

Preparation And Characterization Of Modified Calcium Oxide From Natural Sources And Their Application In The Transesterification Of Palm Oil

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Abstract: Calcium oxide catalysts were prepared from natural calcium sources such as limestone and mud creeper shell and the catalytic activities were evaluated in the transesterification of palm oil. The raw material which mainly composed of calcium carbonate can be easily converted to calcium oxide (CaO) after calcination above 1000 K for few hours. Abundant, cheap sources, benign, high conversion and nontoxic become main advantages of these catalysts. The catalysts were characterized by XRF, TGA, XRD, CO₂-TPD, SEM, and BET methods. Thermal decomposition of CaCO₃, will produced CaO which later will be converted into calcium hydroxide (Ca(OH)₂) via simple hydration technique. Under optimum reaction condition (methanol to oil ratio 15:1, catalyst loading 3 wt.%, reaction temperature 338 K for 5 hours), the highest conversion of palm oil to methyl ester recorded were 98% and 94% when using modified limestone and mud creeper shell respectively. The results observed an increment up to 80% by using modified catalysts with characterization results showed high in basicity and surface area. Hence, promising materials via simple and cheap method can be achieved.

Index Terms: Biodiesel production, Calcium hydroxide, Heterogeneous, Hydrolysis, Limestone, Methyl ester, Mud creeper shell, Palm oil

1. INTRODUCTION

Rapid population and gradually increased industrial sector are the main reasons that caused the fast diminishing of energy resources. The transportation sector worldwide alone consumed 57.7% of fossil fuel usages, which make one-fifth of global carbon dioxide (CO₂) emissions [1]. Therefore, concerns over increasing energy demands, continuous global warming effects, declining petroleum reserves, petroleum price hike and scarcities have raised the critical need to search for alternative, renewable and environmentally friendly fuels. Renewable energy has been highlighted in the last decade because of its potential to replace fossil fuel especially for transportation. Biodiesel is considered as renewable fuels, as they are derived at least partially from parts of dead organisms such as plants, animals and etc. [2]. It is non-toxic and environmentally benign since it does not contain sulfur, aromatic hydrocarbons, metals or crude oil residues [3]. This is in contrast with conventional diesel, which contains 20-40 wt.% aromatic compounds and as high as 500 ppm sulfur that resulted in black smoke particulate together with SO₂ emissions [4]. Chemically, biodiesel is defined as the mono alkyl esters of long chain fatty acids, typically produced through the reaction (i.e.: transesterification) of vegetable oils or animal fats with methanol or ethanol in the presence of catalyst to yield methyl or ethyl esters (biodiesel) and glycerol as a by-product. Biodiesel production is dominated by homogeneous base catalyst, such as sodium methoxide (CH₃ONa), sodium hydroxide (NaOH) or potassium hydroxide (KOH) [5][6]. Sodium methoxide is the most widely used homogeneous base catalyst in biodiesel production with more than 60% of industrial plants using this catalyst because of its high catalytic activity in moderate reaction condition. However, one of the major problems of acid and alkali homogeneous

catalysts is that the catalyst takes place in one phase reaction system, thus they cannot be reused or regenerated. The catalyst is mixed with the reaction medium and the separation of catalyst from products is difficult which result in higher production cost. Even separation processes do take place, it is not environmentally and economically friendly because a large amount of water is needed, which results in loss of FAME, consume more energy and generate a huge amount of waste water [7]. In contrast, less number of unit operations by means of simple product separation and purification steps with no neutralization process can be obtained using heterogeneous catalyzed transesterification processes. Since, heterogeneous catalysts take place in three-phase system (oil, methanol and catalyst), the catalyst can be easily separated and regenerated. Various studies using heterogeneous catalysts have been investigated in biodiesel production. Mutreja et al., (2011) [8] reported that the biodiesel yield of more than 98% was achieved in only 20 min by using KOH impregnated on MgO as catalyst. Park et al., (2008)[9] reported that, the conversion of 85% of FAME was gained by using WO₃/ZrO₂. Among heterogeneous base catalysts, calcium oxide (CaO) is the most studied and widely used as it presents many advantages such as longer catalyst life, high activity and requires only moderate reaction conditions. However, due to low mechanical strength and stability, several modifications of calcium oxide catalysts such as incorporating active promoters or support materials were investigated. Watkins et al., (2004)[10] evaluated Li-loaded CaO in the transesterification of glyceryl tributyrates to methyl butanoate. The doping of lithium on CaO was found to increase the basicity of the catalyst. Umdu et al., (2009)[11] used Al₂O₃ supported CaO and MgO as basic heterogeneous catalysts. The researchers found that supported CaO and MgO showed higher in catalytic activity than unsupported CaO and MgO. Among the tested catalyst systems, CaO/Al₂O₃ at 80 wt.% loading system gave the best yield (97.5%) at methanol:oil molar ratio (30:1) in 4 h reaction time. The author has concluded that the basic site density and basic strength are the factors driving to its high catalytic activity. Recently, hydration technique was reported to be a facile and efficient technique for increasing the transesterification activity of CaO. Within one hour of reaction time, 93.9 wt.% of methyl esters

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content was gained by using hydrated-decomposed calcium oxide compares to 75.5 wt.% of methyl esters content using calcined calcite[12]. Recently, Niju et al., (2014)[13] reported that eggshells which were subjected to calcination-hydration-dehydration treatment was able to obtain high methyl ester conversion of 94.52% compared to 67.57% when using commercial CaO. Hydration followed by thermal decomposition technique yielded a new solid CaO with a surface area twice than that of conventional thermal decomposition of CaO. However, the water treatment did not change significantly the pore characteristic, although both surface area and pore volume increased intensively [12]. The main objective of this research is to produce calcium-based catalyst with high basicity via simple and cheap hydration technique and employ the prepared catalysts in the transesterification reaction of palm oil.

2. EXPERIMENTAL

2.1. Materials

Palm oil was purchased from Seri Murni, Malaysia. The analytical grade methanol (J.Kollin Chemical) was used in the transesterification reaction. Limestone and mud creeper shell were bought from local quarry and market.

2.2. Catalysts preparation

Limestone was cleaned and crushed while mud creeper shell were washed thoroughly with tap water to remove impurities and fleshy portion adhered on its surface and inner shells, and further rinsed with distilled water. The clean shells and limestone were dried in air at 353 K for an overnight before undergoing calcination at 1073 K and 1173 K respectively. The calcined catalysts were denoted as SS (i.e.: mud creeper shells) and LS (i.e.: limestone). Later, all calcined catalysts were undergoing modification via a hydration method [12] in different medium such as water, ammonia hydroxide solution and sodium hydroxide solution. Approximately 5 g of each calcined catalysts were refluxed in 40 mL of reflux medium for 6 h at 333 K. Then, the catalysts were dried in oven at 383 K for overnight. All samples were denoted as shown in Table 1.

2.3. Transesterification reaction

A typical reaction was carried out in a 25 mL two-neck round bottom flask equipped with a condenser and a magnetic stirrer. For all reactions, the reaction mixture which was consisted of approximately 10 g of vegetable oil (100% palm oil; Seri Murni), 3 wt.% of catalyst loading, a molar ratio of methanol to oil 15:1 were took place in oil bath at 338 K for 5 h. Once the reaction was completed, the catalyst was separated from the mixture by centrifugation. Then, excess methanol was evaporated from the mixture by heating above 338 K for few hours before the biodiesel (FAME) and by-product (glycerol) were separated. The conversion of biodiesel was calculated based on the amount of glycerol produced [14][15]. Transesterification reaction was carried out over differently prepared calcium oxide catalysts before and after modification under the same reaction condition (methanol: oil ratio of 15:1; catalyst loading of 3 wt.%; 5 h reaction time at 338 K).

Table 1. Designated sample name before and after modification of limestone and mud creeper shell.

Raw material	Calcined	Reflux medium		
		Distilled water	Ammonia hydroxide solution	Sodium hydroxide solution
Limestone	LS	HLS	NLS	OLS
Mud creeper shell	SS	HSS	NSS	OSS

2.4. Reusability test

The reusability test was conducted only on the catalyst that gave the highest biodiesel conversion using the same reaction condition as stated above. After the first reaction was done, the catalyst was separated from the reaction product. The catalyst was then washed with acetone for three times to remove the non-polar compounds attached on the catalyst. The catalyst was dried in oven for overnight and further used in the next transesterification reaction. The procedures were repeated until no conversion can be recorded.

2.5. Analysis of biodiesel

In this study, the product (biodiesel) was analyzed by using Shidmadzu gas chromatography equipped with flame ionization detector (FID). The GC was equipped with the HP-Innowax capillary column (30 m length, 0.25 mm I.D., 0.25 μ m film) for separation of methyl ester species. The oven temperature was programmed with two steps of temperature increment. Initially, the temperature was set at 333 K and held for 5 min, then, increased to 473 K at 283 K min^{-1} . Again, the oven temperature was increased up to 513 K at 278 K min^{-1} and held for 5 min. The injector and detector port was set at 523 K where nitrogen gas was utilized as the carrier gas. The sample was dissolved in η -hexane and 1 μ L of sample was injected into the system for analysis. The total operating time was about 18.5 min.

2.6 Catalysts characterization

The elemental compositions of the catalysts were determined by XRF spectrometry by using Shidmadzu EDX-720 spectrometer. Thermogravimetric analysis (TGA) is used to determine the thermal transition and decomposition of materials. TGA curves of limestone and mud creeper shells were recorded by using Perkin-Elmer Thermogravimetry Analyzer TGA7. The samples were analyzed under the temperature range of 323 K to 1273 K at a heating rate of 283 K min^{-1} with nitrogen gas flow rate of 50 mL min^{-1} . A Shidmadzu XRD- 6000 Diffractometer was used to identify the crystalline phase of synthesized catalysts. The XRD patterns were analyzed by using the Joint Committee on Powder Diffraction Standards (JCPDS) files to identify the sample of solid materials by comparing their diffraction lines and intensities. The basic strength and total basicity of all prepared catalysts were evaluated by using the temperature programmed desorption of CO₂ (Thermo Finnigan TPD/R/O 1100). Prior to analysis, approximately 0.05 g catalysts were pretreated under a nitrogen stream at 393 K for 5 min (303 K min^{-1} , 30 mL min^{-1}). Next, a flow of pure CO₂ (30 mL min^{-1}) was subsequently introduced into the reactor for 2 h. The TPD of CO₂ analysis was carried out starting from 303 K up to 1123 K under a helium flow (30 mL min^{-1}), and the desorbed CO₂ species was detected by thermal conductivity detector (TCD), hence, the respective TPD spectrum was recorded.

Meanwhile, Thermo Finnigan Sorptomatic Instrument model 1900 was used to determine the surface area, pore volume and pore size distribution of the samples by N₂ adsorption-desorption technique. The morphology of all catalysts before and after modification was observed under a scanning electron microscope using LEO 1455 VP electron microscope operated at 30 kV. Prior to analysis, the samples were coated with a thin layer of aurum using BIO-RAS Sputter Coater.

3. RESULTS AND DISCUSSION

3.1. Catalysts characterization

From Table 2, it shows that limestone has the highest percentage of calcium (99.98%) followed by mud creeper shells (91.43%). Only strontium was detected as minor compound in limestone while other elements such as iron, silica, potassium and scandium were detected in mud creeper shell. Based on XRF analysis, it is proven that the chosen raw materials in this study are rich in calcium.

Table 2. Elemental compositions (%) of raw limestone and mud creeper shell.

Raw material	Composition (%)						
	Ca	Fe	Si	Sr	K	Sc	Others
Limestone	99.98	-	-	0.02	-	-	-
Mud creeper shell	91.43	4.12	2.39	0.98	0.37	0.59	0.11

Based on the TGA curves shown in Fig. 1, limestone and mud creeper shells generated similar pattern of two distinct phases of weight loss at around 450 – 620 K and around 760 – 1100 K, regardless the calcium sources. Barros *et al.* (2009)[16] in his study reported that shells (i.e.: seashells) will experience initial weight loss at temperature around 373 – 413 K due to the trapped moisture that physically adsorbed on the sample. However, in this study, no significant weight loss was recorded at temperature below 400 K, since all the samples have undergone drying prior to the analysis. The first significant weight loss at 450 – 600 K can be attributed to the released of chemisorbed water [17] and volatile material [18]. As the temperature increase above 750 K, the remaining organic material also started to dissociate and finally at around 900 - 1100 K, the major weight loss occurs which is attributed to the decomposition of CaCO₃ into CO₂ and CaO [17][19]. From calculation, it was found that the value of total weight loss and theoretical weight loss of all samples were equivalent. Based on TGA analysis, raw limestone was calcined at 1073 K while raw mud creeper shell was calcined at 1173 K.

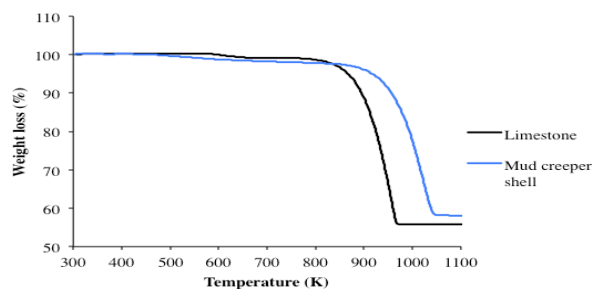


Fig. 1. TGA curves of raw limestone and mud creeper shell.

From XRD patterns (Fig. 2), uncalcined limestone were mainly composed of calcium carbonate, CaCO₃ in the form of calcite with main reflection peaks appeared at 2 θ = 23.2°, 29.6°, 36.1°, 39.5°, 43.3°, 47.6°, 48.7°, 60.8° and 65.7° (JCPDS No. 00-001-0837). Meanwhile mud creeper shell consists of CaCO₃ in the form of aragonite. The main reflection peaks appeared at 2 θ = 26.4°, 27.4°, 33.3°, 36.3°, 38.0°, 45.98°, 48.6°, 52.6° and 53.2° (JCPDS No. 00-003-0425). This analysis verifies the fact that the raw materials are composed of CaCO₃ and it will be transformed to calcium oxide [20][21] when subjected to high temperature calcination. After calcination, limestone and mud creeper shells showed intense sharp peaks of cubic CaO (JCPDS No. 00-004-0777) at 2 θ = 32.2°, 37.4°, 53.8°, 64.2° and 67.4° as shown in Fig. 3 and 4, respectively.

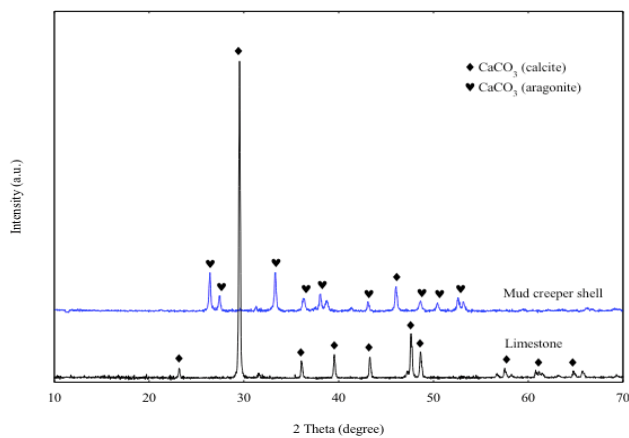


Fig. 2. XRD patterns of raw limestone and mud creeper shell.

Upon treatment in different reflux medium, the evolution of characteristic peaks of Ca(OH)₂ was clearly seen in all samples and suppress the peak characteristics of CaO. All of the peaks that appeared at 2 θ = 18.3°, 28.9°, 34.3°, 47.3°, 51.0°, 54.6°, 62.8°, 64.5° and 72.0° are well indexed to the calcium hydroxide with a hexagonal crystal structure (JCPDS No. 00-004-0733). Based on the XRD analysis, the calculated Scherrer's crystallite size of CaO and Ca(OH)₂ ranging between 28 – 42 nm (Table 3). In general, all modified catalysts show a slight decrease in the crystallite size after being modified in the different reflux medium.

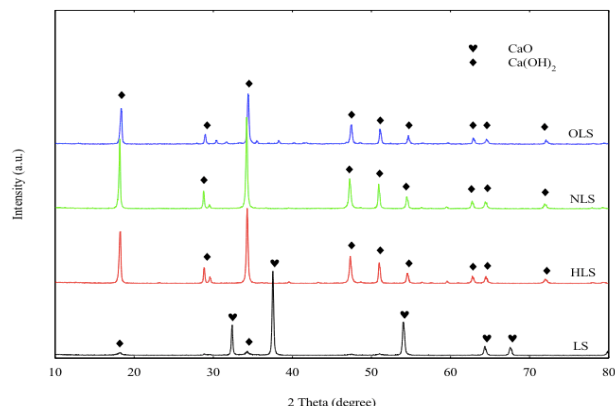


Fig. 3. XRD patterns of calcined and modified limestone.

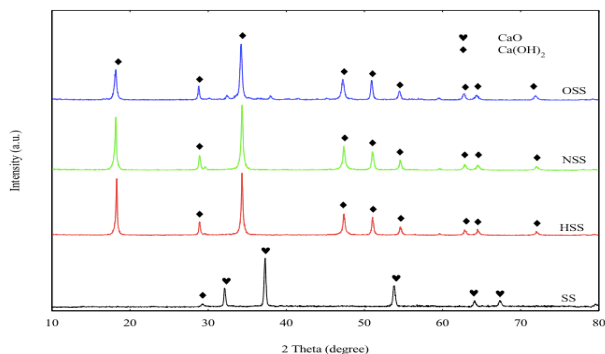


Fig. 4. XRD patterns of calcined and modified mud creeper shell.

From the temperature desorption of CO₂ analysis (Fig. 5 and Fig. 6), calcined limestone and mud creeper shells have shown a remarkable increase in basic sites amount when they were treated with different hydroxide precursors (i.e.: distilled water > ammonia hydroxide solution > sodium hydroxide solution) as shown in Table 4. All of the catalysts were regarded as having high basic strength since the maximum desorption temperature (T_{max}) is ranging from 990 K and above. According to Di Serio *et al.*, (2006)[22] a very broad desorption band extending from 400 – 700 K could be assigned as interaction of carbon dioxide with sites of weak and medium basic strength. While narrower band at higher temperature from 700 – 900 K can be attributed to the presence of much stronger basic sites. Interestingly, all the prepared CaO catalysts in this study revealed much higher basic sites than what has been reported by [23] on commercial CaO. The commercial CaO recorded only 450 μmol g⁻¹ at T_{max} of 848 K.

Table 3. Crystallite size (nm) of all synthesized catalysts

Catalyst		Crystallite size (nm)
Limestone	LS ^a	41.97
	HLS ^b	37.88
	NLS ^b	42.47
	OLS ^b	36.20
Mud creeper shell	SS ^a	42.70
	HSS ^b	42.62
	NSS ^b	35.14
	OSS ^b	28.07

^a CaO peak (200) reflection

^b Ca(OH)₂ peaks of (101) reflection

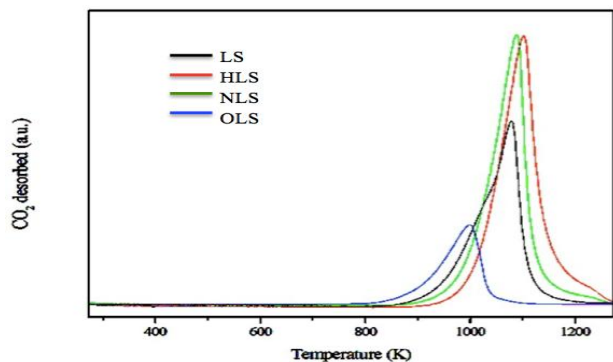


Fig. 5. TPD profiles of calcined and modified limestone.

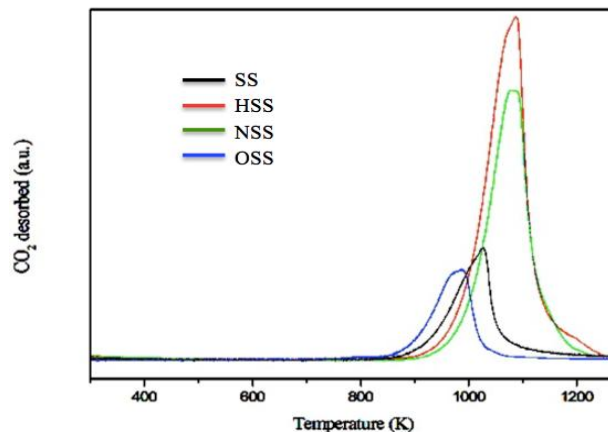


Fig. 6. TPD profiles of calcined and modified mud creeper shell.

Table 5 depicts the surface area, pore volume and average pore diameter of all catalysts. The surface area analysis revealed that there is no significant trend in surface area, pore volume and average pore diameter observed for calcined and modified catalysts. For calcined samples, limestone possesses the largest surface area of 88.0 m² g⁻¹ followed by mud creeper shells (12.7 m² g⁻¹). In this study, the calcined limestone (LS) achieved almost six times larger surface area than what has been reported by Ngamcharussrivichai *et al.*, (2011)[24] which was 13.8 m² g⁻¹ with average pore size of 21.4 nm and average pore volume of 0.09 cm³ g⁻¹. Even so, in this study, the BET surface area does not become the main parameter of concern because the catalyst surface area does not have a direct impact on the biodiesel. This was confirmed by few reported studies by Shu *et al.*, (2010)[25] and Hattori, (2004)[26]. In transesterification reaction, it has been agreed by many researchers [27][28][29][30], which said that the most critical factor that affected the transesterification reaction is the acidity and basicity of the catalyst.

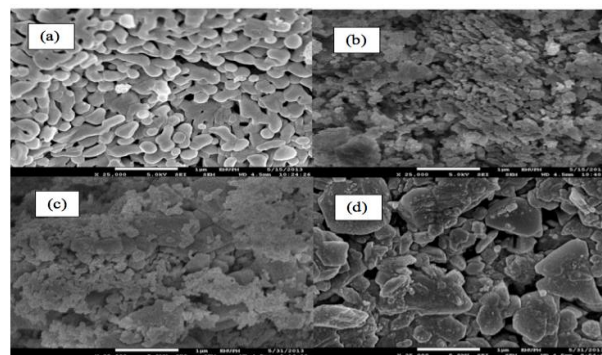
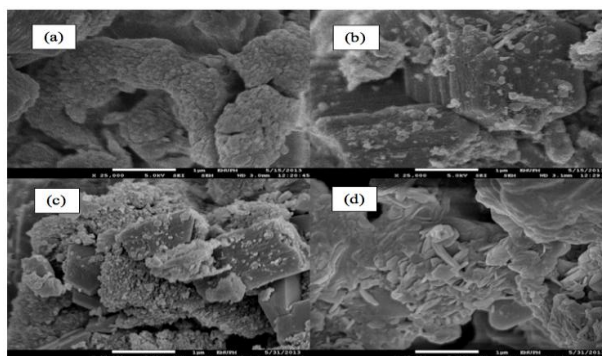
Catalyst		CO ₂ -TPD		
		T _{max} (K)	T _{min} (K)	CO ₂ uptake (μmol g ⁻¹)
Limestone	LS	860	1078	24,142
	HLS	920	1100	31,229
	NLS	860	1085	30,874
	OLS	820	1000	13,983
Mud creeper shell	SS	860	1027	28,499
	HSS	900	1087	30,285
	NSS	900	1077	30,874
	OSS	860	990	9,637

Table 4. Amount of CO₂ uptake (μmol g⁻¹) for limestone and mud creeper shell before and after modification.

Table 5. Surface area ($m^2 g^{-1}$), pore volume ($cm^3 g^{-1}$) and average pore diameter (nm) of all synthesized catalysts.

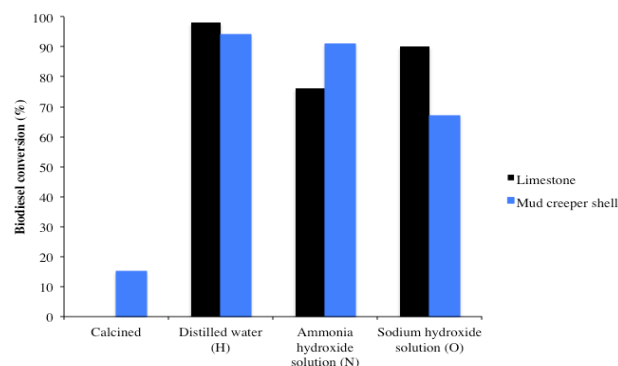
Catalyst	CO ₂ -TPD			
	T _{onset} (K)	T _{max} (K)	CO ₂ uptake ($\mu mol g^{-1}$)	
Limestone	LS	860	1078	24,142
	HLS	920	1100	31,229
	NLS	860	1085	30,874
	OLS	820	1000	13,983
Mud creeper shell	SS	860	1027	28,499
	HSS	900	1087	30,285
	NSS	900	1077	30,874
	OSS	860	990	9,637

Meanwhile, Fig. 7 and Fig. 8 depicted the SEM morphology of unmodified and modified catalysts prepared from limestone and mud creeper shells respectively. It can be seen clearly that calcined limestone (LS) showed a distinctive feature of uniform, smooth surface of the rod-dumbbell shape particles. This feature was obtained after limestone being calcined at 1073 K in air. The smooth surface of the rod-dumbbell like particles of LS changes to the rough surface of irregular particles after it was modified with distilled water (HLS), ammonia hydroxide solution (NLS) and sodium hydroxide solution (OLS). A mixture of small and big hexagonal-like plates were formed with clear structure was observed for OLS. SEM image of calcined mud creeper shells (Fig. 8(a)) demonstrated bulky substances with surface roughness and fracture was observed. The surface roughness was probably due to the high calcination temperature of the catalyst (i.e.: 1173 K) while liberating CO₂. Ngamcharussrivichai *et al.*, (2010)[31] also stated that the increase in fracture and surface roughness of dolomite CaMg(OH)₂ coincides with the increase in the calcination temperature. Modification of mud creeper shell in distilled water, ammonia hydroxide solution and sodium hydroxide solution have dissolved the bulky substance into smaller particles scattered on a cluster of thin plates as depicted in Fig. 8(b) and Fig. 8(c), respectively. Much clearer image of a hexagonal-like plate was observed for the OSS sample (Fig. 8 (d)). Upon modification via hydration technique, the structure of bulky particles has crumbled forming smaller particles scattered on a bigger pallet. The formation of hexagonal-like plates were observed for all modified catalysts which coincides with the hexagonal Ca(OH)₂ phase determined by XRD analysis. Catalysts modified in both distilled water and ammonia hydroxide solutions show more or less similar morphological structure, with more noticeable hexagonal-like plate can be observed for sodium hydroxide modified catalysts.

**Fig. 7.** SEM images for (a) LS, (b) HLS, (c) NLS and (d) OLS.**Fig. 8.** SEM images for (a) SS, (b) HSS, (c) NSS and (d) OSS

3.2. Transesterification reaction

The prepared catalysts were subsequently tested for their catalytic activity in the transesterification of palm oil with methanol in the reaction parameters are as follows; methanol to oil molar ratio of 15:1, catalyst loading of 3 wt.%, reaction temperature of 338 K and reaction time of 5 h. In general, it can be clearly seen that the catalysts that undergoing hydration treatment showed much higher biodiesel conversion than that of unmodified catalysts regardless the hydroxide precursor types. The biodiesel conversion of more than 70% was achieved for all modified catalysts except for OSS catalyst, which displayed 67% of biodiesel conversion (Fig. 9). Meanwhile, the product from the reaction catalyzed by calcined limestone (LS) cannot be obtained due to saponification that resulted in difficulty to separate the product and glycerol.

**Fig. 9.** Biodiesel conversion (%) of calcined and modified limestone and mud creeper shell

Kouzu and Hidaka, (2012)[32] stated that the leaching of CaO catalyst will display a homogeneous contribution toward the base-catalyzed transesterification and thus biodiesel produced will be contaminated with the leached Ca species which make the recovery of the biodiesel and glycerol is difficult. A general trend was observed for the modified catalysts, whereby the catalysts that have been treated with distilled water recorded the highest biodiesel conversion followed by an ammonia hydroxide solution and sodium hydroxide solution. The highest biodiesel conversion of 98% was exhibited by calcined limestone treated with distilled water (HLS), while calcined mud creeper shell treated with sodium hydroxide solution showed the least conversion of about 67%. The highest biodiesel conversion catalyzed by HLS could be attributed to the highest number of basic sites determined by TPD-CO₂ analysis. Although, from all mediums that were used to modify the CaO catalysts, sodium hydroxide solution shows the least biodiesel conversion, it still shows better biodiesel conversion than unmodified catalysts (LS and SS). Hence, as expected the hydration technique that was applied in this study has proven to improve the catalytic activity of the prepared catalysts, due to the increase in basic sites as supported by TPD-CO₂ analysis.

3.3. Biodiesel characterization

Table 6 shows comparison for both methyl ester standard and synthesized methyl ester (biodiesel) based on GC chromatogram. From the table, the retention time of the synthesized methyl ester was found in agreement with the biodiesel standard, suggesting that all triglycerides from palm oil have successfully transesterified into biodiesel.

3.4. Reusability

Since HLS showed the highest biodiesel conversion of 98%, its reusability was examined by carrying out subsequent reaction cycles using similar reaction condition to that of transesterification reaction. No thermal activation was conducted on the used catalyst before it was used for the next cycle. The results revealed that the HLS could be used up to three consecutive times before the biodiesel conversion decreased dramatically. For the first cycle, 98% of biodiesel conversion was obtained, followed by 96% and 88% for the second and third run, respectively. However, at fourth cycle, no activity was recorded. From observation, the deactivation of catalyst was due to the loss of nearly half of the catalyst mass after third cycle. The loss of catalyst was probably due to the catalyst was partially soluble in methanol which subsequently affects the recovery of glycerol. Since the catalyst was reused without any reactivation, the catalyst was poisoned by reaction mixture (i.e.: glycerol, oil, methyl ester) and absorbed water [33]. The moisture and the formation of glycerol on the surface of the catalyst prevented the interaction between the glycerides molecules, methanol and active sites of the catalyst. Therefore, careful washing step and thermal activation is required prior to each cycle to maintain high reusability.

Table 6. Retention time (min) of standard and synthesized methyl esters.

Types of methyl ester	Methyl ester retention time (min)	
	Standard	Synthesized
Myristate (C14:0)	7.277	7.296
Palmitate (C16:0)	8.408	8.539
Stearate (C18:0)	9.557	8.985
Oleate (C18:1)	9.624	9.821
Linoleate (C18:2)	9.783	9.939

4. CONCLUSION

In this study, highly active catalysts were prepared from limestone and mud creeper shells by using modified hydration method. The HLS catalyst was found to be an efficient catalyst for the transesterification and significantly increase the conversion of biodiesel due to the presence of high basic sites with good reusability over three cycles.

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REFERENCES

- [1] Goldemberg, J. (2008). Environmental and ecological dimensions of biofuels. In: Conference on the ecological dimensions of biofuels, Washington (DC).
- [2] Sawanidou, E., Zervas, E. and Tsagarakis, K.P. (2010). Public acceptance of biofuels. Energy Policy 38:3482-3488.
- [3] Dubei, M.A., Tremblay, A.Y. and Liu, J. (2007). Biodiesel production using a membrane reactor. Bioresource Technology 98:639-647.
- [4] Phan, A. N, and Phan, T.M. (2008). Biodiesel production from waste cooking oils. Fuel 87: 3490-3496.
- [5] Alamu, O.J., Waheed, M.A. and Jekayinfa, S.O. (2008). Effect on ethanol-palm kernel oil ratio on alkali-catalysed biodiesel yields. Fuel 87:1529-1533.
- [6] Dmytryshyn, S.L., Dalai, A.K. and Chaudhari, S.T. (2004). Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties. Bioresource Technology 92:55-64.
- [7] Vicente, G., Martínez, M. and Aracil, J. (2007). Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. Bioresource Technology 98(9):1724-1733.
- [8] Mutreja, V., Satnam, S. and Amjad, A. (2011).

- Biodiesel from mutton fat using KOH impregnated MgO as heterogeneous catalysts. *Renewable Energy* 36(8):2253- 2258.
- [9] Park, Y.M., Lee, D.W., Kim, D.K., Lee, J.S. and Lee, K.Y. (2008). The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catalysis Today* 131(1–4):238- 243.
- [10] Watkins, R.S., Lee, A.F. and Wilson, K. (2004). Li–CaO catalysed tri-glyceride transesterification for biodiesel applications. *Green Chemical* 6:335–40.
- [11] Umdu, E.S., Tuncer, M. and Seker, E. (2009). Transesterification of *Nannochloropsis oculata* microalga's lipid to biodiesel on Al₂O₃ supported CaO and MgO catalysts. *Bioresource Technology* 100:2828–31.
- [12] Yoosuk, B., Udomsap, P., Puttasawat, B. and Krasae, P. (2010a). Improving transesterification activity of CaO with hydration technique. *Bioresource Technology* 101(10):3784-3786.
- [13] Niju, S., Meera, K.M., Begum, S. and Anantharaman, N. (2014). Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society* 18(5):702-706.
- [14] Kotwal, M.S., Niphadkar, P.S., Deshpande, S.S., Bokade, V.V. and Joshi, P.N. (2009). Transesterification of sunflower oil catalyzed by flyash-based solid catalysts. *Fuel* 88:1773–1778.
- [15] Vyas, A.P., Subrahmanyam, N. and Patel, P.A. (2009). Production of biodiesel through transesterification of *Jatropha* oil using KNO₃/Al₂O₃ solid catalyst. *Fuel* 88:625–628,
- [16] Barros, M.C., Bello, P.M., Bao, M. and Torrado, J.J. (2009). From waste to commodity: transforming shells into high purity calcium carbonate. *Cleaner Production* 17(3):400-407.
- [17] Shengyang H., Yun W. and Heyou H. (2011). Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production. *Biomass and Bioenergy* 35: 3627-3635
- [18] Naemchan, K., Meejo, S., Onreabroy, W. and Limsuwan, P. (2008). Temperature effect on chicken egg shell investigation by XRD, TGA and FTIR. *Advance Material Research* 55:333–336.
- [19] Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N. and Faungnawakij, K. (2010). Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresource Technology* 101(10):3765-3767.
- [20] Roschat, W., Kacha, M., Yoosuk, B., Sudyoasuk, T. and Promarak, V. (2012). Biodiesel production based on heterogeneous process catalyzed by solid waste coral fragment. *Fuel* 98:194-202.
- [21] Sharma, Y.C., Singh, B. and Korstad, J. (2010). Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from *Pongamia pinnata* oil. *Energy Fuels* 24:3223–31.
- [22] Di serio M., Ledda M., Cozzolino M., Minutillo G., Tesser R. and Santacesaria E. (2006). Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Industrial & Engineering Chemistry Research* 45:3009-14.
- [23] Reyero I., Arzamendi G. and Gandía L. M. (2014). Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. *Chemical Engineering Research and Design* 92(8):1519-1530.
- [24] Ngamcharussrivichai, C., Warakorn, M., Anawat, K., Kunn, K. and Suchada, B. (2011). Preparation of heterogeneous catalysts from limestone for transesterification of vegetable oils—Effects of binder addition. *Journal of Industrial and Engineering Chemistry* 17(3):587-595.
- [25] Shu, Q., Gao, J., Nawaz, Z., Liao, Y. and Wang, D. (2010). Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon based solid acid catalyst. *Applied Energy* 87: 2589-2596.
- [26] Hattori, H. (2004). Solid base catalysts: generation, characterization, and catalytic behaviour of basic sites. *Journal of the Japan Petroleum Institute* 47(2):67-81.
- [27] Hashemizadeh, I. and Ahmad Zuhairi A. (2013). Alkaline Earth Metal Oxide Catalysts for Biodiesel Production from Palm Oil: Elucidation of Process Behaviors and Modeling Using Response Surface Methodology. *Iranian Journal of Chemistry and Chemical Engineering* 32(1):113-126.
- [28] Reckha S., Babu N.S., Prasad S.P.S. and Lingaiah N. (2009). Transesterification of edible and non-edible oils over basic solid Mg/Zr catalysts. *Fuel Processing Technology* 90:152-7.
- [29] Yan S., Sally S.O. and Ng K.Y.S. (2009a). Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts. *Applied Catalysis A: General* 353:203-12.
- [30] Yan, S., Kim, M., Salley, S.O. and Simon Ng K.Y. (2009b). Oil transesterification over calcium oxides modified with lanthanum. *Applied Catalysis A: General* 360:163–70.
- [31] Ngamcharussrivichai, C., Nunthasanti, P. Tanachai, S. and Bunyakiat, K. (2010). Biodiesel production through transesterification over natural calciums.

Fuel Processing Technology 91(11):1409-1415.

- [32] Kouzu, M. and Hidaka, J.S. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: a review. Fuel 12.
- [33] Lee H. V., Joon C. J., Nurul F. A., Rabiah N. and Taufiq-Yap Y.H. (2014). Heterogeneous base catalysts for edible palm and non-edible Jatropha-based biodiesel production. Chemistry Central Journal 8:30.