (equation 5) is measured by using the R-squared (R^2), where the R^2 value for the model is obtained at 0.9607, pointing that 96.07% of the actual experimental data can be interpreted by equation (5). The values of the adjusted and predicted R^2 are also respectively monitored at 0.9506 and 0.9317, indicating that the predicted and experimental FAEE yields are in a good agreement. Table 2 shows that the average standard error of estimate (SEE) between the two corresponding responses is observed at 1.24% (n = 45), indicating sufficient data accuracy. Figure 2 (b.1) – (b.3) further prove that both experimental and predicted plots share a similar response profile. Therefore, 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 m_c = 3.87 wt%, t = 3.58 h, and m_{eo} = 12:1. The computed response at this condition is obtained at 97.87 wt%, with desirability = 1.0 (Figure 4). To confirm the plausibility of the mathematical model, triplicate experiments are carried out at the optimum condition. The average FAEE yield is found at 98.72 ± 0.36 wt%, with the purity of 98.57 ± 0.41 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 relatively

short reaction time (t = 3.58 h) and low catalyst amount (m_c = 3.87 wt%) is highly beneficial in practice, as these variables directly influence the production efficiency.

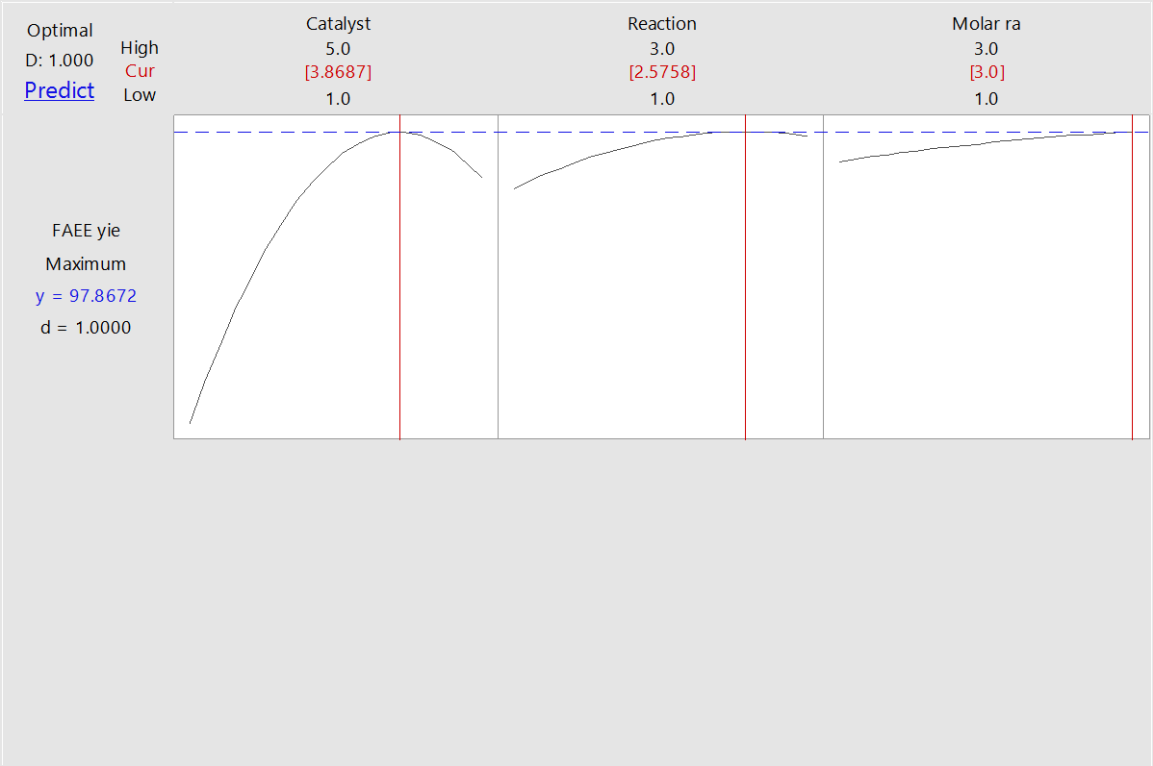

Figure 4. The optimization plot of the reaction variables

The recyclability of CS-based catalysts is presented in Figure 5, where the results show that the regenerated CS-based catalyst can maintain a high yield of FAEE (> 90 wt%) until the fourth run, before significantly decline to 89.35 wt% in the fifth cycle. The FAEE yields for the first four cycles are 98.72 wt%, 98.22 wt%, 96.57 wt%, 95.97 wt%, with the respective purity of 98.57 wt%, 98.89 wt%, 97.33 wt, 98.19 wt%. The deactivation of CS-based catalyst is probably due to the clogged pores, caused by the deposition of deactivation-induced molecules, e.g., free glycerol, acyl glycerides, and biodiesel. The FFA content may as well deactivate the basic sites of CS-based catalyst through neutralization [5] to form calcium carboxylate.

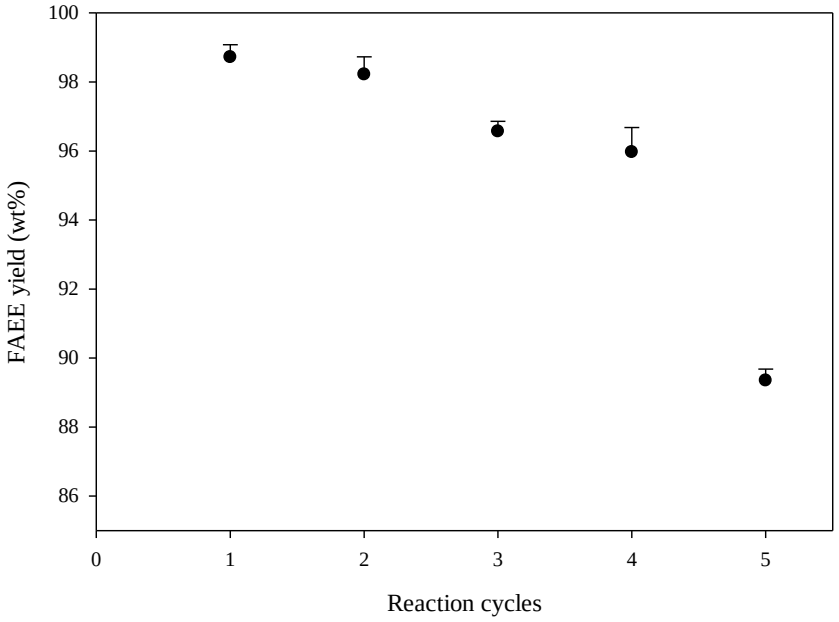

Figure 5. The catalytic activity of recycled CS-based catalyst

3.4 Characteristics of LTW-based biodiesel

Table 6 presents the fuel properties of LTW-based biodiesel generated using CS-based CaO as a catalyst. All measurements indicate that the resulting biodiesel product has equivalent properties with those of the commercial biodiesel. A high flash point shows that the product can be treated, stored, and transported safely. Its calorific value, 44.671 MJ/kg, is also within the range required in the petroleum diesel fuel (42 – 46 MJ/kg) [40]. The chemical compositional analysis of the LTW-based FAEE using GC-FID shows that there are ten distinguished peaks in the chromatogram: myristic acid ethyl ester (C14:0), myristoleic acid ethyl ester (C14:1), palmitic acid ethyl ester (C16:0), palmitoleic acid ethyl ester (C16:1), heptadecanoic 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). The presence of myristoleic acid ethyl ester (C14:1) in the optimized LTW-based FAEE product might be caused by the degradation of the unsaturated fatty acid with a longer carbon chain into shorter ones during the reaction.

Table 6. The properties of LTW-based biodiesel

Properties	Methods	LTW-based biodiesel	ASTM D6751	Diesel fuel (ASTM D975-08)
Kinematic viscosity (at 40°C), mm^2/s	ASTM D445	2.11	1.9 – 6.0	1D: 1.3 – 2.4 2D: 1.9 – 4.1
Flash point, °C	ASTM D93	167.2	93 min	1D: 38 min 2D: 52 min
Cetane number	ASTM D613	53.4	47 min	46 min
Acid value, mg KOH/g	ASTM D664	0.22	0.50 max	-
Calorific value, MJ/kg	ASTM D240	44.671	-	-

4. CONCLUSIONS

Successful conversion of LTW to biodiesel is achieved using CS-based catalyst, with the highest FAEE yield of 98.72 ± 0.36 wt% (purity of 98.57 ± 0.41 wt%) obtained at the following reaction condition: m_c = 3.87 wt%, t = 3.58 h, and m_{eo} = 12:1. The CS-based catalyst shows good recyclability; the FAEE yield stays above 90 wt% for four reaction cycles. The fuel properties of LTW-based FAEE comply with ASTM D6751 and ASTM D975-08. The valorization of CS and LTW will prominently reduce the waste and meanwhile offers an environmentally benign route to produce high value-added renewable energy.

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EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH

--Manuscript Draft--

Manuscript Number:	JBAB-D-21-00045R1
Article Type:	Research paper
Keywords:	leather tannery waste; crab shell; biodiesel; waste-derived fuel; reusability; optimization study
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Abstract:	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 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% (purity of 98.6 ± 0.4 wt%) using the following operating condition: reaction time t = 3.58 h, catalyst amount mc = 3.87 wt%, and a molar ratio of ethanol to LTW meo = 12:1. The CS-based CaO shows good reusability with FAEE yield staying above 90 wt% for four cycles. The fuel properties of LTW-based biodiesel meet ASTM D6751 and ASTM D975-08 standards, with the ethyl ester ranging from C14 to C20.
Response to Reviewers:	We have addressed the major concerns of the reviewers and revised the manuscript accordingly. The detailed responses have been uploaded along with the revised manuscript.

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May 17, 2021

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On behalf of my co-author, I am writing to submit the revised manuscript for publication consideration in *Biomass & Bioenergy*. The details of the manuscript are as follows:

Title of Manuscript: **EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH**

Authors: Maria Yuliana, Shella Permatasari Santoso (shella_p5@yahoo.com), Felycia Edi Soetaredjo (felyciae@yahoo.com), Suryadi Ismadji (suryadiismadji@yahoo.com), Aning Ayucitra (aayucitra@yahoo.com), Chintya Gunarto (chintya95@yahoo.com), Artik Elisa Angkawijaya (artikelisa@mail.ntust.edu.tw), Yi-Hsu Ju (yhju@mail.ntust.edu.tw), Chi-Thanh Truong (tcthanh@ctu.edu.vn)

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Keywords: *leather tannery waste; crab shell; biodiesel; waste-derived fuel; reusability; optimization study*

Word counts: 5427 words (excluding references)

We greatly appreciate the constructive comments and suggestions given by the editor and reviewers. We have addressed the major concerns of the reviewers and revised the manuscript accordingly. We also know of no conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. Furthermore, we have strictly prepared the manuscript in accordance with the journal and ethical guidelines.

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Thank you for your consideration. I am looking forward to hearing from your positive response.

Sincerely yours,

Maria Yuliana

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Journal: *Biomass and Bioenergy*

Title: **EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH**

Dear Editor,

We appreciate your useful comments and suggestions on our manuscript. We have modified the manuscript accordingly, and detailed corrections are listed below:

Editor

1) There are numerous minor English language errors which detract from the content. These must be corrected. Note that only one revision is permitted and so if this is not addressed in the revision the paper may be rejected.
   Response: The manuscript has been edited by an English-speaking native to improve its grammar and readability.
2) A clear comparison to the current standard/accepted process is needed to show how this catalyst maintains/improves performance
   Response: We have provided a table (Table 6, p.22) to compare this work with the other biodiesel preparation processes, especially ones converted from waste. The authors have also added a brief explanation of the table in p.21 line 357-361.

Reviewer #3

1) I agree with the scope of this manuscript that utilizing waste as a source of catalyst to covert waste feedstock to biofuel; fascinating idea. This is overall well-constructed manuscript with a few revision suggestions
   Response: We appreciate the suggested modifications and have carefully revised the manuscript in view of the constructive reviewer's comments as outlined in detail below.
2) Lines 70-71; 74-77-- Need references
   Response: We have added several references for the two sentences (p.4 line 68-69 and line 72-74).
3) Line 94 -- Cs2O@ noanoparticles? What does "@" mean in here?

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Response: We have revised the name of the catalyst. It should be Cs_2O-loaded Fe_3O_4 nanoparticles, as shown in p.5 line 100.

4) Lines 94-95 -- What is "soak liquor micro bacteria"?
Response: This refers to the silica-immobilized micro bacteria soaked into a mixture of inorganic nutrients (e.g., $MgSO_4$, $FeSO_4$, $CoCl_2$, $MnCl_2$, $CaCl_2$, and $(NH_4)_6Mo_7O_{24}$). The authors have revised the term in p.5 line 100-102.
5) Lines 96-97 -- Authors are presenting CS as a feed stock for catalyst production and LTW as a feed stock for biodiesel production but it doesn't read this way. Please revise.
Response: We have revised the sentence in p.6 line 111-113.

Reviewer #4

1) The manuscript number JBAB-D-21-00045 named "EFFICIENT CONVERSION OF LEATHER 1 TANNING WASTE TO BIODIESEL 2 USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH" reports the potential use of CS-based catalysts to prepare biodiesel with commercial yield and specification from leather tanning waste in one-pot transesterification. The authors are dealing with an innovative approach for converting leather tanning waste into biodiesel. The transesterification of lipid to biodiesel was performed by using CaO (coming from crab shells) catalyst. After carefully reading the manuscript, the reviewer thinks that the information concerning the transesterification process provided in this paper is good. Therefore, the subject is interesting for JBAB. However, to justify its publication, some aspects should be clarified in the revised manuscript
Response: We greatly appreciated the constructive comments given by the reviewer. We have addressed the major concerns of the reviewer with the detailed responses provided below.
2) The specifications of biodiesel are described by at least 16 properties listed in the norm ASTM D6751. Please explain why authors report only 5 properties in Table 6.
Response: We have added several properties in Table 7 (p.24); the selection of the measured properties is based on the significance on the product storage, handling, and performance stability during use.
3) Modelling complex processes and optimizing their performances is a challenging task. This kind of problems can be solved by using some of the

followings empirical approaches based on experimental design methodology (including complete and fractional factorial design, central composite design, Doehlert matrix, among others) and/or artificial neural networks (ANN). Indeed, there are several statistical and mathematical approaches available to solve complex process. Although, the approach discussed in the submitted paper is working reasonably well, a deeper justification of the methodology applied in the manuscript is missing. Indeed, which was the main reason to choose the statistical methodology that they have applied/documented in their manuscript? This should be discussed (and supported with references) in the introduction section.

Response: We have provided the justification of the statistical approach applied in the manuscript in p.6 line 116-123.

Reviewer #5

1) The content of this paper is technically accurate and sound.
   Response: The authors appreciate the reviewer's comments. They are especially encouraging for the authors.
2) The presence of mistakes in some punctuation marks in text.
   Response: We have corrected the typing mistakes throughout the manuscript.
3) The list of abbreviations must be present before the introduction section, as some abbreviations in the text need to know.
   Response: We have added the abbreviation list as the footnote of the introductory section (p.3).

Reviewer #6

1) Abbreviations should be in the alphabetical order.
   Response: We have sorted the abbreviations in the alphabetical order (p.3).
2) Where is the equation (1)? The text should be written again.
   Response: We have revised the equation number throughout the manuscript (p.9 line 197-198 and 201-203, p.10 line 224, p.11 line 228-229, p.18 line 313-314, p.19 line 328 and 330).

Reviewer #7

1) This manuscript presents generically good quality research, and addresses important waste management and renewable energy provision problems.

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Response: We are grateful for the reviews provided by the reviewer. The detailed responses to the comments are provided below.

2) There is much higher focus on the catalyst than on the feedstock for biodiesel. The Introduction section should be enriched with more citations to previously published research related to leather tanning waste and animal fat valorization through biodiesel production. Also, citation to higher number of references published in the past 5 years should be done.
   Response: We have enriched the introduction section with the leather tanning waste-related research, and added a number of new references to the text (p.5 line 88-93, line 95-98; p.5-6 line 104-111).
3) The organization of the manuscript must be improved - there are results shown in the Methods section, while they should only be presented (and discussed) in the Results and Discussion section.
   Response: We have moved Table 1 to section 3.2 (p.16 line 278-279), and changed its title to Table 4. Meanwhile, the authors agree to keep the DOE matrix table (Table 2) in the methods section, as this table lists the input reaction parameters which directly correlates to the procedure of the statistical design experiments. We have also revised the numbering of the table in the text accordingly.
4) Concerning biodiesel characterization - further analysis should be done, and the values of important parameters should be included, at least for the biodiesel produced under the optimum conditions.
   Response: We have added the characterization analysis for the LTW-based biodiesel which is obtained under the optimum conditions, shown in Table 7 (p.24).
5) Some lumped lists of references must be rearranged, or some additional details should be added to show why each cited reference is relevant and, therefore, must be cited.
   Response: We have rearranged the lumped lists of references according to the input from the reviewer in p.4 line 62-67 and line 76-77; p.16 line 283-286.
6) On the other hand, there are some references that have been inadequately cited, as they are not related to the statement they should be supporting, so they should be replaced with suitable references.

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Response: We have also added relevant and suitable references for several statements in p.4 line 68-69, and line 72-74, p.5 line 103-104, p.16 line 283-286, p.17 line 291-293, p.18 line 303-306.

7) There are at least two justifications - noted in the commented version of the manuscript - that do not seem adequate in the context of this research.

   (1) *Abstract line 36-38: "The fuel properties of LTW-based biodiesel meet ASTM D6751 and ASTM D975-08 standards, with the ethyl ester ranging from C14 to C20"* → not sure this is true, as many important parameters have not been determined/shown.

   Response: We have added several properties in Table 7 (p.24).

   (2) *P.15 line 301:* But high excess alcohol hinders phase separation, leading to an apparently lower biodiesel yield.

   Response: We have added a statement and reference in p.18 line 303-306.

   (3) *P.18 line 348 – 349: "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%"* → *Maybe it is not only loss of catalyst activity but loss of catalyst itself. When recovering the catalyst, maybe there is some loss. Can you confirm there was no catalyst loss?*

   Response: During the reusability experiments, we adjust the amount of LTW and ethanol according to the regenerated catalyst. Therefore, the authors confirm that there was no catalyst loss during the experimental run, and the yield and purity results stated in the manuscript are valid.

   (4) *P.19 line 362: "the range required in the petroleum diesel (42 – 46 MJ/kg)"* → in fact, there is no specification on the calorific value of biodiesel or diesel. This must be rephrased.

   Response: We have rephrased the sentence in p.23 line 374-375.

   (5) *P.21 line 391: Reference #1* → *add language*

   Response: We have added the English translations for the title of the article in p.25 line 398-402.

8) Figure 1 looks blurred

   Response: We have improved the imaging quality of Figure 1 (p.14)

9) Number of significant digits must be checked along the whole document - it must not always be 2.

   Response: We have revised the number of significant digits for all values presented in the manuscript.

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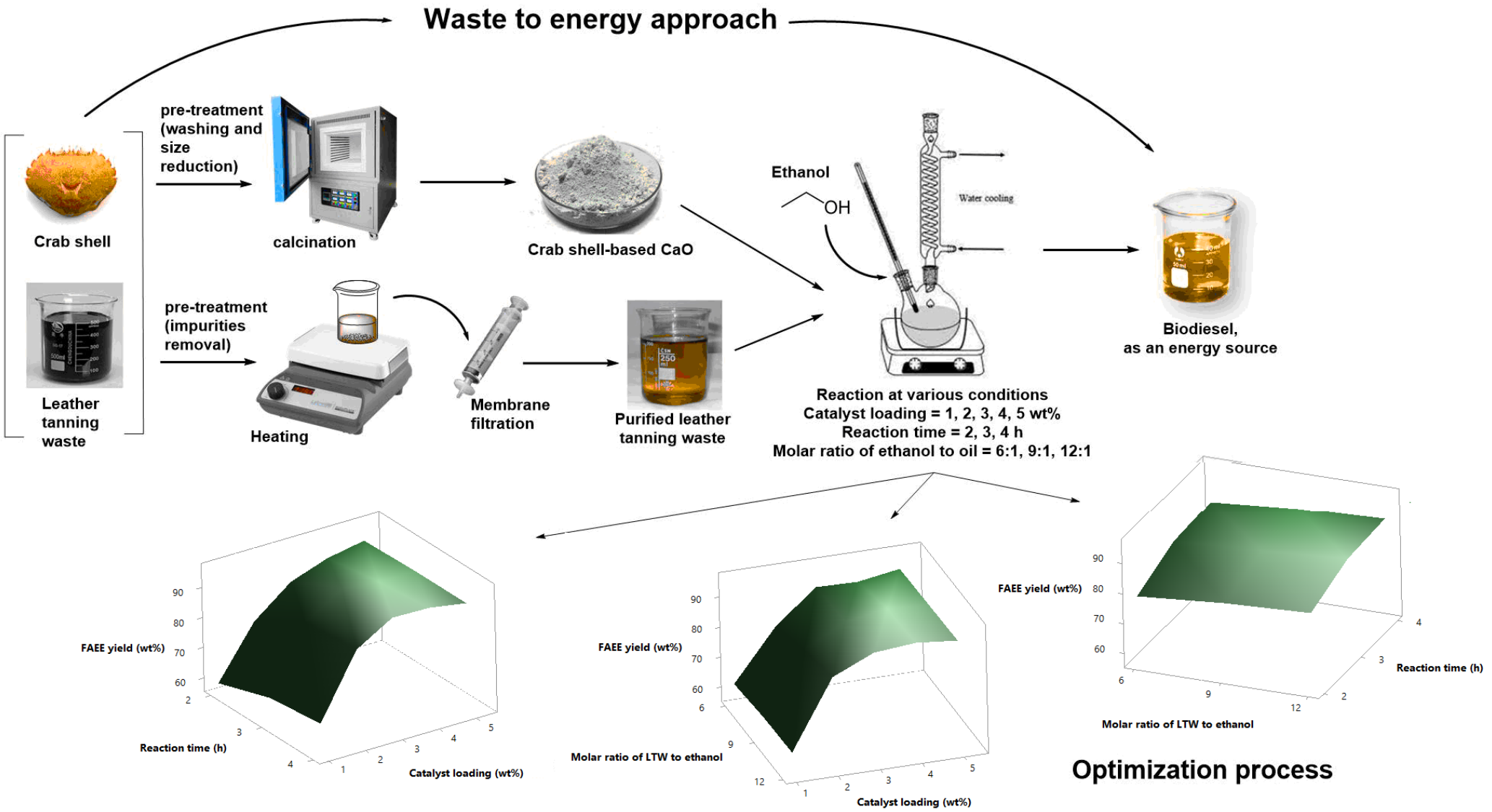
10) Authors used the word "recyclability" concerning catalyst "reusability" - the crab shell was recycled to a new catalyst, that in turn was reused 5 times (in the first 4 times there was no significant activity loss) - this concept must be amended.
Response: We have revised the term of "recyclability" to "reusability" in the manuscript text.
11) Some typos (spaces missing) and some citations to references must be improved (no need to add date after the Author name)
Response: We have revised the citations following the reviewer's suggestions (p.9 line 193-194, p.13 line 242, p.15 line 249-250 and 264, p.16 line 286). The authors have also corrected the typos throughout the manuscript.
12) Must add a space between the numerical value and its units (exception is for %).
Response: We have added a space between all numerical values in the manuscript and their units.
13) Maybe Authors can provide a Graphical Abstract to make this manuscript more appealing.
Response: We have added the graphical abstract to improve the understanding of the readers on this manuscript.
14) I believe the Highlights should be improved - including acronyms without previous definition does not allow to clearly show the relevance of the achievements.
Response: We have revised several points of highlights to improve their relevance to the manuscript, and removed the acronyms as well.

The manuscript has been resubmitted to your journal. We look forward to your positive response.

Sincerely yours,

Maria Yuliana

Graphical Abstract



- The tannery and aquaculture wastes are successfully utilized to produce biodiesel
- The highest biodiesel yield of 98.7 wt% is achieved from this waste-to-energy act
- The optimum operating condition: t = 3.58 h, m_c = 3.87 wt%, and m_{eo} = 12:1
- The crab shell-based CaO has good reusability up to the fourth run (yield > 90 wt%)
- The properties of the resulting biodiesel are following the standard of ASTM D6751

EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH

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ABSTRACT

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 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% (purity of 98.6 ± 0.4 wt%) using the following operating condition: reaction time t = 3.58 h, catalyst amount m_c = 3.87 wt%, and a molar ratio of ethanol to LTW m_{eo} = 12:1. The CS-based CaO shows good reusability with FAEE yield staying above 90 wt% for four cycles. The fuel properties of LTW-based biodiesel meet ASTM D6751 and ASTM D975-08 standards, with the ethyl ester ranging from C14 to C20.

Keywords: leather tannery waste; crab shell; biodiesel; waste-derived fuel; reusability; optimization study

1. INTRODUCTION[1]

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 transesterification 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.

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[1] **Abbreviation**

ANOVA	Analysis of variance
CaO	Calcium oxide
CS	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
MLFD	Multilevel factorial design
RSM	Response surface methodology
SEE	Standard error of estimate
TGA	Thermogravimetric analysis

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 be 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 simpler use in the transesterification process, many heterogeneous catalysts 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 investigated [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 conducted 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 utilization 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 focuses 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 utilization 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 (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 substantial amount of crude fat (>60 wt%) [18] that can be converted to biodiesel; which renders it an abundant raw material to prepare biodiesel. A number of valorization approaches have been previously conducted to prepare biodiesel from LTW, namely using supercritical methanol [20], Cs_2O-loaded Fe_3O_4 nanoparticles [21], solid-state fermentation using silica-immobilized micro bacteria soaked in inorganic nutrients (e.g., $MgSO_4$, $FeSO_4$, $CoCl_2$, $MnCl_2$, $CaCl_2$, and $(NH_4)_6Mo_7O_{24}$) [22], and conventional basic catalyst (e.g., potassium methoxide [23], sodium and potassium hydroxide [24,25], and methanolic 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 challenges 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 transesterification. 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 three independent processing variables (catalyst loading m_c, reaction time t, and the molar ratio of ethanol to LTW m_{eo}) on the yield of fatty acid ethyl esters (FAEE) is studied. The optimization approach is conducted using a combination of response surface methodology (RSM) and 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 variables at all levels, and (2) offers more flexibility in assessing these interactions 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 pulverized to a powder and 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, 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 analysis 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 (> 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 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-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. Meanwhile, the textural properties of CS-based CaO, such as its specific surface area and pore volume, were obtained using Micromeritics ASAP 2010 Sorption Analyzer at 77 K. The XRD diffractogram of the catalyst was acquired in 2θ = 15 ° - 90 ° using an X'PERT Panalytical Pro X-Ray diffractometer (Philips-FEI, Netherlands). The wavelength of monochromatic Cu $K\alpha_1$ radiation (λ) is set at 0.154 nm. The voltage and tube current is adjusted at 40 kV and 30 mA, respectively. To measure its thermal stability, six milligrams of CS-based CaO powder were placed in a platinum pan and subjected to a Perkin Elmer TG/DTA Diamond (Perkin Elmer, 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 (velocity 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 AOAC 991.36, ASTM D5555-95, and AOCS Ca 2e-84, respectively. LTW is also further analyzed for its fatty acid (FA) profile using GC-2014 (Shimadzu Ltd., Japan), following the method of ISO 12966. Restek Rtx-65TG (30 m x 0.25 mm ID x 0.10 µm film thickness, Restek, USA) was selected as the separation column to identify the FA profile in LTW.

2.3 Biodiesel preparation using LTW and CS-based CaO

Ethanol as the alcohol source and LTW at m_{eo} = 6:1, 9:1, and 12:1 was added into a three-neck flask, fully installed along with a condenser, magnetic stirrer, and heater. A specified amount of CS-based CaO (m_c = 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 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 glycerol, excess ethanol, and other undesirable by-products. The separated FAEE-rich phase was then subjected to vacuum evaporation to obtain the biodiesel product.

Using the optimized reaction condition obtained in section 2.5, a repetition of transesterification using the same catalyst was performed until the yield of FAEE reached below 90 wt% to measure the reusability of the CS-based CaO. All runs were conducted in triplicates.

2.4.Compositional analysis of LTW-based biodiesel using GC-FID

The FAEEs composition in the LTW-based biodiesel was identified by 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 x 0.25 mm ID x 0.25 µm film thickness, Agilent Technology, CA). Before analysis, 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 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).

$$\text{FAEE Purity } (F_p, \text{wt\%}) = \left(\frac{\sum A_{FAEE} - A_{IS}}{A_{IS}} \times \frac{V_{IS} C_{IS}}{m_{FAEE}} \right) \times 100\% \quad (1)$$

Where $\sum A_{FAEE}$ is the area sum of FAEE peaks, A_{IS} is the area of methyl heptadecanoate peak, V_{IS} is the volume of methyl heptadecanoate solution (ml), C_{IS} 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).

$$\text{FAEE Yield (wt\%)} = \left(\frac{m_{FAEE}}{m_{LTW}} x\ F_p \right) \times 100\% \quad (2)$$

Where m_{FAEE} is the final FAEE mass obtained (g), m_{LTW} is the initial mass of LTW (g) and F_p 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 yield of FAEE as the response. The input variables, namely m_c (wt%), t (h), and m_{eo} (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 m_{eo} are separated into three levels: low (1), middle (2), and high (3), m_c is classified into five levels with an ascending order to accurately observe the influence of the parameter on the yield of FAEE (wt%). Table 1 presents the encoded parameters and their actual values.

Table 1. The encoded reaction parameters and their corresponding values

Variables	Encoded factor	Factor level				
		1	**2**	**3**	**4**	**5**
Catalyst loading (m_c, wt%)	*A*	1	2	3	4	5
		1		**2**		**3**
Reaction time (t, h)	*B*	2		3		4
Molar ratio of ethanol to LTW (m_{eo})	*C*	6:1		9:1		12:1

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 reproducibility and accuracy, the experimental runs were carried out in triplicates and randomized order. Analysis 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 goodness-of-fit analysis on the generated mathematical model is also evaluated using the R-squared value.

The following equation (3) shows the correlation between the predicted response (FAEE yield, wt%) and the input variables, where Y_{FAEE} is the predicted FAEE yield (wt%); k_0, k_i, k_{ii}, k_{ij} are the coefficients for the intercept, linear, quadratic, and two-way interactions

of the input variables, respectively; X_i and X_j are the encoded reaction variables (*A*, *B*, *C*). While the value of *i* lies between 1 and 3 for *t* and m_{eo}, it ranges from 1 to 5 for m_c.

$$Y_{FAEE} = k_0 + \sum_{i=1}^{3} k_i X_i + \sum_{i=1}^{3} k_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} k_{ij} X_i X_j \quad (3)$$

Table 2. The DOE matrix based on MLFD

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

[a] 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.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of CS-based CaO

Figure 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 (Figure 1 (a)). The calcination 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 aggregated, resulting in non-uniform particle size. Valverde et al. [32] stated that the presence of carbon in the CS-based CaO will induce the formation of CO_2 during the calcination. This CO_2 gas will then react with the CaO product to produce calcium carbonate, the primary cause of particle aggregation.

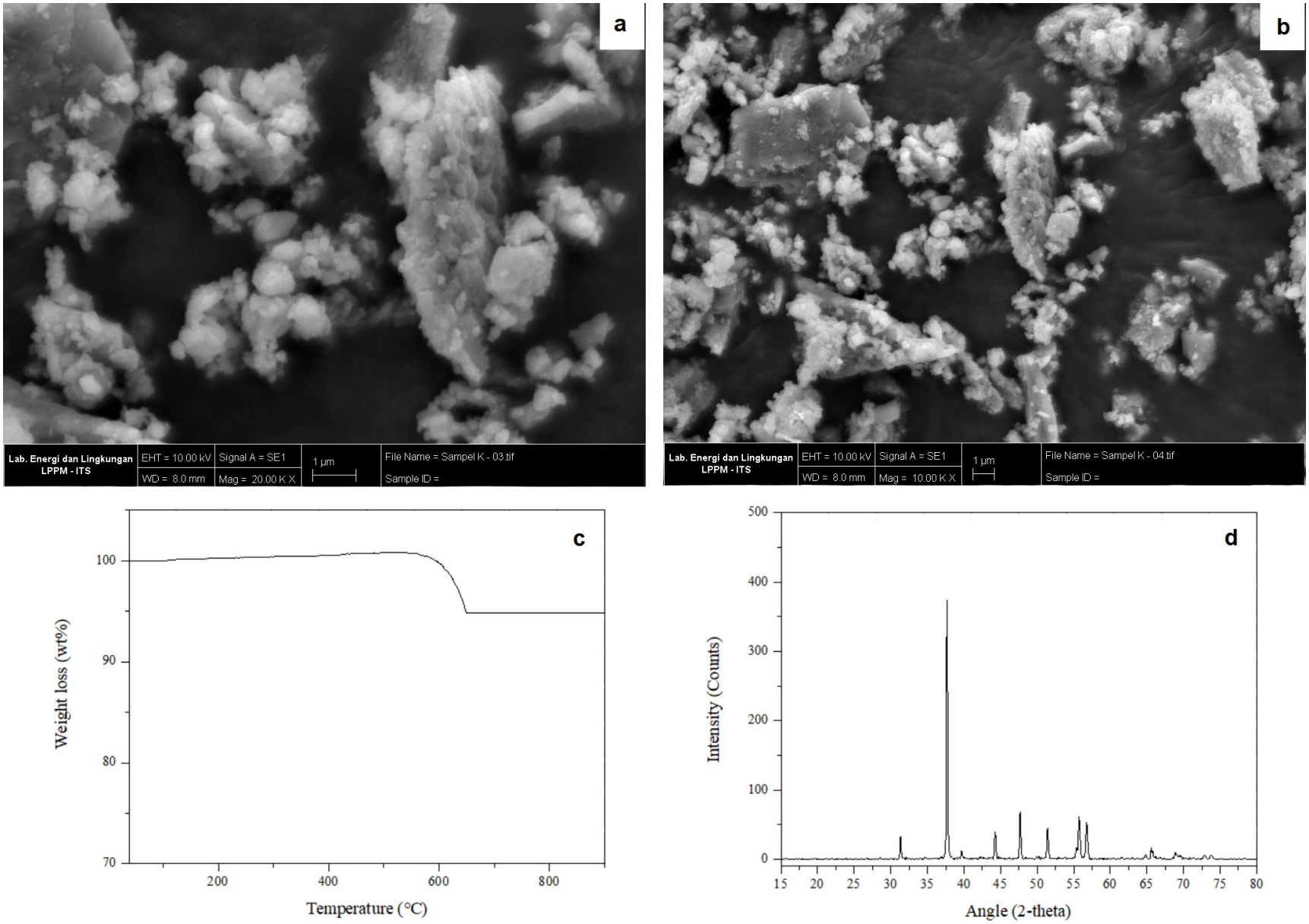

Figure 1. (a) – (b) FESEM images, (c) TGA analysis, (d) XRD pattern of CS-based CaO

The textural properties of CS and CS-based CaO analyzed by nitrogen sorption are provided in Table 3. The CS-based CaO has superior properties 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 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.

Table 3. The textural properties of CS and CS-based CaO

Materials	Specific surface area (S_{BET}, m^2/g)	Pore volume (V_p, cm^3/g)
CS	0.91	0.022
CS-based CaO	12.47	0.081

To demonstrate the thermal stability of the CS-based CaO, a thermogravimetric analysis (TGA) was carried out, and its profile is presented in Figure 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 ($CaCO_3$) to CaO [11]. As the complete decomposition of $CaCO_3$ can be achieved at the temperature of around 700 °C; the selection of 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 (Figure 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 palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1) as the three principal fatty acids constituting LTW.

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 esterification to generate FAEE from the FFA content in LTW, and (2) base-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, therefore efficient conversion from LTW to FAEE can be achieved in a single step.

Table 4. The chemical properties of LTW

Parameters	Result
Moisture, wt%	11.45
FFA, wt%	18.89
Total crude fat, wt%	69.66
Molecular mass, g/mol	798.5
FA composition, wt%	
C14:0	4.30
C16:0	28.70
C16:1	2.60
C17:0	0.70
C18:0	13.40
C18:1	43.50
C18:2	4.90
C18:3	1.80
C20:0	0.10

Figure 2 presents the yield of FAEE obtained at various m_c, t, and m_{eo}. The experimental results indicate that the catalyst amount, specifically the number of active sites offered by CS-based CaO, is proportional to the yield of FAEE (Figure 2 (a.1) - (a.2)). Its value increases with m_c when m_c is within 3 wt%. A stagnant FAEE yield at m_c > 3 wt% is monitored, which is probably contributed by (1) the 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.

Figures 2 (a.1) and (a.3) show a mild increase of the FAEE yield by 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 conversion of acyl glycerides and FFA into FAEE. From another viewpoint, lengthening the duration of the reaction also gives the catalyst enough time to adsorb the reactants and desorb the resulting product [39].

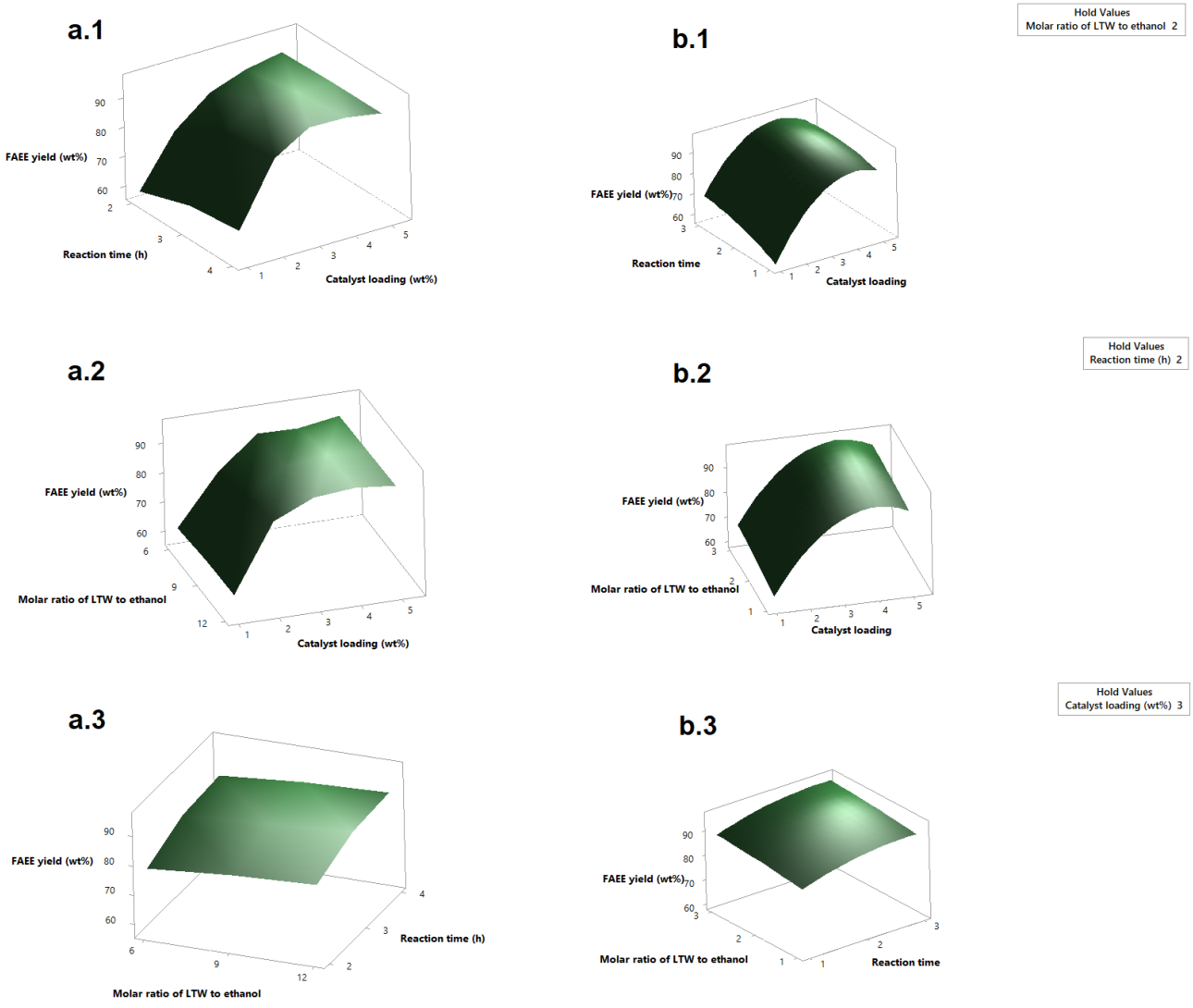

Figure 2. (a) The experimental and (b) the predicted FAEE yield (wt%), based on their interaction between (1) catalyst loading m_c (wt%) and reaction time t (h), (2) catalyst loading m_c (wt%) and molar ratio of ethanol to LTW m_{eo}, (3) reaction time t (h) and the molar ratio of ethanol to LTW m_{eo}

The influence of m_{eo} is depicted in Figure 2 (a.2) – (a.3). As seen from the figure, having excess ethanol from m_{eo} = 6:1 to m_{eo} = 12:1 contributes to a slightly higher FAEE yield, and its prominence is incomparable to the effect of m_c. 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 (m_c, t, m_{eo}). Table 2 presents the relation between the responses and their corresponding input variables. Using the least square analysis, the experimental responses are found to fit into a second-order polynomial model as follows:

$$Y_{FAEE}(FAEE\ yield, wt\%) = 13.23 + 29.67(A) + 15.51(B) + 4.23(C) - 3.358(A^2) - 2.127(B^2) - 0.347(C^2) - 1.095(A)(B) - 0.307(A)(C) - 0.105(B)(C) \quad (4)$$

where Y_{FAEE} is the predicted FAEE yield (wt%) which is presented in Table 2; A, 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 (A^2, B^2, C^2, (A)(B), (A)(C), (B)(C)) reduce the response. The statistical ANOVA results presented in Table 5 shows that all terms, except that of C^2, (A)(C), and (B)(C), are prominent to the reaction (p-value < 0.05), with the significance order of $A > A^2 > B > C >$ (A)(B) > B^2 as shown in Figure 3.

Table 5. The three-way ANOVA study of the tested variables

Term	Coef	SE Coef	T-Value	P-Value
Constant	92.76	1.01	92.25	0.000
A	13.433	0.561	23.95	0.000
B	3.507	0.486	7.22	0.000
C	1.713	0.486	3.53	0.001
A^2	-13.432	0.948	-14.17	0.000
B^2	-2.127	0.841	-2.53	0.016
C^2	-0.347	0.841	-0.41	Non-significant
(*A*)(*B*)	-2.190	0.687	-3.19	0.003
(*A*)(*C*)	-0.613	0.687	-0.89	Non-significant
(*B*)(*C*)	-0.105	0.595	-0.18	Non-significant
R-squared (R^2)			0.9607	
Adjusted R-squared (Adj-R^2)			0.9506	
Predicted R-squared (Pred-R^2)			0.9317	

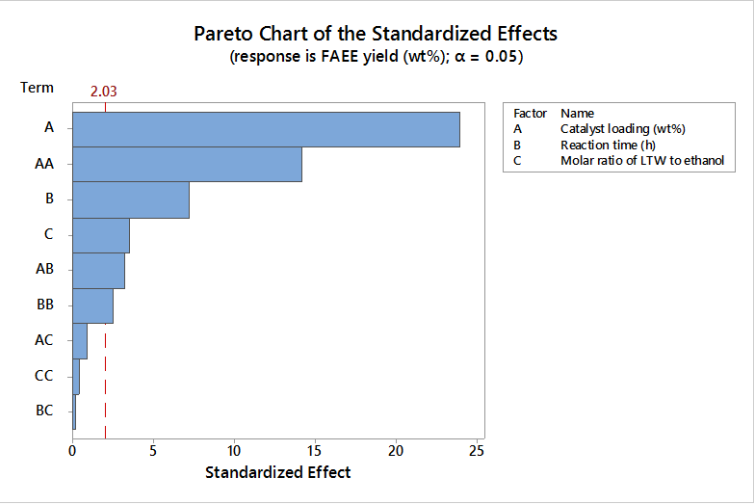

Figure 3. The Pareto chart of the standardized effect showing the significance order of various reaction variables

The goodness-of-fit analysis for the fitted equation (equation (4)) is measured by using the R-squared (R^2), where the R^2 value for the model is 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 R^2 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 standard error of estimate (SEE) between the two corresponding responses is observed at 1.24% (n = 45), indicating sufficient data accuracy. Figure 2 (b.1) – (b.3) further prove that both experimental and predicted plots share a similar response profile. Therefore, 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 m_c = 3.87 wt%, t = 3.58 h, and m_{eo} = 12:1. The computed response at this condition is obtained at 97.9 wt%, with desirability = 1.0 (Figure 4). To confirm the plausibility of the mathematical model, triplicate experiments are carried out at the optimum condition. The average FAEE yield is 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 relatively short reaction time (t = 3.58 h) and low catalyst amount (m_c = 3.87 wt%) is highly beneficial in practice, as these variables directly influence the production efficiency.

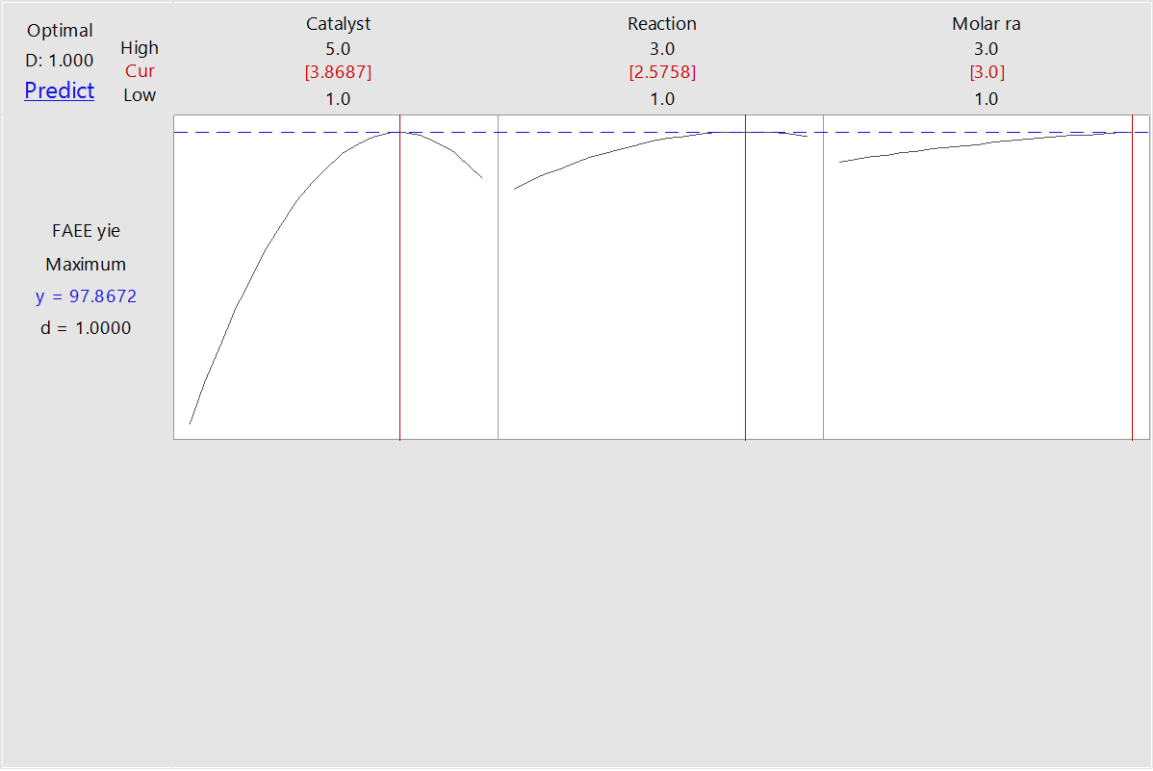

Figure 4. The optimization plot of the reaction variables

The reusability of CS-based CaO is presented in Figure 5, where the results show that the regenerated CS-based CaO can maintain a high yield of FAEE (> 90 wt%) 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 glycerol, 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. A 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 comparable performance with the other preparation processes, indicated by its high product yield (higher than 90 wt%) and reusability number.

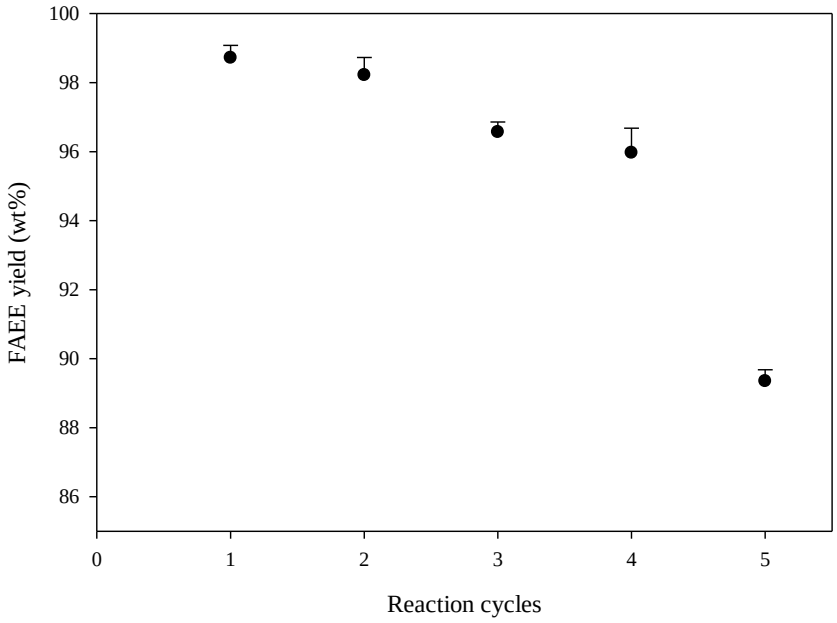

Figure 5. The catalytic activity of reused CS-based CaO

Table 6. The performance of various techniques for the production of biodiesel from waste-originated materials

Lipid material	Catalyst type	Operating condition	Biodiesel yield (wt%)	Catalyst reusability	Reference
Vegetable oil wastewater sludge	N/A *(Subcritical methanol)*	T = 215°C, P = 6.5 MPa, m_{mo}[b] = 5:1, t = 12 h	92.7	-	[41]
Waste cooking oil	Zn-doped waste-egg shells CaO	T = 65°C, m_c = 5 wt%, m_{mo}[b] = 20:1, t = 4 h	96.7	2	[42]
Tallow fats	KOH	T = 60°C, m_c = 0.8 wt%, m_{mo}[b] = 6:1, t = 2 h	90.8	-	[43]
LTW	N/A[a] *(Supercritical ethanol)*	T = 374.6°C, P = *15 MPa*, m_{eo} = 40.02:1, t = 47.4 min	98.9	-	[16]
LTW	CS-based CaO	T = 60°C, m_c = 3.87 wt%, m_{eo} = 12:1, t = 3.58 h	98.7	4	This work

[a] Not available

[b] m_{mo} stands for molar ratio of methanol to oil

3.4 Characteristics of LTW-based biodiesel

Table 7 presents the fuel properties of LTW-based biodiesel generated using CS-based CaO as a catalyst. The measurements indicate that the properties of the resulting biodiesel product are 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 acid ethyl ester (C14:0), myristoleic acid ethyl ester (C14:1), palmitic acid ethyl ester (C16:0), palmitoleic acid ethyl ester (C16:1), heptadecanoic 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).

Table 7. The properties of LTW-based biodiesel

Properties	Methods	LTW-based biodiesel	ASTM D6751	Diesel fuel (ASTM D975-08)
Kinematic viscosity (at 40°C), mm^2/s	ASTM D445	2.1	1.9 – 6.0	1D: 1.3 – 2.4 2D: 1.9 – 4.1
Density (at 15°C, kg/m^3)	ASTM D1298	865	-	-
Flash point, °C	ASTM D93	167	93 min	1D: 38 min 2D: 52 min
Cloud point	ASTM D2500	10.2	-	-
Cetane number	ASTM D613	53	47 min	46 min
Water and sediment, vol%	ASTM D2709	0.01	0.05 max	0.05 max
Acid value, mg KOH/g	ASTM D664	0.22	0.50 max	-
Iodine value, g I_2/100 g	AOCS Cd 1-25	52.9	-	-
Ester content, wt%	EN 14103	98.7	-	-
Linolenic acid ethyl ester content, wt%	EN 14103	1.2	-	-
Polyunsaturated ethyl ester content, wt%	EN 15779	6.1	-	-
Total glycerine, wt%	ASTM D6584	0.16	0.24 max	-
Free glycerine, wt%	ASTM D6584	0.01	0.02 max	-
Sulfur, ppm	ASTM D5453	3.67	15 max (S15) 500 max (S500)	1D and 2D: 15 max (S15) 500 max (S500)
Phosphorus, ppm	ASTM D4951	0.21	10 max	-
Carbon residue, wt%	ASTM D4530	0.002	0.05 max	1D: 0.15 max 2D: 0.35 max
Oxidation stability, h	EN 14112	12.7	3 min	-
Calorific value, MJ/kg	ASTM D240	44.67	-	-

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% (purity of 98.6 ± 0.4 wt%) obtained at the following reaction condition: m_c = 3.87 wt%, t = 3.58 h, and m_{eo} = 12:1. The CS-based CaO shows good reusability; the FAEE yield stays above 90 wt% for four reaction cycles. The fuel properties of LTW-based FAEE comply with 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.

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Ms. Ref. No.: JBAB-D-21-00045R1
Title: EFFICIENT CONVERSION OF LEATHER TANNING WASTE TO BIODIESEL USING CRAB SHELL-BASED CATALYST: WASTE-TO-ENERGY APPROACH
Biomass and Bioenergy

Dear Dr. Maria Yuliana,

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