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THE UTILIZATION OF WASTE CAPIZ SHELL (*Amusium Pleuronectes*) - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL: ZERO-WASTE APPROACH AND ITS SIMPLE VIABILITY STUDY

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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 2,600 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 biodiesel was 93.4%, obtained at 60°C, 4 h reaction time, 3% catalyst loading and ethanol to LTW molar ratio of 6:1. High biodiesel yield (> 90%) 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.

Keywords: biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study

1. INTRODUCTION[1]

The financial and environmental costs for waste disposal from typical manufactures can be burdensome and costly. Manufactures generate a huge amount of waste. Therefore, establishing a zero-waste act in the industrial sector to reduce the environmental impact can be done through careful planning, which entails recycling, reusing, or composting as many as possible of the materials used. Reusing and converting waste materials into highly valorized products is one way to conduct this zero-waste act. This research proposed a zero-waste approach and particularly studied the feasibility to utilize waste capiz-shell (WCS) as a heterogeneous catalyst for the conversion of leather tanning waste (LTW) into ethyl esters, or widely known as biodiesel. It will certainly promote a new strategy for waste management and subsequently provide a positive significance in solving both environmental and energy problems. From another point of view, the utilization of these two waste materials will give a positive relation to the recycling of natural mineral resources.

Currently, the major drawback in the use of biodiesel is in its economic factor, which is mostly due to its high expense of raw material and operation including the cost of catalyst

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[1] **Abbreviation**

WCS	Waste capiz-shell
LTW	Leather tanning waste
RPO	Refined palm oil
FAEE	Fatty Acid Ethyl esters
TG	Triacylglyceride(s)
FFA	Free fatty acid
CaO	Calcium oxide

and separation process [1]. Conventional biodiesel production is generally employed in industrial scale, with edible oil used as raw materials and NaOH or KOH solution in methanol as a homogenous alkali catalyst. Therefore, the use of LTW as the raw material and WCS as the catalyst source ensure a declining operational expenditure.

While the homogenous catalyst provides faster reactions and mild processing conditions [2], 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. Furthermore, the regeneration of heterogeneous catalyst after the transesterification process is easier and produces less toxic wastewater, leading to a more environmentally friendly process. Calcium oxide (CaO) is one of the promising heterogeneous catalysts in biodiesel production since it is cheap, available abundantly in nature, renewable and possesses comparable catalytic activity to several homogenous catalysts [3]. In this study, we use WCS as the alternative source of CaO because it contains high calcium content, reaching almost 20% and can be used as an alternative source of calcium oxide [4].

In Indonesia, the production of capiz-shell reached more than 4,000 tons annually. The average weight of its shells is approximately 65% (w/w) and they are commonly discarded as waste. Based on the data above, it is predicted that there will be a minimum of 2,600 tons of WCS is annually produced [5]. Currently, the utilization of this WCS in the food sector has been so far reviewed by Agustini et al. (2011) to develop calcium-rich food based on WCS [4]. Besides its wide studies in food-related area, Suryaputra et al. (2013) also studied the possibility of using WCS as raw material for new heterogeneous catalyst production in the biodiesel production using refined palm oil (RPO), with the maximum yield (93 ± 2.2%) obtained at 6 h reaction time and 3% (w/w) catalyst loading [6].

To complete the zero-waste act, LTW was also co-used as the raw lipid material. 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%. 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 [7,8], solid-catalyzed transesterification using Cs_2O loaded nano-magnetic particle [9], solid-state fermentation using micro bacterium species from soak liquor [10], and catalyst-free supercritical ethanol [11].

As the government plans to achieve sustainable development goals in 2030 which includes affordable and clean energy, maintaining climate and protect the ecosystem, this 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. The recyclability of the catalyst was also studied at the operating condition giving the maximum yield.

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 lipid source for the biodiesel preparation. Several pretreatment steps of LTW was performed before use according to the following procedures: (1) LTW was repeatedly washed with deionized water 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 biodiesel sample 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-6500F (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. The characteristics of LTW are presented in Table 1.

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 conducting the catalytic transesterification of LTW to FAEE at various operating conditions. The procedure was carried out as follows: Ethanol and LTW at various 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. Certain amount of WCS-based CaO (1%, 2%, 3%, 4%, 5% of LTW, w/w) 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 purified biodiesel.

The analysis of biodiesel 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 x 0.25 mm ID x 0.25 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 biodiesel 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 biodiesel 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:

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

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 weight of the biodiesel sample (g). According to the F_p measured from equation (1), the determination of FAEE yield can be performed using equation (2):

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

Where m_{FAEE} is the final biodiesel weight (g), m_{LTW} is the initial weight of LTW (g) and F_p is the FAEE purity obtained from equation (1).

2.5 Recyclability study of WCS-based CaO

To measure the catalyst lifetime, the recyclability of WCS-based CaO was determined by reusing the catalyst for the transesterification process at the condition giving the maximum yield of biodiesel. 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 biodiesel yield obtained was below 90% 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 Figure 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. Figure 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 [12]. 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 [12,13]. 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 (Figure 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 [14].

Figure 1

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 [15]. 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 [12,13].

Table 2

The WCS-based CaO was further analyzed by XRD and its diffraction pattern is shown in Figure 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 Figure 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 [16], decomposition of $CaCO_3$ and its phase transition to CaO [12]. This result is consistent 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 [16,17]. 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 [12].

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%. Among those percentages, the FFA value covers around 14.20% of the total mass of LTW, leaving around 65.82% 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 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 [18], making it possible to reach a high yield of conversion using only one-step process.

Figure 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 biodiesel yield (93.4%) with the purity of 97.8% was obtained at the following conditions: 60°C, 4 h, 3% catalyst loading and 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% to 3% 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 [19,20] which further reacted with the excess ethanol to form $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. This component deactivates the catalytic activity of CaO since it possesses lower basic strength. Therefore, further addition of catalyst loading from 3% to 5% gave an unfavorable influence to the yield of FAEE as it declines from ~90% to around 70%, since excess CaO equals to a higher amount of CaO reacting with glycerol to form $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$ which lowers the activity of CaO as a catalyst and leads to a lower yield of biodiesel [6,20]. 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 [21]. Therefore, adding more catalyst is not favorable to increase the yield of biodiesel.

The effect of reaction duration was investigated at three different levels from 2 h to 4 h. Figure 2 presented that longer duration of reaction promoted a moderate enhancement of the biodiesel 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 ideal 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 and gain high product yield within a short time, since transesterification itself is a reversible reaction [1,22]. As described in Figure 2 (a) – (b), the influence of ethanol to LTW molar ratio gave beneficial results on the biodiesel yield at the lower half of catalyst loading (1 – 2%). 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 biodiesel when the catalyst loading used is 3 – 5%. 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 biodiesel yield. Hu et al. (2011) reported similar phenomena in their study that excess alcohol to lipid ratio seems to be favorable to the biodiesel yield only to a certain extent and reaches a stagnant line thereafter [12]. 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 [1].

Figure 2

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, several subsequent reaction cycles were performed, with the following operating conditions: reaction temperature of 60°C, 4 h reaction time, 3% 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 Figure 3. The results indicated that high biodiesel conversion of above 90% was achieved until the third run, and it declines rapidly in the fourth run, reaching only 64.4% of biodiesel 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 [3]. 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 [19]. Moreover, as previously mentioned above, the presence of glycerol in the reaction mixture drives the formation of a less active catalyst, $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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 methanol-oil emulsion [3].

Figure 3

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.

Table 3

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 above, approximately 2,600 tons of WCS and 100,000 tons of LTW 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 grams of LTW contains lipid fraction of 80.02 grams that can be converted into biodiesel with the maximum yield of 93.4% (74.74 grams) at the following conditions: temperature of 60°C, reaction time of 4 h, catalyst loading of 3% 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 1.5% of the total biodiesel demand in Indonesia, with the total WCS-based catalyst amount of 2,242.2 tons (3% of LTW, w/w), 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 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, 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, and (2) solid-liquid filter, dryer and furnace for the catalyst regeneration section, while its yearly production costs are divided into the expenditures of (1) LTW as the raw material, (2) WCS as the catalyst material, (3) energy required to prepare and regenerate the catalyst. 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 four major expenses, namely RPO as feedstock, sodium methylate (1.67% of RPO, w/w) as homogenous catalyst, hydrochloric acid (1.2% of RPO, w/w) and liquid caustic soda (0.12 % of RPO, w/w) 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.

Table 4

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 1.7 folds as compared to process B, since process A requires more processing equipments. However, the economic analysis of their operating costs (Table 5) showed that the total processing cost of process A takes only 1.65% of that for process B, even though the energy consumption of process A is more than 3 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 [1,23]. Therefore, the 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 biodiesel yield was 93.4%, obtained at the temperature of 60°C and 4 h reaction time using catalyst loading of 3% and ethanol to LTW molar ratio of 6:1, with the purity of 97.8%. 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.

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

Parameters	Result
Water content, % (w/w)	13.48
FFA, % (w/w)	14.20
Crude fat, % (w/w)	65.82
Fatty acid profile, % (w/w)	
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

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

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
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		
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	**246,557**	**362**
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

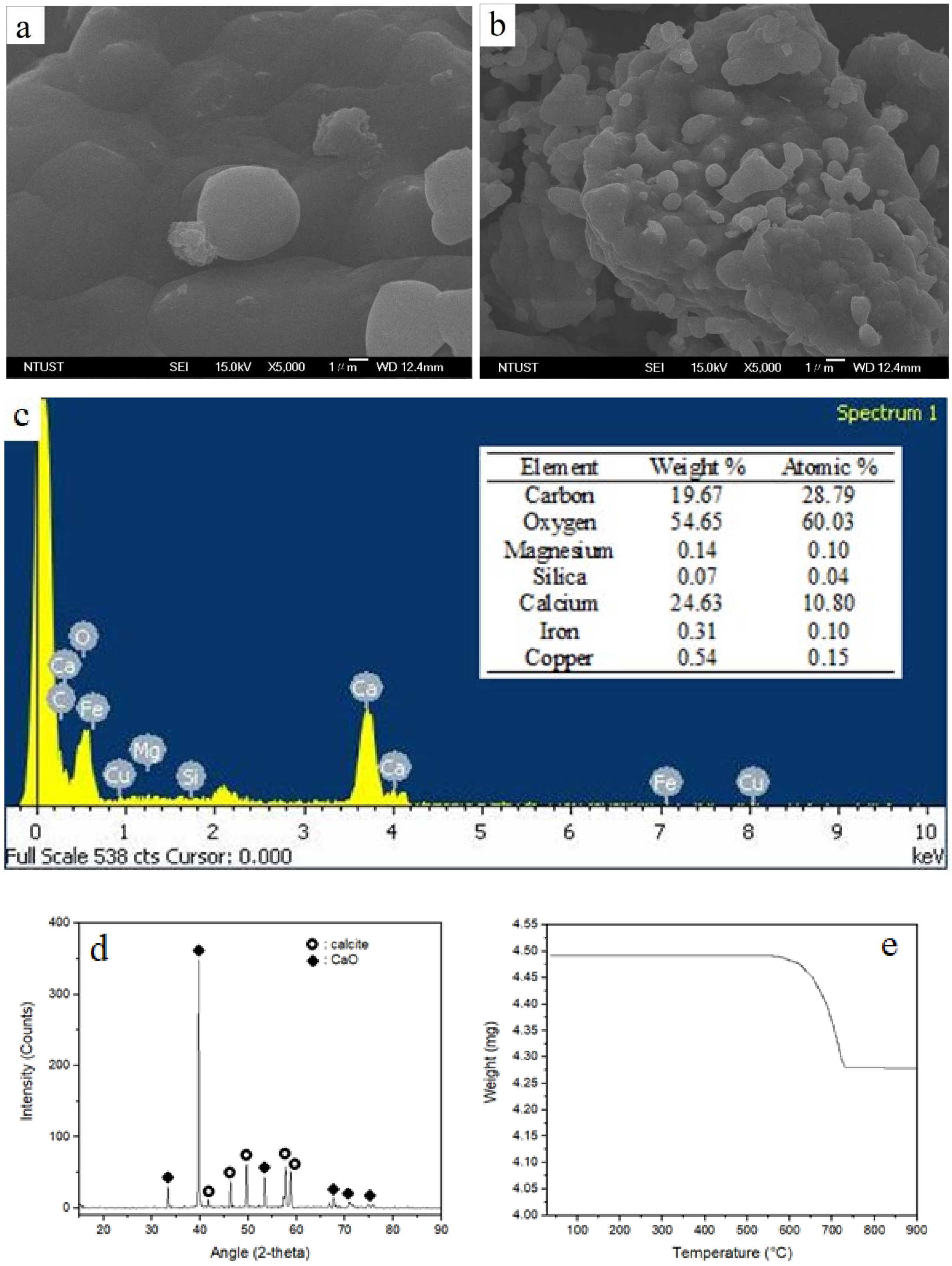
Table 5. Economic analysis of operational costs for process A and B

Input	Required amounts	Unit price (US$)	Cost (US$)
Process A			
LTW (ton)	100,000	-	-
WCS (ton) [1]	747.4	900	672,660
Energy cost (kWh)	2,867,040	0.11	315,374.4
Total operating cost [2]			**988,034.4**
Process B [3]			
RPO (ton)	74,740	750	56,055,000
Sodium methylate (ton)	1,248.16	2,500	3,120,395
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 [2]			**59,540,471.7**

[1] The required amount of WCS was expressed by the total WCS needed to convert the main product divided by the number of recyclability of the catalyst

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

[3] The required amount of supporting materials in process B and its prices were obtained from a local biodiesel manufacturer, PT. Batara Elok Semesta Terpadu



Element	Weight %	Atomic %
Carbon	19.67	28.79
Oxygen	54.65	60.03
Magnesium	0.14	0.10
Silica	0.07	0.04
Calcium	24.63	10.80
Iron	0.31	0.10
Copper	0.54	0.15

Figure 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

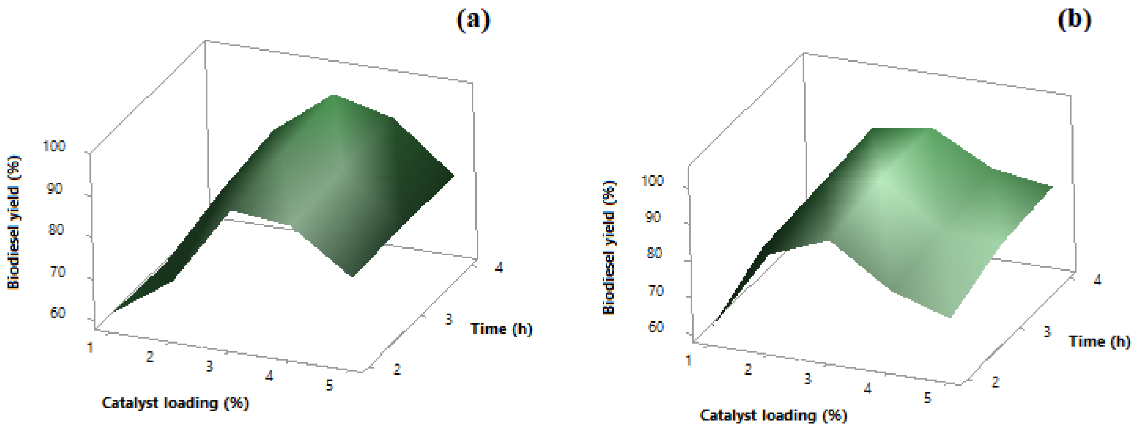


Figure 2. The yield of biodiesel (%) based on the experimental results with the interaction between catalyst loading (%) and time (h) at ethanol to LTW molar ratio of (a) 6:1 and (b) 12:1

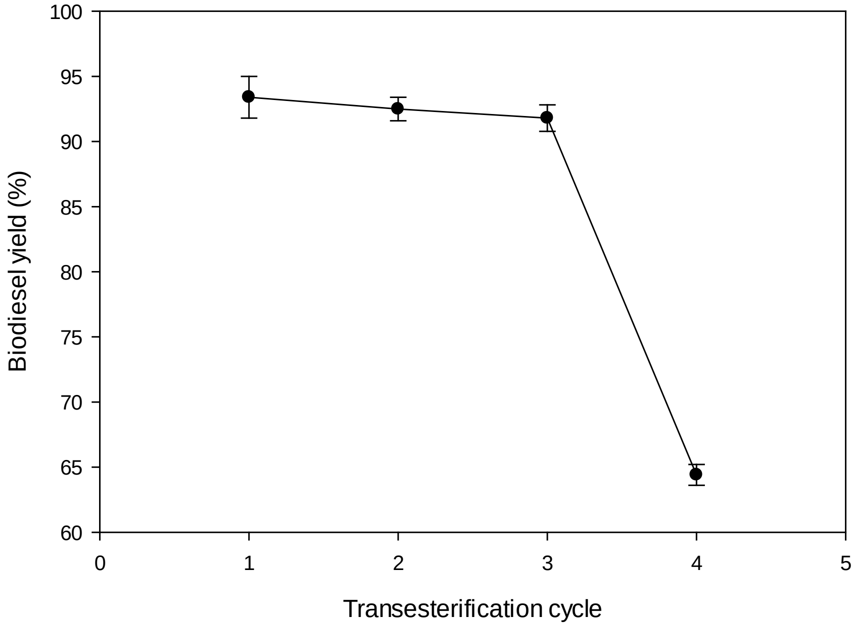


Figure 3. The recyclability of WCS-based CaO as the catalyst for biodiesel preparation from LTW at the transesterification condition of 60°C, 4 h, catalyst loading of 3% and ethanol to LTW molar ratio 6:1

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Article Type: Research Paper

Keywords: biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study

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 2,600 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 biodiesel was 93.4%, obtained at 60°C, 4 h reaction time, 3% catalyst loading and ethanol to LTW molar ratio of 6:1. High biodiesel yield (> 90%) 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.

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Highlights:

- The use of WCS and LTW in energy sector is beneficial for the zero-waste act
- WCS has been successfully used as catalyst for biodiesel production from LTW
- WCS-based catalyst has comparable activity to the other heterogeneous catalyst
- WCS-based catalyst can be reused until the third run with > 90% FAEE yield
- 93.4% FAEE yield with 97.8% purity was obtained in the proposed technique

THE UTILIZATION OF WASTE CAPIZ SHELL (*Amusium Pleuronectes*) - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL: ZERO-WASTE APPROACH AND ITS SIMPLE VIABILITY STUDY

Maria Yuliana[1*], Shella Permatasari Santoso[1,2], Felycia Edi Soetaredjo[1,2], Suryadi Ismadji[1,2], Artik Elisa Angkawijaya[3], Wenny Irawaty[1], Yi-Hsu Ju[2,3,4], Phuong Lan Tran-Nguyen[5], Sandy Budi Hartono[1*]

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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 2,600 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 biodiesel was 93.4%, obtained at 60°C, 4 h reaction time, 3% catalyst loading and ethanol to LTW molar ratio of 6:1. High biodiesel yield (> 90%) 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.

Keywords: biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study

1. INTRODUCTION[1]

The financial and environmental costs for waste disposal from typical manufactures can be burdensome and costly. Manufactures generate a huge amount of waste. Therefore, establishing a zero-waste act in the industrial sector to reduce the environmental impact can be done through careful planning, which entails recycling, reusing, or composting as many as possible of the materials used. Reusing and converting waste materials into highly valorized products is one way to conduct this zero-waste act. ~~This research proposed a zero waste approach and particularly studied the feasibility to utilize waste capiz shell (WCS) as a heterogeneous catalyst for the conversion of leather tanning waste (LTW) into ethyl esters, or widely known as biodiesel. It will certainly promote a new strategy for waste management and subsequently provide a positive significance in solving both environmental and energy problems. From another point of view, the utilization of these two waste materials will give a positive relation to the recycling of natural mineral resources.~~

Currently, the major drawback in the use of biodiesel is in its economic factor, which is mostly due to its high expense of raw material and operation including the cost of catalyst and separation process [1]. Conventional biodiesel production is generally employed in

---

[1] **Abbreviation**

WCS	Waste capiz-shell
LTW	Leather tanning waste
RPO	Refined palm oil
FAEE	Fatty Acid Ethyl esters
TG	Triacylglyceride(s)
FFA	Free fatty acid
CaO	Calcium oxide

industrial scale, with edible oil used as raw materials and NaOH or KOH solution in methanol as a homogenous alkali catalyst. Therefore, the use of LTW as the raw material and WCS as the catalyst source ensure a declining operational expenditure.

While the homogenous catalyst provides faster reactions and mild processing conditions [2], 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. Furthermore, the regeneration of heterogeneous catalyst after the transesterification process is easier and produces less toxic wastewater, leading to a more environmentally friendly process. Calcium oxide (CaO) is one of the promising heterogeneous catalysts in biodiesel production since it is cheap, available abundantly in nature, renewable and possesses comparable catalytic activity to several homogenous catalysts [3]. In this study, we use WCS as the alternative source of CaO because it contains high calcium content, reaching almost 20% and can be used as an alternative source of calcium oxide [4].

In Indonesia, the production of capiz-shell reached more than 4,000 tons annually. The average weight of its shells is approximately 65% (w/w) and they are commonly discarded as waste. Based on the data above, it is predicted that there will be a minimum of 2,600 tons of WCS is annually produced [5]. Currently, the utilization of this WCS in the food sector has been so far reviewed by Agustini et al. (2011) to develop calcium-rich food based on WCS [4]. Besides its wide studies in food-related area, Suryaputra et al. (2013) also studied the possibility of using WCS as raw material for new heterogeneous catalyst production in the biodiesel production using refined palm oil (RPO), with the maximum yield (93 ± 2.2%) obtained at 6 h reaction time and 3% (w/w) catalyst loading [6].

To complete the zero-waste act, LTW was also co-used as the raw lipid material. 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%. 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 [7,8], solid-catalyzed transesterification using Cs_2O loaded nano-magnetic particle [9], solid-state fermentation using micro bacterium species from soak liquor [10], and catalyst-free supercritical ethanol [11].

As the government plans to achieve sustainable development goals in 2030 which includes affordable and clean energy, maintaining climate and protect the ecosystem, this 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. The recyclability of the catalyst was also studied at the operating condition giving the maximum yield.

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 lipid source for the biodiesel preparation. Several pretreatment steps of LTW was performed before use according to the following procedures: ~~(1)~~ LTW was repeatedly washed with deionized water 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 biodiesel sample 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-6500F (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. The characteristics of LTW are presented in Table 1.

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 conducting the catalytic transesterification of LTW to FAEE at various operating conditions. The procedure was carried out as follows: Ethanol and LTW at ~~various~~ 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. Certain amount of WCS-based CaO (1%, 2%, 3%, 4%, 5% of LTW, w/w) 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 purified biodiesel.

The analysis of biodiesel 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 x 0.25 mm ID x 0.25 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 biodiesel 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 biodiesel 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:

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

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 weight of the biodiesel sample (g). According to the F_p measured from equation (1), the determination of FAEE yield can be performed using equation (2):

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

Where m_{FAEE} is the final biodiesel weight (g), m_{LTW} is the initial weight of LTW (g) and F_p is the FAEE purity obtained from equation (1).

2.5 Recyclability study of WCS-based CaO

To measure the catalyst lifetime, the recyclability of WCS-based CaO was determined by reusing the catalyst for the transesterification process at the condition giving the maximum yield of biodiesel. 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 biodiesel yield obtained was below 90% 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 Figure 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. Figure 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 [12]. 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 [12,13]. 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 (Figure 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 [14].

Figure 1

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 [15]. 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 [12,13].

Table 2

The WCS-based CaO was further analyzed by XRD and its diffraction pattern is shown in Figure 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 Figure 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 [16], decomposition of $CaCO_3$ and its phase transition to CaO [12]. This result is consistent 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 [16,17]. 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 [12].

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%. Among those percentages, the FFA value covers around 14.20% of the total mass of LTW, leaving around 65.82% 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 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 [18], making it possible to reach a high yield of conversion using only one-step process.

Figure 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 biodiesel yield (93.4%) with the purity of 97.8% was obtained at the following conditions: 60°C, 4 h, 3% catalyst loading and 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% to 3% 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 [19,20] which further reacted with the excess ethanol to form $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. This component deactivates the catalytic activity of CaO since it possesses lower basic strength. Therefore, further addition of catalyst loading from 3% to 5% gave an unfavorable influence to the yield of FAEE as it declines from ~90% to around 70%, ~~since excess CaO equals to a higher amount of CaO reacting with glycerol to form $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$ which lowers the activity of CaO as a catalyst and leads to a lower yield of biodiesel~~ [6,20]. 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 [21]. Therefore, adding more catalyst is not favorable to increase the yield of biodiesel.

The effect of reaction duration was investigated at three different levels from 2 h to 4 h. Figure 2 presented that longer duration of reaction promoted a moderate enhancement of the biodiesel 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 ~~ideal~~ 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 and gain high product yield ~~within a short time~~, since transesterification itself is a reversible reaction [1,22]. As described in Figure 2 (a) – (b), the influence of ethanol to LTW molar ratio gave beneficial results on the biodiesel yield at the lower half of catalyst loading (1 – 2%). 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 biodiesel when the catalyst loading used is 3 – 5%. 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 biodiesel yield. Hu et al. (2011) reported similar phenomena in their study that excess alcohol to lipid ratio seems to be favorable to the biodiesel yield only to a certain extent and reaches a stagnant line thereafter [12]. 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 [1].

Figure 2

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, ~~several~~ subsequent reaction cycles were performed, with the following operating conditions: reaction temperature of 60°C, 4 h reaction time, 3% 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 Figure 3. The results indicated that high biodiesel conversion of above 90% was achieved until the third run, and it declines rapidly in the fourth run, reaching only 64.4% of biodiesel 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 [3]. 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 [19].

Moreover, as previously mentioned above, the presence of glycerol in the reaction mixture drives the formation of a less active catalyst, $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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 methanol-oil emulsion [3].

Figure 3

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.

Table 3

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 ~~above~~, approximately 2,600 tons of WCS and 100,000 tons of LTW 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 grams of LTW contains lipid fraction of 80.02 grams that can be converted into biodiesel with the maximum yield of 93.4% (74.74 grams) at the following conditions: temperature of 60°C, reaction time of 4 h, catalyst loading of 3% 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 1.5% of the total biodiesel demand in Indonesia, with the total WCS-based catalyst amount of 2,242.2 tons (3% of LTW, w/w), 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 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, 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, and (2) solid-liquid filter, dryer and furnace for the catalyst regeneration section, while its yearly production costs are divided into the expenditures of (1) LTW as the raw material, (2) WCS as the catalyst material, (3) energy required to prepare and regenerate the catalyst. 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 four major expenses, namely RPO as feedstock, sodium methylate (1.67% of RPO, w/w) as homogenous catalyst, hydrochloric acid (1.2% of RPO, w/w) and liquid caustic soda (0.12 % of RPO, w/w) 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.

Table 4

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 1.7 folds as compared to process B, since process A requires more processing equipments. However, the economic analysis of their operating costs (Table 5) showed that the total processing cost of process A takes only 1.65% of that for process B, even though the energy consumption of process A is more than 3 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 [1,23]. Therefore, the 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 biodiesel yield was 93.4%, obtained at the temperature of 60°C and 4 h reaction time using catalyst loading of 3% and ethanol to LTW molar ratio of 6:1, with the purity of 97.8%. 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.

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

Parameters	Result
Water content, % (w/w)	13.48
FFA, % (w/w)	14.20
Crude fat, % (w/w)	65.82
Fatty acid profile, % (w/w)	
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

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

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
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		
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	**246,557**	**362**
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

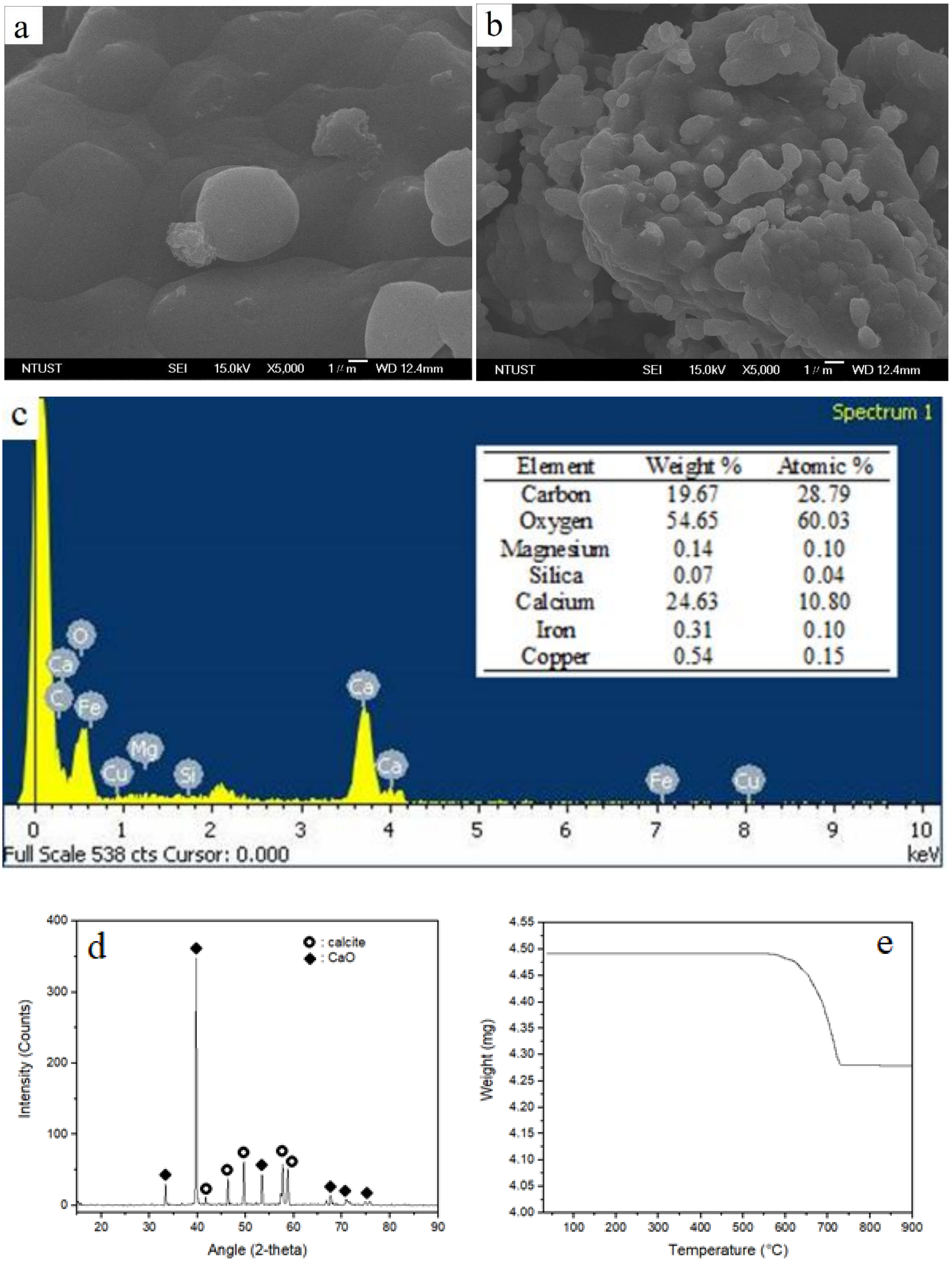
Table 5. Economic analysis of operational costs for process A and B

Input	Required amounts	Unit price (US$)	Cost (US$)
Process A			
LTW (ton)	100,000	-	-
WCS (ton) [1]	747.4	900	672,660
Energy cost (kWh)	2,867,040	0.11	315,374.4
Total operating cost [2]			**988,034.4**
Process B [3]			
RPO (ton)	74,740	750	56,055,000
Sodium methylate (ton)	1,248.16	2,500	3,120,395
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 [2]			**59,540,471.7**

[1] The required amount of WCS was expressed by the total WCS needed to convert the main product divided by the number of recyclability of the catalyst

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

[3] The required amount of supporting materials in process B and its prices were obtained from a local biodiesel manufacturer, PT. Batara Elok Semesta Terpadu



Element	Weight %	Atomic %
Carbon	19.67	28.79
Oxygen	54.65	60.03
Magnesium	0.14	0.10
Silica	0.07	0.04
Calcium	24.63	10.80
Iron	0.31	0.10
Copper	0.54	0.15

Figure 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

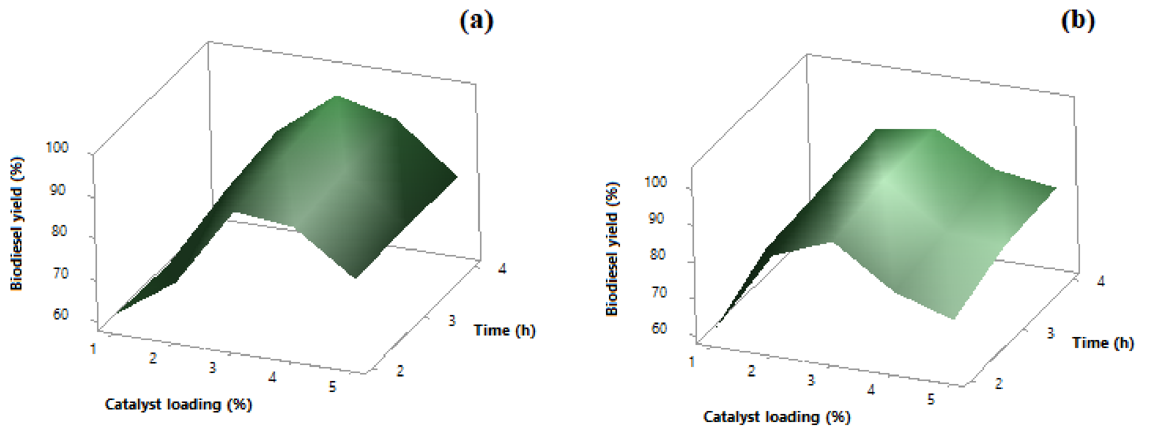


Figure 2. The yield of biodiesel (%) based on the experimental results with the interaction between catalyst loading (%) and time (h) at ethanol to LTW molar ratio of (a) 6:1 and (b) 12:1

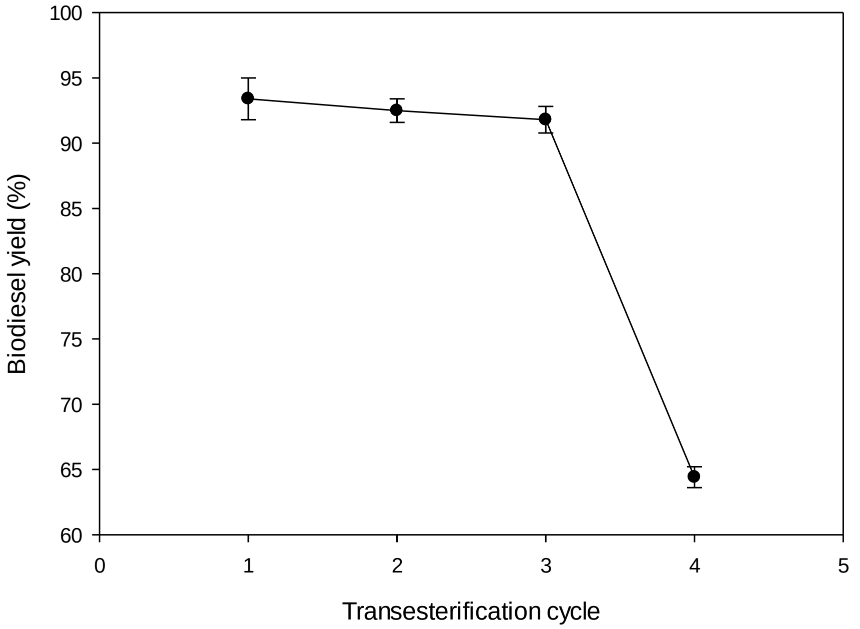


Figure 3. The recyclability of WCS-based CaO as the catalyst for biodiesel preparation from LTW at the transesterification condition of 60°C, 4 h, catalyst loading of 3% and ethanol to LTW molar ratio 6:1

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Your Submisison - JECE-D-20-00671R1

1 message

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Ms. Ref. No.: JECE-D-20-00671R1
Title: THE UTILIZATION OF WASTE CAPIZ SHELL (Amusium Pleuronectes) - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL: ZERO-WASTE APPROACH AND ITS SIMPLE VIABILITY STUDY
Journal of Environmental Chemical Engineering

Dear Dr. Yuliana,

Thank you for submitting the above paper to Journal of Environmental Chemical Engineering. Your manuscript needs major revisions.

The reviewers comments are included below for your attention. Please carefully address the issues raised in the comments. I invite you to submit your revised manuscript.

The due date for submitting your revised manuscript is May 13, 2020

If you are submitting a revised manuscript, please also:

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AND

b) provide a suitable rebuttal to each reviewer comment not addressed

In order to facilitate the check of your manuscript, all the changes made during revision should appear in a different color. That is, the font color should be changed from black to red or blue (directly in the text) rather than using the track changes in Microsoft Word. A response letter for the revised manuscript should be sent to the editor along with your responses to the reviewer comments. These two steps are mandatory for the further review of the manuscript.

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I look forward to receiving your revised manuscript.

Yours sincerely,

Guilherme Luiz Dotto, Ph.D
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Journal of Environmental Chemical Engineering
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Reviewers' comments:

Reviewer #1: The paper "The Utilization of Waste Capiz Shell (Amusium Pleuronectes) - Based Catalyst for the Conversion of Leather Tanning Waste Into Biodiesel: Zero-waste Approch and Its Simple Viability Study" investigate the FAEE production from tannery residue and catalyzed by heterogeneous alkaline compound obtained from capiz shell. The manuscript is well written, structured, the proposal of the research is interesting and addresses an important topic. However, in order to allow the publication of the work, some major issues must be revised, especially in relation to the cost analysis presented by the authors:

1. In my opinion, the title is a little long. Suggestion of a more concise and informative title: "UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL";

2. The authors must highlight in the Introduction Section what is the novelty of the research in relation to what has already been published about the subject. The synthesis of acyl esters (biodiesel) from waste material using heterogeneous alkaline catalysis is a well-established topic. No approach in this regard has been made;

3. Why did the authors choose to work with ethanol? Although it is a "greener" acyl acceptor, the results could be more promising if methanol had been used, once its higher reactivity would reduce considerably the reaction time required to achieve a favorable biodiesel yield. Methanol also has lower costs of production, which would bring more economic advantages to their process.

4. Page 3, line 31. In the second paragraph of the Introduction, the issue "biodiesel" is inserted in the manuscript very abruptly. Firstly, there should be a contextualization the theme to thereby to mention the problems in relation to the costs of the raw material used by the industries;

5. Page 4, line 20. "Calcium oxide (CaO) is one of the promising heterogeneous catalysts in biodiesel production". The use of CaO in the synthesis of biodiesel is not something "promising" since for several years the use of this compound has been addressed in researches on the subject. Please, rewrite this sentence.

6. There are many statements and data mentioned in the manuscript without reference. Please, review this.

7. Specify and standardize throughout the text the metric unit for mass concentration, especially for the parameter "catalyst concentration". I assume that the maximum yield obtained by the authors was for a catalyst concentration of 3 wt% although in the text only "3%" was used;

8. Page 7, line 27 to 39. How was defined the range of variation of the investigated parameters (reaction time, catalyst load and the two EtOH to LTW molar ratios)? Have preliminary tests been performed or chosen according to values usually adopted in similar researches? Please, clarify this in the manuscript;

9. Page 7, line 29. Why did the authors choose to investigate only two EtOH to LTW molar ratios? The excess of alcohol used in the process is a much more important parameter than the reaction time, where obviously an increase in the reaction time leads to an increase in the biodiesel yield. It would be more interesting to use at least four EtOH:LTW molar ratios (6:1; 8:1, 10:1, 12:1, for example) and define a fixed reaction time for all tests (4 h, for example).

10. Page 8, Equation 1 and 2. I am not convinced that the form the authors calculated the biodiesel yield obtained in the tests is coherent. Usually, the FAEE (or FAME) yield for a biodiesel synthesis reaction is calculated using only equation 1, which the authors named "FAEE purity". Equation 2 seems to me to be more a calculation of losses in the process, since by chromatography, the authors demonstrated that 97.8% of the sample is FAEE. Please, explain this methodology adopted.

11. The discussion of the results is well written. However, the presentation of results could be improved. Figure 2 is a fundamental part of the discussion and, in my opinion, the way it is presented restricts the results interpretation. The presentation of these graphs (Figure 2a and b) in the usual way (in two dimensions instead of three) seems to me to be a better option.

12. Page 14, line 10. "[…] resulting in the generation of calcium-carboxylate, a component that is miscible in the lipid phase and induces the formation of methanol-oil emulsion". Was not used in the tests ethanol? Please, review this sentence.

13. Page 14, Table 3. A comment regarding the FAEE cloud point obtained by the authors should be mentioned, since the value presented of 10.1 °C is considerably high. In countries with severe winter, this can be a problem, and a suggestion to overcome this inconvenience could be presented by the authors in order to enrich the discussion of the results. Many alternatives from different companies are currently offered to correct this problem.

14. Page 14, Table 3. The authors used a residue with high acidity (14.2 wt%) as raw material for the process. However, no comments regarding the final acid value for the synthesized FAEE was made. Usually, regulatory standards impose a maximum acid value of 0.5 mg KOH/g. As it is an easy analysis to be performed, I suggest that the authors add to Table 3 the acid value of the biodiesel produced in the tests.

15. The costs evaluation of the process, while being simple, presents an interesting discussion for the manuscript. However, some points observed by me show divergences that must be considered in order to allow the publication of this analysis in the manuscript. Points to be reviewed:

- The authors did not consider for Process A the costs for feedstock purification: washing, water evaporation and filtration of impurities;
- For process A, the reuse of the catalyst for successive cycles was considered. However, after two batches, according presented in Figure 3, data for FAEE yield tend to be below what regulatory standards require to the esters concentration (usually > 97 %);
- From my own experience, I say that the homogeneous alkaline process widely used in industries around the world usually employs 0.5 wt% of sodium methylate (the authors considered 1.67 wt%);
- For process B, it was considered a refined raw material to be converted into biodiesel. However, biodiesel industries use degummed raw materials ("less pure" than refined ones) in the process, often blended with other fatty materials, reducing production costs. Therefore, I believe that the value of the costs related to the raw material of process B are overestimated;
- The authors accomplished the economic analysis considering ethanol as process reagent. However, biodiesel industries (Process B) use methanol as reagent, which has a much lower production cost than ethanol;

As the results and discussion are presented, it is difficult to believe that the heterogeneous process has a total production cost of only 1.65 % in relation to the homogeneous one.

Additional suggestions are found in the attached file "JECE-D-20-00671R1"

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Maria Yuliana <mariayuliana@ukwms.ac.id>

Submission Confirmation for JECE-D-20-00671R2

1 message

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Title: UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL
Journal of Environmental Chemical Engineering
Research Paper

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Manuscript Number: JECE-D-20-00671R2

Title: UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL

Article Type: Research Paper

Keywords: biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study

Corresponding Author: Dr. Maria Yuliana, Ph.D.

Corresponding Author's Institution: Widya Mandala Catholic University Surabaya

First Author: Maria Yuliana, Ph.D.

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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 2,600 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.

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April 29, 2020

Professor Guilherme Luiz Dotto
Editor
Journal of Environmental Chemical Engineering

Dear Professor Dotto,

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

Title of Manuscript: **UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL**

Authors: Maria Yuliana, Shella Permatasari Santoso (shella_p5@yahoo.com), Felycia Edi Soetaredjo (felyciae@yahoo.com), Suryadi Ismadji (suryadiismadji@yahoo.com), Artik Elisa Angkawijaya (artikelisa@mail.ntust.edu.tw), Wenny Irawaty (wenny_i_s@ukwms.ac.id), Yi-Hsu Ju (yhju@mail.ntust.edu.tw), Phuong Lan Tran-Nguyen (tnplan@ctu.edu.vn), Sandy Budi Hartono (sandy@ukwms.ac.id)

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   E-mail: sandy@ukwms.ac.id

Keywords: *biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study*

In this manuscript, we proposed a zero-waste act by utilizing waste capiz-shell (WCS) and leather tanning waste (LTW) to produce bioenergy, particularly biodiesel. WCS-based catalyst has been successfully synthesized and used to convert LTW into biodiesel. This catalyst possesses comparable catalytic activity as the other heterogeneous catalysts. WCS-based catalyst can be reused until the third run with more than 90% biodiesel yield. The viability study concluded that the positive utilization of WCS and LTW in the energy-related sector is beneficial for the zero-waste act and is a potential key in solving both energy and environmental problems. 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 renewable energy and environmental science.

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 we have also acknowledged the significant financial support for this work. Furthermore, we have read, understood and adhered to the Ethical Guidelines, and we have strictly prepared the manuscript in accordance with the journal guidelines.

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

Sincerely yours,

Maria Yuliana

Widya Mandala Catholic University Surabaya
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Website: http://www.ukwms.ac.id

Journal: *Journal of Environmental Chemical Engineering*

Title: **Utilization of waste capiz shell-based catalyst for the conversion of leather tanning waste into biodiesel**

Dear Editor,

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

Reviewer #1

1) The paper "The Utilization of Waste Capiz Shell (Amusium Pleuronectes) - Based Catalyst for the Conversion of Leather Tanning Waste Into Biodiesel: Zero-waste Approch and Its Simple Viability Study" investigate the FAEE production from tannery residue and catalyzed by heterogeneous alkaline compound obtained from capiz shell. The manuscript is well written, structured, the proposal of the research is interesting and addresses an important topic. However, in order to allow the publication of the work, some major issues must be revised, especially in relation to the cost analysis presented by the authors.

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

2) In my opinion, the title is a little long. Suggestion of a more concise and informative title: "UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL".

   Response: We have revised the title to "UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL".

3) The authors must highlight in the Introduction Section what is the novelty of the research in relation to what has already been published about the subject. The synthesis of acyl esters (biodiesel) from waste material using heterogeneous alkaline catalysis is a well-established topic. No approach in this regard has been made

Response: We have rewritten the introductory section and highlighted the novelty of our research.

4) Why did the authors choose to work with ethanol? Although it is a "greener" acyl acceptor, the results could be more promising if methanol had been used, once its higher reactivity would reduce considerably the reaction time required to achieve a favorable biodiesel yield. Methanol also has lower costs of production, which would bring more economic advantages to their process.

   Response: As the reviewer mentioned, ethanol is certainly greener alcohol than methanol, since it can be obtained from renewable sources. It is also known that transesterifications of biodiesel have very different behavior depending on the alcohol used in the system. While with methanol, the system is biphasic, we have a homogenous reaction system by using ethanol, which is able to increase the reaction rate and is favorable in the reaction system using heterogeneous catalysts.

   We have added a statement and relevant articles to briefly explain our purpose in using ethanol in p.6 line 10-17.

5) Page 3, line 31. In the second paragraph of the Introduction, the issue "biodiesel" is inserted in the manuscript very abruptly. Firstly, there should be a contextualization the theme to thereby to mention the problems in relation to the costs of the raw material used by the industries

   Response: We have rewritten the paragraph in p.3 line 24 to p.4 line 15.

6) Page 4, line 20. "Calcium oxide (CaO) is one of the promising heterogeneous catalysts in biodiesel production". The use of CaO in the synthesis of biodiesel is not something "promising" since for several years the use of this compound has been addressed in researches on the subject. Please, rewrite this sentence.

   Response: We have rewritten the sentence in p.4 line 46-51.

7) There are many statements and data mentioned in the manuscript without reference. Please, review this.

   Response: We have added relevant references for the statements and data mentioned in the manuscript.

8) Specify and standardize throughout the text the metric unit for mass concentration, especially for the parameter "catalyst concentration". I assume that the maximum yield obtained by the authors was for a catalyst concentration of 3 wt% although in the text only "3%" was used.

Response: We have standardized the unit for mass concentration throughout the manuscript.

9) Page 7, line 27 to 39. How was defined the range of variation of the investigated parameters (reaction time, catalyst load and the two EtOH to LTW molar ratios)? Have preliminary tests been performed or chosen according to values usually adopted in similar researches? Please, clarify this in the manuscript.

Response: We have added a statement on how we defined the range of variation of the investigated parameters in p.8 line 31-41.

10) Page 7, line 29. Why did the authors choose to investigate only two EtOH to LTW molar ratios? The excess of alcohol used in the process is a much more important parameter than the reaction time, where obviously an increase in the reaction time leads to an increase in the biodiesel yield. It would be more interesting to use at least four EtOH:LTW molar ratios (6:1; 8:1, 10:1, 12:1, for example) and define a fixed reaction time for all tests (4 h, for example)

Response: An increase of FAEE yield was monitored when the molar ratio of ethanol to LTW decreases from 12:1 to 6:1 at 3% (w/w) catalyst loading. Judging from the results, level addition of ethanol to LTW molar ratio between 6:1 and 12:1 would not alter the FAEE yield significantly since the maximum yield obtained at a molar ratio of 6:1 has already reached 93.4 wt%. Meanwhile, level addition lower than 6:1 will encounter its lower limit, which is fixed by the stoichiometric ratio of the transesterification process. Therefore, we chose to investigate only two ethanol to LTW molar ratios.

11) Page 8, Equation 1 and 2. I am not convinced that the form the authors calculated the biodiesel yield obtained in the tests is coherent. Usually, the FAEE (or FAME) yield for a biodiesel synthesis reaction is calculated using only equation 1, which the authors named "FAEE purity". Equation 2 seems to me to be more a calculation of losses in the process, since by chromatography, the authors demonstrated that 97.8% of the sample is FAEE. Please, explain this methodology adopted.

Response: Yield of FAEE (wt%) is defined as the mass of pure FAEE divided by the mass of raw material (LTW). As explained in section 2.3, the final biodiesel product after transesterification was obtained by overnight settling and vacuum evaporation; and is directly measured gravimetrically. The measured mass of the final biodiesel product cannot be regarded as the mass of pure FAEE since it may contain impurities. Therefore, the purity of FAEE (wt%) in the final *biodiesel product was then acquired from gas chromatography analysis and determined using equation (2). The mass of pure FAEE in the final biodiesel product can be calculated by multiplying the results from equation (2) with the mass of final biodiesel product; hence, the yield of FAEE can be determined by dividing the mass of pure FAEE in the final biodiesel product with the mass of raw material (LTW), as expressed in equation (3).*

To avoid misinterpretation, we have revised the term m_{FAEE} *in equation (3) to* m_{BD}*, where* m_{BD} *is the weight of the final biodiesel product in gram (p.9 equation (3) and p.10 line 1).*

12) The discussion of the results is well written. However, the presentation of results could be improved. Figure 2 is a fundamental part of the discussion and, in my opinion, the way it is presented restricts the results interpretation. The presentation of these graphs (Figure 2a and b) in the usual way (in two dimensions instead of three) seems to me to be a better option
Response: We have revised Figure 2 into two-dimensional graphs.
13) Page 14, line 10. "[…] resulting in the generation of calcium-carboxylate, a component that is miscible in the lipid phase and induces the formation of methanol-oil emulsion". Was not used in the tests ethanol? Please, review this sentence
Response: We have corrected the typing error and revised it to ethanol (p.15 line 29).
14) Page 14, Table 3. A comment regarding the FAEE cloud point obtained by the authors should be mentioned, since the value presented of 10.1 °C is considerably high. In countries with severe winter, this can be a problem, and a suggestion to overcome this inconvenience could be presented by the authors in order to enrich the discussion of the results. Many alternatives from different companies are currently offered to correct this problem.
Response: We agree with the reviewer that in countries with severe winter, a cloud point of 10.1°C could be a problem. Therefore, we have added several suggestions to overcome the problem in p.15 line 44-59.
15) Page 14, Table 3. The authors used a residue with high acidity (14.2 wt%) as raw material for the process. However, no comments regarding the final acid value for the synthesized FAEE was made. Usually, regulatory standards impose a

maximum acid value of 0.5 mg KOH/g. As it is an easy analysis to be performed, I suggest that the authors add to Table 3 the acid value of the biodiesel produced in the tests.

Response: The acid value of LTW-based biodiesel was found to be 0.21 mg KOH/g. We have added this number to Table 3 (p.31).

16) The costs evaluation of the process, while being simple, presents an interesting discussion for the manuscript. However, some points observed by me show divergences that must be considered in order to allow the publication of this analysis in the manuscript. Points to be reviewed:

a. The authors did not consider for Process A the costs for feedstock purification: washing, water evaporation and filtration of impurities

Response: We have revised the discussion according to the reviewer's suggestions (in p.17 line 12-15) and added the equipment costs for feedstock purification in Table 4 (p.32). Moreover, we have also considered the cost of process water in the LTW purification step and additional energy requirement, as presented in the discussion section (p.17 line 19-22) and Table 5 (p.33).

b. For process A, the reuse of the catalyst for successive cycles was considered. However, after two batches, according presented in Figure 3, data for FAEE yield tend to be below what regulatory standards require to the esters concentration (usually > 97 %)

Response: According to Figure 3, the FAEE yield for the 1st to the 3rd run was found to be slightly declined from 93.4 wt% to 91.8 wt% at 60°C, 4 h reaction time, 3 wt% catalyst loading and ethanol to LTW molar ratio of 6:1. However, the purity of FAEE still ranges from 97.1-97.8 wt%, higher than that required in the standard. We have added the results of FAEE purity during the recyclability analysis in p.15 line 2-5.

Meanwhile, to maintain the FAEE yield constant in process A, we have also revised the calculation in Table 5 (p.33) where we assume that there is no recycled WCS-based CaO used in the transesterification process.

c. From my own experience, I say that the homogeneous alkaline process widely used in industries around the world usually employs 0.5 wt% of sodium methylate (the authors considered 1.67 wt%)

Response: We agree with the reviewer that the industries usually employ 0.5 wt% of pure sodium methylate as the catalyst. However, in this manuscript, *we regarded sodium methylate as sodium methylate 30% solution in methanol, which is industrially available for biodiesel production. Therefore, we considered the catalyst to be 1.67 wt%.*

To avoid misinterpretation, we have corrected the term of sodium methylate to sodium methylate 30% solution in methanol, in both text (p.17 line 32-34) and Table 5 (p.33).

d. For process B, it was considered a refined raw material to be converted into biodiesel. However, biodiesel industries use degummed raw materials ("less pure" than refined ones) in the process, often blended with other fatty materials, reducing production costs. Therefore, I believe that the value of the costs related to the raw material of process B are overestimated

Response: We have consulted with PT. BEST (a local biodiesel company which is one of the biodiesel suppliers for Pertamina, a state-owned and biggest petroleum company in Indonesia) regarding the industrial processing steps and feedstock selection for biodiesel production. Refined palm oil (RPO, with FFA and water content less than 0.1 wt%) is very much preferable than the degummed materials (with higher FFA and water content) for conventional mass production since it will produce less soap (leads to easier separation) and give a stable biodiesel yield. Therefore, we decided to use RPO as the feedstock for process B.

e. The authors accomplished the economic analysis considering ethanol as process reagent. However, biodiesel industries (Process B) use methanol as reagent, which has a much lower production cost than ethanol

Response: We have added both methanol and ethanol in our economic analysis, as shown in Table 5 (p.33).

As the results and discussion are presented, it is difficult to believe that the heterogeneous process has a total production cost of only 1.65 % in relation to the homogeneous one.

Response: We have revised the calculation according to your constructive suggestions and we found that the total operating cost of process A is 17.4% of that for process B, in p.18 line 17.

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

Sincerely yours,

Maria Yuliana

Highlights:

- The use of WCS and LTW in energy sector is beneficial for the zero-waste act
- WCS has been successfully used as catalyst for biodiesel production from LTW
- WCS-based catalyst has comparable activity to the other heterogeneous catalyst
- WCS-based catalyst can be reused until the third run with > 90% FAEE yield
- 93.4% FAEE yield with 97.8% purity was obtained in the proposed technique

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 2,600 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.

Keywords: biodiesel; catalyst; waste capiz-shell; leather tanning waste; zero-waste approach; viability study

1. INTRODUCTION[1]

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

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[1] **Abbreviation**

WCS	Waste capiz-shell
LTW	Leather tanning waste
RPO	Refined palm oil
FAEE	Fatty Acid Ethyl esters
TG	Triacylglyceride(s)
FFA	Free fatty acid
CaO	Calcium oxide

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 mesoporous 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 4,000 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 2,600 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-6500F (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:

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

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.

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 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 x 0.25 mm ID x 0.25 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:

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

Where $\sum A_{\text{FAEE}}$ 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 equation (2), the determination of FAEE yield can be performed using equation (3):

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

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 equation (2).

2.5 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 Figure 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. Figure 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 (Figure 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].

Figure 1

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].

Table 2

The WCS-based CaO was further analyzed by XRD and its diffraction pattern is shown in Figure 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 Figure 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 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].

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.

Figure 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 $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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. Figure 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 and gain high product yield, since transesterification itself is a reversible reaction [18,59]. As described in Figure 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].

Figure 2

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 Figure 3. The results indicated that high FAEE yield of above 90 wt% was achieved until the third run with the purity of FAEE ranges from 97.1 – 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, $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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].

Figure 3

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].

Table 3

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 2,600 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 grams of LTW contains lipid fraction of 80.02 grams that can be converted into FAEE with the maximum yield of 93.4 wt% (74.74 grams) 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[2]), sodium methylate 30% solution in methanol (1.67 wt% of RPO[3]) as the homogenous catalyst, hydrochloric acid (1.2 wt% of RPO[4]) and liquid caustic soda (0.12 wt% of RPO[5]) 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.

[2, 3, 4, 5] The required composition of supporting materials in process B were obtained from a local biodiesel manufacturer in Indonesia.

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.

Table 4

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 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.

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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

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

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) [1]	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 [2]			**11,169,508.4**
Process B [3]			
RPO (ton)	74,740	750	56,055,000
Sodium methylate 30% solution in methanol (ton)	1,248.16	2,500	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 [2]			**64,383,623.7**

[1] 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

[2] 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)

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

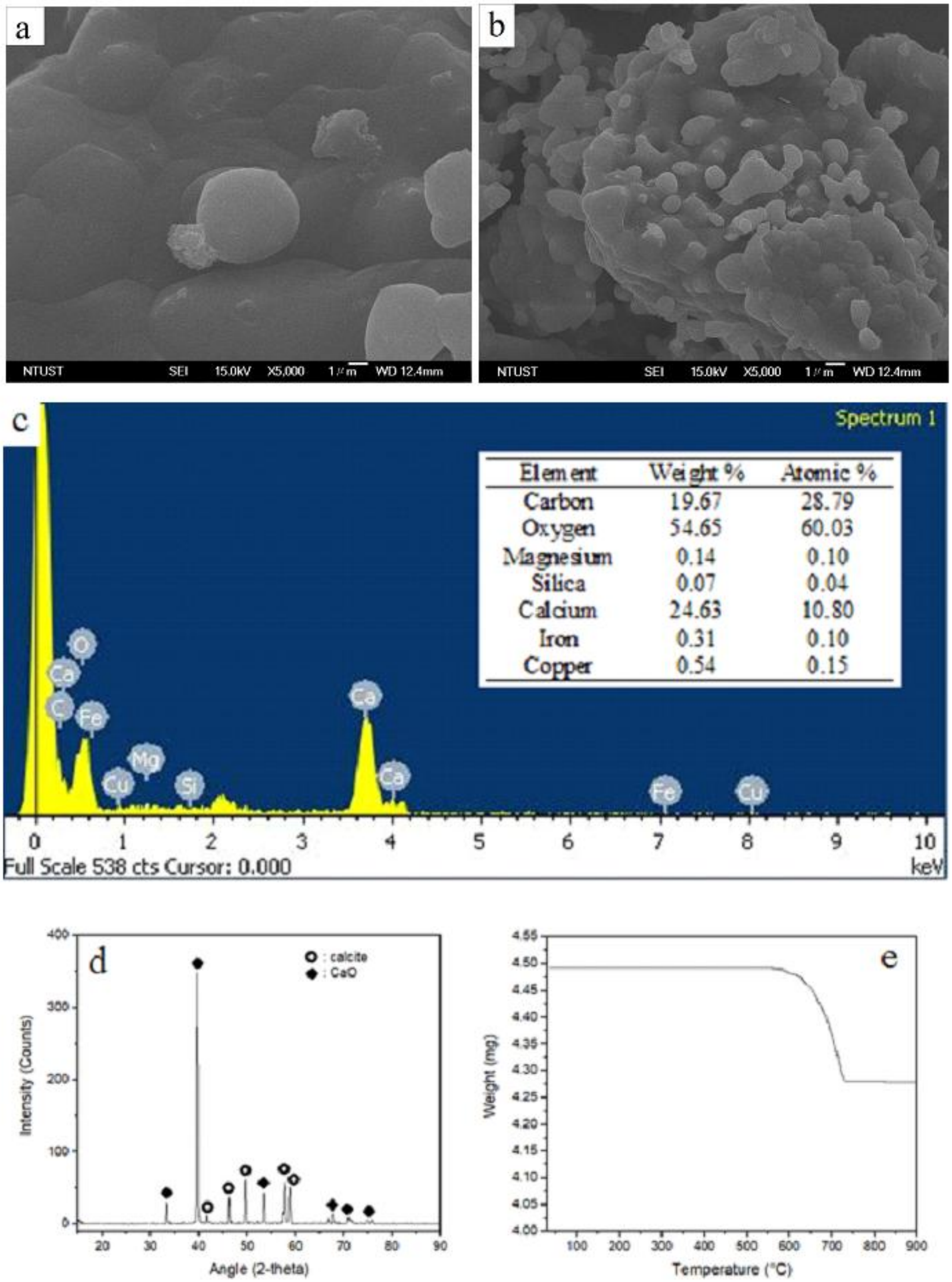
Figure captions.

Figure 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

Figure 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

Figure 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

Figure 1



Element	Weight %	Atomic %
Carbon	19.67	28.79
Oxygen	54.65	60.03
Magnesium	0.14	0.10
Silica	0.07	0.04
Calcium	24.63	10.80
Iron	0.31	0.10
Copper	0.54	0.15

Figure 2

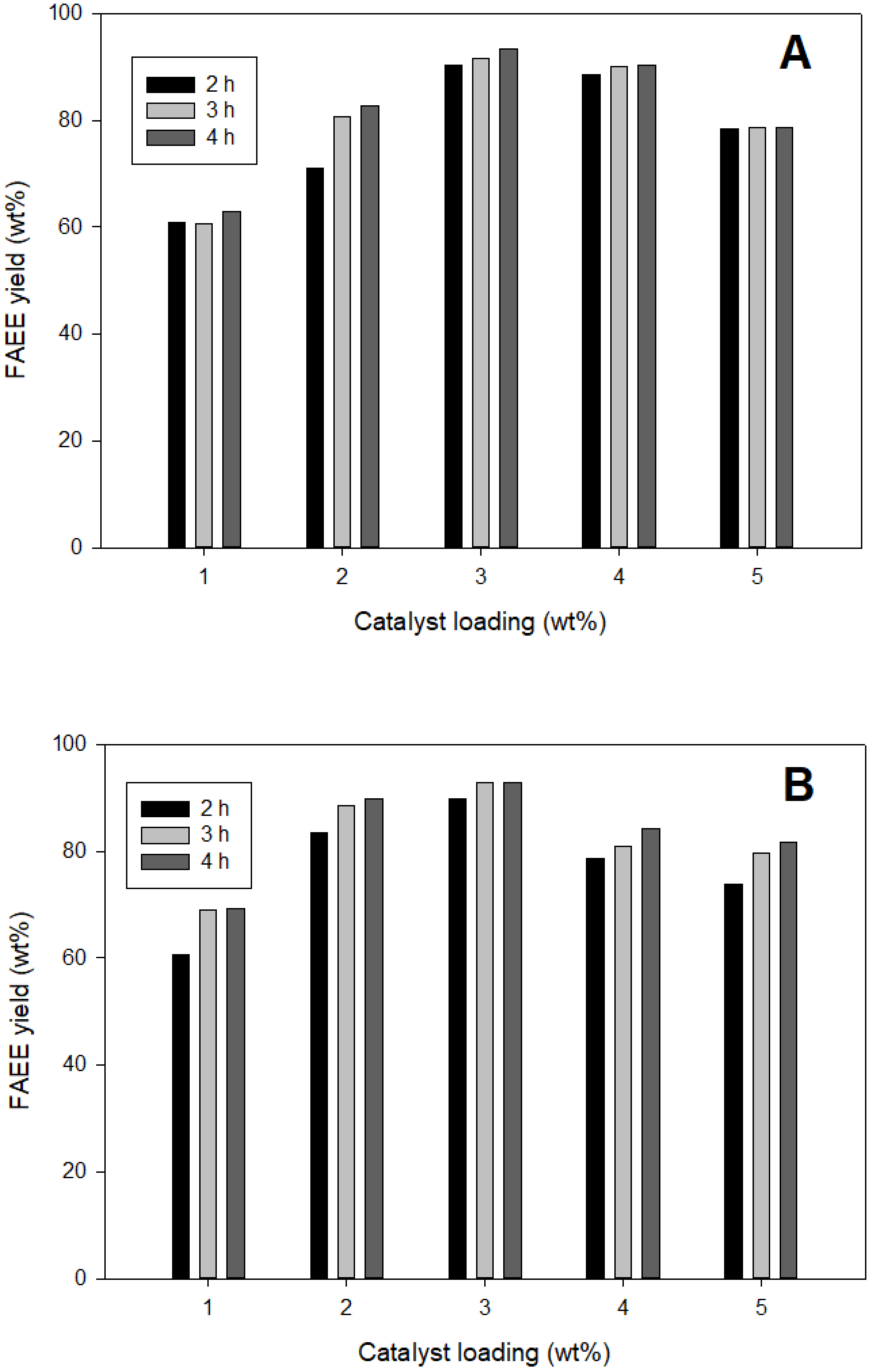


Figure 2

Figure 3

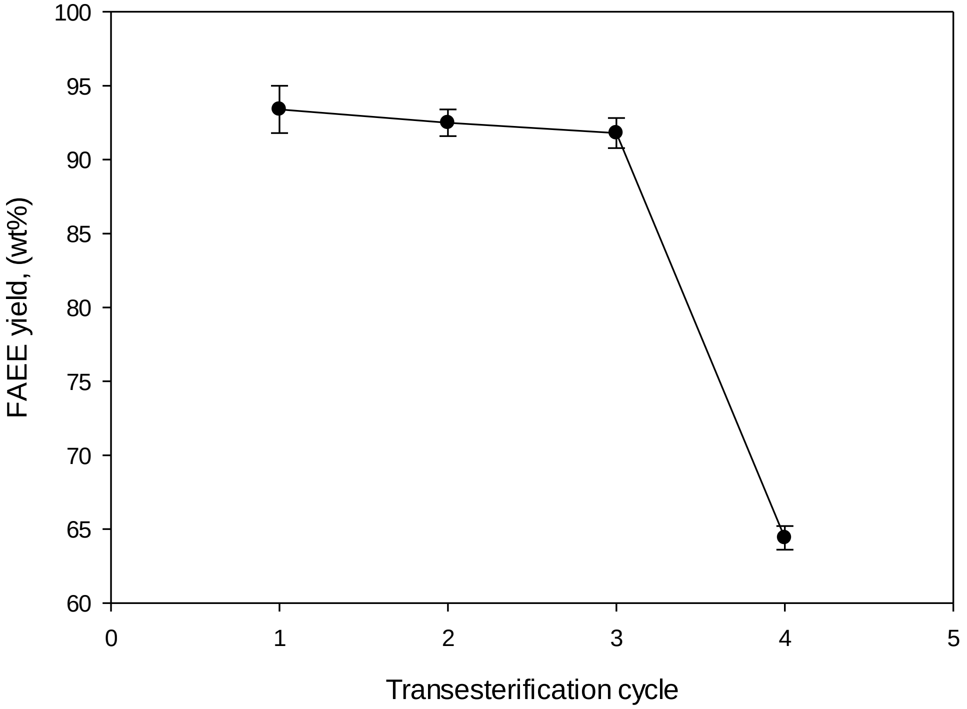


Figure 3

CREDIT AUTHOR STATEMENT

Maria Yuliana - Conceptualization, methodology, software, visualization, investigation, writing – original draft
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Felycia Edi Soetaredjo - Resources, data curation
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***Declaration of Interest Statement**

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Dear Dr. Yuliana,

I am pleased to inform you that your manuscript "UTILIZATION OF WASTE CAPIZ SHELL - BASED CATALYST FOR THE CONVERSION OF LEATHER TANNING WASTE INTO BIODIESEL" has been accepted for publication in Journal of Environmental Chemical Engineering.

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Maria Yuliana Liauw, ST., Ph.D. <mariayuliana@ukwms.ac.id> Mon, May 11, 2020 at 3:38 PM
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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

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Abbreviations: WCS, waste capiz-shell; LTW, leather tanning waste; RPO, refined palm oil; FAEE, Fatty Acid Ethyl esters; TG, triacylglyceride(s); FFA, free fatty acid; CaO, calcium oxide

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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 mesoporous 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 pretreatment, 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 x0.25 mm ID x0.10 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:

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

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:

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

Where $\sum A_{\text{FAEE}}$ 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):

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

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.

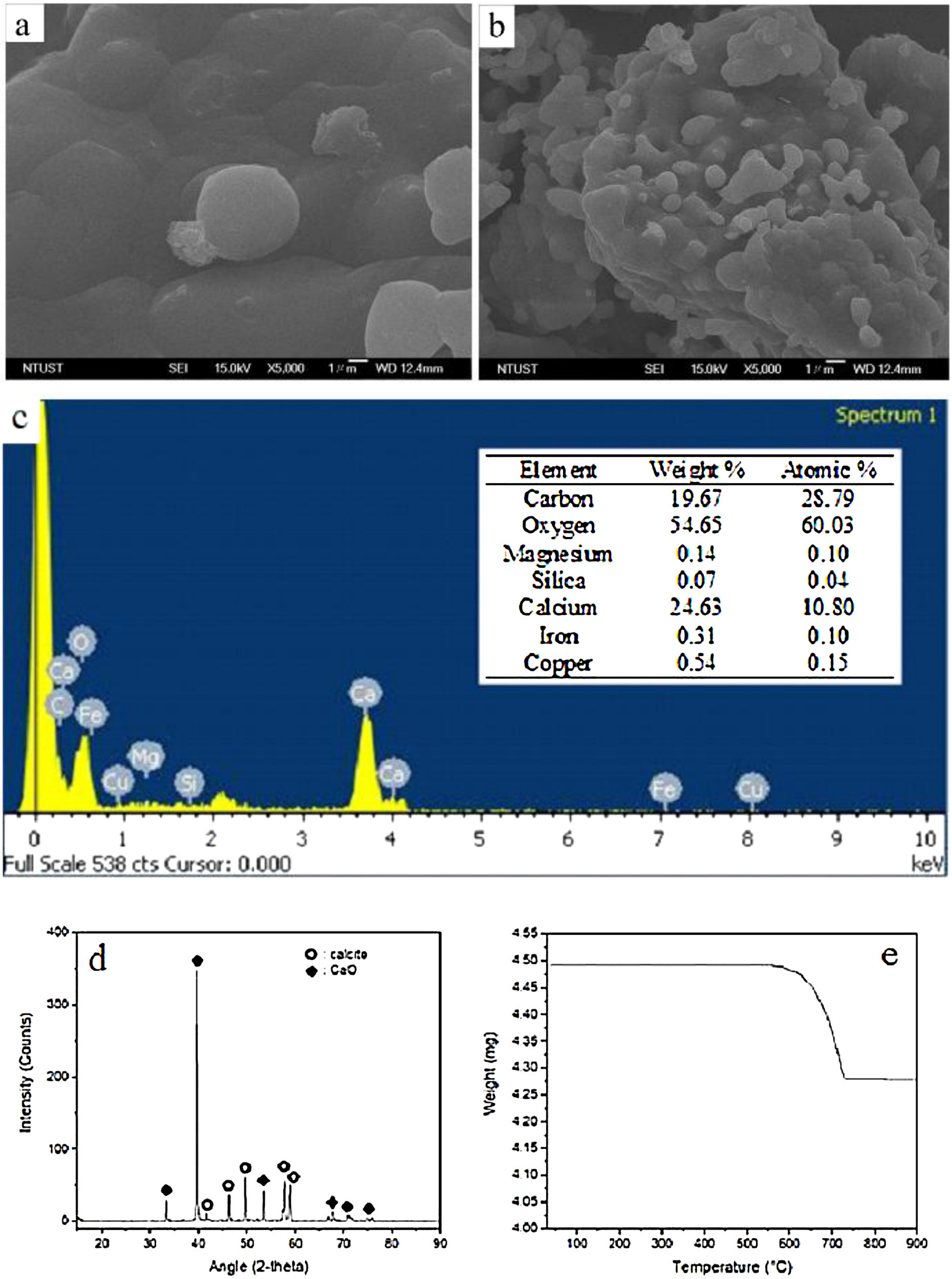
3. Results and discussions

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



Element	Weight %	Atomic %
Carbon	19.67	28.79
Oxygen	54.65	60.03
Magnesium	0.14	0.10
Silica	0.07	0.04
Calcium	24.63	10.80
Iron	0.31	0.10
Copper	0.54	0.15

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 $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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 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].

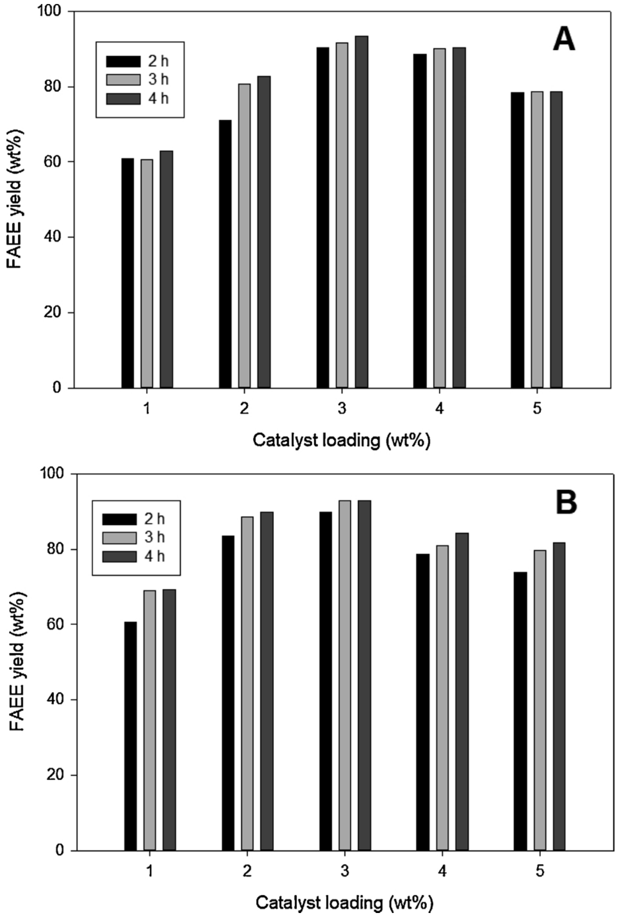


Fig. 2. The FAEE yield (wt%) based on the experimental results with the interaction between catalyst loading (wt%) and time (h) at ethanol to LTW molar ratio of (a) 6:1 and (b) 12:1.

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

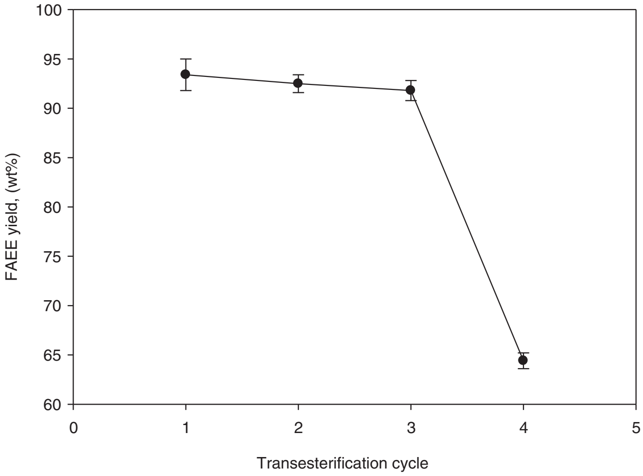


Fig. 3. The recyclability of WCS-based CaO as the catalyst for biodiesel preparation from LTW at the transesterification condition of 60 °C, 4 h, catalyst loading of 3 wt% and ethanol to LTW molar ratio 6:1.

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, $C_2H_5O\text{-}Ca\text{-}O(OH)_2C_3H_5$. 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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