CALCIUM OXIDE AS A SOLID BASE CATALYST FOR TRANSESTERIFICATION OF TRA CATFISH FAT

Le Thi Thanh Huong(1), **Huynh Van Tien**(1), **Phan Minh Tan**(2), **Tran Thi Viet Hoa**(3)
(1) Ho Chi Minh City University of Industry
(2) Department of Science and Technology HCMC
(3) University of Technology, VNU-HCM

ABSTRACT: *In our work, biodiesel was prepared from Tra fat by methanolysis reaction using activated calcium oxide as solid base catalyst. Effects of various process parameters on biodiesel production such as molar ratio of methanol to fat, catalyst concentration, temperature and time of reaction and the active mechanism of CaO catalyst for the transesterification reaction were investigated. The results show that CaO has strong basicity and high catalytic activity as a heterogeneous solid base catalyst and the transesterification reaction takes place on basic sites of calcium diglyceroxide formed due to the reaction between CaO and the by-produced glycerol. The biodiesel yield achieves 92.95 % at 60 °C, 90 minutes, 8:1 molar ratio of fat to methanol, and 6 % CaO catalyst. Important fuel properties of the produced biodiesel meet the specifications of ASTM D 6751 biodiesel standard*

1. INTRODUCTION

Biodiesel production is based on the transesterification reaction of triglycerides with methanol in the presence of a catalyst, to yield the corresponding fatty acid methyl esters (FAME) and glycerine as co-product. Current technology uses homogeneous basic catalysts such as NaOH and KOH. However, the high cost of biodiesel is a barricade to commercialize biodiesel. Nowadays, studies have found solutions to reduce the biodiesel cost like the recovery of crude glycerine and methanol, the use of heterogeneous catalysts, supercritical methanol, cosolvents, and etc [1,2,3]. Heterogeneous basic catalysts could be easily separated from the reaction mixture by filtration and then reused. Also, they are less corrosive, leading to safer, cheaper, and more environment-friendly operations. When heterogeneous catalysts were used, most of studies demonstrated that strict conditions including high reaction temperature, long reaction time, high molar ratio of methanol to oil, high pressure or adding cosolvent were still needed. As a consequence, it is still necessary to explore new heterogeneous catalysts [4,5,6].

Our object is to study biodiesel production by methanolysis reaction of Tra fat obtained in Mekong Delta, Vietnam, using activated calcium oxide as solid base catalyst. The activation mechanism of CaO catalyst was also investigated.

2. EXPERIMENTAL

2.1. Materials

Fat of Tra Catfish used in the experiments was obtained from An Giang Agriculture and Food Export Company (Afiex). Pure methanol (99%) was obtained from Vietnam. The CaO catalyst with pure grade (92%) was purchased from China. Gas chromatograph standards for methyl esters were obtained from Fulka (United Kingdom) and Sigma (Spain). Chemicals used for analysis were supplied from Merck (Germany).

2.2. Preparation of catalyst

A commercial calcium oxide was milled to 90 μm and then activated by calcination at 1000 °C for 4 hours to remove absolutely the surface carbonate and hydroxyl groups. Then it was stored in a closed flask in the presence of KOH pellets to diminish the rehydration and the adsorption of CO_2 (fresh catalyst). The basic strength and the basicity of the prepared catalyst

(H_) were determined by using Hammett indicator. The X-ray diffraction (XRD) of the catalyst was performed on a Siemen D-5000 using the Cu-Kα radiation, over a 2θ range of 20°-74° with a step size of 0.03° at a scanning speed of 0.8°/s. The specific surface area of the catalyst was measured using the Brunauer-Emmett-Teller (BET) method with QUANTACHROME TRRWIN V1.0. KBr pellet technique was applied for determining IR spectra of the catalyst. Spectra were recorded on a spectrometer with 4 cm^{-1} resolution by BRUCKER system. After the completed transesterification reaction, the catalyst was collected through filtration and then washed with methanol to remove the stains such as FAME and glycerine. For identifying the active mechanism of catalyst, calcium diglyceroxide, as a reference sample, was prepared by the reaction of CaO and glycerine in the presence of methanol. The solubility of CaO was determined by the EDTA titration method.

2.3. Transesterification

The transesterification process from Tra fat with methanol using CaO catalyst was performed according to Fig. 1. After filtered off catalyst, the rest of production mixture was neutralized by 18 % HCl solution to reject the remaining CaO catalyst. Production mixture then settled to separate into two phases for 4 h by separator funnel. The upper layer was neutralized again by 10% KOH solution to eliminate absolutely the remains of HCl and free fatty acids. Subsequently, crude biodiesel was washed by hot distillated water (60 – 70°C) until the washing was neutral. Finally, biodiesel product was dried by household microwave oven SANYO Fan-Assisted 1200 W [7].

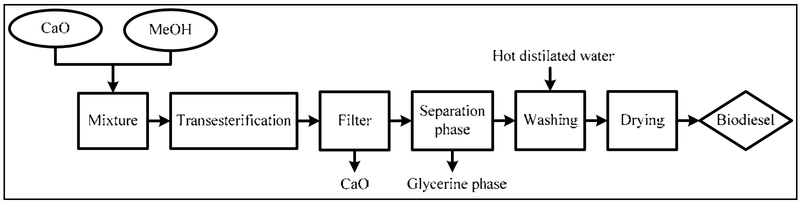


Fig. 1. Schema of the transesterification from Tra fat

2.4. Analytical methods

Physicochemical properties of biodiesel were determined using standard test methods according to ASTM D 6751 [8].

The production yield (H):

$$H(\%) = \frac{m_{biodiesel} \times C}{\frac{3m}{M} \times M_{FAME}} \times 100\%$$

$m_{biodiesel}$: amount of biodiesel product

m: amount of Tra fat

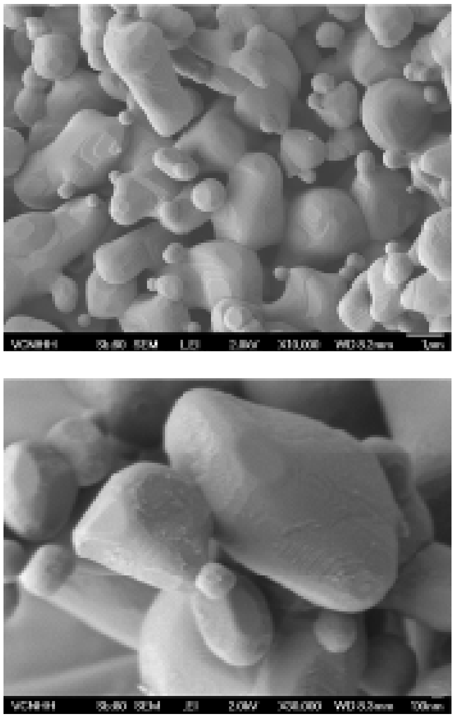
M and M_{FAME}: average amount of a Tra fat molecule and FAME molecule

3. RESULTS AND DISCUSSION

3.1. Characterizations of activated CaO catalyst

The activated CaO catalyst is characterized by the physicochemical parameters such as the specific surface area of 3.55 m^2/g, the basic strength of 7.55mmol/g, the amount of basic of $15 < pH < 18.4$ and the solubility degree in methanol of 0.01 %. The shape of commercial CaO is irregular [9]. After activation process, the shape is still irregular but the morphologies become similar to each other, and the grains are sintered (Fig. 2a).

a.Commercial CaO



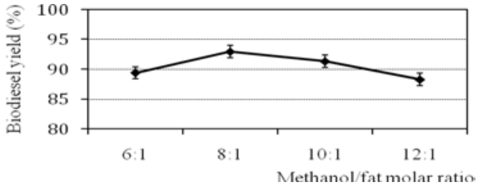
b.Activated CaO catalyst

Fig. 2. SEM images of CaO catalyst

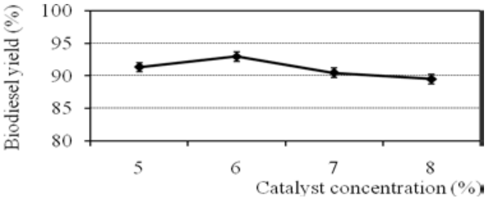
3.2. Effect of parameters on transesterification reaction

3.2.1. Effect of molar ratio of methanol to fat

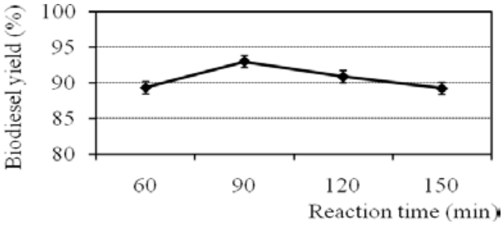
The fixed factors were 6 % CaO, reaction temperature of 60 ^{o}C, and reaction time of 90 minutes. The molar ratios of methanol to fat were ranged from 6:1 to 12:1. The results as shown in Fig. 3a indicate that the biodiesel yield increases with increases in molar ratio. The maximum yield (92.95 %) achieves at 8:1 methanol:fat molar ratio. It should be noted that in presence of heterogeneous catalysts, the reaction mixture is a three-phase fat/methanol/catalyst system. With an increase in the methanol loading amount, the ability to have good phase contact increases, which results in increasing biodiesel yield. However, further increases in methanol:fat molar ratio (higher than 8:1) decrease the conversion yield. Furthermore, higher methanol:fat molar ratios could make separating and washing step of biodiesel from glycerine phase complicated due to the formation of emulsion of excessive methanol with glycerine. In addition, much energy is needed to recover the large amount of unreacted methanol. Therefore, the best methanol/fat molar ratio is 8:1.



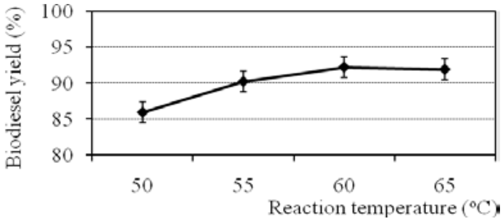
a. Effect of molar ratio of methanol to fat



b. Effect of catalyst concentration



Effect of reaction time



Effect of reaction temperature

Fig. 3. Effect of reaction parameters on the biodiesel yield

3.2.2. Effect of catalyst concentration

The fixed factors were reaction temperature of 60 ^{o}C, reaction time of 90 minutes, and the above optimized molar ratio of methanol to fat (8:1). The catalyst concentration of CaO was changed from 5 % to 8 %. As we can see the results presented in Fig. 3b, the maximum transesterification yield (92.95 %) achieves at 6 % CaO catalyst concentration. When catalyst concentration is greater than the best value (6 %), the biodiesel yield reduces due to the decrease in the ability to have a good phase contact. Hence, the best methyl ester yield is obtained at 6 % CaO catalyst.

3.2.3. Effect of reaction time

The methanolysis of Tra fat was carried out during different periods of time such as 60, 80, 90 and 120 minutes. In all experiments, other parameters like molar ratio of methanol to fat and catalyst concentration were the optimal results achieved in the previous sections. The results as shown in Fig. 3c indicate that the conversion reaction is fast and the obtained biodiesel yield is more than 80% with reaction time of 60 minutes. The maximum yield of transesterification also is 92.95 % for reaction time of 90 minutes. As conversion reaction achieves the maximum yield, if reaction time is continuously increased, the conversion yield will decrease due to long reaction time at high temperature (60 ^oC) nearby the boiling point of methanol, so methanol could be easily undergone some loss.

3.2.3. Effect of reaction temperature

The temperature of transesterification reaction was ranged from 50 ^oC to 65 ^oC. In all experiments, other parameters like molar ratio of methanol to fat, catalyst concentration, and reaction time were the optimal results achieved in the previous sections. The results as shown in Fig. 3d indicate that the maximum yield of production biodiesel achieves 92.95 % at 60 ^oC. After the best reaction temperature, the production yields are almost constant because the transesterification reaction achieved the equilibrium state. Hence, the best reaction temperature for transesterification of Tra fat using CaO is 60 ^oC.

3.3. The active mechanism of CaO catalyst

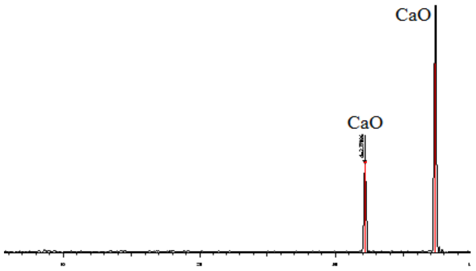


Fig 4a. Fresh CaO

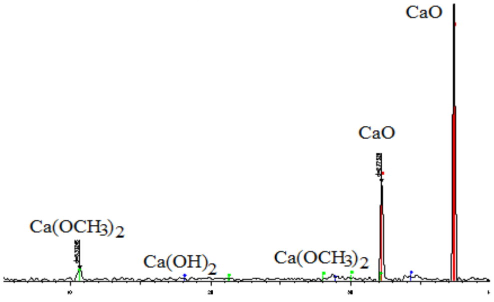


Fig 4b. CaO and MeOH

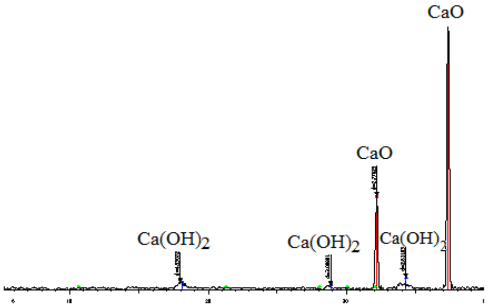


Fig 4c. Collected CaO after reaction time of 20 min

Fig. 4 shows XRD patterns of the fresh catalyst, collected catalyst, and the reference samples. It finds that the chemical composition of CaO catalyst is significantly transformed into some other calcium compounds during the transesterification process. Comparing the fresh catalyst (Fig 4a) with the catalyst activated for 20 min with MeOH (Fig. 4b), we could find small diffraction peaks, attributable to $Ca(OH)_2$ and $Ca(CH_3O)_2$, but most of CaO remained as is. This implies that a small amount of CaO has reacted with methanol to form $Ca(OH)_2$ and $Ca(CH_3O)_2$ as follows: $CaO + 2CH_3OH \rightarrow Ca(CH_3O)_2 + H_2O$; $CaO + H_2O \rightarrow Ca(OH)_2$. The transesterification is progressed due to the catalytic activation of $Ca(CH_3O)_2$. However, no peak of $Ca(CH_3O)_2$ could be found after reaction time of 20 min (Fig. 4c).

Interestingly, only component is noticed after the transesterification reaction is completed. Characteristic peaks of calcium methoxide are not found (Fig. 4c). Furthermore, glycerine as a by-product is a trihydric alcohol; it can react with CaO to form CaO-glycerine complex. Obvious peaks appeared with 2θ values of 8 ^{o}, 10 ^{o}, 21 ^{o}, 24 ^{o}, 26 ^{o}, and 39 ^{o} (Fig. 4d), which are almost the same as that of calcium diglyceroxide prepared as the reference sample (Fig. 4e).

Calcium diglyceroxide composing the collected catalyst could be produced by combining calcium oxide with the by-produced glycerine ($CaO+2C_3H_8O_3 \rightarrow (C_3H_7O_3)_2Ca + H_2O$. In addition, it is also noticed that more soaps are produced by the saponification of the $Ca(OH)_2$ catalyst with free fatty acids contained in Tra fat ($Ca(OH)_2 + 2RCOOH \rightarrow (RCOO)_2Ca + 2H_2O$. The experiments prove that calcium oxide is more reactive with glycerine than with methanol because the reaction of calcium oxide with methanol in the presence glycerine produces only calcium diglyceroxide.

From these results, it is clear that the probable activation mechanism of the transesterification using CaO catalyst is as follows. First, CaO is activated by methanol and a small amount of CaO is converted into $Ca(CH_3O)_2$ which activates the transesterification reaction to form the by-produced glycerine. The produced glycerine reacts with CaO and a calcium diglyceroxide is formed. The participation of calcium diglyceroxide as a high active catalyst promotes the rate of the transesterification. It could be explained that the continuous withdraw of glycerine makes the equilibrium of the transesterification shift to the product side; as a result, the reaction time is significantly reduced in comparison with other heterogeneous catalysts. Thus, CaO catalyst is activated by methanol as an intitiating reagent for the reaction to produce glycerine; then, the calcium dilgyceroxide, which is formed from the generated glycerine and CaO, functions as the main catalyst of the transesterification reaction.

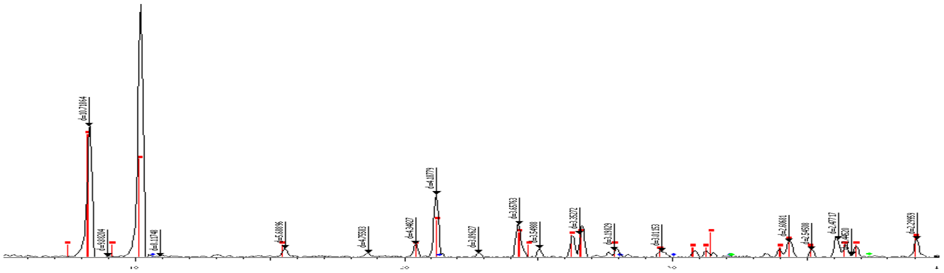


Fig 4e. Calcium diglyceroxide from reaction of CaO and glycerine in the presence of MeOH

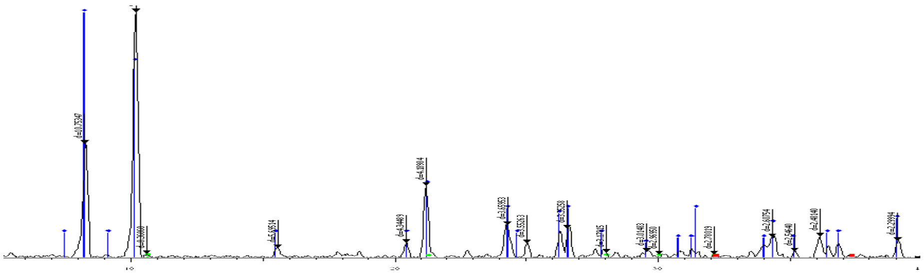
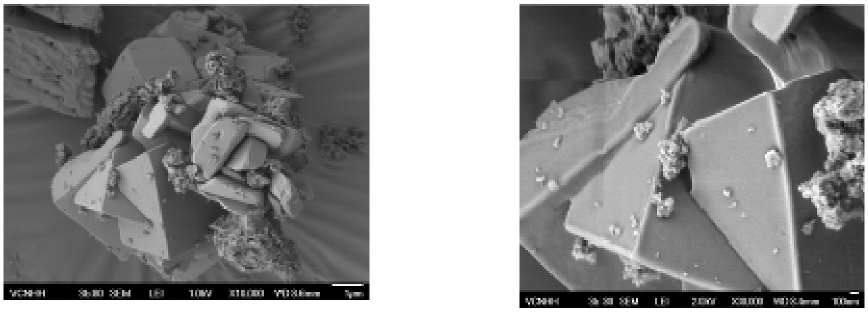


Fig 4d. CaO collected after reaction

Fig. 4. XRD patterns of collected CaO catalyst and reference sample

SEM images of CaO collected after the transesterification reaction and reference sample of calcium diglyceroxide as shown in Fig. 5 indicate that the morphology of CaO catalyst is evidently changed after the transesterifiaction reaction. Most particles are in the shape of angular rock (Fig. 5b). It is similar to the shape of calcium diglyceroxide (Fig. 5a).

a.Calcium diglyceroxide



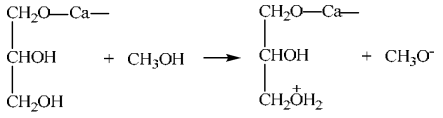
b.The collected catalyst

Fig. 5. SEM images of calcium diglyceroxide and the collected catalyst

Fig. 5 illustrates a proposed mechanism on the transesterification using calcium oxide as a solid base catalyst. The catalyzed transesterification spends two stages. At the first stage, calcium diglyceroxide is produced.

$CaO + 2CH_3OH \rightarrow Ca(CH_3O)_2 + H_2O$
$CaO + H_2O \rightarrow Ca(OH)_2$
$Ca(CH_3O)_2 \rightarrow Ca^{2+} + CH_3O^-$
$CH_3O^- + RCOOR \rightarrow RCOOCH_3 + ROH$ (Glycerine - $C_3H_8O_3$)
$2C_3H_8O_3 + CaO \rightarrow (C_3H_7O_3)_2Ca + H_2O$

At the second stage, calcium diglyceroxide would play the catalyst role for the transesterification.



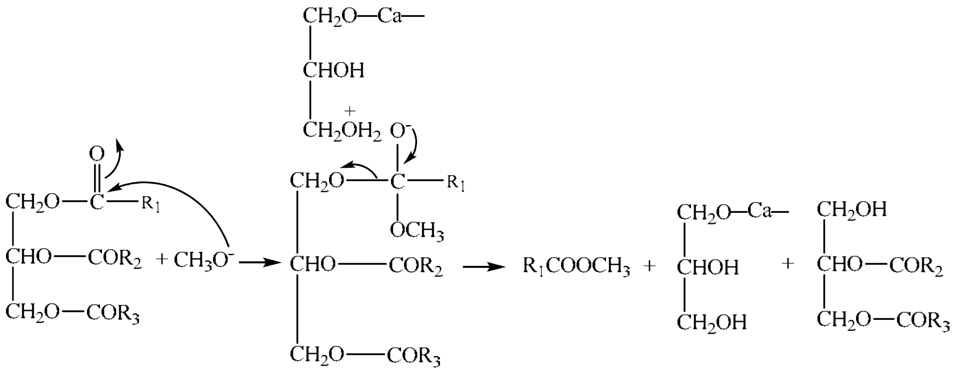


Fig. 6. Possible mechanism for transesterification of Tra fat using CaO catalyst

Some researchers have proposed the mechanisms on the transesterification using calcium oxide as a heterogeneous catalyst, however most of them are suggestive [5,6,8,9,10].

4. CONCLUSIONS

This study indicates that CaO catalyst is the potential heterogeneous catalyst for the biodiesel production on large scale due to its abundance, availability, cheap cost, and high basic strength. The main factors affecting the transesterification are molar ratio of methanol to fat, catalyst concentration, reaction temperature and reaction time. The maximum yield of 92.95 % could be achieved at 8:1 molar ratio of methanol to fat and the activated CaO catalyst of 6 % at 60 °C for 90 minutes. Calcium diglyceroxide, which is formed by the reaction of calcium oxide with the by-produced glycerine, functions as the main catalyst for the the transesterification reaction. However, the active surface sites of CaO are poisoned with CO_2 and covered with H_2O; thus the CaO catalyst has thermally treated at 1000 °C before being used for the transesterification.

ĐIỀU CHẾ BIODIESEL TỪ MỠ CÁ TRA XÚC TÁC DỊ THỂ CaO

Lê Thị Thanh Hương[(1)], Huỳnh Văn Tiến[(1)], Phan Minh Tân[(2)], Trần Thị Việt Hoa[(3)]
(1) Trường Đại học Công nghiệp TP.Hồ Chí Minh
(2) Sở Khoa học và Công nghệ
(3)rường Đại học Bách Khoa TP.HCM

TÓM TẮT: *Nghiên cứu này khảo sát khả năng sử dụng CaO như là một xúc tác baz rắn cho phản ứng điều chế biodiesel từ mỡ cá Tra. Nội dung nghiên cứu gồm các yếu tố ảnh hưởng đến phản ứng chuyển hóa este như tỷ lệ metanol/mỡ, hàm lượng xúc tác, thời gian và nhiệt độ phản ứng và cơ chế hoạt động của xúc tác CaO. Kết quả cho thấy CaO là một xúc tác baz rắn mạnh có hoạt tính xúc tác cao. Phản ứng chuyển hóa được thực hiện chủ yếu trên các tâm baz của hợp chất canxi diglyxeroxid mà được tạo thành từ xúc tác CaO và glyxerin sinh ra trong phản ứng. Hiệu suất biodiesel cao nhất 92,95 % đạt được ở điều kiện: tỷ lệ mol metanol:mỡ là 8:1, 6 % CaO trong thời gian 90 phút và ở nhiệt độ 60 ^{o}C. Các tính chất quan trọng của sản phẩm biodiesel đều đáp ứng được tiêu chuẩn ASTM D 6751.*

REFERENCES

[1]. J. Gerpen, B. Shanks, R. Prusko, and D. Clements, Biodiesel Production Technology, Report of National Renewable Energy Laboratory **(NREL/SR-510-36244)**, (2004).

[2]. H. Fukuda H, Kondo A, and Noda H, Review Biodiesel Fuel Production by Transesterification of Oil, Biodiesel and Bioengineering, 92, 405-416 (2001).

[3]. U. Schuchardt, R. Serchelia, R. Vargas, Transesterification of Vegetable Oils: a Review, Journal of Brazilian of Chemical Society, **9**(1), 199-210, (1998).

[4]. E. Lotero, J. Goodwin, A.Bruce Jr, K. Suwannakarn, Yijun Liu, and D. Lopez, The Catalysis of Biodiesel Synthesis, Catalysis, **19**, 50-58 (2006).

[5]. M. L. Granados, M. D, Z. Poves, and et al, Biodiesel from sunflower oil by using activated calcium oxide, Applied Catalysis B: Environmental, **73**, 317-326 (2007).

[6]. X. Liu, H. He, and et al, Calcium methoxide as a solid base catalyst for transesterification of soybean oil to biodiesel with methanol, Fuel **87**(7), 1076-1082 (2008).

[7]. L. T. T. Huong, P. M. Tan, T. T. V. Hoa, S. Lee, Biodiesel production from fat of Tra catfish and Basa catfish, Journal of the Korean Oil Chemists' Society, **25**(3), 418-428 (2008).

[8]. L. T. T. Huong, P. M. Tan, T. T. V. Hoa, Biodiesel production from fat of Tra catfish with KOH catalyst assisted by microwave, Tạp chí Hóa học, **47**(2A), 440-446, (2009).

[9]. S. Yan, M. Kim, S. O. Salley, K.Y. Simon Ng, Oil transesterification over calcium oxides modified with lanthanum, Applied Catalysis A: General, **360**, 163–170 (2009).

[10]. J. Lengyel, Z. Cvengrošová, J. Cvengroš, Transesterification of triacyglycerols over calcium oxide as heterogeneous catalyst, Petroleum & Coal, 51(3), 216-224, (2009).

[11]. B. P. Lim, G. P. Maniam, Biodiesel from adsorbed waste oil on spent bleaching clay using CaO as a heterogeneous catalyst, European Journal of Scientific Research, **33**(2), 347-357, (2009).