Malaysian Journal of Analytical Sciences, Vol 23 No 4 (2019): xxx - xxx
DOI: https://doi.org/10.17576/mjas-2019-2304-zz

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society

ISSN
1394 - 2506

RARE EARTH METAL DOPED CaO AS CATALYST FOR THE TRANSESTERIFICATION REACTION OF COOKING OIL

(Logam Nadir Bumi Dop CaO sebagai Mangkin untuk Tindak Balas Transesterifikasi Minyak Masak)

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Received: 31 March 2018; Accepted: 17 April 2019

Abstract

Biodiesel has been introduced as an alternative fuel to replace the depletion of diesel oil and environmental pollution. Thus, the production of biodiesel is in demand and usually, conducted through base catalysed transesterification reaction towards the low grade cooking oil. In this research, bimetallic oxide cerium-calcium catalyst supported on activated carbon (AC) was prepared using impregnation method. Optimum catalytic parameter was observed with 30 wt.% of cerium loading on Ce/Ca/AC catalyst calcined at 500 °C and gave the highest free acid methyl ester (FAME) yield of 73.5% with fixed reaction conditions (65 °C, 1:18 wt.% oil to methanol ratio, 6 wt.% catalyst loading and 3 hours of reaction time). The enhanced activity of Ce/Ca/AC catalyst can be ascribed to the uniform needle-like morphology and well dispersion of the Ce-Ca on the support surface as indicated by FESEM images. XRD showed that the Ce/Ca/AC catalyst was in amorphous phase with BET surface area of 149.18 m^2/g. These results showed Ce/Ca/AC catalyst has promising potential to be used for production of FAME from low grade cooking oil.

Keywords: bimetallic oxide, Ce-Ca catalyst, cooking oil, transesterification, biodiesel

Abstrak

Biodiesel telah diperkenalkan sebagai bahan api alternatif bagi menggantikan pengurangan minyak diesel dan juga pencemaran alam sekitar. Oleh itu keperluan terhadap penggunaan biodiesel semakin meningkat, dan kebanyakan proses penghasilan biodiesel dilakukan melalui tindak balas transesterifikasi beralkali ke atas minyak masak bergred rendah. Melalui kajian ini, mangkin oksida dwilogam serium-kalsium berpenyokong karbon teraktif (AC) disediakan menggunakan kaedah pengisitepuan basah. Parameter optimum bagi mangkin dapat dilihat dengan kehadiran 30 wt.% kandungan serium dalam mangkin Ce/Ca/AC yang dikalsinkan pada suhu 500 °C, dan menghasilkan kadar penukaran asid bebas metil ester (FAME) sebanyak 73.5% dengan keadaan tindak balas tetap (65 °C, 1:18 wt.% nisbah minyak kepada metanol, 6 wt.% kuantiti mangkin dalam tempoh 3 jam tindak balas). Peningkatan aktiviti transesterifikasi adalah disebabkan oleh morfologi mangkin Ce-Ca yang berbentuk sepeti jarum dan sekata pada permukaan penyokong seperti yang ditunjukkan oleh imej FESEM. XRD pula menunjukkan bahawa mangkin Ce/Ca/AC berada di dalam fasa amorfus dengan luas permukaan BET sebanyak 149.18 m^2/g. Ini menunjukkan, mangkin Ce/Ca/AC adalah berpotensi untuk digunakan dalam pengeluaran FAME dari minyak masak bergred rendah.

Kata kunci: oksida dwilogam, mangkin Ce-Ca, minyak masak, transesterifikasi, biodiesel

Introduction

Concerns over the global oil price fluctuations, the depletion of natural fuel sources and the rising issues of climate pollution caused by greenhouse gas emissions have pushed for a transition to a better energy source. The government continues to update energy policies as an effort to ensure the efficiency and sustainability of national energy supplies, including replacing them with renewable energy sources [1, 2]. Biodiesel is seen as the best alternative fuel source in replacing petroleum-based diesel. Compared to diesel fuel, biodiesel is seen as environmentally friendly as it is free of sulfur and aromatic, making it non-toxic and biodegradable with lower emissions [3-5].

Almost all biodiesel is produced by base catalyzed transesterification as it is the most economical process since low temperatures are required, resulting in a high conversion yield. Furthermore, base catalyzed transesterification proceeds faster than acid catalyzed reaction [6, 7]. However, the costs of biodiesel production are still quite high in comparison to petroleum diesel. This is due to the use of homogenous catalyst in existing biodiesel production process. Homogeneous catalysts that commonly used such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) causes saponification process and requires a lot of water to be separated from the product of the reaction [8]. Hence, studies on the use of solid-based or heterogeneous catalysts have been widely conducted to reduce the dependency towards homogeneous catalysts in the biodiesel production industry. Among the benefits in using the heterogeneous catalysts are no side effects that can pollute the environment apart from being easily isolated from the resulting biodiesel. Separated catalyst can then be reused in a continuous reactor in comparison to the homogeneous catalysts used in the batch reactor [9, 10].

Extensive studies of heterogeneous catalysts have been conducted for biodiesel synthesis over the last decade, including alkaline metals, transition metals, rare earth metals, amino acid-based polymers, and micro-promoted alkaline and silicon/aluminate mesoporous [11]. However, the use of dopant from transition metals group to base catalysts is still poorly utilized in the transesterification reaction. Among the heterogeneous catalysts, Ca-based catalysts are mostly mixed with MgO, BaO, La_2O_3, SnO_2 whereas less attention was paid on the potential rare earth metal as a dopant even though this metal oxide offers good performance [12]. Hence, this study will focus on the heterogeneous catalyst production from alkaline earth metals with added rare earth metal dopant through wet impregnation methods. The incorporation of cerium and calcium species into the functionalized activated carbon (AC) perhaps can enhance the interaction between catalyst particles and support. The catalytic performance of Ce/Ca/AC was then compared in the transesterification of low grade cooking oil.

Materials and Methods

Materials

Calcium nitrate tetrahydrate $Ca(NO_3)_2{\bullet}4H_2O$, cerium nitrate hexahydrate $Ce(NO_3)_3{\bullet}6H_2O$, hydrophosphoric acid (H_3PO_4), methanol and *n*-hexane were purchased from Merck. All chemicals and solvents were used without further purification. Low grade cooking oil and palm kernel shells were obtained from the local market.

Catalyst Preparation

The activated carbon was initially synthesized using chemical activation process. The palm kernel shells were pre-treated with H_3PO_4 for 20 hours followed by purification with distilled water till the solution adjusted to neutral pH. Before introducing metal precursors, the carbon support was functionalized at 200 °C calcination temperature. The activated carbon was then immersed in nitrate salts aqueous solution of calcium and cerium at various ratios (10 wt.%, 20 wt.% and 30 wt.%) and aging in the oven at 80-90 °C for 24 hours. Then, the samples were calcined at various temperatures of 500, 700 and 1000 °C for 5 hours using a ramp rate of 5 °C/min to eliminate all the metal precursor impurities.

Catalytic reaction and characterization

The transesterification reaction was carried out using batch-reflux reactor method. Approximately, 10 g of low grade cooking oil the calculated amount of Ce/Ca/AC catalyst and methanol were mixed and heating up to 65 °C for 3 hours of reaction time. The mixture was distilled to remove excess of methanol followed by centrifuged at 3000 rpm for 30 minutes to separate the FAME and glycerol. Catalytic activity performance for all the prepared catalysts were measured using GC-FID equipped with SP-2560 capillary column (100 m × 0.25 mm × 0.20 µm) to determine the percentage FAME conversion of low grade cooking oil at fixed reaction conditions. The column temperature was programmed at 140°C for min and increased up to 240 °C for 15 minutes. meanwhile, the injector and detector temperatures were set up at 260 °C. The identified composition was compared with Supelco 37 component FAME mix standards.

The potential catalyst was characterized using X-ray diffraction (XRD) to identify the crystallography of Ce/Ca/AC while the specific surface area and pore distribution of the catalyst were determined by the Brunauer-Emmet-Teller (BET) using N_2 adsorption/desorption analyser. Field emission scanning electron microscopy (FESEM-EDX) to identify the morphology and elemental composition study.

Results and Discussion

Figure 1 shows the XRD pattern for all prepared Ce/Ca/AC catalysts after calcination at 500, 700 and 1000 °C. Overall, the XRD diffractogram of each calcination temperature presented the similar pattern, which was amorphous structure. The surface morphologies of Ce/Ca/AC catalysts at different calcination temperatures were examined by FESEM and shown in Figure 2. Overall, it could be seen that all the Ce/Ca/AC catalysts have a rough surface morphology, consisting of larger and smaller particle sizes, thus confirming the amorphous structure as mentioned by the previous XRD analysis. Figure 2(a) of Ce/Ca(30:70)/AC catalyst calcined at 500 °C showed the formation of smaller like-needle aggregated on the catalyst support. This characteristic should provide the spacious area for active site distribution on the catalyst surface. However, particle shape changed when the catalyst was calcined at 700 °C as shown in Figure 2(b). The catalyst was composed of coarse and non-uniform particles of different grain sizes, scattered on the catalyst surface. Reaching the calcination temperature to 1000 °C, the morphology structure of the catalyst altered and form more agglomeration and non-uniformly distributed on the surface of the catalyst. The dense packed surface at higher calcination temperature deteriorated the surface area as well as catalytic performance [13]. These changes were expected to have an effect on the transesterification reaction. The element composition of the Ce/Ca(30:70)/AC catalyst calcined at 500 °C was studied by EDX analysis (Figure 2(d)).

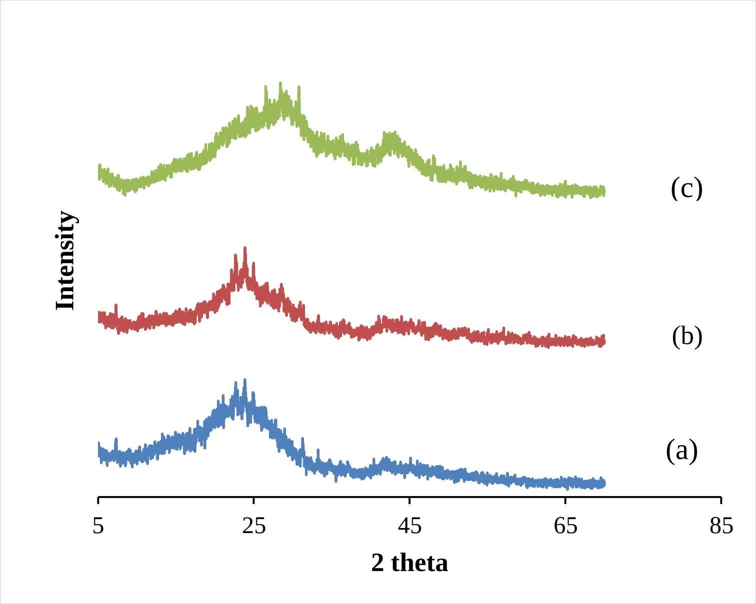

Figure 1. XRD diffractogram for Ca/Ce (30:70)/AC catalyst at calcination temperature of (a) 500 °C, (b) 700 °C and (c) 1000 °C

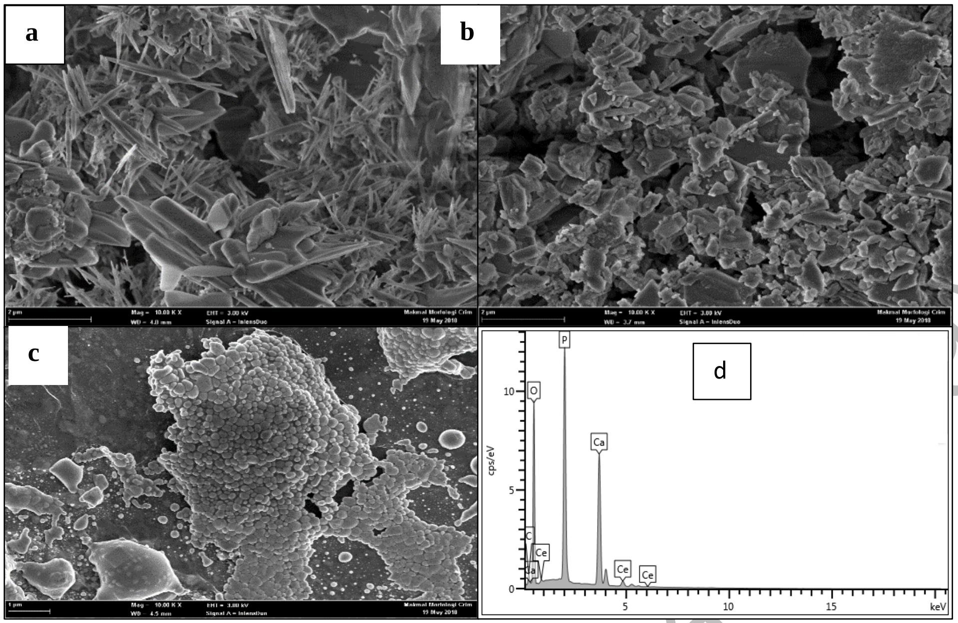

Figure 2. FESEM image for Ce/Ca (30:70)/AC catalysts calcined at (a) 500 °C, (b) 700 °C and (c) 1000 ℃ for 5 hours and (d) EDX result of Ce/Ca (30:70)/AC catalysts calcined at 500 °C

High performance catalysts are usually relied on materials with high surface area and associated with particle size below than 100 nm. The specific surface area (BET) and pore volumes of Ca/Ce (30:70)/AC catalysts are summarized in Table 1. The results of Ca/Ce (30:70)/AC showed gradually reduced of surface area and pore volume upon increasing of calcination temperature from 500 °C to 1000 °C while maintained the concentration of both Ce and Ca species. This observation might be due to the pore structure collapsed or most of the active site sitting on the bulk matrices instead of well-distributed on the catalyst surface.

Table 1. The specific surface area of Ce/Ca (30:70)/AC catalysts calcined at 500 °C, 700 °C and 1000 °C

Calcination T (°C)	**BET Surface area (m^2/g)**	**Pore Size (Å)**	**Pore Volume (cm^3/g)**
1000	70.28	19.13	0.034
700	127.65	19.74	0.063
500	149.18	20.16	0.082

Effect of cerium loading

Figure 3 illustrates the influence of cerium loading on Ca-based catalyst on the transesterification reaction. It was clearly observed that the triglyceride reduction was significantly increased as the cerium content of the catalyst increased from 10 wt.% to 30 wt.%, wherein more than 70% of FAME conversion was produced. These results, therefore, suggested the transesterification of low grade cooking oil was dependable on appropriate percentage of Ce/Ca ratio. In contrary, this ascending trend of transesterification activity was against the findings obtained by Kamal et al. [14] where the optimal transesterification was achieved with less than 20 wt.% of dopant loading. Increasing the amount of dopant gave no further performance towards transesterification reaction. They found that the excessive dopant loading caused agglomeration on catalyst surface and blocking the pores and the number of active sites.

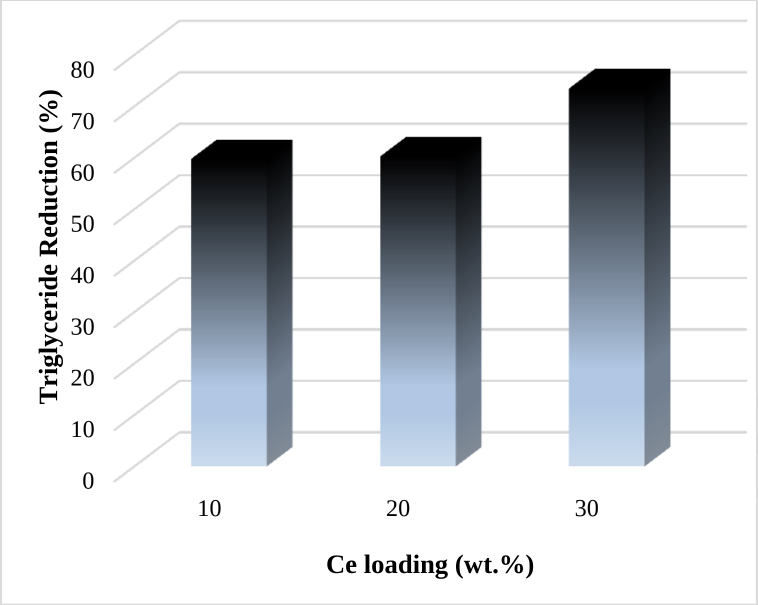

Figure 3. Effect of Ce loading of Ce/Ca/AC catalysts on the transesterification reaction

Effect of calcination temperature

Since calcination temperature affects the catalytic activity, the catalysts were calcined at different temperatures to determine the optimum calcination temperature for each based catalysts that could enhance the transesterification reaction. All the catalysts were calcined at different temperatures of 500, 700 and 1000 °C, while the cerium loading was varied at 10, 20 and 30 wt.%. Catalytic performances of all the catalysts were indicated in Table 2 which represented the percentage conversion of cooking oil at different calcination temperatures and various cerium loadings. At calcination temperature of 700 °C and 1000 °C, all catalysts showed low oil conversions. However, at lower calcination temperature of 500 ^{o}C, the oil conversion greatly increased for all catalysts. Among the prepared catalysts, the catalytic activity of Ce/Ca/AC catalysts calcined at 500 ^{o}C was the most promising catalyst for the transesterification reaction of low grade cooking oil to biodiesel compared to other catalysts. This might be due to the agglomeration of particles that occur on the surface of the catalyst during the calcination process, thus reducing the active sites of the catalyst [15].

Table 2. Effect of calcination temperature (CT) of Ce/Ca/AC catalyst on the transesterification reaction

	Triglyceride Reduction (%)		
Ce loading (wt.%)	**CT 500 °C**	**CT 700 °C**	**CT 1000 °C**
10	59.78	59.73	48.52
20	60.29	54.50	53.23
30	73.50	64.45	42.55

Effect of catalyst dosage

Catalyst dosage is another crucial factor that contribute to the higher conversion of FAME or biodiesel. From the previous findings, a variety of catalyst dosage affected the conversion percentage of biodiesel [16]. In this study, a range of 2 wt.% to 12 wt.% of Ce/Ca/AC catalyst was examined on the transesterification of low grade cooking oil. Based on the results, the ascending trend of triglyceride reduction or FAME conversion could be observed in Figure 4. The percentage yield from 2 wt. to 10 wt.% of FAME conversion was rapidly increased as catalyst provided more active sites for the transesterification reaction. 10 wt.% was considered as optimum catalyst dosage for reaching the maximum conversion of FAME due to its possibility to contact more between solid catalyst and reactant during adsorption-desorption process. However, there was no increment when the catalyst dosage was beyond 10 wt.%, This was probably due to the catalyst reached its maximum catalyst loadings for the reaction and leaching effect start to occur.

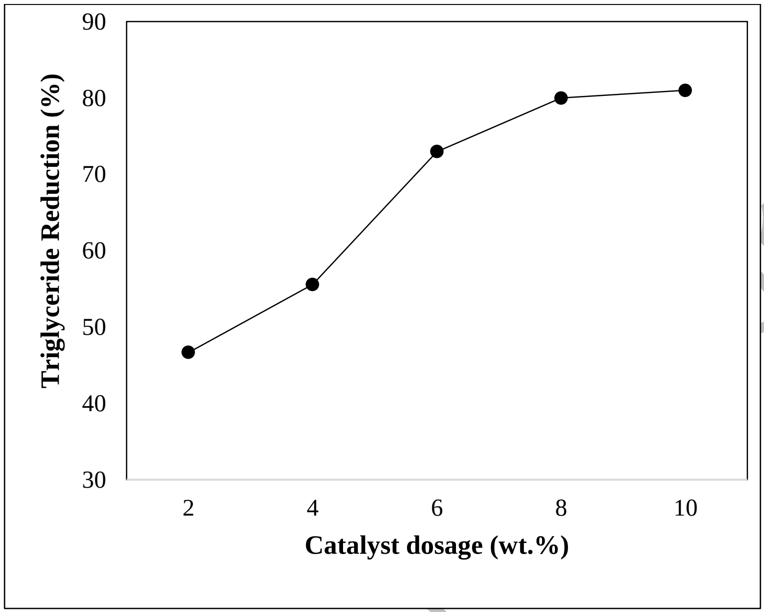

Figure 4. Effect of catalyst dosage on the reduction of triglyceride

Conclusion

As a conclusion, the optimum catalytic conditions for transesterification reaction was achieved with 30 wt.% of cerium on Ce/Ca/AC, calcined at 500 °C under the reaction conditions of 65 °C, 1:18 wt.% oil to methanol ratio, 6 wt.% catalyst loading and 3 hours of reaction time. Under these optimal conditions, almost 70% of FAME conversion was completed successfully. A high surface area of 149.18 m^2/g with needle-like shape and amorphous phase characteristics influenced the catalytic performance of Ce/Ca/AC towards transesterification reaction of low grade cooking oil.

Acknowledgement

The authors would like to acknowledge Universiti Kebangsaan Malaysia (UKM) for the financial support under Geran Galakan Penyelidik Muda (GGPM-2017-030).

References

1. Cai, Z. Z., Wang, Y., Teng, Y. L., Chong, K. M., Wang, J. W., Zhang, J. W. and Yang, D. P. (2015). A two-step biodiesel production process from waste cooking oil via recycling crude glycerol esterification catalyzed by alkali catalyst. *Fuel Processing Technology*, 137: 186-193.
2. Ezebor, F., Khairuddean, M., Abdullah, A. Z. and Boey, P. L. (2014). Esterification of oily-FFA and transesterification of high FFA waste oils using novel palm trunk and baggase-derived catalysts. *Energy Conversion and Management*, 88: 1143-1150.
3. Marinković, D. M., Stanković, M. V., Veličković, A. V., Avramović, J. M., Miladinović, M. R., Stamenković, O. O. and Jovanović, D. M. (2016). Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. *Renewable and Sustainable Energy Reviews*, 56: 1387-1408.

4. Bankovic-Ilic, I., Miladinovic, M., Stamenkovic, O. and Veljkovic, V. (2017). Application of nano CaO-based catalysts in biodiesel synthesis. *Renewable & Sustainable Energy Reviews*, 72: 746-760.
5. Kesic, Z., Lukic, I., Zdujic, M., Mojovic, L. and Skala, D. (2016). Calcium oxide based catalysts for biodiesel production: A review. *Chemical Industry & Chemical Engineering*, 22(4): 391-408.
6. Kwong, T. L. and Yung, K. F. (2015). Heterogeneous alkaline earth metal–transition metal bimetallic catalysts for synthesis of biodiesel from low grade unrefined feedstock. *RSC Advances*, 5(102): 83748-83756.
7. Macala, G. S., Robertson, A. W., Johnson, C. L., Day, Z. B., Lewis, R. S., White, M. G. and Ford, P. C. (2008). Transesterification catalysts from iron doped hydrotalcite-like precursors: Solid bases for biodiesel production. *Catalysis Letters*, 122(3-4): 205-209.
8. Ullah, F., Dong, L., Bano, A., Peng, Q. and Huang, J. (2016). Current advances in catalysis toward sustainable biodiesel production. *Journal of the Energy Institute*, 89(2): 282-292.
9. Maneerung, T., Kawi, S., Dai, Y. and Wang, C.H. (2016). Sustainable biodiesel production via transesterification of waste cooking oil by using cao catalysts prepared from chicken manure. *Energy Conversion and Management*, 123: 487-497.
10. Marinković, D. M., Avramović, J. M., Stanković, M. V., Stamenković, O. S., Jovanović, D. M. and Veljković, V. B. (2017). Synthesis and characterization of spherically-shaped Cao/Γ-Al_2O_3 catalyst and its application in biodiesel production. *Energy Conversion and Management*, 144: 399-413.
11. Abeti, M., Wan Daud, W. M. A. and Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 90(6): 770-777.
12. Warintorn T., Thawatchai M. and Sibudjing K., (2015). Highly active and durable Ca-doped Ce-SBA-15 catalyst for biodiesel production. *Energy*, 89: 946-956.
13. Abdullah, W. N. W., Azelee, W. A. W. A., Ali, R., Mokhtar, W. N. A. W. and Omar, M. F. (2017). Catalytic oxidative desulfurization technology of supported ceria based catalyst: Physicochemical and mechanistic studies. *Journal of Cleaner Production*, 162: 1455-1464.
14. Kamal, N. M., Bakar, W.A.W.A. and Ali, R. (2017). Catalytic optimization and physicochemical studies over Zn/Ca/Al_2O_3 catalyst for transesterification of low grade cooking oil. *Energy Conversion and Management*, 137: 113-120.
15. Rosid, S. J. M., Bakar, W. A. W. A. and Ali, R. (2015). Physicochemical study of supported cobalt–lanthanum oxide-based catalysts for Co_2/H_2 methanation reaction. *Clean Technologies and Environmental Policy*, 17(1): 257-264.
16. Wang, L. and Yang, J. (2007). Transesterification of soybean oil with Nano-MgO or not in supercritical and subcritical methanol. *Fuel*, 86: 328-333.