

Fatty acid methyl ester (FAME) production from soybean oil under ambient conditions using strontium loaded bovine bone



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ABSTRACT

Energy- and cost efficient processes are desirable for the large scale production of fatty acid methyl ester (FAME) for fuel applications. This work reports the utilization of Sr loaded bovine bone as effective and reusable catalyst for FAME production at low temperatures (30–65 °C), in high yields (>90%). Loading of Sr(NO₃)₂ into bovine bone (as a porous support) followed by calcination (500–1100 °C) affords a series of catalytically active materials. Material calcined at 750 °C (denoted as SrC750) gives optimum performance, with very high FAME yields (96.5%) after 1 h at 65 °C, and can be reused up to 10 times without yield decrease or need for regeneration. High yields of FAME (>93%) are also achieved at ambient temperature (30 °C) using SrC750, with products meeting ASTM 6751 and EN 14214 requirements suggesting their applicability as fuels in diesel engines.

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1. Introduction

Heterogeneous catalysis has enormous potential in production of fatty acid methyl ester (FAME), which constitutes the major chemical component of biodiesel fuels. Current homogenous processes utilize alkali metal hydroxides or mineral acids whose corrosive nature can result in equipment wear and the potential for toxic waste stream generation. Utilizing heterogeneous catalytic systems could therefore reduce process costs and environmental impact since the catalysts are easy to separate from the liquid fatty acid methyl ester (FAME) product, and are potentially reusable [1–3]. Heterogeneous base catalysts developed thus far for the transesterification of triglycerides to FAME include alkali earth oxides [2,4–6] and alkali, or alkaline earth oxides embedded in matrix material [5–9]. Several studies have reported that the

catalytic activity of metal oxides is related to the specific area [10,11] and the surface basicity of the material as quantified by Hammett indicators [6,12,13]. An investigation of the ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxides (CaO, SrO and BaO) found that the catalytic activity of the catalyst was strongly dependent on the Hammett basic strength (CaO < SrO < BaO) [6]. In addition, Liu and co-workers employed SrO (calcined SrCO₃ at 1200 °C for 5 h) as a solid base catalyst for the methanolysis of soybean oil, and >95% conversion was obtained at 65 °C in 30 min with a catalyst loading of 1.5% wt: a fact they claimed was attributed to the higher basicity of SrO compared to other homogeneous catalysts NaOH, KOH, NaOCH₃, and KOCH₃ [4]. In terms of reusability, SrO showed excellent catalytic activity over multiple cycles, with a slight decrease in FAME yields during each process being attributed to physical catalyst loss. Although SrO is highly active, its solubility in biodiesel (and thus as a contaminant) severely limits its industrial potential [14,15]. Therefore, supporting active metal (eg. Sr) oxides within a stable, insoluble but porous carrier may avoid this issue, while allowing for the dispersibility of the active species. Zinc oxide [16], magnesia [17,18], SiO₂ [5] and hydroxyapatite [19] have

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been used as catalyst support systems. Chen et al. found that incorporation of SrO into SiO₂ (SrO/SiO₂) results in its catalytic activity being maintained in FAME production from olive oil, with superior catalyst stability (less metal oxide leaching) compared to SrO alone [5]. Moreover, Wei and coworkers reported the use of synthetic hydroxyapatite loaded with Sr for conversion of soybean oil to FAME in high yield, with the porous structure of the hydroxyapatite supporting the active phase (Ca_xSr_{1-x}O), allowing for high catalyst activity [19]. However, preparation of this material required multiple steps and chemical processing which increases cost, and generates waste. Recently, Smith et al. reported a catalyst system derived from waste bovine bone, which requires only one calcination step to activate the raw material [20]. Very high FAME yields (97%) can be obtained from soybean oil, with the catalyst being reused for up to four cycles without the need for regeneration, or significant yield reduction. Calcium oxide (CaO) in the calcined bovine bone is believed to be the catalytically active phase however the basic strength (Hammett indicator, H₁₀–13) of the composite material is lower than that of CaO itself (H₁₅–18) [6,13]. This present study builds on the utility of bovine bone waste as a catalyst platform, focusing on improving its catalytic activity and usability profile through incorporation of higher activity metal centers (Sr) into the porous bone structure. Additionally, the effect of different calcination temperatures on the phase compositions, morphologies, surface properties, and catalytic activity of the material was investigated with the view to optimize the efficiency of this system for FAME production.

2. Experimental

2.1. Materials

Bovine bone in particulate form was purchased from Rung Ruang Co., Ltd. (Samutprakarn, Thailand). The obtained material was dried at 100 °C for 24 h prior to grinding and sieving into a smaller particle size (400 mesh) for use as support material. Strontium nitrate (AR grade) was purchased from Himedia, India, whereas magnesium silicate (Florisil® 100/200 mesh) was supplied from Supelco Inc., USA. Soybean oil (commercial edible grade, Morakot, Thailand), and methanol (reagent plus, Burdick & Jackson, Korea) were used as received.

2.2. Catalyst preparation

The catalyst was prepared using a modified version of a procedure for incorporation of Sr into hydroxyapatite [19]. Five grams of dried bovine bone was added to a 6 mmol/l aqueous Sr(NO₃)₂ solution, and the suspension rapidly stirred for 24 h at ambient temperature. Following this the solid was allowed to settle, and then was collected by filtration. After drying at 105 °C for 12 h the solid was calcined using a furnace (Lenton UAF 17/12) for 6 h in an atmosphere of air, at one of several different temperatures (550, 650, 750, 850, 950 or 1100 °C). A series of calcined samples was thus obtained (SrC550–SrC1100) whose codes correspond to each calcination temperature.

2.3. Catalyst characterization

Phase identification in the powdered samples was investigated using powder X-ray diffraction (PXRD) on a Bruker AXS model D8 Advance diffractometer (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$), operating at 40 mA and 40 kV with 2-theta range = 5°–60°, step = 0.075°, and scan step rate = 0.0375°/s. The crystalline phases for all samples were identified based on reference data obtained from the Joint Committee on Powder Diffraction Standards (JCPDS), and

Inorganic Crystal Structure Database (ICSD) databases. Catalyst morphology analyses were carried out using a scanning electron microscope (SEM; Philips: XL30&EDAX) with the samples being coated with gold prior to observation. The chemical composition of the bovine bone samples was analyzed using infrared spectroscopy (Perkin Elmer; PE 2000 FT-IR) with elemental analysis being carried out using flame atomic absorption spectroscopy (Perkin Elmer 3100). Brunauer–Emmett–Teller (BET) analysis (Quantachrome surface analyzer) was employed to determine the specific surface area of the samples. In addition, basicity of catalysts was quantified using the benzoic acid titration method as previously described [21].

2.4. Catalytic activity testing

The transesterification reaction of soybean oil with methanol was carried out to investigate the catalytic activity of strontium loaded bovine bone. The reaction procedure was performed at the equilibrium vapor pressure of the reaction mixture in a sealed thick-wall borosilicate glass tube under conditions utilized for calcined bovine bone (BV) [20] to allow direct activity comparisons of both materials to be made. An appropriate amount of methanol (6:1 methanol to oil molar ratio) and catalyst (8 wt % with respect to oil) was added to the tube. Subsequently, soybean oil was added, the tube was sealed and the mixture heated at 65 °C for 3 h while stirring at 500 rpm with a magnetic stirrer bar. After this time stirring was discontinued, the tube was cooled, opened and the phases allowed to separate. Quantification of FAME yields was determined by sampling the top layer and analysis using ¹H NMR spectroscopy (Bruker AVANCE 300; Chloroform-d reference) using a published protocol [22].

2.5. Catalyst reusability and chemical stability

The catalyst reusability was probed through investigation of a series of transesterification reactions at 65 °C and 30 °C, where the catalyst was reused after recovery from a previous batch process. A comparison of FAME yields from these provided an indication of the catalyst activity, stability and reusability. Firstly, on completion of a transesterification process using fresh catalyst, the liquid products were decanted away and the used catalyst was subjected to subsequent transesterification processes without any regeneration. In each subsequent process, fresh soybean oil and methanol were added in identical quantities as initially used, and the FAME yield was determined. For comparative purposes, the catalyst reusability for the transesterification reactions at 65 °C was examined for 1 h and 3 h to allow for more in-depth profiling of the catalytic process. Secondly, 3 h transesterification reactions were performed at ambient temperature (30 °C) and the spent catalyst was either reused, or regenerated prior to use in subsequent cycles. To regenerate the catalyst, the recovered (spent) catalyst was stirred with methanol at 65 °C for 1 h. After decantation of methanol from the reactor tube, the regenerated catalyst was subsequently utilized for a further transesterification process using fresh reagents.

The presence of active species (calcium and strontium) in both fresh and spent catalyst was examined using flame atomic absorption spectroscopy. To determine the solubility (catalyst leaching) of calcium and strontium in methanol, the catalyst (0.5 g) was heated in methanol (25 mL) at 65 °C for 3 h in the closed tube (as used in the transesterification reactions). After cooling and filtering, the methanol solution was diluted with water (50% v/v) prior to measuring the degree of leaching.

2.6. Biodiesel purification method

The transesterification reactions resulted in three phases being formed: excess methanol, FAME, and glycerol in increasing order of density. Decantation was used to remove glycerol, with methanol being distilled off on heating the liquid mixture at 70 °C for 1 h. Purification of the remaining crude FAME was conducted following established procedures, where magnesium silicate adsorbent was added into the FAME product to effectively remove residual glycerol, glycerides, methanol, free fatty acids, and metal ions [23,24]. For each batch, 2 wt % of adsorbent (with respect to the FAME weight) was suspended in, and stirred with, the crude FAME for 24 h. Subsequently, the mixture was filtered and the FAME stored in a sealed container prior to characterization of its physico-chemical properties using standard test protocols [25].

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns for Sr loaded bovine bone in uncalcined (SrBV), and calcined forms (SrC650, SrC750) are shown in Fig. 1a. From these patterns the uncalcined, and SrC650 samples mainly consist of crystalline calcium carbonate and poorly crystalline hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), and presumably $\text{Sr}(\text{NO}_3)_2$ which shows reflections at $2\theta = 33^\circ$ and 40° (masked by HAP). Calcination at higher temperatures ($\geq 750^\circ\text{C}$) resulted in enhanced HAP crystallinity, consistent with results previously reported [5], and complete decomposition of the $\text{Sr}(\text{NO}_3)_2$ phase as noted in previous studies [10,11,17]. However, the diffraction pattern of SrC650 is more complex, showing reflections from the presence of HAP, and possibly CaO and CaCO_3 . Wei and co-workers report evidence of a $\text{Ca}_x\text{Sr}_{1-x}\text{O}$ phase ($2\theta = 37^\circ$) on calcination of HAP loaded with high (>20% wt) levels of Sr^{2+} [19]. Comparisons of the PXRD pattern of SrC650 with ICSD simulated patterns for CaO, SrO, and CaSrO (not shown) indicate the absence of all of these apart from CaO, a phase believed responsible for the catalytic activity and which also appears at $2\theta = 37^\circ$. SrO, while reported to be the product of $\text{Sr}(\text{NO}_3)_2$ decomposition at 600 °C [17], was not observed in the PXRD pattern of SrC650. The Sr loading (7.95 ± 0.26 wt%), as determined by flame atomic absorption

spectroscopy, is higher than the detection limit for XRD measurements, suggestive of amorphous Sr containing compounds in this sample. Reflections for all crystalline Sr species described above were also absent at higher calcination temperatures (SrC750–SrC1100).

3.1.2. FT-IR spectra

Fourier transform infrared (FT-IR) spectra of all samples are shown in Fig. 1b, and these show a large degree of similarity to that of calcined bovine [20]. Uncalcined Sr loaded bone (SrBV) shows evidence of organic material (as indicated by C–H stretching bands at 2918 and 2850 cm^{-1}), and water (3430 cm^{-1}) which are largely removed on calcination. Other peaks at 1092, 1039, and sharp peaks at 602 and 566 cm^{-1} due to phosphate groups from HAP are evident in all samples. Adsorptions due to CO_3^{2-} species (1463, 1417 and 880 cm^{-1}) [26] are present in all samples up to a calcination temperature of 750 °C. However, the intensity of these relative to the phosphate peaks at 1092, 1039 cm^{-1} decreases as the calcination temperature is raised (SrC650 \rightarrow SrC750), such that they are almost entirely absent at 1100 °C (SrC1100) which correlates with the thermal decomposition of CaCO_3 [27]. In addition to the OH peak of HAP at 3574 cm^{-1} , a peak at 3650 cm^{-1} attributed to $\text{Ca}(\text{OH})_2$ [28,29] was observed in samples calcined above 650 °C. This is in contrast with the findings of Wei et al., who ascribe this frequency to the substitution of Sr^{2+} for Ca^{2+} sites in HAP at high Sr^{2+} loadings (>20% wt) [19]. However, due to the absence of PXRD evidence for a $\text{Ca}_x\text{Sr}_{1-x}\text{O}$ phase and the low Sr loading (ca. 7% wt.) it is unlikely that this peak is related to extensive Sr substitution in the calcined bone. In addition, the FT-IR spectrum of reused catalyst shows characteristic peaks assigned to hydrocarbon compounds, as expected from the catalyst surface being coated by organic material (products and by-products) from the reaction.

3.1.3. Catalyst morphology and surface properties

SEM images of BV samples are shown in Fig. 2. Whereas uncalcined Sr-loaded BV (Fig. 3a), and material calcined at 550 °C (SrC550) have irregular granular structures, higher temperatures result in further morphological changes including the generation of plate-like (SrC650), and regular prismatic crystallites (SrC750–SrC1100). The uniform crystallinity of SrC750–SrC1100 can be attributed to the crystalline HAP framework, as present in their diffraction patterns (Fig. 1a). Calcination temperatures higher than

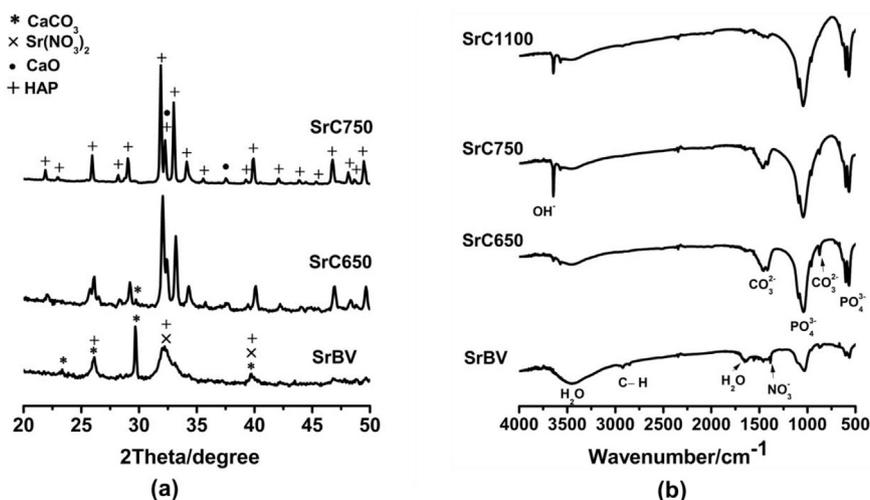


Fig. 1. (a) Powder XRD patterns of Sr loaded waste bovine bone derived catalysts obtained through calcination at different temperatures and (b) FT-IR spectra of SrBV and calcined samples at different temperatures.

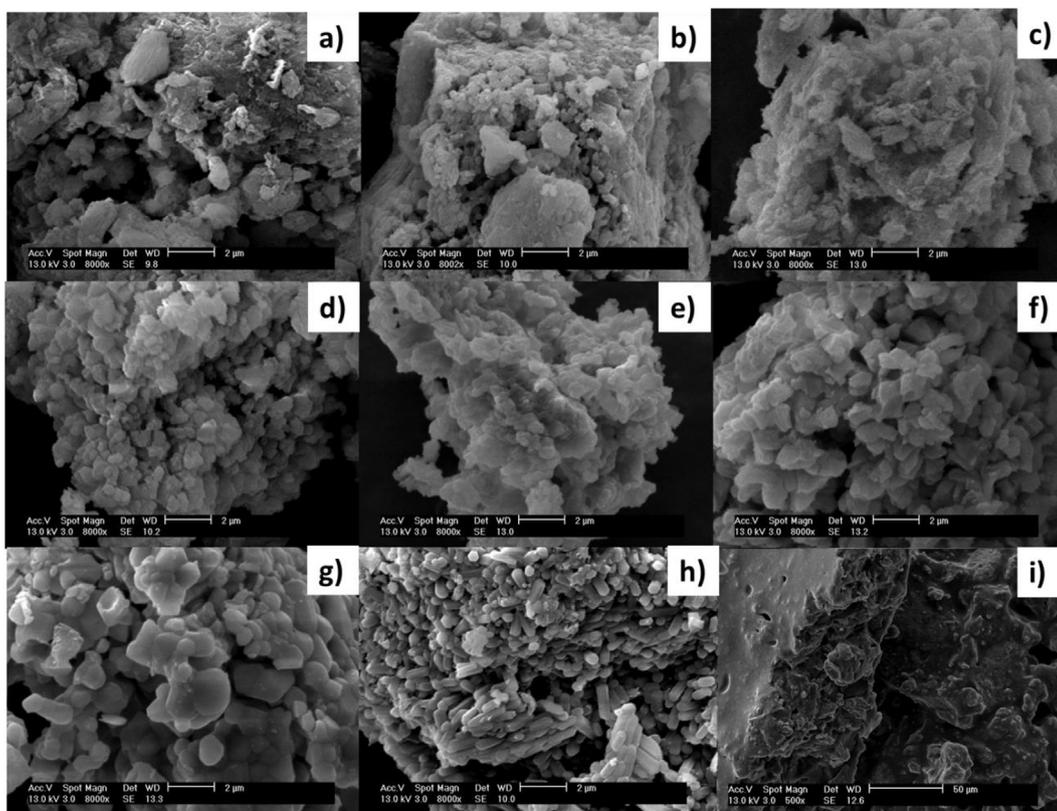


Fig. 2. SEM images of BV catalyst materials: a) SrBV; b) SrC550, c) SrC650, d) SrC750, e) SrC850, f) SrC950, g) SrC1100, h) calcined BV (unloaded), i) spent (reused) SrC750.

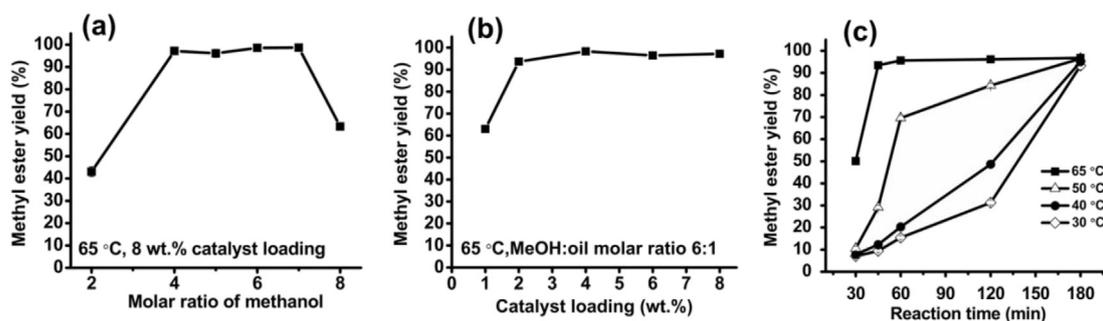


Fig. 3. FAME yields (%) from transesterification reactions of soybean oil and methanol catalyzed by SrC750. Effects of: (a) methanol/oil molar ratio; (b) catalyst loading; and (c) reaction time and temperature variations.

950 °C result in surface smoothing, and aggregation of the crystallites to resemble globular formations in excess of 2 μm in size (SrC1100, Fig. 2g). The morphology of calcined sample depends on calcination temperatures. As shown in Fig. 2d, SrC750 is comprised of non-uniform globular aggregates, whereas calcined BV at 750 °C is composed of uniform rod-like particles (Fig. 2h).

The surface properties (Table 1) mirror the morphologies of the samples as obtained by SEM imaging. SrC650 has the largest surface area, and is the most porous of the BV materials on the basis of pore volume and average pore diameter. As the calcination temperature is increased, these parameters steadily decrease indicating a reduction in surface porosity. This is most noticeable in SrC1100 which shows appreciable surface smoothing and particle aggregation (Fig. 2g), in comparison with other samples.

3.2. Catalytic activity

3.2.1. Activity screening

Screening tests were performed to probe the catalytic activity of SrC650–SrC1100 and the obtained results are shown in Table 1. For comparison, both uncalcined and calcined catalysts were employed to catalyze FAME production, with process parameters as employed in a previous report (65 °C, 3 h, 8 wt.% catalyst loading with respect to oil weight, methanol to oil molar ratio of 6:1) [20]. The results indicate that uncalcined, and samples calcined at lower temperatures (550–650 °C) are not ideal catalysts for FAME production (<90% conversion). The poor catalytic activity of these samples is attributable to their composition: CaCO₃ and Sr(NO₃)₂ are not active catalysts for FAME production [13]. The calcination temperature of 650 °C and below are too low for effective conversion of

Table 1
Surface properties of catalyst samples, and FAME yields (%) obtained from transesterification of soybean oil and methanol. All reactions utilized catalyst loading of 8% wt. and methanol to oil molar ratio of 6:1. ^a Smith et al. [20]. ND = not determined.

Sample	Surface area (m ² /g)	Total pore volume (cc/g)	Average pore diameter (Å)	FAME yield (%)			
				After 3 h reaction			
				Rx temp.30 °C	Rx temp.40 °C	Rx temp.50 °C	Rx temp.65 °C
SrBV	ND	ND	ND	ND	ND	0	0
SrC550	ND	ND	ND	ND	ND	0	0
SrC650	9.49	0.1063	448.2	ND	76.81 ± 1.05	82.02 ± 1.93	86.26 ± 0.57
SrC750	4.80	0.0188	157.3	93.32 ± 1.74	95.06 ± 0.39	96.53 ± 1.56	98.55 ± 1.26
SrC850	3.48	0.0124	142.8	87.72 ± 1.02	94.69 ± 1.28	97.61 ± 3.06	96.81 ± 1.43
SrC950	3.92	0.0127	130.2	82.34 ± 2.24	97.14 ± 0.96	94.56 ± 2.50	96.60 ± 3.55
SrC1100	2.62	0.0059	90.2	ND	ND	65.59 ± 1.52	77.84 ± 5.26
Calcined BV (at 750 °C) ^a	3.06	0.0017	153.1	ND	ND	84.0 ± 4.3	97.3 ± 2.1

CaCO₃ and Sr(NO₃)₂ to oxide (CaO, SrO) active sites [20,27]. From these results, samples calcined at 750–950 °C gave highest FAME yields (>95%) due to the presence of greater numbers of active sites whereas calcination at 1100 °C resulted in lower yields, arising from low porosity related to surface smoothing and aggregation (Fig. 2g).

The FAME yields obtained at 65 °C, in Table 1, suggest that both bovine bone and Sr loaded bone samples require calcination at 750 °C (at the lowest) to be catalytically active. As previously reported [20], calcined bovine bone gave very low FAME yields from transesterification reactions at temperatures lower than 65 °C. Therefore, employing SrC750–SrC950 catalysts in transesterification reactions at lower reaction temperatures would benefit probing the advantages of Sr loading. The tests showed no difference in FAME yields at reaction temperatures of 40 °C and 30 °C. By further decreasing the temperature to 30 °C, variations in the catalytic activity of SrC750–SrC950 could then be observed. As indicated in Table 1, SrC750 gave the highest catalytic activity (>93%) of these systems at 30 °C, with FAME yields increasing with temperature (except in the case of SrC950, which proved more variable possibly due to the decrease in pore size and pore volume). As lower operating temperatures would result in significant economic benefits to industry, SrC750 was chosen as the most promising candidate for FAME production and was used in subsequent experiments to map out optimum reaction parameters.

3.2.2. Influence of reaction parameters on FAME yield

Parameters potentially impacting the production of FAME from soybean oil include the methanol to oil molar ratio, catalyst loading, reaction temperature and reaction time. The impact of the molar ratio of methanol to oil on the FAME process catalyzed by SrC750 (65 °C, 3 h) is shown in Fig. 3a. Increasing the methanol to oil molar ratio from 2:1 to 4:1 resulted in a marked increase in FAME yield, although the rate of increase tapers off as the ratio is increased further (4:1 to 7:1). However, higher ratios (e.g. 8:1) were found to negatively influence the FAME yield. Previous studies have suggested that this phenomenon could possibly be attributed to insufficient mixing of reactants and products with the solid catalyst, as well as the decrease in catalyst concentration [30]. Quantification of the optimum catalyst loading level is important for determining the efficiency of a catalytic process. Accordingly, various catalyst loading levels (1.0 wt % to 8.0 wt % with respect to oil) were utilized in this study. The reaction profile shown in Fig. 3b indicates that oil to FAME conversion increases markedly in when increasing catalyst loading from 1.0 wt% to 2.0 wt%, but remains almost constant at higher values. Based on these results, the calcined Sr loaded bovine bone has higher catalytic activity than calcined bovine bone, which requires 8 wt % loading to achieve >90% FAME yields under the same conditions [20]. High FAME yields (>90%), are obtainable at low loadings (2.0 wt%) of SrC750

and at lower methanol to oil ratios (4:1) than are required for calcined BV reactions (6:1) under the same conditions. These results indicate the advantages of Sr loading.

The influence of reaction time, and temperature on FAME yield are shown in Fig. 3c. High FAME yields (>93%) were obtained after only 45 min at 65 °C, with reactions being substantially slower at lower reaction temperatures. However, high FAME yield can be achieved at temperatures of 30–50 °C, with sufficient reaction time (3 h). These findings highlight the superior performance profile of SrC750 over calcined BV, and several other Sr loaded materials. Calcined BV provides FAME yields of only 65% after 1 h at 65 °C, and 97.3% after 3 h at this temperature [20]. The system employed by Wei and co-workers (synthetic Sr loaded hydroxyapatite) affords 85% yield of FAME after 5 h at 70 °C [19]. Additionally, Yang et al. utilized Sr loaded ZnO to give high (94.7%) yields of FAME at 65 °C after 5 h [16]; significantly longer than the time taken to obtain comparable yields using SrC750 (1 h). Moreover, it is interesting to note that SrC750 gave high FAME yields (93.32%) under ambient conditions (30 °C) after 3 h, as compared to Sr loaded MgO which provided only 65% FAME at 32 °C after 3 h [17]. The catalytic activity of BV systems correlates with basicity, which increases from 0.14 mmol/g in calcined BV to 0.44 mmol/g in SrC750, highlighting the influence of even low loadings of Sr incorporation within the porous matrix.

3.3. Catalyst reusability

Reusability is a necessary property of heterogeneous catalysts used in industrial applications. Probing the lifetime and chemical stability of the Sr-loaded BV catalyst is a crucial step in assessing its practicality towards large scale FAME production. The catalyst from a FAME batch process was employed in a series of subsequent processes under identical conditions, without prior purification or regeneration. Using the same reaction conditions (65 °C, 3 h) as employed previously for calcined BV [20], SrC750 maintained its activity over a longer lifetime (6 processes) and was more active (>90%) than calcined BV which provides high activity over only four successive processes. Catalyst reusability becomes more favorable for shorter processing times: SrC750 catalyzes the formation of FAME in high yields (>90%) in 1 h at 65 °C for up to 10 successive processes before any significant decrease in activity is observed (Fig. 4a). Activity loss after this point is likely to be due to accumulation of reactants and products in the active sites, as indicated by the change in morphology of spent SrC750 (Fig. 2i).

As the solubility of SrC750 in methanol (measured using flame atomic absorption spectroscopy) is very low (0.00093% for Ca, 0.00002% for Sr), this would indicate that leaching is not a factor in catalyst activity loss over time. However, longer reaction times (3 h) also resulted in a shortened reusability profile for SrC750, with

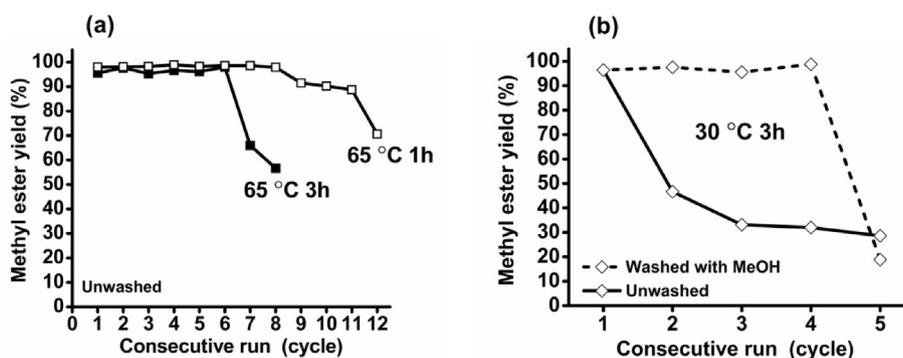


Fig. 4. FAME yields (%) obtained from successive processes catalyzed by reused SrC750 (reaction conditions: methanol/oil molar ratio 6:1, catalyst loading 8 wt%); (a) reused at 65 °C and (b) reused at 30 °C for 3 h.

Table 2

Physico-chemical properties of synthesized biodiesel from soybean oil (at 65 °C after 3 h catalyst loading of 8% wt. and methanol to oil molar ratio of 6:1) compared with standard ranges (^aas quantified by GC).

Property	ASTM D-6751	EN 14214	Synthesized FAME
^a Ester content (%)	>96.5	>96.5	99.17
Kinematic viscosity (mm ² /s, 40 °C)	1.9–6.0	3.5–5.0	4.64
Flash point (°C)	>130.0	>120.0	156.0
Cloud point (°C)	–	–	3.3
Pour point (°C)	–	–	–4.0

catalytic activity decreasing rapidly after the 6th successive run. This may be due to accumulation of reactants and products on catalyst surface. As discussed earlier, SrC750 is highly active even at 30 °C. From a practical perspective it is interesting to examine whether the catalyst can be reused at such low temperatures. From the results in Fig. 4b, although the transesterification reaction can be carried out at ambient temperature (30 °C) giving very high FAME yields (93.32%) in the first cycle, the conversion declined sharply in the second reaction run (<50%). However, it proved possible to regenerate spent SrC750 by washing with methanol to remove absorbed glycerol molecules from the catalyst surface [31]. As seen in Fig. 4b, the regenerated catalyst can be reused up to 4 times while maintaining high FAME yields (>90%).

3.4. Properties of FAME

The properties of synthesized FAME are reported in Table 2. Comparison of these with industry specifications for FAME used in biodiesel applications (ASTM and EN) indicate that SrC750 catalyzed processes have the potential to be utilized for the production of fuel quality FAME.

4. Conclusion

Strontium loaded bovine bone calcined at 750 °C (SrC750) is highly active for FAME production. This report emphasizes the advantages of naturally available hydroxyapatite in waste bone over synthetic hydroxyapatite: bovine bone is cheap and abundant, and its porosity renders it an attractive support for incorporation of Sr ions into the bone matrix. Sr loading is facile, with the catalytic system obtained being reusable over multiple passes. Current investigations are underway into developing immobilized forms of SrC750 for application in process scale-up.

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References

- [1] M. Agarwal, G. Chauhan, S.P. Chaurasia, K. Singh, Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production, *J. Taiwan Inst. Chem. Eng.* 43 (2012) 89–94.
- [2] X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, *Fuel* 87 (2008) 216–221.
- [3] H.-J. Kim, B.-S. Kang, M.-J. Kim, Y.M. Park, D.-K. Kim, J.S. Lee, K.-Y. Lee, Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst, *Catal. Today* 93–95 (2004) 315–320.
- [4] X. Liu, H. He, X. Wang, S. Zhu, Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst, *Catal. Commun.* 8 (2007) 1107–1111.
- [5] C.-L. Chen, C.-C. Huang, D.-T. Tran, J.-S. Chang, Biodiesel synthesis via heterogeneous catalysis using modified strontium oxides as the catalysts, *Bioresour. Technol.* 113 (2012) 8–13.
- [6] H. Mootabadi, B. Salamatina, S. Bhatia, A.Z. Abdullah, Ultrasonic-assisted biodiesel production from palm oil using alkaline earth metal oxides as the heterogeneous catalysts, *Fuel* 89 (2010) 1818–1825.
- [7] S. Benjapornkulapong, C. Ngamcharussrivichai, K. Bunyakiat, Al₂O₃-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil, *Chem. Eng. J.* 145 (2009) 468–474.
- [8] M.C.G. Albuquerque, I. Jiménez-Urbistondo, J. Santamaría-González, J.M. Mérida-Robles, R. Moreno-Tost, E. Rodríguez-Castellón, A. Jiménez-López, D.C.S. Azevedo, C.L. Cavalcante Jr., P. Maireles-Torres, CaO supported on mesoporous silicas as basic catalysts for transesterification reactions, *Appl. Catal. A-Gen.* 334 (2008) 35–43.
- [9] S. Yan, H. Lu, B. Liang, Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production, *Energy Fuels* 22 (2008) 646–651.
- [10] C. Reddy, V. Reddy, R. Oshel, J.G. Verkade, Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides, *Energy Fuels* 20 (2006) 1310–1314.
- [11] D.E. López, J.G. Goodwin Jr., D.A. Bruce, E. Lotero, Transesterification of triacetin with methanol on solid acid and base catalysts, *Appl. Catal. A-Gen* 295 (2005) 97–105.
- [12] X. Li, G. Lu, Y. Guo, Y. Guo, Y. Wang, Z. Zhang, X. Liu, Y. Wang, A novel solid superbase of Eu₂O₃/Al₂O₃ and its catalytic performance for the transesterification of soybean oil to biodiesel, *Catal. Commun.* 8 (2007) 1969–1972.
- [13] M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, J. Hidaka, Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production, *Fuel* 87 (2008) 2798–2806.

- [14] S.J. Yoo, H. Lee, B. Veriansyah, J. Kim, J.-D. Kim, Y.-W. Lee, Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts, *Bioresour. Technol.* 101 (2010) 8686–8689.
- [15] E. Rashtizadeh, F. Farzaneh, Transesterification of soybean oil catalyzed by Sr-Ti mixed oxides nanocomposite, *J. Taiwan Inst. Chem. Eng.* 44 (2013) 917–923.
- [16] Z. Yang, W. Xie, Soybean oil transesterification over zinc oxide modified with alkali earth metals, *Fuel Process. Technol.* 88 (2007) 631–638.
- [17] J. Tantirungrotechai, S. Thepwatee, B. Yoosuk, Biodiesel synthesis over Sr/MgO solid base catalyst, *Fuel* 106 (2013) 279–284.
- [18] B. Yoosuk, P. Krasae, B. Puttasawat, P. Udomsap, N. Viriya-empikul, K. Faungnawakij, Magnesia modified with strontium as a solid base catalyst for transesterification of palm olein, *Chem. Eng. J.* 162 (2010) 58–66.
- [19] C. Wei, H. Zhiliang, L. Yu, H. Qianjun, Preparation and characterization of a novel solid base catalyst hydroxyapatite loaded with strontium, *Catal. Commun.* 9 (2008) 516–521.
- [20] S.M. Smith, C. Oopathum, V. Weeramongkhonlert, C.B. Smith, S. Chaveanghong, P. Ketwong, S. Boonyuen, Transesterification of soybean oil using bovine bone waste as new catalyst, *Bioresour. Technol.* 143 (2013) 686–690.
- [21] R. Rahul, J.K. Satyarthi, D. Srinivas, Lanthanum and zinc incorporated hydroxalates as solid base catalysts for biodiesel and biolubricants production, *Indian J. Chem. Sect. A* 50A (2011) 1017–1025.
- [22] G. Gelbard, O. Brès, R.M. Vargas, F. Vielfaure, U.F. Schuchardt, ^1H Nuclear magnetic resonance determination of the yield of the transesterification of rapeseed oil with methanol, *J. Am. Oil Chem. Soc.* 72 (1995) 1239–1241.
- [23] C.S. Faccini, M.E. Cunha, M.S.A. Moraes, L.C. Krause, M.C. Manique, M.R.A. Rodrigues, E.V. Benvenuti, E.S. Caramão, Dry washing in biodiesel purification: a comparative study of adsorbents, *J. Braz. Chem. Soc.* 2 (2011) 558–563.
- [24] M.C. Manique, C.S. Faccini, B. Onorevoli, E.V. Benvenuti, E.S. Caramão, Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil, *Fuel* 92 (2012) 56–61.
- [25] M. Canakci, H. Sanli, Biodiesel production from various feedstocks and their effects on the fuel properties, *J. Ind. Microbiol. Biotechnol.* 35 (2008) 431–441.
- [26] G. Xu, I.A. Aksay, J.T. Groves, Continuous crystalline carbonate apatite thin films. A biomimetic approach, *J. Am. Chem. Soc.* 123 (2001) 2196–2203.
- [27] I. Halikia, L. Zoumpoulakis, E. Christodoulou, D. Prattis, Kinetic study of the thermal decomposition of calcium carbonate by isothermal methods of analysis, *Eur. J. Min. Proc. Environ. Prot.* 1 (2001) 89–102.
- [28] A.M. Kalinkin, E.V. Kalinkina, O.A. Zalkind, T.I. Makarova, Chemical interaction of calcium oxide and calcium hydroxide with CO_2 during mechanical activation, *Inorg. Mater.* 41 (2005) 1071–1079.
- [29] B.O. Fowler, Infrared studies of apatites. II. Preparation of normal and isotopically substituted calcium, strontium and barium hydroxyapatites and spectra-structure-composition correlations, *Inorg. Chem.* 13 (1974) 207–214.
- [30] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, *J. Am. Oil Chem. Soc.* 61 (1984) 1638–1643.
- [31] W. Xie, T. Wang, Biodiesel production from soybean oil transesterification using tin oxide-supported WO_3 catalysts, *Fuel Process. Technol.* 109 (2013) 150–155.