The utilization of hydroxyapatite-supported CaO-CeO₂ catalyst for biodiesel production

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Abstract

The study investigated the effect of a bimetallic supported catalyst in biodiesel production. Calcined waste bone derived hydroxyapatite (HAP), a solid waste from animal, was served as the support for CaO-CeO₂ catalyst. Various characterization techniques such as FT-IR, BET, SEM-EDS, CO₂-TPD and XRD analysis were used to analyse the activity of this heterogeneous catalyst. The effect of main parameters in preparation process such as calcination temperature and active component loading on catalyst performance were discussed to obtain the optimal preparation conditions. Under the optimal reaction conditions (11 wt.% dosage of 30%CaO-CeO₂/HAP-650 catalyst and 9:1 methanol to oil molar ratio at 65 °C for 3 h) the highest biodiesel yield of 91.84% was obtained. Stability test indicated that the yield (84.4%) of fatty acid methyl ester was produced after 8 re-used cycles due to the low leaching of catalyst components.

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20 The experimental results showed that biodiesel production cost might be lowered while producing
21 relatively high yield at the present of long life-span catalyst.

22 **Keywords:** Biodiesel; Transesterification; Hydroxyapatite; Heterogeneous catalyst; Bone

23

24 1. Introduction

25 Due to the limited oil reserves and the increasing associated environmental issues, biodiesel has
26 been deemed to be a sustainable alternative fuel and therefore has attracted considerable attention in
27 last decade. Biodiesel has several merits such as renewability, biodegradability, non-toxicity and it
28 can be used directly in engines without any modification [1, 2]. Biodiesel, i.e., fatty acid methyl
29 esters (FAME), is a principal product produced from the catalytic transesterification reaction
30 between triglycerides (vegetable oils or animal fats) and methanol [3, 4]. Among various influence
31 factors on biodiesel production via transesterification reaction, the development of catalysts
32 definitely played a core role. Therefore, extensive researches were conducted to improve the activity,
33 stability and economic benefits of catalysts.

34 Previously, the transesterification reaction has already been conducted on a commercially scale
35 using homogeneous acids and bases, such as H_2SO_4 , HCl , NaOH , CH_3ONa , etc. Bases were more
36 active and less corrosive than acids, and hence were preferred in transesterification [5].
37 Unfortunately, homogeneous bases proved to be sensitive to free fatty acids and water resulting in
38 saponification, which have a negative effect on the performance of the catalyst [6-8]. Besides, a
39 water washing process was needed for removal of both homogeneous acids and bases from
40 biodiesel after transesterification reaction, and thus a large amount of wastewater was generated [9,
41 10].

42 In contrast, heterogeneous catalysts have been found to be easily separated from reaction mixture,
43 thereby simplifying the production process, leading to their global employment in biodiesel
44 production [11-13]. At present, to decrease the synthesis cost of heterogeneous catalysts, various
45 heterogeneous solids derived from waste shells, such as egg shell [14, 15], mussel shell [16],
46 scallop shell [17], angel wing shell [18], obtuse horn shell [7] and shrimp shell [19] in which the

major active component is CaO, have drawn much attention. However, the deactivation problem caused by leaching of Ca^{2+} has been a drawback of CaO-based catalysts [20, 21]. Hence, methods were conducted to improve the stability of bulk CaO. One of the measures was to develop another low-cost and long-term animal bone derived catalyst (such as sheep bone [11], chicken bone [21], bovine bone [22], etc.). However, in order to acquire desirable yield of biodiesel, more derived bone catalysts consumption and longer reaction time must be used, and all of these conditions could in turn increase the cost of biodiesel production. Thus it is essential to explore other methods to improve the activity of waste bone derived catalysts. Another measure was to modify CaO by doping with other metals. Previously, researchers have exploited various metal oxides conjugated with CaO (such as $\text{CaO-La}_2\text{O}_3$ [23], CaO-MgO [24], CaO-ZrO_2 [25], etc.) to enhance the interaction and create the bi-functional catalytic site.

Pig bone is one of available waste bone from meat production in China, Hydroxyapatite (HAP), accounting for 30 wt.% of pig bones, which is the main composition was considered to be a good dispersed supporter [26] due to its strong ion-exchange capability, acid–base adjustability, non-toxicity, adsorption capacity and thermal stability [27]. Several researches have been done using HAP as a support for heterogeneous catalyst production. Sebti and co-researchers [28] reported that HAP was an excellent solid support for the Knoevenagel condensation without solvent. Successful application of HAP serving as a catalyst support for ruthenium to complete hydrogenation of quinolone was detailed by Sun et al. [29]. Fish bone derived natural hydroxyapatite-supported copper exhibited excellent efficacy in the semi-batch esterification of oleic acid with ethanol [30]. Thus HAP was preferred as a supporter for catalyst during transesterification reaction. Meanwhile, among modified CaO-based catalysts mentioned above, CaO-CeO_2 is seen as a promising catalyst which presented excellent performance and stability due

70 to the intensive interaction and lattice distortions created by substitution between Ca^{2+} and Ce^{4+}
71 with different valence, especially at the Ca/Ce molar ratio of 1:1 [31-33]. As a result, it's reasonably
72 enough to assume that HAP supported CaO-CeO_2 catalyst could perform well in catalyzing
73 transesterification reaction for biodiesel production with low cost. To the best of my knowledge this
74 kind of research has never been reported before.

75 A series of $\text{CaO-CeO}_2/\text{HAP}$ catalysts were prepared and their activities towards
76 transesterification reaction were examined in this work. FT-IR, BET, SEM, EDS, CO_2 -TPD and
77 XRD characterizations were conducted to determine the physical/chemical properties of the
78 catalysts. Besides, the catalyst preparation conditions (calcination temperature and loading
79 amounts), reaction parameters (catalyst dosage, methanol to oil molar ratio and reaction time) and
80 stability were also studied in detail.

81 **2. Experimental**

82 **2.1 Materials**

83 Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), methanol and hexane were
84 purchased from Tianjin Chemical Reagent Factory (Tianjin, China), of analytical reagent (AR)
85 grade. Refined palm oil was obtained from a local market. Pig bones were collected from a cafeteria
86 inside Tianjin University.

87 **2.2 Catalyst preparations**

88 In order to remove the impurities attached on the surface of bones, the collected bones were
89 washed thoroughly using hot deionized water, and then dried in an oven at $105\text{ }^\circ\text{C}$ for 6 h. After that
90 the dried bones were grounded to desired powders using agate mortar and were calcined in a muffle
91 furnace at $1000\text{ }^\circ\text{C}$ for 4 h. The fine calcined bones powders were stored for the subsequent catalyst
92 preparation and experimental runs.

93 A series of CaO-CeO₂/HAP catalysts were synthesized using wet impregnation method. To
94 produce 30%CaO-CeO₂/HAP catalyst, 5.71g of Ce(NO₃)₃·6H₂O and 3.10g of Ca(NO₃)₂·4H₂O were
95 dissolved in deionized water according to Ca/Ce molar ratio of 1:1. 1 M calcium nitrate solution
96 and 1 M cerium nitrate solution were well mixed followed by impregnating with 7g of dried bone
97 powders at the continuous stirring rate of 500 rpm for 3 h. According to [31] calcium oxide and
98 cerium oxide are obtained from calcination of calcium nitrate and cerium nitrate at 873K for 5h
99 respectively. So the bones which had absorbed nitrates were dried in an oven at 105 °C for 12h
100 followed by calcinations with varying temperatures (500 °C, 650 °C, 800 °C) at the rate of 2 °C/min
101 for 5 h. After that, the catalysts were stored in the vacuum oven for further experimental runs. The
102 loading mount of CaO-CeO₂ as 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% could be calculated based
103 on the amounts of initial material [34-36]. The catalysts were labeled as xCaO-CeO₂/HAP-y, where
104 x and y represented the amount of CaO-CeO₂ (Ca/Ce molar ratio of 1:1) loaded on the catalyst and
105 the calcination temperature, respectively.

106 2.3 Characterizations of catalysts

107 The FTIR spectra were detected on a Shimadzu IR-Prestige-21 Spectrometer in the wavenumber
108 range of 400-4000 cm⁻¹ following the KBr pellet method. The surface area and particle size
109 distribution analysis of the samples were conducted using a Quantachrome Autosorb-iQ Analyzer at
110 77.3 K according to N₂ adsorption-desorption. And then the results were calculated using
111 Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) computing method
112 automatically. The surface micrographs and element compositions were determined by S-4800
113 Scanning Electron Microscopy coupled with Energy Disperse Spectroscopy Instrument (Hitachi,
114 Japan). Furthermore, the basic properties of samples were determined using temperature
115 programmed desorption of CO₂, which were operated in the temperature-programmed mode of

116 120 °C-10 °C/min-1000 °C and flushing with the flowing (30 ml/min) helium continually. Phase
117 analysis of the synthesized catalysts were qualitatively analyzed using a D/MAX-2500 X-ray
118 Diffract-meter (Rigaku, Japan) coupled with Cu K α radiation(λ =1.5418 Å, 40 mA, 40 kv) and a
119 step-scan pattern (scanning range: 2 θ , 10 °-80 °; scanning speed: 4 °/min). To characterize the
120 physicochemical properties of produced biodiesel, density was determined using specific gravity
121 bottle, kinematic viscosities were determined by an Ubbelohde Viscometer, flash point was
122 measured by closed flash point automatic tester, and acid number was determined by acid base
123 titration method.

124 **2.4 Transesterification procedure**

125 The transesterification reaction of palm oil and methanol was carried out in a 100 ml
126 round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The constant
127 temperatures were kept at 65 °C in water bath, and the agitation speed was controlled
128 approximately at 600 rpm simultaneously. 30 g of the oil with a 9:1 of the methanol to palm oil
129 molar ratio and 11 wt.% of catalyst dosage (based on the weight of oil) were placed inside the flask
130 while stirring and refluxing for 3 h. when the reaction completed, the catalysts were separated by
131 centrifugation, and the remaining liquid products were divided into two layers in a separating funnel.
132 Biodiesel floated on the top layer while glycerol at the bottom. The desirable biodiesel obtained was
133 further purified by distillation to remove the excess methanol.

134 The obtained biodiesel products were quantitatively analyzed using Gas Chromatography
135 (Agilent 7890A, USA) fitted with an FID detector operating at 340 °C. Before GC analysis, 20mg
136 of the prepared biodiesel and 10mg of Methyl salicylate were diluted by 2mL of n-hexane. 1 μ L of
137 the diluted liquid was injected into a capillary column DB-5HT (30 m $\times$ 0.25 mm $\times$ 0.1 μ m) which
138 was operated in a temperature-programmed mode of 100 °C (0 min)–30 °C/min–330 °C (10 min).

139 The reference, solvent and carrier gas were methyl salicylate, n-hexane and pure helium
 140 correspondingly. The yield of fatty acid methyl ester (FAME) was calculated using equation (1) [37]
 141 with the standard deviation of ± 0.01 mass.

$$142 \quad Yield \% = \frac{M_a}{M_t} \times 100\% = \frac{M_{ester}}{M_{oil}} \times 100\% \quad (1)$$

143 Where, M_a is the actual mass of FAME, and M_t is the theoretical mass. While M_{ester} and
 144 M_{oil} stand for weight of fatty acid methyl ester (g) produced and weight of oil used (g),
 145 respectively.

146 **3. Results and discussion**

147 **3.1 Characterizations**

148 **3.1.1 FT-IR absorption spectra analysis.**

149 The comparison of FTIR spectra between calcined bone and 30%CaO-CeO₂/HAP-650 catalysts
 150 were presented in Fig. 1. The band at 3570 cm⁻¹ corresponds to stretching vibration of OH⁻¹ groups
 151 in the HAP structure [38]. The broad bands appeared at 569 cm⁻¹, 603 cm⁻¹, 672 cm⁻¹ and 1045 cm⁻¹
 152 in both catalyst were assigned to P-O group stretching vibration [39, 40]. The band which appeared
 153 at 3640 cm⁻¹ in CaO-CeO₂/HAP catalyst was not prominent in the FTIR spectra of calcined bone.
 154 This band might be associated with stretching vibration of OH groups contained in Ca(OH)₂, which
 155 can be formed by decomposition of nitrate followed by its reaction with water [38]. It was noted
 156 that the bands related to vibrational model of Ce group did not appear in the testing range of 400
 157 cm⁻¹-4000 cm⁻¹ possibly due to (1) Ce-O groups may appear at about wavenumbers lower than 400
 158 cm⁻¹ [41]; (2) The frequency of Ce-O might be reduced by the formation of mixed binary metal
 159 oxide [42].

Fig. 1. FTIR spectra comparison (calcined bone and 30%CaO-CeO₂/HAP-650 catalysts)

3.1.2 BET surface area analysis

The BET surface areas and pore volumes of the various catalysts with different loadings and diverse calcination temperatures were shown in Table 1. As the active component CaO-CeO₂ impregnated from 0 wt.% to 40 wt.%, the surface area and pore volume of the samples decreased significantly from 104.615 m²·g⁻¹ to 10.053 m²·g⁻¹ and 0.104 cc·g⁻¹ to 0.016 cc·g⁻¹, respectively. This result might be ascribed to the loaded oxides which blocked the smaller pores on the surface of the catalysts. Besides, with the calcination temperature increased from 500 °C to 650 °C, the surface area decreased gradually from 16.560 m²·g⁻¹ to 13.501 m²·g⁻¹. Such decrease was expected since the atoms of small particles could diffuse to the boundary and fuse other particles together to form larger particles at high temperature [9]. When the calcination temperature increased to 800 °C, the surface area of CaO-CeO₂/HAP catalyst decreased dramatically (from 13.501 m²·g⁻¹ to 7.625 m²·g⁻¹). It may be attributed to sintering of catalyst particles at higher calcination temperature.

174 **Table 1** BET surface area, pore volume of catalysts

Samples	Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cc} \cdot \text{g}^{-1}$)	FAME yield (%)
Calcined bone (HAP)	104.615	0.104	83.53
10%CaO-CeO ₂ /HAP-650	27.076	0.032	85.36
20%CaO-CeO ₂ /HAP-650	18.830	0.021	87.8
30%CaO-CeO ₂ /HAP-650	13.501	0.019	91.84
40%CaO-CeO ₂ /HAP-650	10.053	0.016	91.3
30%CaO-CeO ₂ /HAP-500	16.560	0.015	88.1
30%CaO-CeO ₂ /HAP-800	7.625	0.018	82.84

175 **3.1.3 Scanning electron microscopy & Energy disperse spectroscopy (SEM-EDS) analysis**

176 The surface micrographs of various catalysts are shown in Fig. 2. The micrograph of CaO-CeO₂
177 catalyst exhibited the packed accumulation of spherical and cluster shape particles, while the
178 micrograph of 30%CaO-CeO₂/HAP catalyst showed the regular blocks and pores, which could be
179 attributed to the porous structure of bones and clustering of metal oxide particles on the calcined
180 bone surface. Besides, it was observed that the particle size of 30%CaO-CeO₂/HAP catalyst
181 calcined at 800 °C was much larger than the one calcined at 650 °C indicating that the crystalline of
182 catalyst could be improved by calcination temperature.

183 The surface element contents of catalysts with different loadings are listed in Table 2. The
184 calcined bone derived catalyst mainly consisted of Ca, P, O, and some minor components such as C,
185 Na and Mg. As CaO-CeO₂ was loaded on the bone, the content of Ce observed on the surface of the
186 loading-mode catalyst increased. As the loading amount increased from 20 wt.% to 40 wt.%, the
187 contents of Ca and Ce were also increased in the range of 21.11%-26.88% and 13.92%-24.63%,
188 respectively. The higher contents indicated that the Ca and Ce were well loaded on the surface of
189 calcined bone.

Fig. 2. SEM images of catalysts: (a) CaO-CeO₂-650 (50.0k); (b) 30%CaO-CeO₂/HAP-650 (50.0k); (c) 30%CaO-CeO₂/HAP-650 (10.0k); (d) 30%CaO-CeO₂/HAP-800 (10.0k)

Table 2 Chemical Compositions of various catalysts

catalysts	Element content (wt. %)							
	Ca	Ce	C	O	Na	Mg	P	Others
Calcined bone	30.87	0	2.36	43.13	1.15	1.48	20.02	0.99
CaO-CeO ₂	7.49	64.45	1.04	20.89	-	-	-	6.13
20%CaO-CeO ₂ /HAP-650	21.11	13.92	2.72	44.83	1.61	2.32	13.03	0.464
30%CaO-CeO ₂ /HAP-650	25.12	22.67	1.32	31.77	1.10	0.70	13.81	3.51
40%CaO-CeO ₂ /HAP-650	26.88	24.63	3.46	30.23	1.60	0.62	9.80	2.78

3.1.4 Temperature programmed desorption of CO₂ (CO₂-TPD) analysis

The basicity of various catalysts e.g., 10%CaO-CeO₂/HAP-650, 20%CaO-CeO₂/HAP-650, 30%CaO-CeO₂/HAP-650 and 40%CaO-CeO₂/HAP-650 are illustrated in Fig. 3. The total amounts of CO₂ desorbed are shown in Table 3. As can be observed, the calcined bone derived catalyst showed two weak desorption peaks at the temperature range of 570–740 °C, with 7.9 μmol/g and 35.1 μmol/g of CO₂ desorbed, implying the low basicity owned in calcined bone. The optimal yield of FAME could be obtained with the rich catalyst dosage of 20 wt.%, which was in good agreement

201 with previous study [11]. As the addition of mixed oxide CaO-CeO₂ increased from 20 wt.% to 40
202 wt.%, a weak desorbed peak of CO₂ at the temperature range of 160-250 °C and a broad desorbed
203 peak of CO₂ at the temperature range of 480-720 °C were clearly observed. The improvement of
204 strong basic site, increased from 431.8 μmol/g to 634.5 μmol/g of CO₂ desorbed and might be
205 attributed to the synergic effect between CaO and CeO₂ [33]. Additionally, it can be observed that
206 the increasing CaO-CeO₂ loadings could contribute to the upward shift of CO₂ desorption
207 temperatures, which also improved the basicity of the catalysts.

208 Fig. 4 demonstrated the basicity of catalysts pretreated in different calcination temperatures
209 (500 °C, 650 °C and 800 °C). As shown in Fig. 4a, except for the aforesaid desorption peak, there
210 was a turning point appeared in the curve at approximately 650 °C, which might be owing to
211 thermal decomposition of 30%CaO-CeO₂/HAP-500 catalyst. When the calcination temperature
212 increased from 650 °C to 800 °C, the amount of CO₂ desorbed at the temperature range of
213 500~700 °C decreased considerably from 441.8 μmol/g to 174.8 μmol/g due to sintering of catalyst
214 particles at higher calcination temperature, which was also supported by the result of BET analysis
215 as shown in Table 2.

Fig. 3. CO₂-TPD analysis of catalysts: (a) calcined bone; (b) 10%CaO-CeO₂/HAP-650; (c) 20%CaO-CeO₂/HAP-650; (d) 30%CaO-CeO₂/HAP-650; (e) 40%CaO-CeO₂/HAP-650

Table 3 Total basicity of various catalysts, expressed in $\mu\text{mol CO}_2/\text{g}$ desorbed

catalysts	Absorbed CO ₂ ($\mu\text{mol/g}$)	Temperature range (°C)	Peak temperature (°C)
Calcined bone	7.9	570-630	587
	35.1	640-740	695
10%CaO-CeO ₂ /HAP-650	427.1	480-720	608
20%CaO-CeO ₂ /HAP-650	9.7	170-230	200
	431.8	500-720	618
30%CaO-CeO ₂ /HAP-650	8.4	160-250	216
	441.8	500-720	620
40%CaO-CeO ₂ /HAP-650	21.2	160-250	230
	634.5	500-720	637
30%CaO-CeO ₂ /HAP-500	14.6	160-250	200
30%CaO-CeO ₂ /HAP-800	471.8	500-760	640
	174.8	500-700	626

Fig. 4. CO₂-TPD analysis of catalysts: (a) 30%CaO-CeO₂/HAP-500; (b) 30%CaO-CeO₂/HAP-650; (c) 30%CaO-CeO₂/HAP-800

3.1.5 X-ray diffraction (XRD) analysis

The XRD patterns of calcined bone, CaO-CeO₂ and CaO-CeO₂/HAP-650 catalysts containing different CaO-CeO₂ loadings from 20 wt.% to 40 wt.% are shown in Fig. 5. According to the Joint Committee on Powder Diffraction Standards, the diffraction peaks which appeared at 10.88°, 32.24°, 32.94°, 39.81°, 46.72° and 49.52° were attributed to the existence of hydroxyapatite [43]. Three obvious peaks at 25.94°, 28.96° and 34.11° were corresponding to β -Ca₃(PO₄)₂ phase [44] confirming that the newly formed β -Ca₃(PO₄)₂ could serve as a base catalyst for transesterification reaction [21, 45]. When the CaO-CeO₂ loaded on the calcined bone, the peaks of CaO ($2\theta = 37.44^\circ$, 53.98°) and CeO₂ ($2\theta = 28.8^\circ$, 48.16° and 57.20°) were clearly found, and the intensities of these peaks increased with the loading increasing from 20 wt.% to 40 wt.%. The narrow and enhanced peaks of CaO and CeO₂ could probably increase the basicity of CaO-CeO₂/HAP catalyst, while counterbalanced by the decrease intensity of hydroxyapatite and β -Ca₃(PO₄)₂ phases.

236 Fig. 6 presented the XRD patterns of 30%CaO–CeO₂/HAP catalysts containing different
 237 calcination temperatures from 500 °C to 800 °C. As shown in Fig. 6, the intensities and sharpness of
 238 CeO₂, CaO, β-Ca₃(PO₄)₂ and hydroxyapatite diffraction peaks increased along with the rising
 239 calcination temperature from 500 °C to 800 °C. This might be because that the higher temperature
 240 was beneficial to decompositions of cerium nitrate and calcium nitrate as well as rearrangement of
 241 oxydic Ce⁴⁺, which enhanced the crystal formation of CeO₂ and CaO phases.

242
 243 **Fig. 5.** XRD patterns of catalysts: (a) CaO-CeO₂-650; (b) calcined bone; (c) 20%CaO–CeO₂/HAP-
 244 650; (d) 30%CaO- CeO₂/HAP-650; (e) 40%CaO- CeO₂/HAP-650

245

246 **Fig. 6.** XRD patterns of catalysts: (a) 30%CaO-CeO₂/HAP-500; (b) 30%CaO-CeO₂/HAP-650; (c)
 247 30%CaO-CeO₂/HAP-800

248

3.2 Influence of catalyst preparation conditions

249

The preparation process of catalyst is crucial to its performance on transesterification reaction.

250

Therefore, the optimizations of synthesized conditions including calcination temperatures (500 °C -

251

800 °C) and active component loadings (10 - 40 wt.%) were investigated.

252

3.2.1 Effect of calcination temperature

253

To determine the relationship between calcination temperature and catalyst activity, the effect of

254

various calcination temperature on catalytic performance were carried out in Table 1. As can be

255

seen, the yield of FAME was slightly increased with the elevation of calcination temperature from

256

500 °C to 650 °C, but decreased remarkably from 91.84% to 82.84% with the increasing

temperature to 800 °C. This result might be ascribed to the more thorough conversion of calcium oxide and cerium oxide from nitrate radicals with the increase of calcination temperature from 500 °C to 650 °C as shown in Fig.6 and the sintering of catalyst with the increasing calcination temperature to 800 °C, which was confirmed by the decreased surface area of 13.501 m²·g⁻¹ to 7.625 m²·g⁻¹ and the increased particle size from surface micrographs of catalysts in Fig. 2(c) and 2(d). Therefore, the optimal calcination temperature of CaO-CeO₂/HAP catalyst was 650 °C.

3.2.2 Effect of active component loading

A series of catalysts prepared with different CaO-CeO₂ loadings ranged from 0 wt.% to 40 wt.% were investigated for transesterification reaction. The yields of FAME were summarized in Table 1. It should be noted that the reaction condition of catalyst dosage of calcined bone and CaO-CeO₂/HAP catalysts were 20 wt.% and 11 wt.%, respectively. As observation, the calcined bone derived catalyst exhibited inferior catalytic performance even with the high catalyst dosage of 20 wt.%. However, there was a rising trend for FAME yield from 83.53% to 85.36% when the loading concentration of CaO-CeO₂ on the calcined bone increased from 0 wt.% to 10wt.%. It might be attributed to (1) the higher basicity of CaO-CeO₂/HAP catalyst conforming to Fig. 3; (2) the vacancies were favorable for CaO-CeO₂/HAP heterogeneous catalyst, which can be created by the substitution of Ca²⁺ in CeO₂ [31-33]. However, the catalyst prepared at higher CaO-CeO₂ loading of 40 wt.% which was used in the biodiesel production process reduced the biodiesel yield slightly. This was possibly due to viscous and emulsified mixture at higher catalyst concentration, which in turn ultimately affects the biodiesel yield adversely [46, 47]. Thus, the maximum yield of FAME was obtained with the CaO-CeO₂ loading of 30 wt.%.

3.3 Optimization of reaction parameters

To obtain the optimum reaction conditions, further experiments were conducted using the

280 pre-optimized 30%CaO-CeO₂/HAP-650 catalyst. For comparison on the catalytic performance,
281 calcined bone was also selected in the investigation. The effects of these reaction parameters on the
282 FAME yield have been recorded as follows.

283 3.3.1 Optimal catalyst dosage

284 The dosage of catalyst is one of main impacts influencing the catalytic performance. Suitable
285 dosage of catalyst can not only improve the efficiency of reaction, but avoid saponification to the
286 greatest extent. The effect of the catalyst dosage on the FAME yield was investigated by varying the
287 catalyst mass ratio from 3 wt.% to 13 wt.%, as displayed in Fig. 7. For calcined bone derived
288 catalyst, the lower yield of FAME of 78.56% was obtained with 13 wt.% catalyst amount, which
289 was mainly ascribed to less available base active sites of HAP (as shown in Fig. 3(a)). For
290 30%CaO-CeO₂/HAP-650 catalyst, the yield of FAME increased from 71.89 % to 91.84 % with the
291 increase of catalyst dosage from 3 wt.% to 11 wt.%. However, further increase of catalyst dosage
292 over 11 wt.% enhanced the viscosity of reaction system and slightly decreased the FAME yield. The
293 reaction mixture became more viscous with high catalyst concentration and might be attributed to:
294 (1) the increased dose may agglomerate the catalyst and decrease the number of active sites; (2) the
295 slight soap formation which inhibited the reaction process as a result of increase in the viscosity of
296 the reactants. Therefore, the optimal catalyst dosage was regarded as 11 wt.%.

297
298 **Fig. 7.** Effect of catalyst dosage on yield of FAME under the following fixed conditions.
299 30%CaO-CeO₂/HAP-650: Methanol to oil molar ratio = 9:1, Reaction time = 3 h, Reaction
300 temperature = 65 °C; Calcined bone: Methanol to oil molar ratio = 15:1, Reaction time = 5 h,
301 Reaction temperature = 65 °C

302 3.3.2 Optimal reaction time

303 The influence of reaction time on FAME yield was indicated with the prolongation of reaction
304 time from 0.5 h to 4 h. As shown in Fig. 8, the FAME yield was 56.11% at the reaction time of 0.5h
305 when 30%CaO-CeO₂/HAP-650 catalyst was used. Then with the increase of reaction time, the
306 FAME yield improved sharply and reached to the maximum value of 91.84% at 3h and the yield
307 asymptotes after extension of reaction time over 3h as the reaction reached the equilibrium. The
308 complete reaction achieved with 30%CaO-CeO₂/HAP-650 catalyst in 3h since the sufficient
309 reaction time was required for mass transfer by the reactant. Hence, the optimal reaction time of
310 30%CaO-CeO₂/HAP-650 catalyst was 3h. The performance of calcined bone derived catalyst was

311 relative poor possibly due to lower basicity as shown in Fig. 3 as compared with
 312 30%CaO-CeO₂/HAP-650 catalyst.

313
 314 **Fig. 8.** Effect of reaction time on yield of FAME under the following fixed conditions.
 315 30%CaO-CeO₂/HAP-650: Methanol to oil molar ratio = 9:1, Catalyst dosage = 11 wt.%, Reaction
 316 temperature = 65 °C; Calcined bone: Methanol to oil molar ratio = 15:1, Catalyst dosage = 20 wt.%,
 317 Reaction temperature = 65 °C

318 3.3.3 Optimal methanol to oil molar ratio

319 Generally, excess amount of methanol favour the forward transesterification reaction thereby
 320 improving the yield of FAME. The effect of the methanol to oil molar ratio of two solid catalysts on
 321 FAME yield was illustrated in Fig. 9. As methanol to oil molar ratio increase from 3:1 to 15:1, the
 322 FAME yield catalyzed by the 30%CaO-CeO₂/HAP-650 catalyst increased gradually until the
 323 maximum values were reached. The best catalytic performance was shown with the methanol to oil

324 molar ratio of 9:1, which achieved the maximum FAME yield of 91.84%, while the highest FAME
 325 yield catalysed by calcined bone was 83% with the ratio fixed at 15:1. Furthermore, slight decrease
 326 in FAME yield was observed when the increased ratio was above 9:1. It was possibly due to the
 327 dilution effect of catalyst and difficulties of heating reaction mixture [48]. Besides, a great quantity
 328 of extra energy was needed to heat and separate the methanol and glycerol resulting in increased
 329 production cost [49].

330

331 **Fig. 9.** Effect of methanol to oil molar ratio on yield of FAME under the following fixed conditions.

332 30%CaO-CeO₂/HAP-650: Catalyst dosage = 11 wt.%, Reaction time = 3 h, Reaction temperature =

333 65 °C; Calcined bone: Catalyst dosage = 20 wt.%, Reaction time = 5 h, Reaction temperature =

334 65 °C

335 3.4 The conversion properties of the produced biodiesel

336 To fully understand the mechanism of conversion for triglyceride to methyl ester, the composition

337 of species of produced biodiesel obtained under optimal conditions were analyzed using

338 30%CaO-CeO₂/HAP-650 catalyst and were listed in Table 4. The retention time and strength of
 339 peaks represented the various methyl ester contents in synthesized biodiesel. Therefore, it could be
 340 summarized that this solid base catalyst was liable for the production of longer carbon chain methyl
 341 esters.

342 **Table 4** Methyl esters composition of the produced biodiesel

Retention time (min)	Identified compounds	Concentration (%)
30.313	Octadecanoic acid methyl ester	25.64925
33.616	Heptadecanoic acid methyl ester	17.59421
33.118	9-Octadecynoic acid methyl ester	14.89034
26.6	Methyl tetradecanoate	11.5912
33.24	9-Octadecenoic acid methyl ester	8.85902
33.299	11-Octadecenoic acid methyl ester	7.47636
22.543	Dodecanoic acid methyl ester	2.77162
29.904	9-Hexadecenoic acid methyl ester	0.71167
41.267	Methyl n-octanoate	0.61137
31.991	Hexadecanoic acid methyl ester	0.59807
36.328	cis-11-Eicosenoic acid methyl ester	0.57858
26.713	Tridecanoic acid methyl ester	0.08284

343 3.5 The stability of catalyst

344 Stability is one of the most important evaluation parameters of catalytic behavior of the catalyst
 345 in biodiesel production as it gives information about performance which is highly depended on
 346 catalyst preparation cost and its stability. To study the stability of the catalyst, the recyclability of
 347 catalysts (30%CaO-CeO₂/HAP-650 and calcined bone) were tested by operating batch run for
 348 consecutive eight times reuse under the optimal reaction conditions. Before reuse, the catalysts were
 349 washed thoroughly by a mixture solution of n-hexane and methanol to remove absorbed polar and
 350 non-polar materials and then the washed catalysts were subjected to drying in an oven overnight at
 351 105 °C. Fig. 10 shows the performance of catalyst, it is observed that the CaO-CeO₂/HAP catalyst
 352 have better performance than calcined bone derived catalyst, especially after five cycles. Compared
 353 with the CaO-CeO₂ catalyst reported [31] earlier, the CaO-CeO₂/HAP catalyst shown better

354 reusability. The yield of FAME with CaO-CeO₂/HAP catalyst was still 84.4% after eight cycles
355 instead of 83% [31] after fourth cycle of CaO-CeO₂ catalyst, which possibly due to the service of
356 stable support HAP. The decrease in yield of FAME for both catalysts (calcined bone and
357 CaO-CeO₂/HAP) with reaction cycles was revealed and could be attributed to (1) the Ca compound
358 leached out during the reactions; (2) the loss of basicity and basic sites on the catalyst surface [13,
359 31, 50].

360 Leaching problem is a major issue encountered by calcium-based catalysts. To evaluate the
361 leaching of catalyst, the concentrations of cerium and calcium species were measured using ICP
362 method after removal of methanol and were presented in Fig. 11. It is observed that, in the first
363 reaction cycle, the concentrations of leached cerium and calcium species were 65 and 100 ppm,
364 respectively. However, with the subsequent reaction cycles, the concentrations of catalyst
365 component leached into the product phase decreased prominently. The decrease of dissolved species
366 concentration might be attributed to (1) the lattice distortion induced by substitution of Ca²⁺ and
367 Ce⁺⁴; (2) well distribution of the Ca and Ce components on the stable support of calcined bone [31,
368 32, 51]. Additionally, the effect of calcination temperature on dissolved cerium specie also indicated
369 that the leaching concentration of cerium specie decreased as the calcination temperature increased.
370 The consistent decrease of leaching concentration was ascribed result of enhancement of interaction
371 between catalyst components [52-57].

372
373 **Fig. 10.** The stability comparison between calcined bone and 30%CaO-CeO₂/HAP-650 catalyst

374
375 **Fig. 11.** The leaching concentrations of calcium and cerium species

376 3.6 The physicochemical properties of produced biodiesel

377 The produced biodiesel was characterized for its physicochemical properties using American

378 Society for Testing and Materials (ASTM) method. The results and recommended values of
379 petro-diesel (ASTM-D975) and biodiesel (ASTM-D6751) were also given in Table 5.

380 **Table 5** physicochemical properties of produced biodiesel

physicochemical properties	unit	petro-diesel (ASTM-D975)	Biodiesel (ASTM-D6751)	produced biodiesel
Density (40 °C)	g/cm ³	0.83	0.86-0.90	0.88
Kinematic viscosity (40 °C)	mm ² /s	1.9-4.1	1.9-6.0	3.71
Pour point	°C	-35 to -15	-15 to 16	+2
Flash point	°C	60-80	≥130	142
Acid number	mg KOH/g	0.5	0.5	0.23

381 As shown in Table 5, the density of produced biodiesel was 0.88 g/cm³ at 40°C, which was
382 comparable to the density of 0.83 g/cm³ of petro-diesel values. Viscosity which is the essential
383 property of produced biodiesel, could affect the fuel injection characteristic in engine. 3.71 mm²/s
384 of the determined kinematic viscosity of produced biodiesel was within the specified range of
385 ASTM values for biodiesel and petro-diesel. The low temperature characteristics of biodiesel and
386 petro-diesel were evaluated by pour point. The pour point of produced biodiesel was 2 °C which is
387 out of range of petro-diesel limits, suggesting the weaker storage, transportation characteristics in
388 low temperature environment. However, compared with petro-diesel, the flash point of produced
389 biodiesel of 142 °C is the guarantee of greater security of produced biodiesel. The acid number of
390 produced biodiesel was 0.23 mg KOH/g and falls in the range of ASTM standards.

391 **4. Conclusions**

392 In summary, a novel heterogeneous catalyst from CaO-CeO₂ loaded onto pig bone-derived HAP
393 was synthesized and utilized in transesterification reaction for biodiesel production. The highest
394 yield of FAME (91.84%) was achieved by combining with the following reaction parameters:
395 catalyst dosage of 11 wt.%, methanol to oil molar ratio of 9:1, and reaction time of 3 h. The catalyst
396 exhibited good performance after eight cycles as the yield of FAME remained 84.4%. Considering

397 that pig bone-based HAP is a solid waste and easily found, the CaO-CeO₂/HAP catalyst which have
398 good life span could be considered as a potential and promising supported bimetallic catalyst for
399 commercialized biodiesel production in the future.

400 The developed supported catalyst in the present study could minimize the dosage of CaO-CeO₂
401 significantly and improve the stability, in light of the use of waste bone. However, the extra cost of
402 HAP preparation might increase the overall cost of catalyst production despite easing the pollution
403 of waste bone. Further research would be conducted to estimate the energetic and economic aspects
404 of the developed catalyst.

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555

556 **Figure captions**

557 **Fig. 1** FTIR spectra of calcined bone and 30%CaO-CeO₂/HAP-650 catalysts

558 **Fig. 2** SEM images of catalysts: (a) CaO-CeO₂-650 (50.0k); (b) 30%CaO-CeO₂/HAP-650 (50.0k);
559 (c) 30%CaO-CeO₂/HAP-650 (10.0k); (d) 30%CaO-CeO₂/HAP-800 (10.0k)

560 **Fig. 3** CO₂-TPD analysis of catalysts: (a) calcined bone; (b) 10%CaO-CeO₂/HAP-650; (c)
561 20%CaO-CeO₂/HAP-650; (d) 30%CaO-CeO₂/HAP-650; (e) 40%CaO-CeO₂/HAP-650

562 **Fig. 4** CO₂-TPD analysis of catalysts: (a) 30%CaO-CeO₂/HAP-500; (b) 30%CaO-CeO₂/HAP-650;
563 (c) 30%CaO-CeO₂/HAP-800

564 **Fig. 5** XRD patterns of catalysts: (a) CaO-CeO₂-650; (b) calcined bone; (c) 20%CaO-CeO₂/HAP-
565 650; (d) 30%CaO-CeO₂/HAP -650; (e) 40%CaO-CeO₂/HAP-650

566 **Fig. 6** XRD patterns of catalysts: (a) 30%CaO-CeO₂/HAP-500; (b) 30%CaO-CeO₂/HAP-650; (c)
567 30%CaO-CeO₂/HAP-800

568 **Fig. 7** Effect of catalyst dosage on yield of FAME under fixed conditions as follows.
569 30%CaO-CeO₂/HAP-650: Methanol to oil molar ratio = 6:1, Reaction time = 3 h, Reaction
570 temperature = 65 °C; calcined bone: Methanol to oil molar ratio = 15:1, Reaction time = 5 h,
571 Reaction temperature = 65 °C

572 **Fig. 8** Effect of reaction time on yield of FAME under fixed conditions as follows.
573 30%CaO-CeO₂/HAP-650: Methanol to oil molar ratio = 6:1, Catalyst dosage = 9 wt.%, Reaction
574 temperature = 65 °C; calcined bone: Methanol to oil molar ratio = 15:1, Catalyst dosage = 20 wt.%,
575 Reaction temperature = 65 °C

576 **Fig. 9** Effect of methanol to oil molar ratio on yield of FAME under fixed conditions as follows.
577 30%CaO-CeO₂/HAP-650: Catalyst dosage = 11 wt.%, Reaction time = 4 h, Reaction temperature =
578 65 °C; HAP: Catalyst dosage = 20 wt.%, Reaction time = 5 h, Reaction temperature = 65 °C

579 **Fig. 10** The stability comparison between calcined bone and 30%CaO-CeO₂/HAP-650 catalysts

580 **Fig. 11** The leaching concentrations of calcium and cerium species

581 **Table 1** BET surface area, pore volume of catalysts

582 **Table 2** Chemical Compositions of various catalysts

583 **Table 3** Total basicity of various catalysts, expressed in $\mu\text{mol CO}_2/\text{g}$ desorbed

584 **Table 4** Methyl esters composition of the produced biodiesel

585 **Table 5** physicochemical properties of produced biodiesel