Synthesis of Cerium Oxide by Colloidal Emulsion Aphrons (CEAs) Method for Biodiesel Production

Wasinee Amesuwan[1] **and Somnuk Jarudilokkul**[2*]
King Mongkut's University of Technology Thonburi, Bang Mod, Thung Kru, Bangkok 10140

* *Corresponding Author : somnuk.jar@kmutt.ac.th*
[1] *Graduate Student, Department of Chemical Engineering, Faculty of Engineering.*
[2] *Associate Professor, Department of Chemical Engineering, Faculty of Engineering.*

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Abstract

This study investigated the use of barium hydroxide doped ceria ($Ba(OH)_2$–CeO_2) as solid base catalyst for the transesterification of palm oil with methanol to produce biodiesel. Cerium oxide was prepared by colloidal emulsion aphrons (CEAs), a type of dispersion method, which was then followed by calcination. The catalyst was evaluated for its activity in terms of the content of fatty acid methyl ester (%FAME). Moreover, the dependence of the %FAME on the reaction parameters, which included the amount of catalyst and reaction time, was studied. Physicochemical characteristics of the catalyst, as revealed by X-ray diffraction, Brunauer-Emmett-Teller analysis, scanning electron microscopy and differential thermal analysis/thermogravimetry, were also examined. The maximum methyl ester content was noted to be 94.65%. The optimal reaction condition for the transesterification used a 30:1 molar ratio of methanol to oil, with an addition of 8 wt.% $Ba(OH)_2$-CeO_2 catalyst and reaction time of 4 h.

การสังเคราะห์ซีเรียมออกไซด์ด้วยวิธีคอลลอยดอลแอฟรอนเพื่อผลิตไบโอดีเซล

วาศิณี เอี่ยมสุวรรณ[1] **และ สมนึก จารุดิลกกุล**[2*]
มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี แขวงบางมด เขตทุ่งครุ กรุงเทพฯ 10140

** Corresponding Author : somnuk.jar@kmutt.ac.th*
[1] *นักศึกษาระดับบัณฑิตศึกษา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์*
[2] *รองศาสตราจารย์ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์*

ข้อมูลบทความ

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รับเพื่อพิจารณา : 23 กรกฎาคม 2562
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บทคัดย่อ

งานวิจัยนี้ศึกษาการใช้ซีเรียมออกไซด์เจือด้วยแบเรียมไฮดรอกไซด์ ($Ba(OH)_2$–CeO_2) ซึ่งเป็นตัวเร่งปฏิกิริยาที่เป็นของแข็งสำหรับการผลิตไบโอดีเซลจากน้ำมันปาล์มโดยกระบวนเอสเทอริฟิเคชันกับเมทานอล โดยเตรียมซีเรียมออกไซด์ด้วยวิธีคอลลอยดอลอิมัลชันแอฟรอน (Colloidal emulsion Aphrons, CEAs) แล้วทำการเผา จากนั้นจึงทดสอบประสิทธิภาพของตัวเร่งปฏิกิริยาด้วยการวัดค่าร้อยละผลผลิตของเมทิลเอสเทอร์ของกรดไขมัน (%FAME) ปัจจัยที่ศึกษา ได้แก่ ปริมาณตัวเร่งปฏิกิริยา และระยะเวลาของการทำปฏิกิริยา นอกจากนี้ยังได้วิเคราะห์คุณลักษณะเชิงเคมี-กายภาพของตัวเร่งปฏิกิริยาที่เตรียมได้ด้วยเทคนิควิเคราะห์การเลี้ยวเบนของรังสีเอ็กซ์ การวัดพื้นที่ผิวจำเพาะและปริมาตรรูพรุน เทคนิคกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด และเทคนิควิเคราะห์สมบัติทางความร้อนของวัสดุ จากการศึกษา พบว่า สภาวะที่เหมาะสมต่อการเกิดปฏิกิริยาคืออัตราส่วนเชิงโมลของเมทานอลต่อน้ำมันเท่ากับ 30:1 ปริมาณตัวเร่งปฏิกิริยาร้อยละ 8 เวลาในการทำปฏิกิริยา 4 ชั่วโมง ซึ่งทำให้ได้ปริมาณเมทิลเอสเทอร์สูงสุดที่ร้อยละ 94.65

1. Introduction

Energy security is one of the most important issues facing the world today, particularly regarding fluctuating fuel costs, with the price of non-renewable fossil fuel resources, including natural gases, oil and coal, increasing in the world market day by day. Moreover, the supply of fossil fuels is expected to be exhausted in the near future. As fossil fuel resources become more and more limited, scientists have been trying to find alternative energy as a replacement. Renewable energy refers to types of energy generated from natural sources that are not finite in amount. Biodiesel produced from palm oil is one such interesting alternative. The conventional biodiesel process uses homogeneous catalysts such as sodium hydroxide which have many drawbacks. The removal of these catalysts from biodiesel fuel is difficult and requires a washing process that uses a large amount of water [1]. Heterogeneous catalysis is an economically and ecologically important area in the wider catalysis research field because these catalysts have many advantages. They are non-corrosive, environmentally benign and present fewer disposal problems than other catalysts. Moreover, they are also much easier to separate from liquid products and can be designed to produce higher activity, more selectivity and longer catalyst lifetimes [2-3]. Many types of heterogeneous catalysts, such as alkaline earth metal oxides and various alkaline metal compounds supported on alumina or zeolite can catalyze transesterification reactions [4-10]. The order of activity among alkaline earth oxide catalysts is BaO>SrO>CaO>MgO [11-13]. Wenlei et al. [13] found that the optimum catalyst of the reaction was Ba–ZnO with a loading of 2.5 mmol/g Ba on ZnO, calcined at 873 K for 5 h; this was able to exhibit the highest basicity and the best catalytic activity. When the transesterification reaction was carried out at reflux of methanol (338 K), with a 12:1 molar ratio of methanol to oil and a catalyst amount of 6 wt. %, the conversion of soybean oil was 95.8%. Beside, Xinhai et al. [15] investigated the use of CaO–CeO_2 mixed oxides as solid base catalysts. The best catalyst was Ce/Ca with a molar ratio of 0.15 and calcined at 973 K. It was regenerated after being reused 5 times; the biodiesel yield was 91%. Meena et al. [16] studied the transesterification of used vegetable oil with barium aluminate. It was found that the maximum %FAME was 93%. The synthesized CeO_2 nanoparticles had high surface areas resulting in the catalyst having higher activity. $Ba(OH)_2$ is a basic catalyst that has a high reaction rate and is not corrosive. Therefore, the combination of $Ba(OH)_2$ and CeO_2 should provide the best performance [17-18].

There have been recent reports of CeO_2 nanoparticles being prepared by various techniques, including mechanochemical reaction, microemulsion, hydrothermal, sol-gel method, glycothermal process, precipitation and spray pyrolysis [19-24]. Colloidal emulsion aphrons (CEAs) are considered as micrometer-sized water-in-oil (W/O) emulsion cores encapsulated by a “soapy shell” consisting of multi-layer surfactant molecules. In this dispersion, the emulsion core sizes are mainly between 10–100 μm and those of the inner phase droplets are between 1–5μm [25-29]. CEAs, which is mild and simple dispersion method, can also be used as a microreactor to synthesize nanoparticle materials.

Preparation of nickel over cerium oxide supported by the use of colloidal emulsion aphrons was studied by Sunisa et al. [29]. The three different methods of synthesis that were investigated were: (1) incipient wetness impregnation; (2) impregnate the support into CEAs loaded with nickel solution, and (3) coprecipitation in CEAs of support and active metal.

The synthesized particles were characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM), surface area and porosity analysis (BET), and inductively coupled plasma (ICP) analysis. The performances of all catalysts were tested with methane steam reforming. It showed that the catalyst prepared by method (2) exhibited the highest methane conversion rate [24]. Transesterification of palm kernel oil (PKO) with methanol over various types of natural calcium, including limestone calcite, cuttlebone, dolomite, hydroxyapatite, and dicalcium phosphate, has been investigated at 60°C and 1 atm. The calcination temperature had a significant effect on physicochemical properties, as evidenced by N_2 adsorption–desorption measurement, TGA, SEM and XRD. It was found that the calcination of dolomite at 800°C resulted in a highly active mixed oxide. Under the suitable reaction conditions, the amount of dolomite was calcined at 800°C of 6 wt.% based on weight of oil, with a methanol to oil molar ratio of 30:1 and reaction time of 3 h, methyl ester content of 98.0% can be achieved [18].

In the present study, cerium oxide was prepared by colloidal emulsion aphrons (CEAs) method followed by calcination and impregnation with $Ba(OH)_2$. The catalytic activity was presented in term of the conversion to methyl ester. Moreover, the dependence of the conversion to methyl ester on the reaction parameters, which included the amount of catalyst and reaction time, was examined.

2. Materials and Methods

2.1 Catalysts preparation

CeO_2 catalyst was obtained from the reduction of $CeCl_3{\bullet}7H_2O$ (Sigma) in colloidal emulsion aphrons (CEAs) as described in Sunisa et al. [29]. Then, mixed $Ba(OH)_2$(Merck)-CeO_2 were prepared using impregnation method. Following typical protocol, an aqueous solution containing barium hydroxide was stirred with CeO_2 catalyst for 6 h and then dried overnight at 100°C. Then, the solid particles were calcined in a muffle furnace at the given temperature for 1 h.

2.2 Catalyst characterization

The crystalline phase of $Ba(OH)_2$-CeO_2 obtained from the preparation was identified by X-ray diffraction (XRD, Bruker: D8 Discover) analysis. XRD patterns were carried out at room temperature using CuKα radiation (λ=1.54056 A°). XRD patterns of nanosized CeO_2 were obtained in 2θ range between 20° and 80° with a step of 0.01° and a scan speed of 2°/min. The particle morphology and the sizes of the $Ba(OH)_2$-CeO_2 were observed by Scanning Electron Microscope (SEM, Jeol Model JEM-2100) method. The surface area, pore size and pore volumes of the particles were measured by BET surface area and porosity analysis (Quantachrome: Autosorb-1).

2.3 Transesterification reaction

The transesterification was carried out in a 250 ml neck round-bottom flask equipped with reflux condensers and a magnetic stirrer. The mixture of palm oil (Oleen, Thailand), methanol and catalyst was stirred vigorously. After reaction, the catalyst was separated by filtration. Then, it was boiled in order to remove methanol. The organic phase was separated by centrifugation. The obtained sample was washed with deionized water and dried with anhydrous Na_2SO_4. Finally, %FAME (Fatty Acid Methyl Ester) was measured by using a gas chromatograph (Agilent 6890) equipped with a flame ionization detector (FID) and a 30-m HP-INNOWAX capillary column. All data from the experiment are based on duplicate sample.

3. Results and discussion

3.1 Biodiesel from palm oil by homogeneous and heterogeneous catalysts

For this experiment, the condition for reaction used a 30:1 molar ratio of methanol to oil, 4 wt% of catalyst, and reaction time of 4 h. Figure 1 reveals the effect of homogeneous and heterogeneous catalyst on %FAME. It was found that %FAME obtained from homogeneous catalyst was 95.68%. As the homogeneous catalyst is a liquid phase, which is the same as substrate, the catalyst can be mixed and made good contact with the substrate. However, a byproduct of this caution was soap which causes difficulty in the separation of glycerin from product [30]. For heterogeneous catalyst, 1.45 %FAME was obtained from CeO_2 which indicated that CeO_2 was a non-active agent for the biodiesel process. As CeO_2 particles have a high surface area and are stable, they can improve thermal stability of various materials [31]; therefore, this was selected as a support. In order to improve the surface properties, oxide of alkaline earth ($Ba(NO_3)$-CeO_2 and $Ba(OH)_2$-CeO_2) was selected as an active agent. It was found that %FAME of $Ba(NO_3)$-CeO_2 and $Ba(OH)_2$-CeO_2 were 20.93%, and 94.65%, respectively. Since the %FAME of $Ba(OH)_2$ was close to % FAME of NaOH, it was this selected as a dopant with CeO_2.

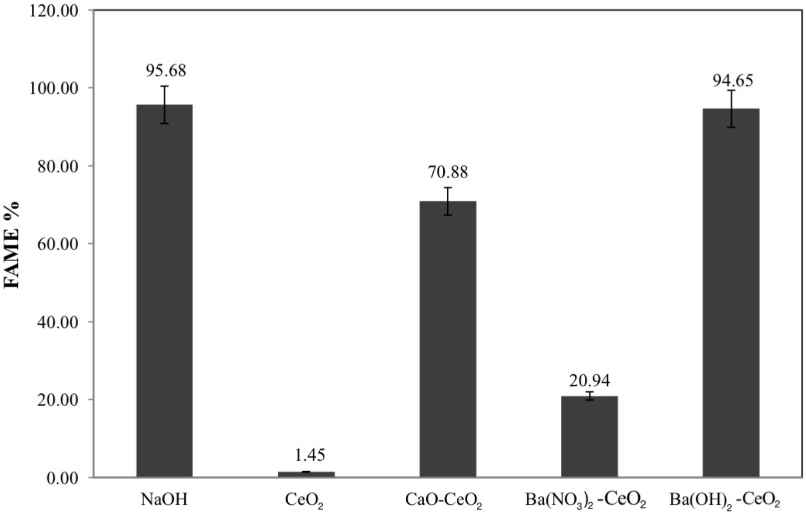


Figure 1 Influence of catalyst type on % FAME

3.2 Influence of catalysts preparation conditions

The influence of catalyst preparation is shown in Figure 2. %FAME obtained from $Ba(OH)_2$ was 95.52%, which is higher than the $Ba(OH)_2$ supported on CeO_2. By way of comparing catalyst support of cerium oxide commercial ($Ba(OH)_2$-CeO_2-com.) and cerium oxide synthesized by Colloidal Emulsion Aphrons ($Ba(OH)_2$-CeO_2-CEAs), it was found that %FAME obtained from $Ba(OH)_2$-CeO_2-com. and $Ba(OH)_2$-CeO_2.CEAs were

79.42% and 94.64 %, respectively. Sunisa et al. [29] reported that CeO_2-CEA particles were spherical in shape and nanometer in scale. Surface area and pore volume of the catalyst were higher than CeO_2-com whereas pore size of the catalyst was less than CeO_2-com., as shown in Table 1. The surface areas of CeO_2-com and CeO_2-CEAs were 0.977 m^2/g and 131.2 m^2/g, respectively. Thus, CeO_2-CEAs provided higher %FAME. It was chosen as a support for the impregnation with $Ba(OH)_2$ for active agent of biodiesel production.

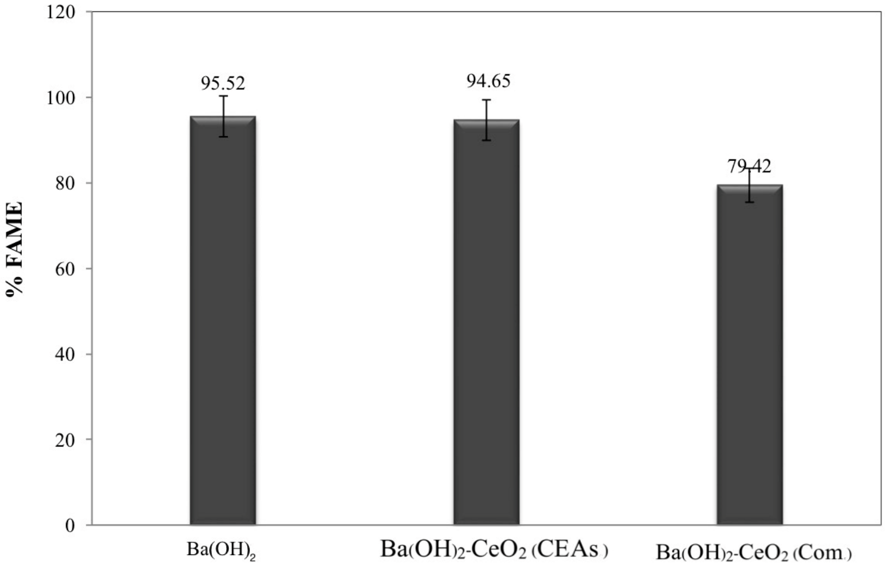


Figure 2 Influence of catalyst preparation condition
A : $Ba(OH)_2$ B : $Ba(OH)_2$-CeO_2 (CEAs.) C : $Ba(OH)_2$-CeO_2 (Com.)

Table 1 The Surface area, Pore volume and Pore size of $Ba(OH)_2$-CeO_2 with different CeO_2

Samples	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
CeO_2 (Com.)[a]	0.977	-	-
CeO_2 (CEAs)[b]	131.2	0.117	35.6
$Ba(OH)_2$-CeO_2 (Com.)	5.731	0.0219	152.80
$Ba(OH)_2$-CeO_2 CEAs	8.217	0.0279	135.70

[a](Navadol et al., 2005)and [b] (Sunisa et al., 2012)

The X-ray diffraction patterns of $Ba(OH)_2$-CeO_2 (com) and $Ba(OH)_2$-CeO_2(CEAs) are shown in Figure 3. The patterns indicated the same element present in the characteristic peaks of both samples. The peak of $Ba(OH)_2$-CeO_2(com) is higher than cerium oxide prepared by $Ba(OH)_2$-CeO_2(CEAs). This indicates that $Ba(OH)_2$-CeO_2(com) has higher crystallinity.

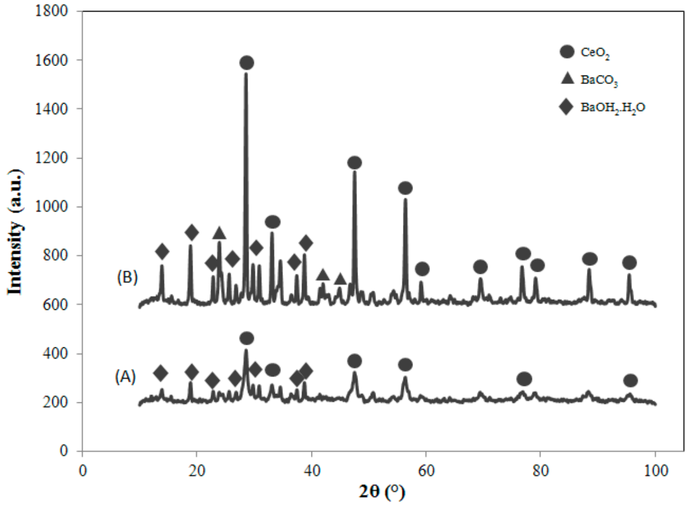
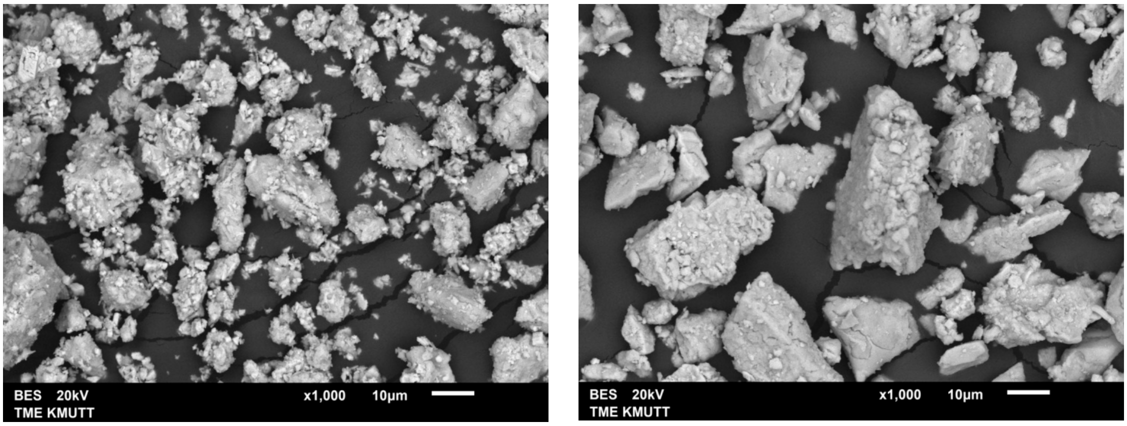


Figure 3 XRD patterns for samples: (A) $Ba(OH)_2$-CeO_2 (CEAs) and (B) $Ba(OH)_2$-CeO_2 (Com.)

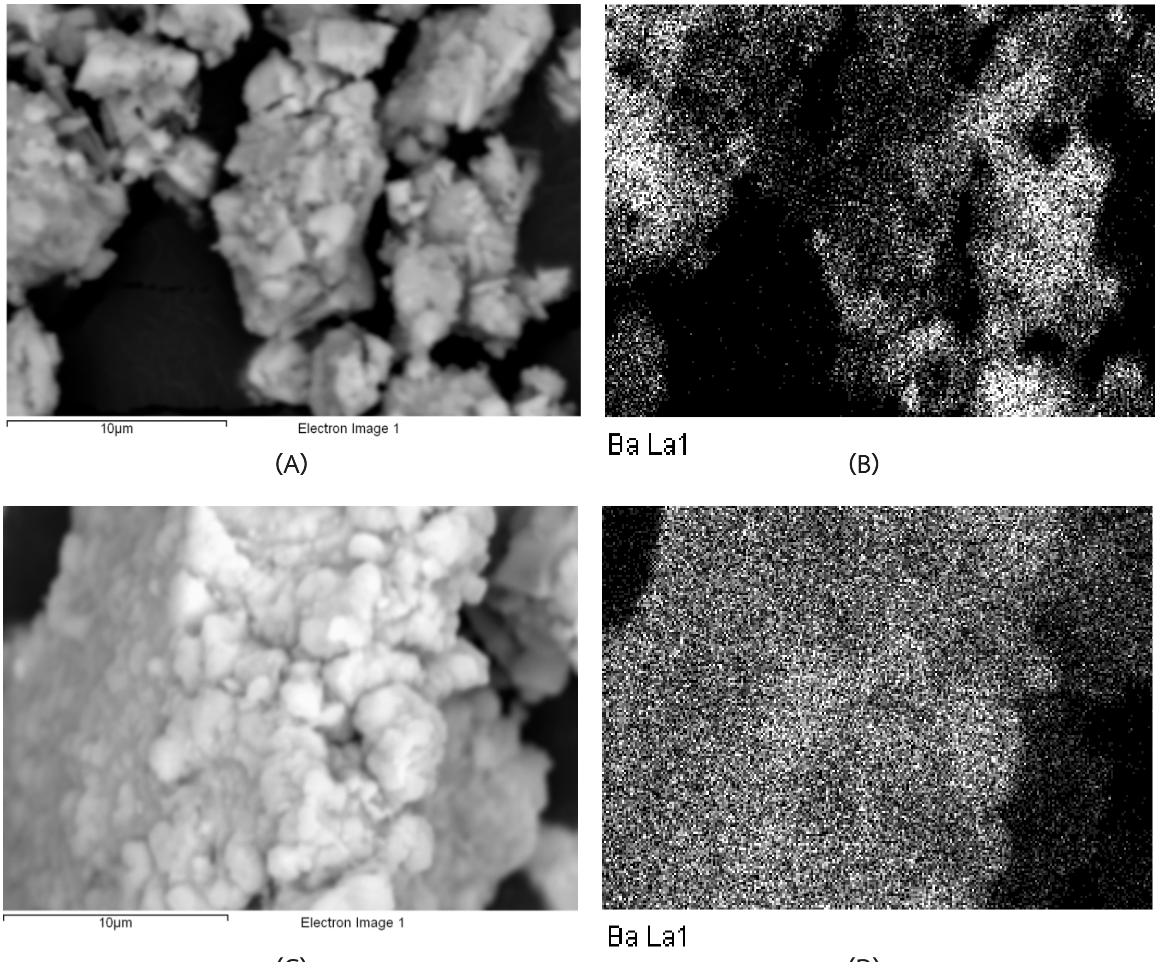
Scanning electron micrographs (SEM) of $Ba(OH)_2$-CeO_2(com) and $Ba(OH)_2$-CeO_2(CEAs) are presented in Figure 4. Both barium - cerium oxide particles are irregular-shaped crystalline particles. The $Ba(OH)_2$-CeO_2(com) particles consist of many small granules attached to aggregate particles.



(A) (B)

Figure 4 SEM images for samples: (A) $Ba(OH)_2$-CeO_2 (Com.) and (B) $Ba(OH)_2$-CeO_2 (CEAs)

In order to investigate the distribution of barium particles on cerium oxide, SEM/EDS was examined, as shown in Figure 5. The barium particles on $Ba(OH)_2$-CeO_2 (CEAs) in Figure 5 (D) were dispersed on the surface of cerium oxide and wee more uniform than that of $Ba(OH)_2$-CeO_2 (Com.), as shown in Figure 5 (B). Surface area and porosity of cerium oxide prepared by CEAs were higher than cerium oxide commercial, therefore, barium was seen to be loaded on the surface cerium oxide and more consistently.



(A) (B)

(C) (D)

Figure 5 SEM image of sample: (A) $Ba(OH)_2$-CeO_2 (Com.), (C) $Ba(OH)_2$-CeO_2(CEAs), and SEM/EDS images of samples: (B) Distribution of $Ba(OH)_2$-CeO_2 (Com.), (D) Distribution of $Ba(OH)_2$ -CeO_2 (CEAs).

The influence of calcination temperature (at the heating rate of 10°C/min) on %FAME is illustrated in Figure 6. It can be seen that %FAME increased with the calcination temperature. However, when the temperature was greater than 500°C, %FAME decreased. The increasing %FAME when the temperature was less than 500°C should be caused by the greater roughness of CeO_2 surface at a high temperature. It should be derived from the decomposition of the carbonate groups, which liberated CO_2 concomitantly resulting in the formation of small pores [17]. At a temperature higher than 500°C, the particle size increases substantially with increasing calcination temperature, indicating an obvious sintering of crystallinity, which results in an unreactive state [15]. Thus, 500°C was an optimum temperature and selected for most experiments.

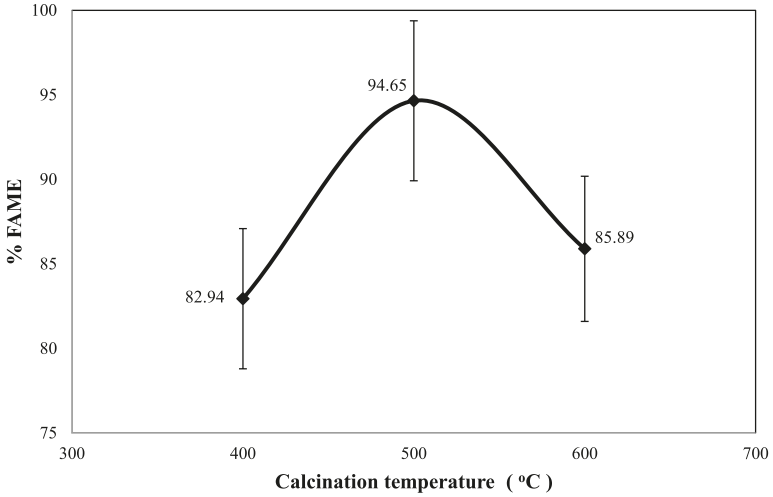
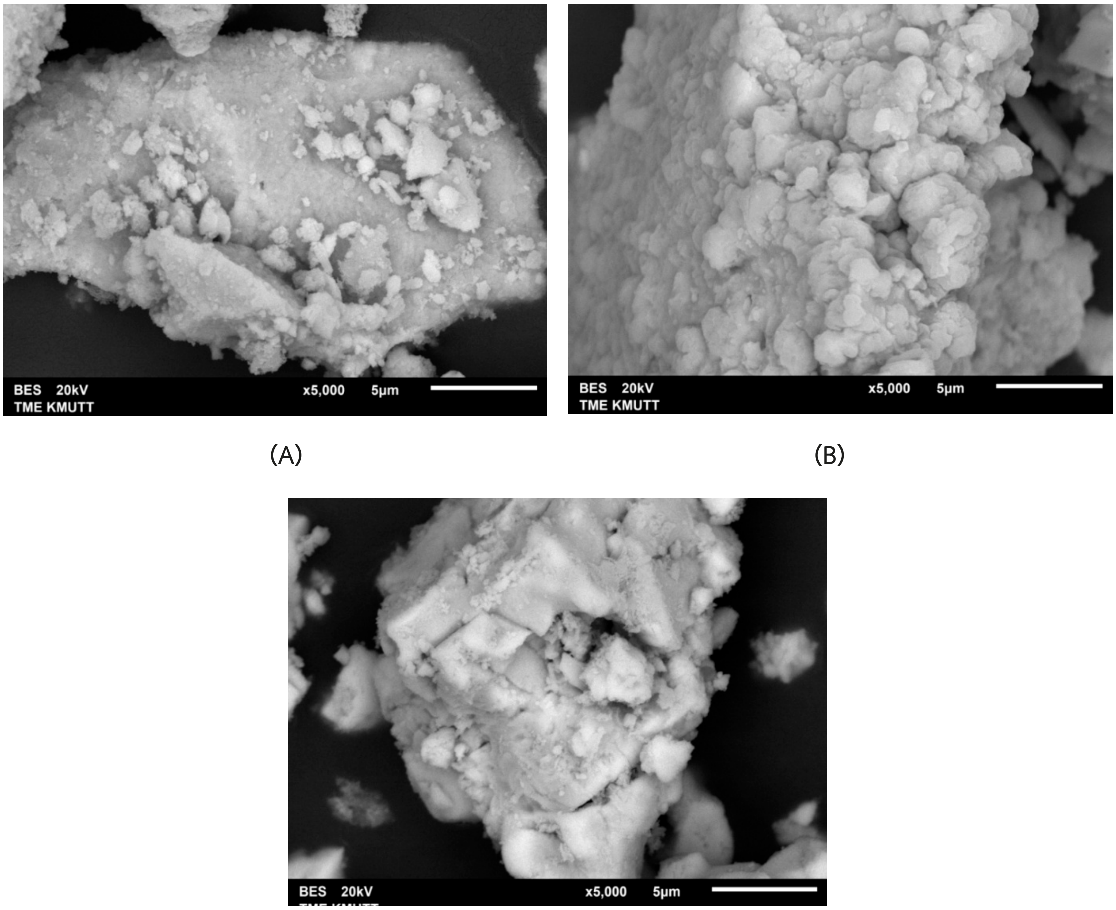


Figure 6 Influence of calcination temperature

Table 2 The Surface area, Pore volume and Pore size of $Ba(OH)_2$-CeO_2 with different calciantion temperatures

Calcination Temp. (°C)	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
400	9.180	0.0497	216.40
500	8.217	0.0279	135.70
600	4.411	0.0152	138.10

N_2 adsorption-desorption measurement is presented in Table 2. The pore sizes of all samples were classified as meso-porous (less than 10 nm). Moreover, an increase of calcination temperature caused a decrease in BET surface area and pore volume which might have been caused by sintering of the particles. The scanning electron micrographs of the calcined samples are presented in Figure 7. Catalysts calcined at high temperatures revealed increased roughness of cerium oxide surface, as shown in Figure 7 (A) and (B). Therefore, increasing the contact area between the catalyst and substrate resulted in a higher %FAME. Large fractures appeared on the surface when calcination temperatures were higher than 500°C, as shown in Figure 7 (C). The surface fraction was reflected by a significant decrease in the average pore volume, which corresponds to the data of BET in Table 1.



(A) (B)

(C)

Figure 7 SEM images for $Ba(OH)_2$-CeO_2:
(A) $Ba(OH)_2$-CeO_2 calcined at 400°C (B) 500°C and (C) 600°C

The X-ray diffraction patterns of calcined $Ba(OH)_2$-CeO_2 samples at different temperatures are depicted in Figure 8. All of the samples presented the peak of cerium oxide. Increasing calcination temperature caused the particles crystallize more. The characteristic peaks of the cerium oxide (2θ = 28.56°, 33.08°, 47.48°, 56.34°, 59.09° and 69.40°) and the characteristic XRD peak of $Ba(OH)_2$ were observed on the samples calcined at 400°C and 500°C in Figure 8 (A) and (B), respectively. Figure 8 (C) shows the increasing calcination temperature up to 600°C. $Ba(OH)_2$ was decomposed to $BaCO_3$ (2θ = 23.90°, 46.77° and 46.99°) and $BaCeO_3$ (2θ = 28.71°, 40.98°, 50.87°, 59.45°, 67.44° and 81.98°). $BaCO_3$ phase occurred by the loaded $Ba(OH)_2$ was decomposed to BaO on the surface of the cerium oxide support; subsequently, the formed

BaO could adsorb atmospheric CO_2 with the formation of $BaCO_3$ phase [14]. However, the BaO phase was not detected by XRD. The trace amounts of BaO phase may have been highly dispersed on the surface of the cerium oxide support as a monolayer [14]. The $BaCeO_3$ phase could be one reason for the lower catalytic activity because of decreased surface area of catalysts.

The representative weight loss (TG) and DTA curves of $Ba(OH)_2$-CeO_2 are presented in Figure 9, which shows DTA peak with the associated mass loss in the temperature ranges of 30-255°C and 255-800°C. At the temperature range of 30-255°C, a mass loss of 10.5% was related to a decrease in the amount of water in the $Ba(OH)_2{\bullet}8H_2O$ whereas at the temperature range of 255-800°C, the mass loss was due to the decomposition of the $Ba(OH)_2$, the solid–state interaction between the guest compound with the support [14]. The related evidence for the solid state interaction of the catalyst and support can also be seen via XRD pattern in Figure 8.

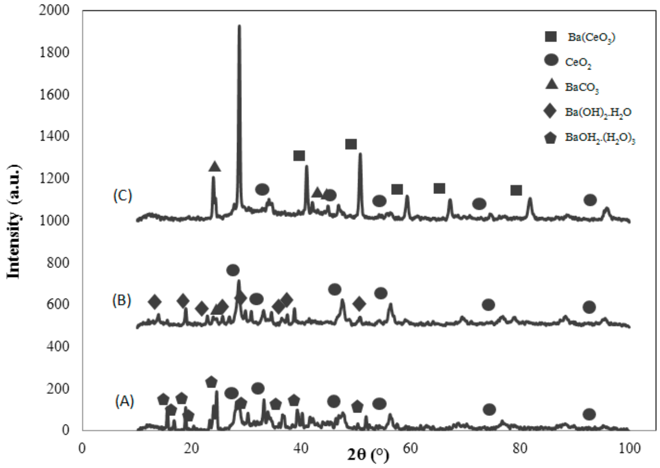


Figure 8 XRD patterns for $Ba(OH)_2$-CeO_2: (A) $Ba(OH)_2$-CeO_2 calcined at 400°C (B) 500°C and (C) 600°C

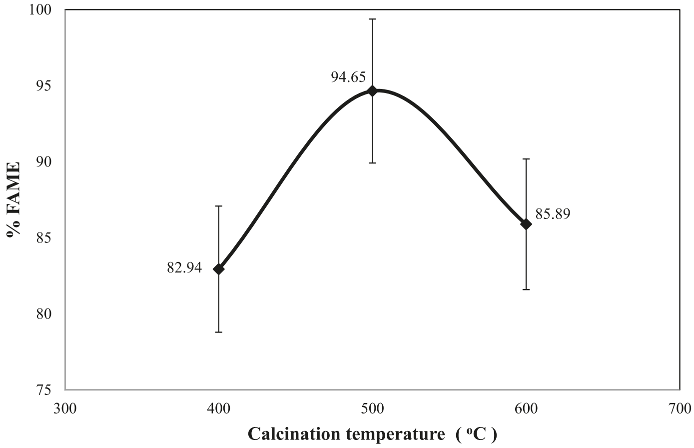


Figure 9 DTA-TG trace of the $Ba(OH)_2$-CeO_2

3.3 Influence of the reaction conditions

The influence of the catalyst amount was examined in the range of 4 - 16 wt. % of initial oil weight, as shown in Figure 10. The %FAME increased from 79.83% to 94.65% with an increase of catalyst amount from 4 wt. % to 8 wt. % which should increase the number of active basic sites. However, when the amount of $Ba(OH)_2$-CeO_2 increased to 12 wt.%, %FAME decreased. This may have been caused by poor diffusion between the methanol-oil-catalyst systems, and higher viscosity of the mixture. [15].

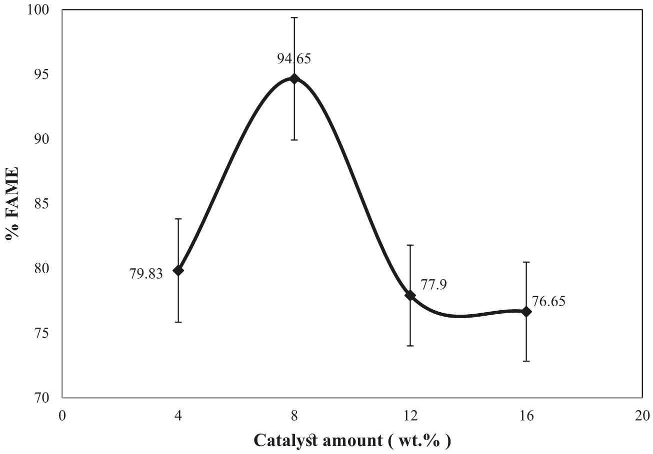


Figure 10 Influence of catalysts amount

The influence of reaction time on %FAME is shown in Figure 11.%FAME increased from 66.55% to 94.65% with an increased reaction time from 3 h to 4 h due to monoglycerides and diglycerides at initial stage retarded the diffusion of reactants and products [31]. Moreover, the rate of the reaction increased directly with reaction time until the reaction time reached 4 h. The decreasing %FAME at 5 h might have been caused by the decreasing amount of triglyceride and reversion of the reaction. Thus, the maximum conversion was achieved at a reaction time of 4 h. The highest %FAME obtained from this condition was higher than the %FAME (86%) obtained from transesterification of palm oil with ZnO [30].

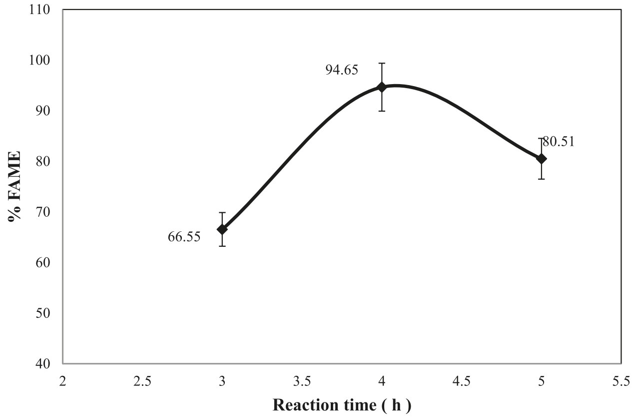


Figure 11 Influence of reaction time

After the completion of the reaction, the solid base catalyst of $Ba(OH)_2$-CeO_2 was recovered by filtration, washed with methanol and dried at 100°C [33] for 1 h. Reusability studies were carried out under the optimal reaction conditions mentioned above (methanol : oil molar ratio of 30 : 1, catalyst amount of 8 wt% and reaction time of 4 h.). The results are shown in Figure 12. The %FAME yield slightly decreased even in the second cycle (89.53%) and the third cycle (76.27%). This decrease in activity may have been due to the active siteblockage by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerol [1] and loss of the active site by methanol leaching [32].

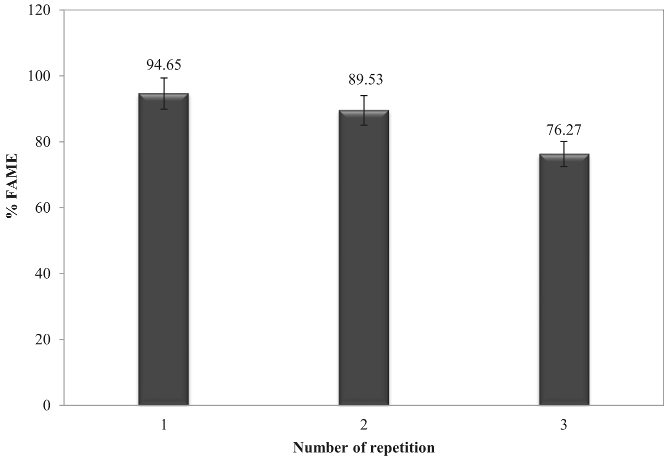


Figure 12 Influence of reusability of $Ba(OH)_2$-CeO_2

4. Conclusions

$Ba(OH)_2$-CeO_2 mixed oxides as solid base and high surface area catalysts can be seen as a good heterogeneous base catalyst for the transesterification of palm oil with methanol to produce biodiesel. The cerium oxides were prepared by colloidal emulsion aphrons (CEAs) method and loaded with $Ba(OH)_2$. The optimum calcination temperature of the catalyst was at 500°C for 1 h. The optimized reaction condition for the transesterification had a 30:1 molar ratio of methanol to oil, with an addition of 8 wt.% $Ba(OH)_2$-CeO_2 catalyst and reaction time of 4 h. The highest %FAME was 94.65% at the optimum condition. The reaction could be completed over a short time under mild temperatures and pressure conditions.

5. References

1. Boonyawan, Y., Parncheewa, U., Buppa, P. and Pawnprapa, K., 2010, "Modification of Calcite by Hydration–dehydration Method for Heterogeneous Biodiesel Production Process: The Effects of Water on Properties and Activity," *Chemical Engineering Journal*, 162 (1), pp. 135-141.

2. Gryglewicz, S., 1999, "Rapeseed Oil Methyl Esters Preparation using Heterogeneous Catalysts," *Bioresource Technology*, 70 (3), pp. 249–253.

3. Tanabe, K. and Holderich, W.F., 1999, "Industrial Application of Solid Acid-base Catalysts," *Applied Catalysis A:General*, 181 (2), pp. 399–434.

4. Schachter, Y. and Herman, P., 1968, "Calcium-oxide-catalyzed Reactions of Hydrocarbons and of

Alcohols," *Jounal of Catalysis*, 11 (2), pp. 147–158.

5. Xie, W., Peng, H. and Chen, L., 2006, "Transesterification of Soybean Oil Catalyzed by Potassium Loaded on Alumina as a Solid-base Catalyst," *Applied Catalysis A:General*, 300 (1), pp. 67–74.

6. Supes, G.J., Dasari, M.A., Doskocil, E.J., Mankidy, P.J. and Goff, M.J., 2004, "Transesterification of Soy-bean Oil with Zeolite and Metal Catalysts," *Applied Catalysis A:General*, 257 (2), pp. 213–223.

7. Zhang G., Hattori H. and Tanabe K., 1988, "Aldol Addition of Acetone, Catalyzed by Solid Base Catalysts: Magnesium Oxide, Calcium Oxide, Strontium Oxide, Barium Oxide, Lanthanum(III) Oxide and Zirconium Oxide," *Applied Catalysis A:General*, 36, pp. 189–197.

8. Iizuka, T., Hattori, H., Ohno, Y., Sohma, J. and Tanabe, K., 1971, "Basic Sites and Reducing Sites of Calcium Oxide and their Catalytic Activities," *Jounal of Catalysis*, 22 (1), pp. 130–139.

9. Kabashima, H., Katou, T. and Hattori, H., 2001, "Conjugate Addition of Methanol to 3-buten-2-one Over Solid Base Catalysts," *Applied Catalysis A: General*, 214, pp. 121–134.

10. Chantrasa, A., Sukphan, A. and Goodwin, J.G., 2011, "The Deactivation of Sulfonated Carbon Catalyst Derived from D-glucose on Amberite XAD1180 during the Biodiesel Synthesis at High Temperature," *KMUTT Research and Development Journal*, 34 (1), pp. 19-29. (In Thai)

11. Cantrell, D.G., Gillie, L.J., Lee, A.F. and Wilson, K., 2005, "Structure-reactivity Correlations in MgAl Hydrotalcite Catalysts for Biodiesel Synthesis," *Applied Catalysis A:General*, 287 (2), pp. 183–190.

12. Seki, T., Kabashima, H., Akutsu, K., Tachikawa, H. and Hattori, H., 2001, "Mixed Tishchenko Reaction Over Solid Base Catalysts," *Jounal of Catalysis*, 204 (2), pp. 393–401.

13. Tsuji, H., Yagi, F., Hattori, H. and Kita, H., 1994, "Self-condensation of n-butyraldehyde over Solid Base Catalysts," *Jounal of Catalysis*, 148 (2), pp. 759–770.

14. Wenlei, X. and Zhenqiang, Y., 2007, "Ba–ZnO Catalysts for Soybean Oil Transesterification," *Catalysis Letters*, 117 (3), pp. 159-165.

15. Xinhai, Y., Zhenzhong, W., Hongliang, L., Shan-Tung, T. and Jinyue, Y., 2011, "Transesterification of Pistacia Chinensis Oil for Biodiesel Catalyzed by CaO–CeO_2 Mixed Oxides," *Fuel*, 90 (5), pp. 1868–1874.

16. Meena, Y. and Yogesh C.S., 2019, "Transesterification of Used Vegetable Oil using BaAl2O4 Spinel as Heterogeneous Base Catalyst," *Energy Conversion and Management*, 198, pp. 111795-111805.

17. Sahani, S., Roy, T. and Chandra Sharma, Y., 2019, "Clean and Efficient Production of Biodiesel Using Barium Cerate as a Heterogeneous Catalyst for the Biodiesel Production; Kinetics and Thermodynamic Study," *Jounal of Cleaner Production*, 237, pp. 117699-117704.

18. Banerjee, M., Dey, B., Talukdar, J. and Chandra Kalita, M., 2014, "Production of Biodiesel from Sunflower Oil using Highly Catalytic Bimetallic Gold–silver Core–shell Nanoparticle," *Energy*, 69 pp. 695–699.

19. Bae, D.S., Lim, B., Kim, B.I. and Han K. S., 2002, "Synthesis and Characterization of Ultrafine CeO_2 Particles by Glycothermal Process," *Materials Letters*, 56 (4), pp. 610–613.

20. Li, Y.X., Zhou, X.Z., Wang, Y. and You, X. Z., 2003, "Preparation of Nano-Sized CeO_2 by Mechanochemical Reaction of Cerium Carbonate with Sodium Hydroxide," *M (3aterial Letters*., 58 (3), pp. 245–249.

21. Kang, H.S., Kang Y.C., Koo, H.Y., Ju, S.H., Kim, D.Y., Hong, S.K., Sohn, J.R., Jung, K.Y. and Park, S.B., 2006, "Nano-Sized Ceria Particles Prepared by Spray

Pyrolysis Using Polymeric Precursor Solution," *Materials Sciences and Engineering* B, 127, pp. 99–104.

22. Yuejuan, W., Jingmeng, M., Mengfei, L., Ping, F. and Mai, H., 2007, "Preparation of High-Surface Area Nano-CeO_2 by Template-Assisted Precipitation Method," *Journal of Rare Earths*, 25 (1), pp. 58–62.

23. Nagy, K. and Dékány I., 2009, "Preparation of Nanosized Cerium Oxide Particles in W/O Microemulsions," *Colloid and Surface A*, 345 (1), pp. 31–40.

24. Yang, Z., Yang Y., Liang, H. and Liu, L., 2009, "Hydrothermal Synthesis of Monodisperse CeO_2 Nanocubes," *Materials Letters*, 63 (21), pp. 1774–1777.

25. Deng, T., Dai, Y. and Wang, J., 2005, "A New Kind of Dispersion—Colloidal Emulsion Aphrons," *Colloids and Surface: Physicochemical and Engineering*, 266, pp. 97–105.

26. Jauregi, P., Gilmour, S. and Varley, J., 1997, "Characterisation of Colloidal Gas Aphrons for Subsequent Use for Protein Recovery," *Chemical Engineering Journal*, 65 (1), pp. 1–11.

27. He, Y., Wu, Z. and Mao, Z.S., 2009, "A General Diffusion Model for Mass Transfer in Colloidal Liquid Aphron Systems," *Colloids and Surface: Physicochemical and Engineering*, 338, pp. 25–32.

28. Srivastava, P., Hahr, O., Buchholz, R. and Worden, R.M., 2000, "Enhancement of Mass Transfer using Colloidal Liquid Aphrons: Measurement of Mass Transfer Coefficients in Liquid–liquid Extraction," *Biotechnology and Bioengineering*, 70, pp. 525–532.

29. Sunisa, S., Virote, B. and Somnuk, J., 2012, "Synthesis of Nanocrystalline CeO_2 Particles by Different Emulsion Methods," *Materials Characterization*, 67, pp. 83– 92.

30. Muhammad, T., SaqibAli, A. and NasirKhalid, 2012, "Activity of Homogeneous and Heterogeneous Catalysts, Spectroscopic and Chromatographic Characterization of Biodiesel:A Review, *Renewable and Sustainable Energy Reviews*, 16 (8), pp. 6303–6316.

31. Asanumaab, H., Polcikc, P., Kolozsvaric, S., Klimashinb, F.F., Riedlb, H. and Mayrhoferb, P., 2017, "Cerium Doping of Ti-Al-N Coatings for Excellent Thermal Stability and Oxidation Resistance," *Surface and Coatings Technology*, 326, pp. 165-172.

32. Chawalit, N., Pramwit, N., Sithikorn, T. and Kunchana, B., 2010, "Biodiesel Production through Transesterification over Natural Calciums," *Fuel Processing Technology*, 9 (11), pp. 1409–1415.

33. Kristaps, M., 2018, "The Potential of K_3PO_4, K_2CO_3, Na_3PO_4 and Na_2CO_3 as Reusable Alkaline Catalysts for Practical Application in Biodiesel Production," *Fuel Processing Technology*, 179, pp. 302–312.