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Development of Sr/Cao catalyst derived from cuttlebone (*Sepia officinalis)* for biodiesel production

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Abstract

Cuttlebone (*Sepia officinalis)* was used as a source of calcium oxide for biodiesel catalyst. The objective of this work is to present the bio-based catalyst prepared from cuttlebone. 1, 3, 5 and 10 %wt of strontium was loaded into calcium oxide powder derived from cuttlebone. Structural properties of Sr/CaO catalyst were evaluated by Fourier transform infrared and X-ray diffraction, respectively. There is no change on morphological properties of catalyst between Sr/CaO and pristine CaO. The homogeneous distribution of strontium was confirmed by EDX mapping technique. The specific surface area of powder was estimated to be 10-30 $m^2 \cdot g^{-1}$. The thermal stability of catalyst was stable up to 300°C. Preliminary investigation of catalyst for biodiesel was conducted by transesterification from commercial palm olein and methanol. The research work was successfully supported on bio-based economy project.

1. Introduction

Due to exponential growth of worldwide population, transportation and industrial development, the energy consumption has been rapidly increased [1]. Utilization of energy was therefore considered as one of the most important aspects for industrial development. Numerous researches from both academic and industrial sectors have been therefore investigated on the feasibility of energy source such as conventional fossil energy, electrical energy, solar energy as well as wind energy. It was remarkable to note that although conventional fossil energy and its derivatives were considered as the most important source of energy research, the high quantity of consumption of fossil energy may face the depletion of petroleum based resource. In addition, fossil energy consumption may result in excessive emission of toxic gas and other pollutants. The concern of environmental issue, ecological system and human health was therefore in crisis.

Recently, biodiesel was considered as one of the most effective alternative energy source. It was renewable and sustainable as well as biodegradable [2]. Moreover, biodiesel production was safe for environment, non-toxicity and discharging of low level of greenhouse gas [3]. Utilization of biodiesel has been pushed to be considered in order to replace traditional fossil energy. From the viewpoint of synthesis, biodiesel can be produced by transesterification of oils and fats as suggested by Boonyuen *et al.* [4]. Several biomasses from natural occurring resource such as palm oil, jojoba seed oil, soybean oil and olive oil were investigated as a source of biodiesel production [5-8]. It was notable that utilization of natural oil for biodiesel production can be encouraged on the use of biomass for valued-added agricultural purpose. In addition, utilization of raw material for biodiesel production can be also extent to microbial oil and waste cooking oil, suggested by Ma *et al.* [9] and Rabie *et al.* [10], respectively. The production can be successfully occurred by using both homogeneous and heterogeneous catalyst. In industry, to use heterogeneous catalyst for biodiesel production was preferable due to easy separation from product. This was consequently allowed for reusable concept [11,12]. Numerous types of heterogeneous catalyst were therefore developed for biodiesel production such as ZnO, Al_2O_3 and ZrO_2, respectively [13-15]. In order to support on the policy of bio-economy; which involved on the use of bio-based chemical; bio-based waste from municipal area has been prepared as a source of heterogeneous catalyst. Eggshell waste was therefore modified for being as heterogeneous catalyst by several research groups [16-20]. CaO derived from eggshell waste was considered as renewable resource with high yield of synthesis, large surface area and environmental stability. This concept can be extent to the use of mollusk shell such as snail shell and oyster shell, respectively [21].

To support bioeconomy, cuttlebone (*Sepia officinalis)* was considered as one of the most effective sources for CaO production. The structure was considered as orthorhombic aragonite, a less-stable polymorphic modification of calcium carbonate as suggested by Cadez *et al.* [22]. It was remarkable to

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note that cuttlebone has outstanding properties of ultra-lightweight, high stiffness and high permeability reported by Cadman *et al.* [23]. The application of cuttlebone was related to adsorbent material and heterogeneous catalyst [24,25]. It was also considered as reinforcing filler in natural rubber and polyurethane as reported by Poompradub *et al.* [26] and Shang *et al.* [27], respectively. With sustainable development concept, to use cuttlebone as a platform for CaO production in heterogeneous catalyst was therefore challenge.

Therefore, the objective of this research work is to develop heterogeneous catalyst from cuttlebone. CaO derived from cuttlebone, its substitution by strontium ion was prepared. To evaluate the potential as heterogeneous catalyst, yield of fatty acid methyl ester (FAME) as biodiesel product was investigated.

2. Experimental

2.1 Chemical reagents

Cuttlebone was collected from local beach in Rayong province, Thailand. Strontium nitrate chloride was purchased from Sigma Aldrich, co. Ltd. Commercial grade of palm olein was purchased from local supermarket in Thailand. Sodium carbonate and methanol were purchased from Sigma Aldrich, co. Ltd and Merck, co. Ltd, respectively. These chemical reagents were used as received without any further purification.

2.2 Methods

2.2.1 Heterogeneous catalyst preparation

Cuttlebone was washed several times with 10 %wt/v of NaOH solution. Then, it was washed with DI water until neutral pH. After that, it was milled and sieved with 120 mesh. The cuttlebone powder was then dissolved into 0.5 M of HNO_3. During reaction, 1, 3, 5 and 10 wt% of $Sr(NO_3)_2$ was poured into the mixture. The reaction was stirred for 2 h at room temperature. Then, Na_2Co_3 was dropped into the mixure. All powders were calcined at 1000°C for 5 h. The powders were stored in desiccator in order to prevent the moisture adsorption.

2.2.2 Transesterification

To determine the ability of catalyst for biodiesel, the synthesis of fatty acid methyl esters (FAME) from palm olein and methanol was conducted in a 100 ml of round bottom flask equipped with a cooled water condenser, mechanical stirrer and hot plate. The molar ratio of methanol and palm olein was set to 9:1. Only 5 wt% of catalyst was poured. The reaction was conducted at 60°C for 3 h. After reaction, the catalyst was separated from mixture by filtration and excess methanol was evaporated by using rotary evaporator. The yield was analyzed by ^{1}H-NMR spectroscopy by means of TMS standard; comparing the ratio peaks of the methoxy protons and the methylene protons. The level of conversion of oil to FAME was calculated using % conversion = $2/3\times(A\ CH_3/B\ CH_2)\times100\%$ where A CH_3 was the integration value of the methoxy protons in the fatty acid methyl esters (FAME) at a chemical shift of 3.68 ppm (singlet peak) and B CH_2 is the integration value of the methylene protons of the triglycerides at a chemical shift of 2.3 ppm (triplet peak). The factors 2 and 3 are derived from the number of attached protons at the methylene and methoxy carbons, respectively. Additional information on this analysis was presented in our previous literature [4].

2.3 Instruments

The surface morphology was determined using a scanning electron microscope (JEOL JSM-7800). Samples were prepared by placement on a stub, which was coated with a thin layer of gold using a JEOL JFC-1100E sputtering device. Investigation on existence of strontium atom was performed by mapping technique and elemental analysis. The specific surface area (BET) of sample was measured using a surface area analyzer (Autosorb 1c, Quantachrome) based on the BET (Brunauer-Emmett-Teller) principle with nitrogen adsorption isotherm at 77 K. The crystal structure of the sample was investigated by X-ray diffraction (XRD, Phillips P.W. 1830 diffractometer), which was employed using nickel-filtered CuKa radiation. The diffraction patterns were recorded over a range from 20° to 80°. The chemical structure was determined using a Fourier transform infrared (FT-IR) spectrophotometer (SPECTRUM ONE, Perkin Elmer). Samples were scanned from 400-4000 cm^{-1} at room temperature at a resolution of 4 cm^{-1}. ^{1}H-NMR spectrum was recorded by a Bruker Ascend TM600 spectrometer operating at 600 MHz using d6-CDCI3 as a solvent. Thermal stability was evaluated using thermogravimetric analysis (209 F3 Tarsus, NETZSCH). Samples were heated from room temperature to 1000°C at a rate of 10°C·min^{-1} under a nitrogen atmosphere.

3. Results and discussion

CaO was successfully prepared from cuttlebone. The powder exhibited the white-color find form. It should be stored in desiccator in order to fine form moisture absorption. Figure 1 presents FTIR spectra of strontium substituted into calcium oxide and the pristine. With the existence of strontium, the wide bands underwent more broadening. It may imply that strontium substituted into calcium oxide provided the structural disorder of calcium oxide, as suggested by Pal *et al.* [28]. The characteristic peak at wavenumber 3642 cm^{-1} and 1200 cm^{-1} was associated with OH stretching. This was due to physisorbed moisture molecule on the surface of powder [29]. The characteristic peaks at wavenumber 1474 cm^{-1} and 713 cm^{-1} were attributed to Ca-O stretching mode of calcium carbonate. These peaks were related to stretching and bending, depending on environment. This discussion was in agreement with previous article reported by Nurhayati *et al.* [30]. The IR spectrum of the strontium modified calcium oxide at wavenumber 523 cm^{-1} was corresponded to the stretching mode of Sr-O. This technique can be employed to imply that calcium oxide was formed after calcination process.

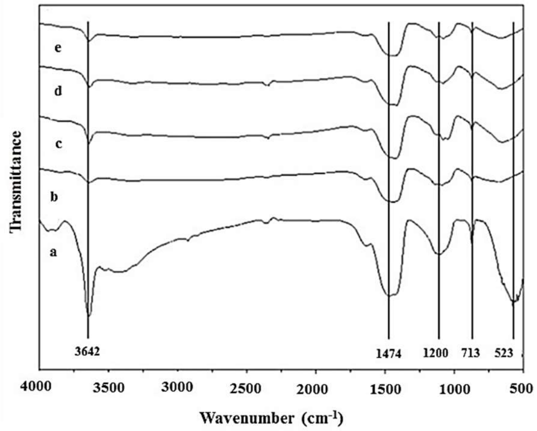

Figure 1. FTIR spectra of (a) CaO derived from cuttlebone, (b) 1% Sr/CaO, (c) 3%Sr/CaO, (d) 5% Sr/CaO, and (e) 10% Sr/CaO.

Figure 2 presents the XRD pattern of strontium substituted calcium oxide powder. The pattern of pristine calcium oxide was provided for comparison. This technique can be used to imply that calcium carbonate from cuttlebone was altered to calcium oxide during calcination step. It was remarkable to note that 1, 3, 5 and 10 %wt of strontium ions were completely substituted into calcium oxide lattice. No significant peak of strontium was observed similar to previous literature reported by Li *et al.* [31]. The characteristic peaks at $2\theta = 32°, 37°, 54°, 64°$ and $68°$ were presented. These characteristic peaks were corresponded (hkl) value (111), (200), (202), (311) and (222), respectively. The XRD spectra of both strontium-substituted into calcium oxide and the pristine were matched with JCPDS card 77-9574. Moreover, the preferential orientation was determined using a texture coefficient (hkl). This result illustrates that the strong peak from XRD pattern was in the (200) plane for the sample, which indicates that the crystal orientation was uniform in the x and z directions. The crystal size of both strontium-substituted calcium oxide and the pristine were estimated by the Scherrer formula $D = K\lambda/\beta\cos\theta$, where D is crystallite size, K is 0.9, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction peak. The statistical average and standard deviation were reported to be 80 nm and 7 nm, respectively.

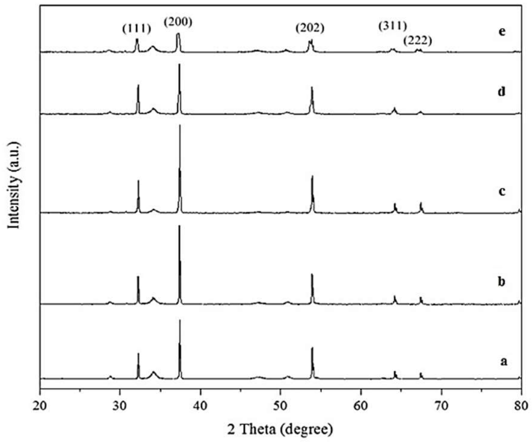

Figure 2. XRD pattern of (a) CaO derived from cuttlebone, (b) 1% Sr/CaO, (c) 3% Sr/CaO, (d) 5% Sr/CaO, and (e) 10% Sr/CaO.

Figure 3 exhibits the morphological properties of strontium substituted calcium oxide and the pristine powder. The particle size range was estimated to be 100-500 nm with non-uniform distribution. No significant between strontium substituted calcium oxide and the pristine can be observed in term of morphological properties. The particle became agglomeration. This was due to the effect of calcination temperature. It can be explained that with high calcination of temperature, calcium carbonate from cuttlebone was changed to calcium oxide powder. CO_2 was then evaporated. The porosity can be observed according to CO_2 gas pathway removal. This discussion was strongly associated with previous article reported by Badnore *et al.* [32].

In addition, Table 1 presents the elemental analysis by EDX. The existence and amount of strontium can be observed. The amount of strontium atom was in the similar trend. The amount of strontium atom was slightly less than preparation step. This was due to lost during preparation step and the area of investigation. However, there is no significant change in the amount of calcium and oxygen atom. During experiment, small amount of carbon atom may also be observed due to incomplete calcination process. The char and residual were then observed.

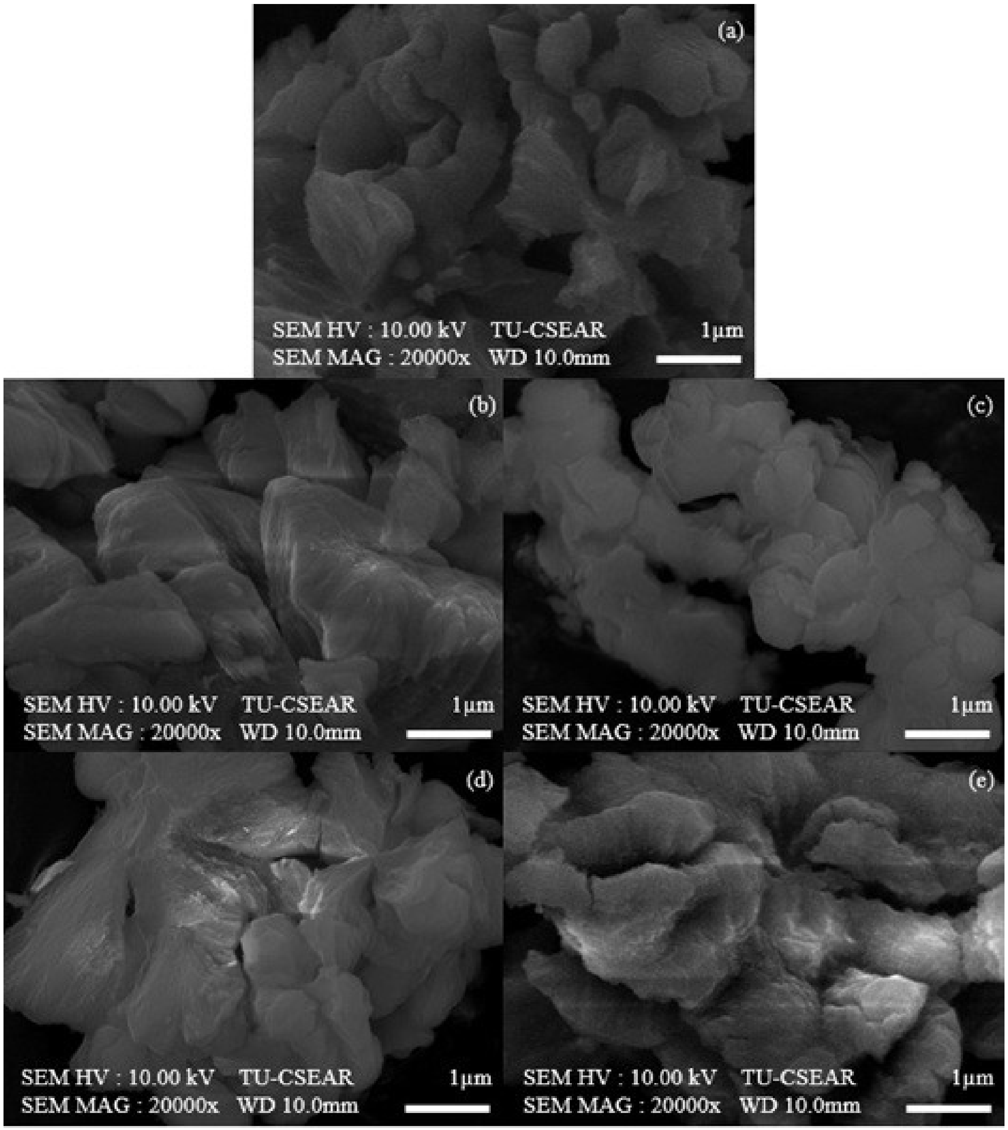

Figure 3. Morphological properties of (a) CaO derived from cuttlebone, (b) 1% Sr/CaO, (c) 3% Sr/CaO, (d) 5% Sr/CaO, and (e) 10% Sr/CaO.

Figure 4 presents mapping experiment of the existence of strontium substituted into calcium oxide powder. The left side and right side were presented morphological properties observed by SEM and the position of strontium atom, respectively. The green color was used to present the existence of strontium substituted into calcium oxide powder. It was remarkable to note that with high amount of strontium, the intensity of green color was subsequently higher, as suggested by Srasri *et al.* [33]. In addition, this technique can be implied the distribution of strontium atom on the surface of calcium oxide powder. Strontium was well distributed on the surface of calcium oxide powder, while the porosity of powder was therefore observed.

Table 1. EDX analysis of CaO derived from cuttlebone, 1% Sr/CaO, 3% Sr/CaO, 5% Sr/CaO, and 10% Sr/CaO.

Catalyst	Calcium (wt%)	Oxygen (wt%)	Strontium (wt%)
CaO	47.00	53.00	-
1% Sr/CaO	42.08	57.39	0.53
3% Sr/CaO	40.48	57.86	1.66
5% Sr/CaO	41.54	55.88	2.58
10% Sr/CaO	35.83	53.06	11.10

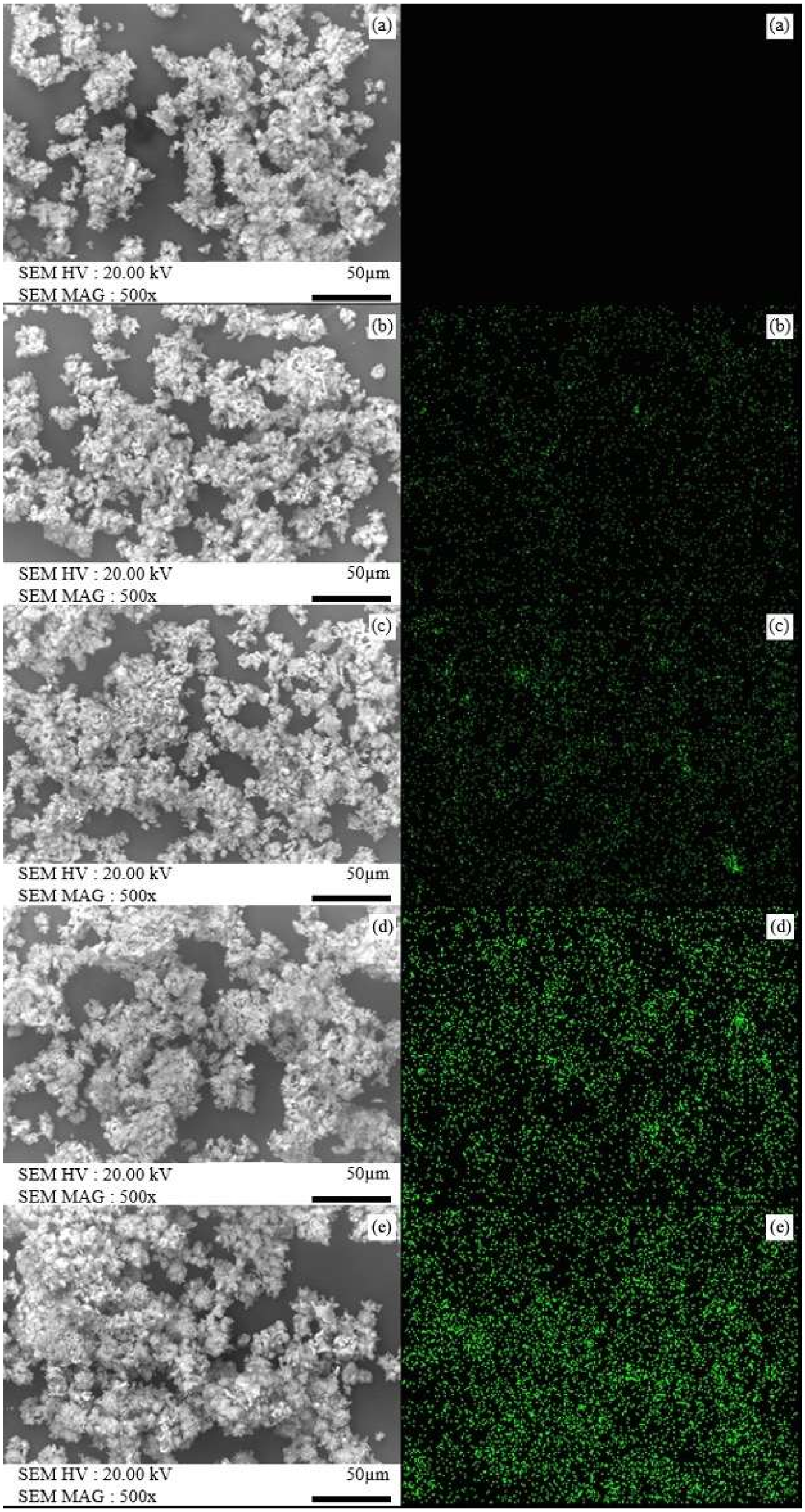

Figure 4. Mapping image of (a) CaO derived from cuttlebone, (b) 1% Sr/CaO, (c) 3% Sr/CaO, (d) 5% Sr/CaO, and (e) 10% Sr/CaO.

Table 2. BET analysis of strontium substituted into calcium oxide powder.

Type	BET Surface Area ($m^2 \cdot g^{-1}$)
CaO	18
1% Sr/CaO	29
3% Sr/CaO	17
5% Sr/CaO	19
10% Sr/CaO	13

One of the most important parameters for catalyst was focused on specific surface area. Table 2 presents BET analysis of strontium substituted into calcium oxide powder, as calculated from nitrogen adsorption isotherm. The range of specific surface area was observed from 12-30 $m^2 \cdot g^{-1}$, similar to previous literature reported by Cho *et al.* [34]. Only 1 wt% of strontium substituted into calcium oxide powder provided the highest technical data on specific surface area. With higher amount of strontium, the data was slightly decreased. The existence of strontium may induce to fusion between calcium oxide powders, leading to agglomeration on surface.

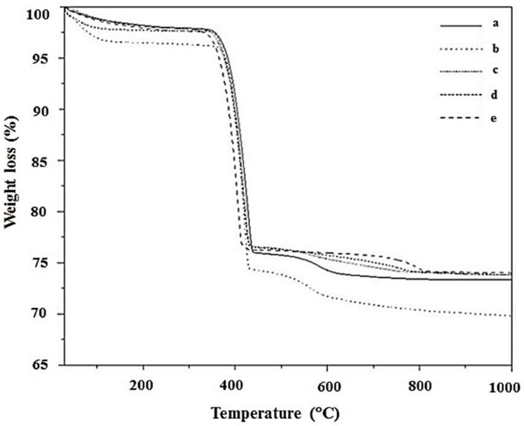

Figure 5. Thermal decomposition of (a) CaO derived from cuttlebone, (b) 1% Sr/CaO, (c) 3% Sr/CaO, (d) 5% Sr/CaO, and (e) 10%Sr/CaO.

Figure 5 presents the thermal decomposition of strontium substituted into calcium oxide powder. The pristine CaO derived from cuttlebone was provided for comparison. The percent yield of residual was estimated to be 75wt%. The region of weight loss can be classified into three different regions. From room temperature to 350°C, small scale of weight loss was observed due to water evaporation. It was therefore important to note that strontium substituted into calcium oxide and also pristine powder were easily adsorbed by humidity, suggesting that powder should be stored in desiccator prior to use. Next to this, with the increment on temperature region to 350-450°C, the wide region of weight loss was observed. This was probably due to the existence of humidity on strontium substituted into calcium oxide powder. It may form $Ca(OH)_2$ as suggested by Azmi *et al.* [35]. Another reason may involve the residual of char after calcination process.

After that, preliminary investigation of catalyst was investigated. The fuel properties of the obtained FAME from tranesterification of palm oil and methanol under optimal conditions are presented in Table 3. The methyl ester content of the obtained biodiesel was estimated to be 80-95%. Significant enhancement of percent conversion was observed due to existence of strontium in CaO catalyst derived from cuttlebone. Moreover, in case of 1% Sr/CaO, the maximum data was presented. This is probably in the similar trend of surface area analysis investigated by BET.

Table 3. Percent conversion of biodiesel.

Catalyst	%Conversion
CaO	49.63
1% Sr/CaO	95.47
3% Sr/CaO	84.59
5% Sr/CaO	87.50
10% Sr/CaO	80.50

4. Conclusions

Cuttlebone was employed as a calcium source of heterogeneous catalyst for biodiesel production. 1, 3, 5 and 10%wt of strontium was successfully incorporated into calcium oxide powder. No significant change was observed by FTIR and XRD analysis. Morphological properties of powder presented as a blocky-like particle. Strontium atom was uniformly distributed on the surface. However, the range of specific surface area was estimated to be 10-30 $m^2 \cdot g^{-1}$. The catalyst presented the excellence in percent conversion of biodiesel synthesis. Preliminary investigation suggested us that utilization of cuttlebone was successfully prepared as an excellent candidate of heterogeneous catalyst for biodiesel production.

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References

[1] A. A. Ayodeji, O. E. Modupe, B. Rasheed, and J. M. Ayodele, "Data on CaO and eggshell catalysts used for biodiesel production," *Data in Brief,* vol. 19, pp. 1466-1473, 2018.

[2] N. Azmi, S. Yusup, and K. M. Sabil, "Effect of water onto porous CaO for CO_2 adsorption: Experimental and extended isotherm model," *Journal of Cleaner Production,* vol. 168, pp. 973-982, 2017.

[3] A. U. Badnore, N. L. Jadhav, D. V. Pinjari, and A. B. Pandit, "Efficacy of newly developed nano-crystalline calcium oxide catalyst for biodiesel production," *Chemical Engineering and Processing-Process Intensification,* vol. 133, pp. 312-319, 2018.

[4] S. Boonyuen, S. M. Smith, M. Malaithong, A. Prkaew, B. Cherdhirunkorn, and A. Luengnaruemoitchai, "Biodiesel production by a renewable catalyst from calcined Turbo jourdani (Gastropoda: Turbinidae) shells," *Journal of Cleaner Production,* vol 177, pp. 925-929, 2018.

[5] V. Čadež, S. D. Škapin, A. Leonardi, I. Križaj, S. Kazazić, B. Salopek-Sondi, and I. Sondi, "Formation and morphogenesis of a cuttlebone's aragonite biomineral structures for the common cuttlefish (Sepia officinalis) on the nanoscale: Revisited," *Journal of Colloid and Interface Science,* vol. 508, pp. 95-104, 2017.

[6] J. Cadman, S. Zhou, Y. Chen, and Q. Li, "Cuttlebone: characterisation, application and development of biomimetic materials," *Journal of Bionic Engineering,* vol. 9, no. 3, pp. 367-376, 2012.

[7] Y. B. Cho, G. Seo, and D. R. Chang, "Transesterification of tributyrin with methanol over calcium oxide catalysts prepared from various precursors," *Fuel Processing Technology,* vol. 90, no.10, pp. 1252-1258, 2009.

[8] J. Corach, E. F. Galván, P. A. Sorichetti, and S. D. Romano, "Estimation of the composition of soybean biodiesel/soybean oil blends from permittivity measurements," *Fuel,* vol. 235, pp. 1309-1315, 2019.

[9] L. Dehghan, M. T. Golmakani, and S. M. Hashem Hosseini, "Optimization of microwave- assisted accelerated transesterification of inedible olive oil for biodiesel productionj," *Renewable Energy*, vol. 18, pp. 915-922, 2019.

[10] I. Fatimah, D. Rubiyanto, A. Taushiyah, F. B. Najah, U. Azmi, and Y. L. Sim, "Use of ZrO_2 supported on bamboo leaf ash as a heterogeneous catalyst in microwave-assisted biodiesel conversion," *Sustainable Chemistry and Pharmacy,* vol. 12, 2019.

[11] J. Goli and O. Sahu, "Development of heterogeneous alkali catalyst from waste chicken eggshell for biodiesel production," *Renewable Energy,* vol. 128, pp. 142-154, 2018.

[12] A. R. Gupta and V. K. Rathod, "Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics," *Waste Management,* vol. 79, pp. 169-178, 2018.

[13] F. Harahap, S. Silveira, and D. Khatiwada, "Cost competitiveness of palm oil biodiesel production in Indonesia," *Energy,* vol. 170, pp. 62-72, 2019.

[14] X. Jia, X. Ma, D. Wei, J. Dong, and W. Qian, "Direct formation of silver nanoparticles in cuttlebone-derived organic matrix for catalytic applications," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 330(2), pp. 234-240, 2008.

[15] S. K. Karmee and A. Chadha, "Preparation of biodiesel from crude oil of Pongamia pinnata," *Bioresource Technology,* vol. 96, no. 13, pp. 1425-1429, 2005.

[16] H. Li, S. Niu, C. Lu, and J. Li, "Calcium oxide functionalized with strontium as heterogeneous transesterification catalyst for biodiesel production," *Fuel,* vol. 176, pp. 63-71, 2016.

[17] A. Linggawati, S. Anita, and T. A. Amri, "Preparation and Characterization of Calcium Oxide Heterogeneous Catalyst Derived from Anadara Granosa Shell for Biodiesel Synthesis," *Knowledge Engaging minds*, vol. 2016, pp. 1-8, 2016.

[18] M. Kirubakaran, and V. Selvan, "Eggshell as heterogeneous catalyst for synthesis of biodiesel from high free fatty acid chicken fat and its working characteristics on a CI engine," *Journal of Environmental Chemical Engineering,* vol. 6, no. 4, pp. 4490-4503, 2018.

[19] Y. Ma, Z. Gao, Q. Wang, and Y. Liu, "Biodiesels from microbial oils: Opportunity and challenges," *Bioresource Technology,* vol. 263, pp. 631-641, 2018.

[20] Y. Y. Margaretha, H. S. Prastyo, A. Ayucitra, and S. Ismadji, "Calcium oxide from pomacea sp. shell as a catalyst for biodiesel production," *International Journal of Energy and Environmental Engineering,* vol. 3, no. 1, pp. 1-9, 2012.

[21] I. M. Mendonça, O. A. R. L. Paes, P. J. S. Maia, M. P. Souza, R. A. Almeida, C. C. Silva, S. Duvoisin, and F. A. de Freitas, "New heterogeneous catalyst for biodiesel production from waste tucumã peels (Astrocaryum aculeatum Meyer): Parameters optimization study," *Renewable Energy,* vol. 130, pp. 103-110, 2019.

[22] A. Pal, P. Nasker, S. Paul, A. Roy Chowdhury, A. Sinha, and M. Das, "Strontium doped hydroxyapatite from Mercenaria clam shells: Synthesis, mechanical and bioactivity study," *Journal of the Mechanical Behavior of Biomedical Materials,* vol. 90, pp. 328-336, 2019.

[23] S. Poompradub, Y. Ikeda, Y. Kokubo, and T. Shiono, "Cuttlebone as reinforcing filler for

natural rubber," *European Polymer Journal,* vol. 44, no. 12, pp. 4157-4164, 2008.

[24] A. M. Rabie, M. Shaban, M. R. Abukhadra, R. Hosny, S. A. Ahmed, and N. A. Negm, "Diatomite supported by CaO/MgO nanocomposite as heterogeneous catalyst for biodiesel production from waste cooking oil," *Journal of Molecular Liquids,* vol. 279, pp. 224-231, 2019.

[25] A. Sandouqa and Z. Al-Hamamre, "Energy analysis of biodiesel production from jojoba seed oil," *Renewable Energy,* vol. 130, pp. 831-842, 2019.

[26] V. Saxena, S. Sharma, and L. M. Pandey, "Fe(III) doped ZnO nano-assembly as a potential heterogeneous nano-catalyst for the production of biodiesel," *Materials Letters,* vol. 237, pp. 232-235, 2019.

[27] R. Shan, L. Lu, Y. Shi, H. Yuan, and J. Shi, "Catalysts from renewable resources for biodiesel production," *Energy Conversion and Management,* vol. 178, pp. 277-289, 2018.

[28] S. Shang, K. L. Chiu, M. C. W. Yuen, and S. Jiang, "The potential of cuttlebone as reinforced filler of polyurethane," *Composites Science and Technology,* vol. 93, pp. 17-22, 2014.

[29] S. Sharma, V. Saxena, A. Baranwal, P. Chandra, and L. M. Pandey, "Engineered nanoporous materials mediated heterogeneous catalysts and their implications in biodiesel production," *Materials Science for Energy Technologies,* vol. 1, no. 1, pp. 11-21, 2018.

[30] E. G. Silveira Junior, V. H. Perez, I. Reyero, A. Serrano-Lotina, and O. R. Justo, "Biodiesel production from heterogeneous catalysts based K_2CO_3 supported on extruded γ-Al_2O_3," *Fuel,* vol. 241, pp. 311-318, 2019.

[31] K. Srasri, M. Thongroj, P. Chaijiraaree, S. Thiangtham, H. Manuspiya, P. Pisitsak, and S. Ummartyotin, "Recovery potential of cellulose fiber from newspaper waste: An approach on magnetic cellulose aerogel for dye adsorption material," *International Journal of Biological Macromolecules,* vol 119, pp 662-668, 2018.

[32] Y. H. Tan, M. O. Abdullah, C. Nolasco-Hipolito, and Y. H. Taufiq-Yap, "Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance," *Applied Energy,* vol. 160, pp. 58-70, 2015.

[33] D. P. van Vuuren, E. Stehfest, D. E. H. J. Gernaat, J. C. Doelman, M. van den Berg, M. Harmsen, and A. Tabeau, "Energy, land-use and greenhouse gas emissions trajectories under a green growth paradigm," *Global Environmental Change,* vol. 42, pp. 237-250, 2017.

[34] N. Viriya-empikul, P. Krasae, B. Puttasawat, B. Yoosuk N. Chollacoop, and K. Faungnawakij, "Waste shells of mollusk and egg as biodiesel production catalysts," *Bioresource Technology,* vol. 101, no. 10, pp. 3765-3767, 2010.

[35] G. Xu, H. Li, X. Ma, X. Jia, J. Dong, and W. Qian, "A cuttlebone-derived matrix substrate for hydrogen peroxide/glucose detection," *Biosensors and Bioelectronics,* vol. 25, no. 2, pp. 362-367, 2009.