Utilization of waste capiz shell – Based catalyst for the conversion of leather tanning waste into biodiesel

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ABSTRACT

Rapid urbanization and technological advancement have led to worrisome challenges associated with increasing waste production, and its management is overly burdensome. Indonesia annually produces 100,000 tons of leather tanning waste (LTW) and 2600 tons of waste capiz-shell (WCS). This study proposed a zero-waste approach by utilizing WCS as the catalyst for biodiesel production from LTW. Based on the characterization results, the WCS-based catalyst is proven to possess high porosity and comparable catalytic activity to the other heterogeneous catalysts. The maximum yield of FAEE was 93.4 wt%, obtained at 60 °C, 4 h reaction time, 3 wt% catalyst loading, and ethanol to LTW molar ratio of 6:1. High FAEE yield (> 90 wt%) can be obtained by reusing the WCS-based catalyst until the third reaction cycle. To examine the feasibility of this zero-waste act, a simple viability study was also performed by comparing this process to the conventional basic transesterification process.

1. Introduction

Leather tanning and aquaculture industries are known to generate a higher amount of waste than products [1–3]. Approximately 80 wt% of the raw hide is generated as waste in leather processing [1,2], while more than 50 wt% of total production in the aquaculture industries is discharged as solid waste [3]. The financial and environmental costs for waste disposal from these industries can be burdensome and costly. Therefore, establishing a zero-waste act in these two industrial sectors to reduce the environmental impact is necessary through careful planning, recycling, reusing, or composting as many as possible of the waste materials. Reusing and converting waste materials into highly valorized products is one way to conduct this zero-waste act.

The valorization of biological sources to biodiesel has attracted extensive interests as it reduces the global petroleum demand and pollution [4,5]. Various types of feedstock, namely edible oils [6–8], non-edible oils [9,10], algae [11–13], industrial fats and greases [14–16], have been developed to produce high-quality biodiesel using sundry of transesterification routes. The transesterification reaction is generally catalyzed by the presence of acids, bases, and enzymes, which can be added to the reaction system in the form of a homogenous or heterogeneous phase [17]. Currently, industrial-scale biodiesel production uses edible oil as raw material and NaOH or KOH solution in methanol as a homogenous alkali catalyst. However, high expenses of raw material and operation including the cost of homogenous catalyst and separation process become the major drawbacks in the use of biodiesel, particularly from the economic viewpoint [18]. Therefore, the use of leather tanning waste (LTW) as the raw material and waste capiz shell (WCS), one of the aquaculture wastes, as the catalyst source in biodiesel production may result in a declining operational expenditure.

While the homogenous catalyst provides faster reactions and mild processing conditions [19], heterogeneous catalyst offers several advantages over the homogenous ones, due to its reusability, easier

separation, and insensitivity to high contaminants, such as FFA, water and other minor components [20]. Furthermore, the regeneration of heterogeneous catalyst after the transesterification process is easier and produces less toxic wastewater, leading to a more environmentally friendly process [21]. Various heterogeneous catalysts for biodiesel production have been reported in literatures, including immobilized intracellular lipase [22], KOH/bentonite composite [23], sulphated zirconia [24,25], base/acid-supported resin [26,27], zeolites [25,28], metal-organic framework [29] and alkali/acid-impregnated meso-porous silica [30]. The main problem for the utilization of these heterogeneous catalysts is in their environmental and economic values since most of these catalysts are synthetic, expensive, and difficult to prepare in large scale production [20]; which restrain their practical implementation in industrial scale. Aside from the above mentioned heterogeneous catalysts, calcium oxide (CaO) has been widely investigated as a low-cost solid catalyst in biodiesel production due to its abundant availability in nature and simple preparation [31–35]. CaO is also known to possess comparable catalytic activity to several homogenous catalysts [36]. Limestone or seashells are common sources to produce CaO [31,33,34,37].

In Indonesia, the production of capiz-shell reached more than 4000 tons annually. The average weight of its shells is approximately 65 wt% and they are commonly discarded as waste [38]. Based on the data above, it is predicted that there will be a minimum of 2600 tons of WCS is annually produced. WCS contains high calcium content, reaching almost 20 wt% and can be used as an alternative source of CaO [39]. Currently, the utilization of WCS in the food sector has been so far reviewed by Agustini et al. (2011) to develop calcium-rich food based on WCS. Besides its wide studies in the food-related area, Suryaputra et al. (2013) studied the possibility of using WCS as raw material for new heterogeneous catalyst production in the biodiesel preparation using refined palm oil (RPO). The maximum methyl ester yield (93 ± 2.2 wt%) was obtained at 6 h reaction time and 3 wt% catalyst loading, indicating that WCS has potential application as a renewable resource of CaO-based catalyst for biodiesel production [20].

However, despite its high catalytic activity in converting refined oil to biodiesel, there has been no further study on the utilization of WCS as a heterogeneous catalyst source to convert a lipid-rich waste into biodiesel. In this study, LTW was co-used as the raw lipid material to complete the zero-waste act. According to the data provided by the Indonesian Ministry of Industry, around 100,000 tons of LTW is produced annually in Indonesia, with a crude fat content of more than 60 wt% [1,40,41]. One of its valorization efforts has been converting the waste into biodiesel. Several studies have been performed to produce LTW-based biodiesel using the following routes: base-catalyzed transesterification [14,42], solid-catalyzed transesterification using Cs_2O loaded nano-magnetic particle [43], solid-state fermentation using micro bacterium species from soak liquor [44], and catalyst-free supercritical ethanol [41].

As the government plans to achieve sustainable development goals in 2030 which include affordable and clean energy, maintaining climate, and protect the ecosystem, the study on the zero-waste approach by exploiting these two waste materials (WCS and LTW) is an interesting topic to be studied. The focus of this study is to observe the potential use of WCS as a catalyst for biodiesel production from LTW. The catalytic activity of WCS-based CaO was monitored at various operating parameters, namely reaction time, catalyst loading, and the molar ratio of LTW to ethanol. Ethanol was selected as the alcohol source instead of methanol, due to its sustainability since ethanol can be obtained from renewable sources [45,46]. The solubility of ethanol in oil will also increase the reaction rate and is favorable in a reaction system using a heterogeneous catalyst [46]. The recyclability of the WCS-based CaO was studied at the operating condition giving the maximum yield. Moreover, a viability study has been also conducted to compare biodiesel preparation in this study with the conventional one.

2. Materials and methods

2.1. Materials

WCS was collected from a local fish market in Gresik, Indonesia, and repeatedly rinsed to remove dirt and unwanted materials prior to pre-treatment, following the procedure conducted by Suryaputra et al. (2013). The WCS-based catalyst powder obtained after the pre-treatment was then stored in a desiccator for further use. Meanwhile, LTW obtained from a leather tanning factory in Bogor, Indonesia was used as a lipid source for biodiesel preparation. Several pretreatment steps of LTW was performed before use according to the following procedures: LTW was washed three times with deionized water (1:1, w/w) to remove gangue and other unwanted impurities. The water content in LTW was then removed by heating at a constant temperature of 120 °C and subsequently subjected to membrane filtration to obtain the treated LTW.

Absolute ethanol and analytical grade n-hexane were purchased from Sigma-Aldrich and Merck (Germany), respectively. All chemicals used for the analysis were of high purity grade and require no further purification. The fatty acid ethyl esters (FAEEs) composition in the final biodiesel product were identified using an external standard pack (10008188) purchased from Cayman Chemicals (Ann-Arbor, MI, USA), while methyl heptadecanoate was used as an internal standard (IS) in the analysis of FAEE purity. Nitrogen (99.99 %) and helium (99.9 %) gases for the gas chromatography-flame ionization detector (GC-FID) analysis were provided by Aneka Gas Industry Pty. Ltd., Surabaya.

2.2. Characterization of WCS based-CaO and LTW

The characterization of WCS-based catalyst (WCS-based CaO) was conducted using field emission scanning electron microscopy (FESEM), X-Ray powder diffraction (XRD) and thermogravimetric analysis (TGA). WCS-based CaO was analyzed for its morphologies using FESEM JEOL JSM-6500 F (Jeol Ltd., Japan), with an accelerating voltage of 15 kV and 12.4 mm working distance. The XRD pattern of the catalyst was acquired in the range of 15° to 90° (2θ angle) by using an X'PERT Panalytical Pro X-Ray diffractometer (Philips-FEI, Netherlands) with monochromatic Cu $K\alpha_1$ radiation at a wavelength (λ) = 0.154 nm, 40 kV of voltage and 30 mA of tube current. The thermal stability of WCS-based CaO was studied using TG/DTA Diamond instrument (Perkin Elmer, Japan). A 6-mg sample was placed in a platinum pan and heated from 30 °C to 900 °C with a rate of 10 °C/min to monitor the decomposition temperature of the catalyst. To maintain the system O_2-free, nitrogen with a velocity of 20 mL/min was purged into the system throughout the entire process.

The determination of fat and FFA content, as well as the fatty acid composition in LTW as raw material for biodiesel preparation, were performed according to the standard methods of AOAC 991.36, ASTM D5555-95 and ISO 12966, respectively. GC-2014 (Shimadzu Ltd., Japan) equipped with Restek Rtx-65TG (30 m x 0.25 mm ID x 0.10 μm film thickness, Restek, USA) as the capillary column was used to measure the fatty acid composition in LTW. Meanwhile, the molar weight of LTW was measured using the equation below:

$$Molar\ weight\ of\ LTW \left(M_{LTW}, \frac{g}{mol}\right) = 56.1\ x\ 1000\ x\ \frac{3}{(SV - AV)} \quad (1)$$

where SV is the saponification value of LTW ($\frac{m_{KOH}}{m_{oil}}$, mg/g) and AV is the acid value of LTW ($\frac{m_{KOH}}{m_{oil}}$, mg/g) [47–49]. The characteristics of LTW are presented in Table 1.

2.3. The study of catalytic activity of WCS-based CaO in various transesterification conditions

The catalytic activity of WCS-based CaO was determined by

Table 1
The characteristics of LTW as the raw material for biodiesel production.

Parameters	Result
Water content, wt%	13.48
FFA, wt%	14.20
Crude fat, wt%	65.82
Molecular weight (g/mol)	878.5
Fatty acid profile, wt%	
C14:0	2.08
C16:0	30.71
C16:1	4.03
C17:0	0.25
C18:0	16.42
C18:1	44.59
C18:2	5.95
C18:3	1.65
C20:0	0.27

conducting the catalytic transesterification of LTW to FAEE at various operating conditions. Three investigated parameters include the reaction time (h), catalyst loading (wt%), and the molar ratio of ethanol to LTW. The range of variation of the parameters was selected based on the study conducted by Suryaputra et al. (2013) and their relevance to the industrial feasibility, both in processing and economic viewpoint [20]. The procedure was carried out as follows: Ethanol and LTW at two molar ratios (6:1 and 12:1) were introduced to a three-neck round bottom flask equipped with a reflux condenser, mechanical stirrer, and heating mantle. A certain amount of WCS-based CaO (1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt% of LTW) was added to the system. The mixture was subsequently heated at 60 °C with continuous stirring at 700 rpm for specified reaction time (2, 3, 4 h). After the reaction completed, the WCS-based CaO was recovered by centrifugation and re-calcined at 900 °C for 2 h, while the filtrate was allowed to settle in the separatory funnel overnight to obtain two layers. The FAEE-rich phase (top layer) was then separated from the bottom layer consisted of glycerol, excess methanol, and other by-products, before being subjected to vacuum evaporation for the excess methanol removal to obtain the final biodiesel product.

The analysis of FAEE purity and composition was carried out using GC-2014 (Shimadzu, Japan), completely equipped with a split/splitless injector and a flame ionization detector (FID). The separation was performed using the narrow bore DB-WAX nonpolar capillary column (30 m x0.25 mm ID x0.25 μm film thickness, Agilent Technology, CA). The column temperature was initially set at 50 °C and maintained isothermal for 15 min, before subsequently ramped to 220 °C at the rate of 4 °C/min. The column temperature was then held constant for another 15 min. The temperature of the injector and detector were adjusted constant at 250 °C and 260 °C, respectively. 100 mg of final biodiesel product was dissolved in 2 mL of internal standard solution (0.01 mg ml^{-1}) and subjected to filtration using polyvinylidene difluoride (PVDF) filter prior analysis. The prepared sample (1 μl) was injected into the GC with a split ratio of 1:50. The velocity of nitrogen (N$_2$, 99.9 %) as the carrier gas was fixed at 30 cm/s at 80 °C. The identification of FAEE composition in the final biodiesel product was conducted by comparing the peaks in chromatogram with the external FAEE standard pack (10008188), while the purity of FAEE was calculated using the following equation:

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

Where $\sum A_{\,FAEE}$ is the sum of the area of FAEE peaks, A_{IS} is the corresponding peak area of IS, V_{IS} is the volume of IS solution (ml), C_{IS} is the concentration of IS solution (g/mL), m is the actual sample weight of the final biodiesel product (g). According to the F_p measured from Eq. (2), the determination of FAEE yield can be performed using Eq. (3):

$$FAEE \; Yield \, (wt\%) \; = \left(\frac{m_{BD}}{m_{LTW}} x \, F_p \right) \times 100\% \qquad (3)$$

Where m_{BD} is the weight of final biodiesel product (g), m_{LTW} is the initial weight of LTW (g) and F_p is the FAEE purity (wt%) obtained from Eq. (2).

2.4. Recyclability study of WCS-based CaO

To measure the catalyst resistance to deactivation, the recyclability of WCS-based CaO was determined by reusing the catalyst for the transesterification process at the condition giving the maximum yield of FAEE. The transesterification product was then analyzed for its purity and yield using GC-FID according to the procedure mentioned in Section 2.4. The repetitive transesterification process was conducted using the same catalyst until the FAEE yield obtained was below 90 wt % with the number of repetitions regarded as the recyclability number of WCS-based CaO. All experiments were carried out in triplicates.

3. Results and discussions

3.1. Characterization of WCS-based CaO

The surface morphologies of natural shell, WCS, and the treated WCS-based CaO were captured by using FESEM, as shown in Fig. 1(a) and (b), respectively. It can be seen from the corresponding figure that the structure of natural WCS is changed significantly from smooth surface and lumpy architecture to a more powdery structure. Fig. 1(b) showed that the CaO catalyst obtained from the calcination treatment of WCS at 900 °C has a honeycomb-like porous and rough surface. The porous structure is probably due to the fact that a large number of bound water in the molecular state is released from the WCS-based CaO during the calcination, creates high porosity in the catalyst [50]. This result is in agreement with the studies conducted by Hu et al. (2011) and Niju et al. (2014) for the treated egg-shells and mussel shells, respectively [50,51]. Some particles seem to be entangled to each other, causing aggregation on the particle and non-uniformity particle size. This phenomenon is likely due to the presence of pure carbon in the WCS, as shown in the EDX pattern (Fig. 1(c)), which was oxidized to carbon dioxide during the calcination and reacted with CaO to form CaCO$_3$ which is the main trigger of the agglomeration [52].

As seen from the BET data which was summarized in Table 2, the specific surface area and pore volume between WCS and WCS-based CaO catalyst also obviously differ each other, which was attributed to the calcination process of the catalyst. WCS-based CaO catalyst possesses 10-folds larger surface area and 5-times higher porosity as compared to the untreated WCS, indicating the occurrence of impurities and bound water removal during the heat-activation treatment which play a vital role in improving the two important parameters related to the porosity of a catalyst. High surface area and pore volume of a solid catalyst have a direct and proportional impact on its catalytic activity [35]. The experimental results showed that the surface area of WCS-based CaO obtained in this study is in the range of the two studies performed by Hu et al. (2011) and Niju et al. (2014), representing that WCS-based CaO has the comparable ability as a catalyst for biodiesel production [50,51].

The WCS-based CaO was further analyzed by XRD and its diffraction pattern is shown in Fig. 1(d). The diffraction pattern of the WCS-based catalyst is in accordance with the characteristics of CaO (JCPDS card NO. 82-1691) and calcite (JCPDS card NO. 29-0306), with CaO as the major component and the remaining calcite after decomposition as the minor phase. The thermal stability of the catalyst was observed from the TGA curve, shown in Fig. 1(e). Only one major weight-loss peak was identified, with a weight loss of around 5% at 571–736 °C, which corresponds to the removal of chemisorbed water [53], decomposition of CaCO$_3$ and its phase transition to CaO [50]. This result is consistent
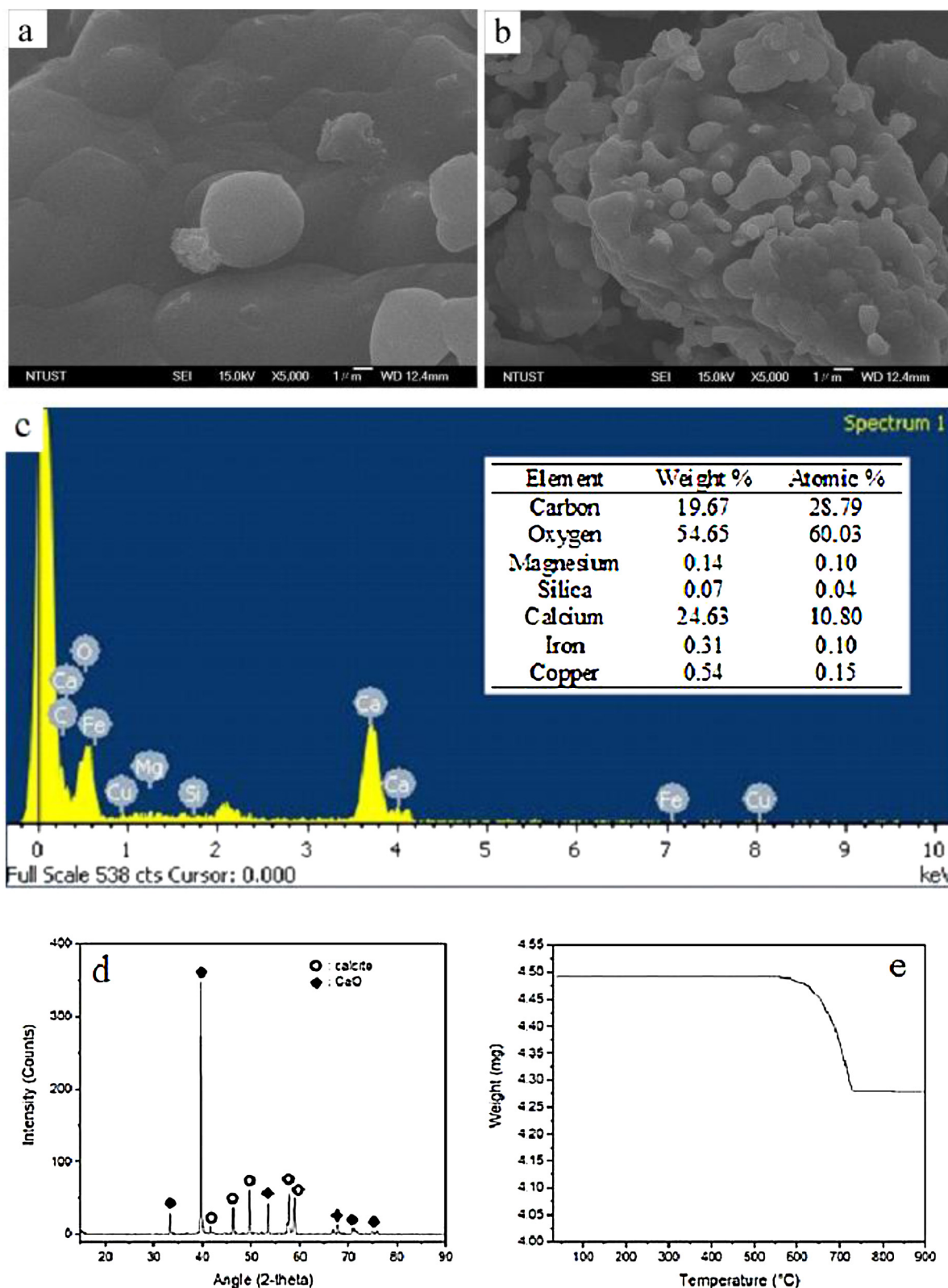
Fig. 1. The characterization results of WCS and WCS-based CaO after calcination at 900 °C for 2 h: (a) SEM image of WCS, (b) SEM image of WCS-based CaO, (c) energy dispersive X-Ray (EDX) spectra of WCS, (d) diffraction pattern of WCS-based CaO, and (e) thermogravimetric analysis (TGA) curve of WCS-based CaO.

with that previously reported by Tang et al. (2013) and Zhu et al. (2011), which reported that the weight remains almost constant after the decomposition of calcite completed in the temperature of around 700 °C [53,54]. Based on the TGA results, it can be concluded that a temperature of 900 °C is suitable for the calcination since it decomposes almost all the calcite and its base derivatives (calcium hydroxide) and forms the porous structure which is desirable for a catalyst. Hu et al. (2011) mentioned that higher activation temperature is also required to escalate the activity of a solid catalyst [50].

Table 2
BET surface area and porosity of WCS and WCS-based CaO.

Materials	S_{BET} ($m^2 g^{-1}$)	V_m ($cm^3 g^{-1}$)
WCS	0.82	0.011
WCS-based CaO	8.49	0.049

3.2. Transesterification of LTW to biodiesel using WCS-based CaO as a catalyst

Table 1 presented the characteristics of LTW as the raw material for biodiesel preparation, and a quite substantial amount of lipid was monitored in LTW, with a value of 80.02 wt%. Among those percentages, the FFA value covers around 14.20 wt% of the total mass of LTW, leaving around 65.82 wt% of crude fat including TG, other acyl glycerides, and minor lipid compounds. The GC chromatogram verified that the major fatty acids constituting LTW are palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1).

Looking at the FFA value, the traditional conversion of LTW to FAEE using homogenous catalyst would require at least two processing steps: (1) esterification to lower the FFA value by converting them into FAEE in the presence of acid catalyst and (2) transesterification to convert the other lipid components into biodiesel using a basic type of catalyst, due to the sensitivity of homogenous catalyst to the presence of impurities, e.g. water and FFA. On the other hand, heterogeneous catalyst shows the insensitive characteristics to the high content of water and FFA in the system [55], making it possible to reach a high yield of conversion using only one-step process.

Fig. 2(a)–(b) summarized the FAEE yield obtained at various reaction time, catalyst loading, and the molar ratio of LTW to ethanol. Based on the experimental results, the maximum FAEE yield (93.4 wt%) with the purity of 97.8 wt% was obtained at the following conditions: 60 °C, 4 h, 3 wt% catalyst loading, and a molar ratio of ethanol to LTW 6:1. It can be seen from the figure that the catalyst loading has an overall positive effect on the FAEE yield. The experimental results demonstrated that the increase of catalyst loading from 1 wt% to 3 wt% greatly escalates the FAEE yield by 1.5 folds in all conditions. WCS-based CaO plays its catalytic function as the alkaline active sites generated from the surface excited the proton from ethanol to form calcium ethylate and hydroxyl ion. The calcium ethylate formed then acts as a nucleophile attacking the carbonyl carbon in the FFA and acyl glycerides chain, leading to the initiation of base-catalyzed reaction to form FAEE and glycerol as a by-product. Once a substantial amount of glycerol was produced, the existing WCS-based CaO in the system reacted with glycerol to produce calcium glyceroxide [56,57] which further reacted with the excess ethanol to form $C_2H_5O-Ca-O(OH)_2C_3H_5$. This component deactivates the catalytic activity of CaO since it possesses lower basic strength. Therefore, further addition of catalyst loading from 3 wt% to 5 wt% gave an unfavorable influence to the yield of FAEE as it declines from ~90 wt% to around 70 wt% [20,57]. Wei et al. (2009) also mentioned that adsorption and desorption of reactants from the catalyst is the actual rate-determining step in the overall reaction [58]. Therefore, adding more catalyst is not favorable to increase the yield of FAEE.

The effect of reaction duration was investigated at three different levels from 2 h to 4 h. Fig. 2 presented that longer duration of reaction promoted a moderate enhancement of the FAEE yield in the constant value of ethanol to LTW molar ratio and catalyst loading. Longer contact between the reactants (alcohol and lipids) and catalyst ensures the conversion of triglycerides and FFA into FAEE. However, its significance is not comparable to the effect of catalyst loading.

Another key parameter in the process is the molar ratio of ethanol to LTW. Theoretically, the stoichiometric molar ratio of ethanol to LTW for biodiesel production is 3:1. However, in practice, the ratio should be higher in order to purposely drive the reaction toward the product side
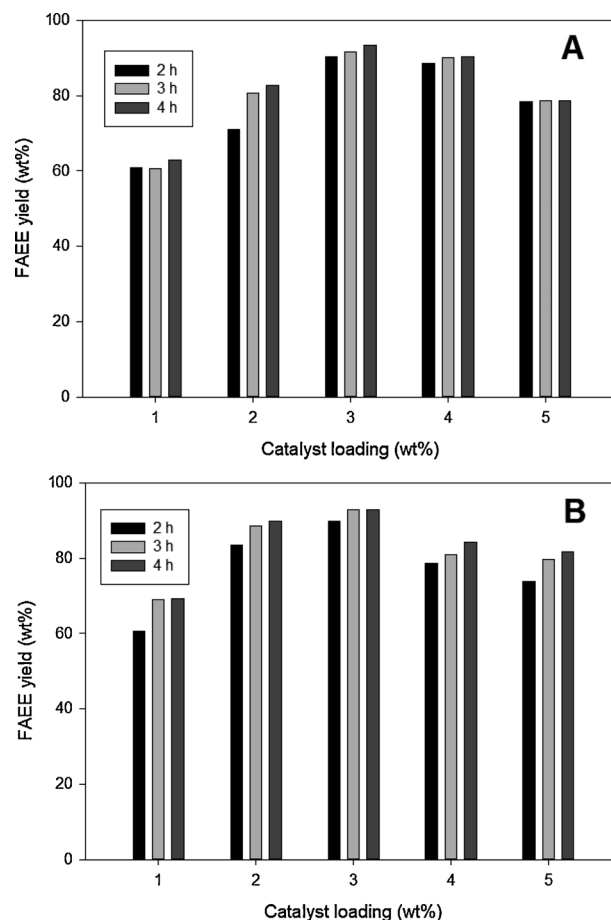

Fig. 2. The FAEE yield (wt%) based on the experimental results with the interaction between catalyst loading (wt%) and time (h) at ethanol to LTW molar ratio of (a) 6:1 and (b) 12:1.

and gain high product yield, since transesterification itself is a reversible reaction [18,59]. As described in Fig. 2(a)–(b), the influence of ethanol to LTW molar ratio gave beneficial results on the FAEE yield at the lower half of catalyst loading (1–2 wt%). Excessive alcohol is desirable to ensure full contact between reactants and catalyst to accelerate the rate of reaction. However, a lower molar ratio of ethanol to LTW (6:1) gave a more favorable effect on the yield of FAEE when the catalyst loading used is 3–5 wt%. It is likely due to the excess of methanol caused the rapid formation of glycerol which will drive the reaction back towards the reactant side, causing lower FAEE yield. Hu et al. (2011) reported similar phenomena in their study that excess alcohol to lipid ratio seems to be favorable to the FAEE yield only to a certain extent and reaches a stagnant line thereafter [50]. As a matter of fact, the higher molar ratio of ethanol to LTW will only escalate the raw material cost and consume larger amounts of energy for the purification and rectification processes [18].

3.3. Recyclability of WCS-based CaO

One of the most important purposes of using heterogeneous catalyst for biodiesel conversion is the recyclability of a catalyst. For the purpose of determining the recyclability of WCS-based CaO, subsequent reaction cycles were performed, with the following operating conditions: reaction temperature of 60 °C, 4 h reaction time, 3 wt% catalyst loading, and the molar ratio of ethanol to LTW 6:1. After each cycle, the solid catalyst was recovered following the method stated in Section 2.4, while fresh reactants were used in every cycle. The experimental results are depicted in Fig. 3. The results indicated that high FAEE yield of
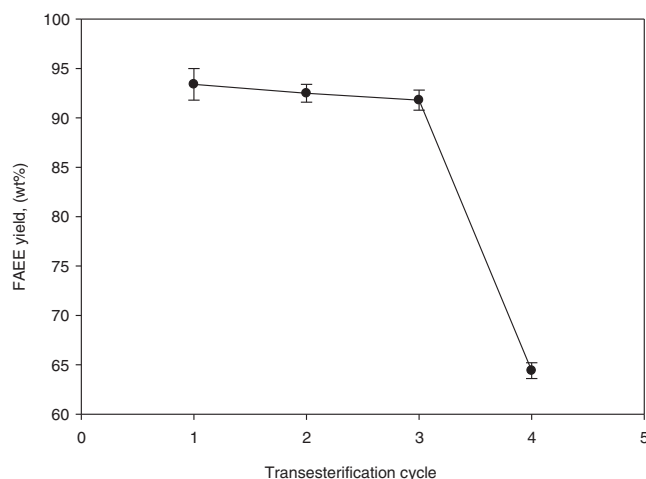
Fig. 3. The recyclability of WCS-based CaO as the catalyst for biodiesel preparation from LTW at the transesterification condition of 60 °C, 4 h, catalyst loading of 3 wt% and ethanol to LTW molar ratio 6:1.

above 90 wt% was achieved until the third run with the purity of FAEE ranges from 97.1 to 97.8 wt%. However, the conversion of FAEE declines rapidly in the fourth run, reaching only 64.4 wt% of FAEE yield. The catalytic deactivation of CaO is generally caused by the direct contact between basic sites on the catalyst surface and the deactivation-induced components [36]. Gaseous CO_2 and water vapor in the ambient air form $CaCO_3$ and $Ca(OH)_2$ when in contact with the oxide catalyst, leading to a decrease in the surface area of the catalyst and subsequently reduce the catalytic activity of CaO [56]. Moreover, as previously mentioned above, the presence of glycerol in the reaction mixture drives the formation of a less active catalyst, C_2H_5O-Ca-O$(OH)_2C_3H_5$. High FFA content in LTW also plays a major role in the deactivation of CaO catalyst because the acidic FFA tends to neutralize basic sites in the surface, resulting in the generation of calcium-carboxylate, a component that is miscible in the lipid phase and induces the formation of ethanol-oil emulsion [36].

The fuel characteristics of LTW-based biodiesel produced using WCS-based CaO as the catalyst and its comparison to the ASTM Standards D6751−19 are reported in Table 3. The measurement results indicated that LTW-based biodiesel possesses a comparable combustion and flow properties to the standard required. High flash point also showed that LTW-based biodiesel can be safely handled, stored, and transported. The cloud point of LTW-based biodiesel was found to be 10.1 °C, which is lower than that required by Indonesian National Standard (SNI 7182:2015, < 18 °C), but still considerably high in countries with severe winter. Several techniques can be industrially applied to improve the cloud point of biodiesel, including cold filtration [60], adsorption using various natural and synthetic sorbent materials [61,62] as well as the addition of cold flow improvers, namely olefin-ester copolymer, poly-methyl acrylate and ethylene-vinyl acetate copolymer [63].

3.4. Simple viability study of the utilization of WCS-based CaO as a catalyst for the biodiesel production from LTW

To highlight the possible utilization of WCS as the catalyst to produce biodiesel from LTW, particularly in Indonesia, a simple viability study was performed. Taking into account the rapid growth of renewable energy consumption and its competitive situation, the non-edible oil including LTW was preferred over the edible ones. Moreover, it is a good addition to use the widely developed heterogeneous catalysts generated from waste-origin.

As mentioned, approximately 2600 tons of WCS [38] and 100,000 tons of LTW [40,41] were annually produced. The market

price of WCS in Indonesia costs around 900 US$ per tons, while in the case of LTW, this type of waste is generally discarded to the environment. Looking at the low market price, the two components possess a high possibility to be used as a replacement for the current edible oils and homogenous catalysts to produce biodiesel. Based on the experimental results, every 100 g of LTW contains lipid fraction of 80.02 g that can be converted into FAEE with the maximum yield of 93.4 wt% (74.74 g) at the following conditions: temperature of 60 °C, reaction time of 4 h, catalyst loading of 3 wt% and molar ratio of ethanol to LTW of 6:1. Therefore, the annual production of biodiesel from LTW is able to reach 74,740 tons and fulfill approximately 1.0 wt% of the total biodiesel demand in Indonesia [64], with the total WCS-based catalyst and ethanol amount of 2,242.2 tons (3 wt% of LTW) and 25,194.7 tons (6:1 ethanol to LTW molar ratio), respectively.

Our viability study compared the proposed technique of using WCS-based CaO as the catalyst to convert LTW into biodiesel (process A) to the conventional base transesterification using a homogenous catalyst to convert RPO into biodiesel (process B) and considered that the processing steps between the two processes are similar, with the major differences in the raw material and its pre-treatment, alcohol, catalyst costs (including the catalyst preparation and regeneration), and the separation steps in biodiesel/by-products purification. The investment costs for process A include (1) the powder mill and furnace for the catalyst preparation section, (2) solid-liquid filter, dryer and furnace for the catalyst regeneration section, and (3) washing vessel, centrifuge and membrane filter for the pre-treatment of LTW, while its yearly production costs are divided into the expenditures of (1) LTW as the raw material, (2) WCS as the catalyst material, (3) ethanol as the alcohol source, (4) energy required to purify LTW, prepare and regenerate the catalyst, and (5) utility, which includes process water for the feedstock pre-treatment. On the other hand, the traditional process B requires (1) mixing vessel and centrifuge for biodiesel purification, and (2) mixing vessel for the neutralization of acidic glycerine (by-product). The annual operational costs of the classic transesterification process B are represented by five major expenses, namely RPO as feedstock, methanol as acyl acceptor (12 wt% of RPO[1]), sodium methylate 30 % solution in methanol (1.67 wt% of RPO[1]) as the homogenous catalyst, hydrochloric acid (1.2 wt% of RPO[1]) and liquid caustic soda (0.12 wt% of RPO[1]) for biodiesel washing and glycerine purification, as well as the energy needed for the separation. The other expenditures are considered negligible since aside from the mentioned operational steps, both of the processes are executed in a similar manner.

Meanwhile, the annual gross revenues for the biodiesel production consists of the sum of credit obtained by selling of main product (biodiesel) and by-products (glycerol and fatty matter). The yield of main and side products in this proposed technique was assumed to be the same as that of the traditional one, leading to a negligible value of the product revenues. The summary of the investment costs of the two processes is presented in Table 4, while the corresponding operating costs are given in Table 5.

As presented in Table 4, having the same capacity of 9.44 tons/h, the investment cost for process A is higher by 2.9 folds as compared to process B, since process A requires more processing equipment. However, the economic analysis of their operating costs (Table 5) showed that the total processing cost of process A takes only 17.4 % of that for process B, even though the energy consumption of process A is more than 4 times higher than its corresponding value for process B. Using waste-originated feedstock and catalyst played the significant role in reducing the operating expenditures. This result is in agreement with the studies reported by Santosa et al. (2019) and Soufi et al. (2017), which stated that the cost of feedstock and supporting chemicals generally pose as the major operating expenditures [18,65]. Therefore, the

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[1] The required composition of supporting materials in process B were obtained from a local biodiesel manufacturer in Indonesia.

Table 3

Fuel Properties of LTW-based biodiesel.

Properties	Methods	Unit	ASTM D6751-19	LTW-based biodiesel
Kinematic viscosity (at 40 °C)	ASTM D445	mm^2 s^{-1}	1.9 – 6.0	4.5
Cetane number	ASTM D613	–	47 min	51.6
Acid value	ASTM D664	mg KOH/g	0.50 max	0.21
Cloud point	ASTM D2500	°C	Location and season dependent	10.1
Flash point	ASTM D93	°C	93 min	171
Heating value	ASTM D240	MJ kg^{-1}	–	44.71

Table 4

The comparison of investment cost between process A and B.

Units	Cost (US$)*	Power (kWh)
Process A		
Pre-treatment of LTW		
Washing vessel	24,590	35
Centrifuge	110,057	33
Membrane filter	70,127	22
Catalyst preparation		
Powder mill	49,946	250
Furnace	51,077	35
Catalyst regeneration		
Solid liquid filter	44,874	38
Dryer	49,583	4
Furnace	51,077	35
Total investment cost	**451,331**	**452**
Process B		
Biodiesel purification		
Washing vessel	24,590	35
Centrifuge	110,057	33
Glycerine purification		
Neutralizing tank	22,375	35
Total investment cost	**157,022**	**103**

* Prices were obtained from the local machinery supplier.

Table 5

Economic analysis of operational costs for process A and B.

Input	Required amounts	Unit price (US$)	Cost (US$)
Process A			
LTW (ton)	100,000	–	–
Water (ton)	300,000	2.99	897,000
WCS (ton)[a]	2,242.2	900	2,017,980
Ethanol (ton)	25,194.7	312	7,860,746
Energy cost (kWh)	3,579,840	0.11	393,782.4
Total operating cost[b]			**11,169,508.4**
Process B[c]			
RPO (ton)	74,740	750	56,055,000
Sodium methylate 30 % solution in methanol (ton)	1,248.16	2500	3,120,395
Methanol (ton)	**8,968.8**	**540**	**4,843,152**
Hydrochloric acid (ton)	896.88	260	233,188.8
Liquid caustic soda (ton)	89.69	470	42,154.3
Energy cost (kWh)	815,760	0.11	89,733.6
Total operating cost[b]			**64,383,623.7**

[a] Assuming that there is no recycled WCS-based CaO used in the process, the required amount of WCS was directly expressed by the total WCS needed to convert the main product.

[b] The total operating costs of process A and B were calculated on the same basis of duration (continuous production for 330 days) and production capacity (74,740 tons of biodiesel).

[c] The required amount of raw/supporting materials in process B and its prices were obtained from a local biodiesel manufacturer in Indonesia.

utilization of LTW and WCS as the materials to produce biodiesel could be significant support for the zero-waste act and the feasible solution to the energy challenge.

4. Conclusions

The WCS-based catalyst was successfully used as a heterogeneous catalyst for biodiesel preparation from LTW. The maximum FAEE yield was 93.4 wt%, obtained at the temperature of 60 °C and 4 h reaction time using catalyst loading of 3 wt% and ethanol to LTW molar ratio of 6:1, with the purity of 97.8 wt%. The study proved that the WCS-based catalyst has comparable activity to the other heterogeneous catalysts. The viability study concluded that the positive use of WCS and LTW in the energy-related sector provided a major benefit for the zero-waste act and is a potential key in solving the energy problems.

CRediT authorship contribution statement

Maria Yuliana: Conceptualization, Methodology, Software, Visualization, Investigation, Writing - original draft. **Shella Permatasari Santoso:** Visualization, Investigation, Writing - original draft. **Felycia Edi Soetaredjo:** Resources, Data curation. **Suryadi Ismadji:** Resources, Writing - review & editing, Supervision. **Artik Elisa Angkawijaya:** Software, Data curation. **Wenny Irawaty:** Software, Validation. **Yi-Hsu Ju:** Writing - review & editing, Supervision. **Phuong Lan Tran-Nguyen:** Writing - review & editing. **Sandy Budi Hartono:** Software, Validation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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