Producción de biodiesel a partir de aceite de palma en un reactor de lecho fijo con metóxido de calcio como catalizador

Biodiesel production from palm oil in a fixed-bed-reactor with calcium methoxide catalyst

**Olga J. Rojas*, Liliana M. Gómez*, José G. López*,
Rolando Barrera-Zapata**, Sonia A. Giraldo*§**

**Centro de Investigaciones en Catálisis, Escuela de Ingeniería Química,
Universidad Industrial de Santander, Bucaramanga, Colombia
**Grupo CERES, Agroindustria y Biorefinerías. Departamento de Ingeniería Química,
Facultad de Ingeniería, Universidad de Antioquia, Colombia
olga.rojas@correo.uis.edu.co, marce_2698@hotmail.com, josegabrieliq@gmail.com,
rolando@udea.edu.co, §sgiraldo@uis.edu.co*

Resumen

En el presente trabajo se analizó el comportamiento del metóxido de calcio como catalizador para la producción de biodiesel a partir de aceite de palma. Inicialmente se establecieron condiciones de operación en un reactor por lotes, como temperatura de activación CaO (25°C), temperatura de reacción (60°C) y relación molar metanol/aceite (10). Se describió el montaje y puesta en marcha de un reactor de lecho fijo y flujo continuo a escala laboratorio; a las condiciones establecidas se obtuvieron rendimientos a métilesteres del 20% con un tiempo de residencia de 60 min. También se analizó el uso de cosolventes como el terbutanol y el acetato de etilo para eliminar las limitaciones de transferencia de masa entre las fases e incrementar los rendimientos a metil ésteres. Se encontró que el uso de etil acetato como cosolvente incrementó el rendimiento a metil esteres hasta el 31 %.

Palabras clave: Biodiesel, cosolvente, oxido de calcio activado, transesterificación.

Abstract

In this research, the behavior of calcium methoxide as catalyst for the production of biodiesel from palm oil in a continuous system was studied. Initially, operating conditions such as CaO activation temperature (25°C), reaction temperature (60°C) and molar ratio methanol-oil (10)were established for a batch reactor. Then, the schematic diagram of the experimental setup and its implementation were described for a packed-bed laboratory scale reactor with continuous flow; for this system, yields of methyl esters of 20% with a residence time of 60 min were obtained. The use of co-solvent such as tert-Bbutanol and ethyl acetate in the continuous reaction system was also investigated, aiming to eliminate mass transfer artifacts between the phases and eventually increasing yields to methyl esters. The use of ethyl acetate as co-solvent increased methyl esters yields up to 31 %.

Keywords: Activated calcium oxide, biodiesel, cosolvent, transesterification.

1. Introduction

Biodiesel is mainly produced at an industrial level by transesterification reactions using basic homogeneous catalysts and discontinuous systems (Canakci, 2007; Balat, M., & Balat, H., 2010). These processes usually present specific drawbacks related with their unfriendly environmental nature due to the challenging to catalyst recoveries. Despite this, most of homogeneous catalytic systems used in transesterification reactions tend to generate corrosion problems and large amounts of waste, in addition to the low quality glycerin obtained as inevitable by-product (Suehara *et al*., 2005). A possible solution for these problems is the use of basic solid catalysts. This kind of catalysts can be recovered and reused in the reaction, allowing to reduce the operational plant costs; hence further process stages, such as catalyst recovering, neutralization, washing, as well as glycerin purification stages can be avoided (Albis *et al*., 2005).

Among the basic solid catalyst commonly used for transesterification reactions, the alkaline earth oxides can be found. The CaO is preferred between the alkaline earth oxide catalyst due its low cost, high catalytic activity and high catalytic stability (Becerra *et al*., 2011).Though a delay in catalytic activity at the beginning of the oil palm transesterification reaction with CaO is observed (latency time), the reaction time necessary for reaching specific biodiesel yields is increased when compared with homogeneous catalysts. In previous works, it was determined that this latency time correspond to the time required for the methoxide ion formation at the solid catalytic surface; consequently, a prior catalyst activation, i.e., the methoxide formation, can accelerate the reaction (Kawashima *et al*., 2009; Granados *et al*., 2007).

It is well known that large industries prefer continuous processes for obtaining high-demand products; therefore, it is important to develop continuous process technologies for the production of biodiesel through heterogeneous catalysis. The present study aims to perform the installation and start-up of a continuous laboratory scale reactor

for the transesterification reaction of palm oil with methanol. In addition, the most relevant parameters that could affect the catalytic activity of calcium methoxide in such reaction were analyzed. Initially, different catalyst activation conditions and reaction conditions were evaluated in a batch system. Then, the installation and start-up of a packed bed reactor with continuous flow was evaluated, including among others, the evaluation of the effect of adding co-solvents to the reaction mixture.

2. Methodology

2.1 CaO characterization

The basic nature of fresh CaO (purity> 99%, Merck) and CaO activated with methanol (purity > 99%, Merck) was determined by the Hammett titration method (Tanabe *et al*., 1989). Three different basic strong indicators were used: bromothymol blue ($7.2 < H < 9.3$), phenolphthalein ($9.3 < H < 15$) and 2.4-dinitroaniline ($15 < H < 18.4$). The procedure for the basic strong determination and the estimation of the number of basic sites consisted in the preparation of a solution indicator – methanol (1 mg indicator/ ml of methanol). Then, 0.1 g of catalyst was mixed with 3 ml of the indicator - methanol solution and the mixture was stirred for stabilization during 2 hours. The change in the mixture color to its basic form was evaluated with benzoic acid 0.01 M. The amount of basic sites was determined by means of Eq. (1).

$$number\ of\ basic\ sites = \frac{acid\ benzoic\ concentation \left[\frac{mmol}{ml}\right] * acid\ benzoic\ volume\ [ml]}{calcium\ oxide\ weight\ [g]} \quad (1)$$

Additionally, Fourier Transformed Infrared spectra (FT-IR Bruker model Tensor 27) were acquired for fresh CaO catalyst and activated CaO catalyst using the KBr pills method. In this way, the presence of methoxide species on the CaO surface was verified.

2.2 Oil palm transesterification

Refined oil palm was supplied by S.I. Saceites Company. The oil palm composition is given in

Table 1. In order to find the most suitable operation conditions for the oil palm transesterification reaction, i.e., CaO activation temperature, reaction temperature and molar ratio methanol/oil palm, a set of reactions were initially performed in batch mode. Then, the previously defined conditions for the batch system were used in the continuous system. The batch reactor consisted in a three-neck rounded glass flask (120 ml) equipped with a magnetic stirrer and immersed in a temperature-controlled oil bath. The glass flask necks were used for the condensation system, temperature measurement and sampling, respectively.

Table 1. Oil palm composition.

Fatty acid	wt. %
Palmitic	38.5
Myristic	1.1
Lauric	0.4
Palmitoleic	0.2
Stearic	3.8
Oleic	44.2
Linoleic	9.5
Linolenic	0.2
Arachidic	0.4
Eicosenic	0.2

The following procedure was used for the batch mode probes: according to previous works recommendations (Becerra *et al*., 2011); a mixture with 0.53 % wt. of CaO was prepared in 14.7 ml of methanol and kept under magnetic stirring (570 rpm) during 1.5 h; in this way the CaO activation took place. In the present work, three different CaO activation temperatures were tested (25, 40 and 60°C). Once the CaO was activated, the oil palm was added to the mixture and the desired reaction temperature was adjusted. The effect of two different reaction temperatures in the oil palm esterification was investigated (45°C and 60°C). The amount of oil palm added to the system was defined in order to test three different molar ratios methanol/oil palm (6.9, 10 and 23).

After defining the suitable CaO activation temperature (25°C), the reaction temperature (60°C) and the molar ratio methanol/oil palm (6.9), the continuous reaction system was developed according to Fig. 1. The continuous reactor consisted in a glass column of 80 cm3 (1.7 cm internal diameter, 35 cm long) packed with 25 g of CaO with average particle size between 1.18-0.6 mm. The catalytic bed of~5 cm long was located between two inert zones using material
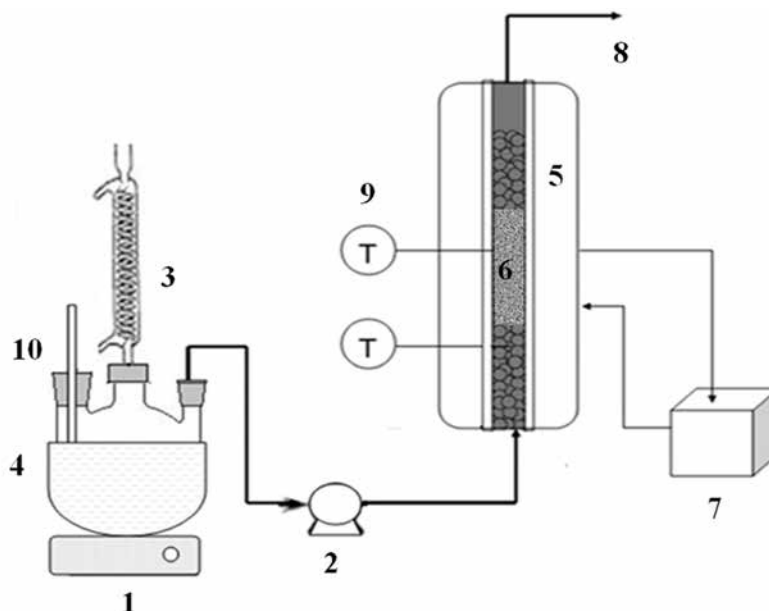

Figure 1. *Continuous reaction system. Heating plate (1), peristaltic pump (2), condensation system (3), three-neck rounded glass flask with temperature-controlled oil bath (4), oven (5), catalytic bed (6), temperature control (7), sample collection system (8), temperature sensors (9), thermometer (10).*

of the same particle size. The feed (600 ml) was loaded in a three-neck rounded glass flask (1000 ml) immersed in a temperature-controlled oil bath. The glass flask was equipped with condensation system; magnetic stirring and temperature control. The isothermal reactor operation was guaranteed by a vertical oven and its respective control artifacts. In addition, the catalytic bed temperature was continually monitored. A feed flow of 0.5 ml/min was used and samples (~0.5 ml) were taken in regular time intervals at the exit of the reactor. It was assumed that stationary state was reached when identical methyl ester yields were found for three consecutive samples.

Two different approaches for the CaO activation were evaluated for the continuous reactor operation: *in-situ* CaO activation and *ex-situ* CaO activation. In-situ CaO activation consisted in loading up the catalytic bed with fresh CaO, then passing methanol during a specified activation time (2, 16 or 60 h), and finally feeding the reaction mixture as previously described. For the ex-situ CaO activation approach, the CaO was activated using the described procedure on batch-mode. After that, the activated CaO was loaded on the catalytic bed and then the reaction mixture was fed.

Finally, the effect on the reaction yield when co-solvents are added to the reaction mixture was evaluated. The use of co-solvents could improve the phase mass transfer between the alcohol, the oil and the solid catalyst, increasing reaction yields. The co-solvents evaluated in this work were tert-Butanol (purity > 99%, Merk), and ethyl acetate (purity> 99%, Sigma-Aldrich). Aspen Plus expert software simulation was used to simulate the LLE for the ternary mixture Alcohol + oil + co-solvent (Fig. 2) and to determine the amount of co-solvent required for ensuring the formation of just one liquid phase. In the simulations, oil palm was assumed to be palmitic oil because it is one of the major oil palm components (Table 1) and is a substance available in the software database. For the tert-Butanol, the molar ratio co-solvent/oil used was 9, and for the ethyl acetate as co-solvent, the co-solvent/oil molar ratio was 4.7.

Reaction products were analyzed by GC (HP 6890) equipped with a FID detector and a capillary column HP-INNOWAX (30 m x 0.32 mm x 0.25 µm). The reaction samples (~0.5 ml) were prepared taking 20 µl from the less dense layer of the sample, which is the layer rich in methyl ester and diluting it in 800 µl of n-heptane. After that, a 2% wt. of
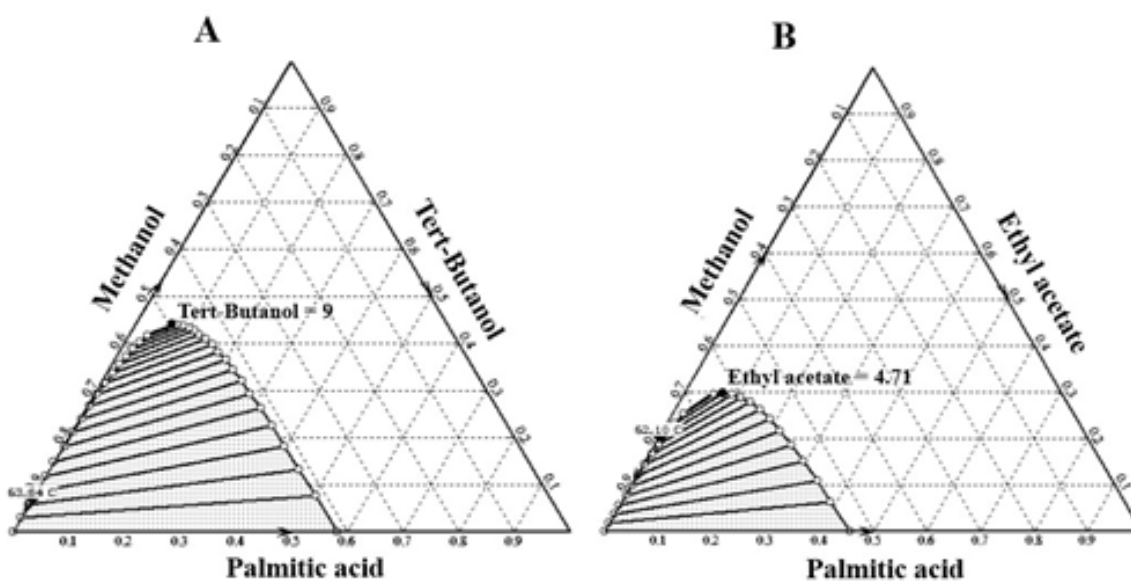

Figure 2. *Liquid-liquid equilibrium to 60 ° C of mixtures: (A) palmitic acid + methanol + ethyl acetate and (B) palmitic acid + methanol + tert-Butanol. Calculations using the simulator Aspen plus 11.1.*
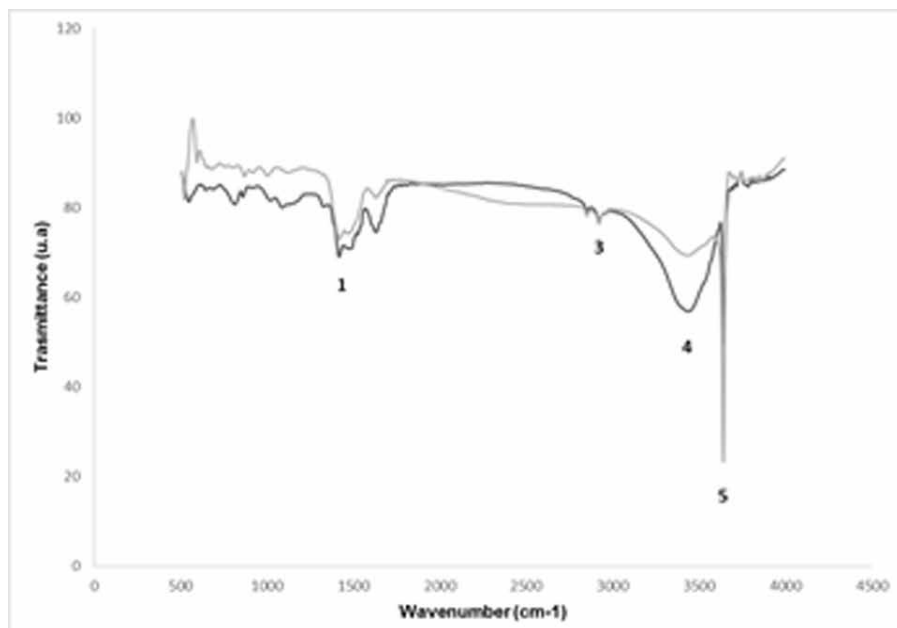
Figure 3. *FTIR spectra of activated CaO (black line) and fresh CaO (gray line), where the numbers indicate the vibrations corresponding to:1 = C-OH, 2 = C-O, 3 = CH-, 4 and 5 =OH-.*

standard (dodecane purity > 99%, Sigma- Aldrich) was added to the sample and analyzed by GC. For quantifications, a standard methyl ester mixture (Fames, Supelco) was used as reference. The catalytic activity was measured in terms of methyl ester yields (%) using Eq. (2). It is important to note that for a total oil conversion, the maximum methyl ester yields could be around 95%.

$$yield[\%] \; = \; \frac{methyl\;ester\;[g]}{oil\;palm[g]} \; x \; 100 \qquad (2)$$

3. Results and discussion

3.1 Catalyst characterization

Fig. 3 shows the FT-IR spectra for fresh CaO catalyst and activated CaO catalyst. A wide band in the 3000 – 3700 cm^{-1} region (bound number 4 on Fig. 3) was observed, which corresponds to the stretching vibrations of OH groups on the Ca(OH)$_2$ (Lutz *et al.*, 1994). It is noticed on Fig. 3 that this band increases its intensity in the activated CaO when compared with the fresh CaO. The band No. 3 in Fig. 3 located between 2800 – 3000 cm^{-1} was assigned to the stretching vibrations for the C-H bond; while the band observed at 1429 cm^{-1} was assigned to the flexion mode of CH$_3$ (Rep *et al.*,

2000). The band No. 2 in Fig. 3 at 1647 cm^{-1} in the activated CaO was assigned to the stretching vibration of C-O bonds (Granados *et al.*, 2010). The presence of these bands on spectra (Fig. 3) can be explained by the methoxide formation on the CaO surface.

Table 2 shows the results for basic sites analyses on the fresh CaO and the activated CaO using different basic indicators. For both catalysts (fresh CaO and activated CaO),the bromothymol blue indicator and the phenolphthalein indicator showed fast color change to their respective conjugated bases, while the 2,4 - dinitroaniline did not show color change. This observation permits to conclude that the activation process on the CaO generated a basic sites increase in the range 7.2 < H < 9.3 and 9.3 < H < 15 with respect to the fresh CaO, without showing a strong basic increase on the catalytic surface. Similar results were found by Kouzu *et al.* (2008), reporting a calcium methoxide basicity in a range of 15.0 to 18.0 using the Hammet indicators method. Thus, basic sites measurements (Table 2) and IR spectra (Fig. 3) demonstrate that the activation process generates a higher amount of basic sites related to the OH group in the catalytic surface.
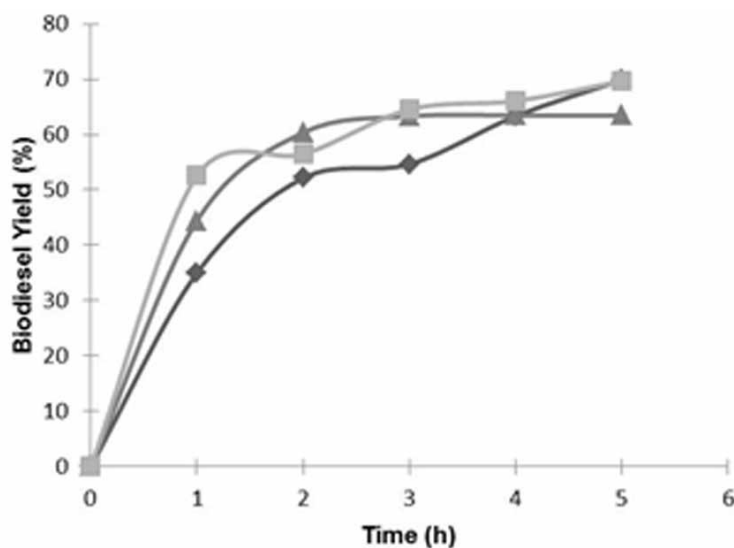
Figure 4. *Effect of activation temperature on the CaO (—◆— 60, —■— 40 y —▲— 25°C) in the methyl ester formation with 0.53% CaO wt, reaction temperature =60°C, molar ratio Alcohol/oil =6.9, molar ratio alcohol/CaO=72.24, activation time =1.5 h.*

Table 2. *Basic sites measurements and basic strength of fresh CaO and activated CaO.*

	Basicity [mmol/ g of CaO]	
catalyst	Bromothymol blue $7.2 < H\_ < 9.3$	Phenolphthalein $9.3 < H\_ < 15.0$
Activated CaO	7.5	11.9
Fresh CaO	2.4	2.6

3.2 Activation temperature

Fig 4 shows the effect of activation temperature on the CaO in the methyl ester formation. It is observed that for the first hour of reaction, a 53% yield to methyl ester is obtained when activation temperature is 25 °C; while only 35% yield to methyl ester is obtained when activation temperature is 60 °C. These results can be explained by the adsorption limitations of
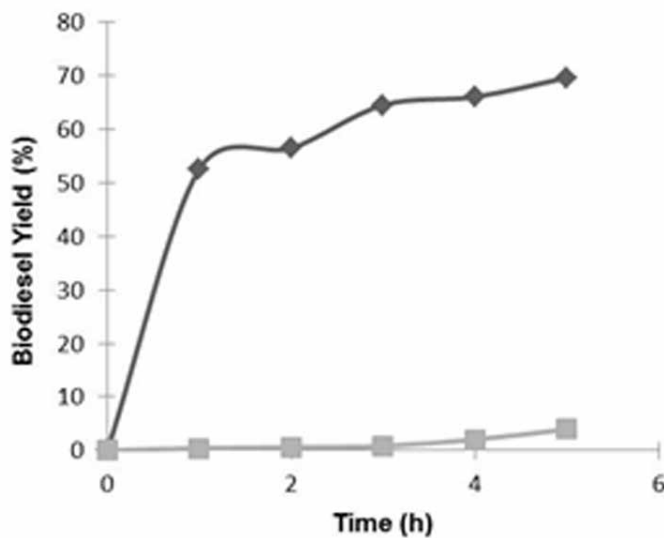

Figure 5. *Effect of reaction temperature (—◆— 60 y —■— 45°C)on the methyl ester yields with 0.53% wt. of CaO, molar ratio Alcohol/oil=6.9, molar ratio Alcohol/CaO=72.24, Activation temperature=25°C, activation time =1.5 h.*
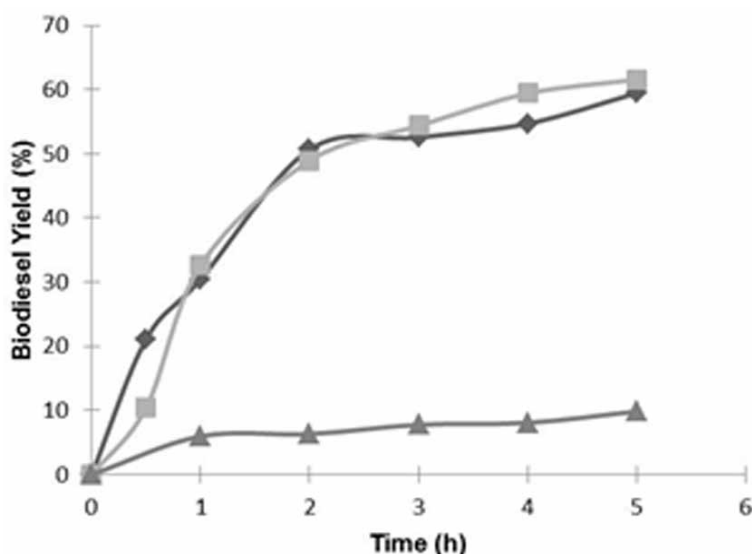
Figure 6. Effect of molar ratio alcohol/oil (6.9,   10 y   22.3) on the methyl ester yields with 0.53% wt. of CaO, molar ratio Alcohol/catalyst =72.24, Activation temperature=25°C, activation time CaO=1.5 h, reaction temperature=60°C

methanol over the catalytic surface at 60 °C. Such adsorption limitations were described by Xiao *et al*., (2010), who found that calcium methoxide formation over CaO surface is a slightly exothermic reaction. Hence, 25 °C was selected in this study as the most appropriate activation temperature for the CaO activation.

3.3 Reaction temperature

The effect of reaction temperature on the methyl ester yields is showed in Fig. 5. It is observed that methyl ester yields for 60 °C are higher when compared with methyl ester yields at 45 °C. This could be explained because raising the temperature favored the increase in reaction rates and decreases possible mass transfer limitations between reactants. These observations coincide with other authors (Liu *et al*., 2008). No higher temperatures than 60 °C were used aiming to avoid passing up the boiling temperature for the solvent (methanol). Hence, 60 °C was chosen as the most suitable reaction temperature.

3.4 Methanol/oil palm ratio

The effect of methanol/oil palm molar ratio on the methyl ester yields is showed in Fig. 6. It is

well known that a methanol excess is necessary for displacing chemical equilibrium to the reaction products; notwithstanding, a very high alcohol/oil (i.e., 22.3) molar ratio shows a methyl ester yield decrease. This behavior could be attributed to the fact that increasing the solubility of the glycerol-methanol system would favor a chemical equilibrium shift to the reactants, and consequently, the methyl ester yield would decrease. Thus, the methanol/oil palm molar ratio chosen in this work was 10.

3.5 Effect of activation approach on the continuous system

The effect of the CaO activation approach (in situ or ex situ) as well as the activation time on the continuous system is presented in Fig. 7. It is observed that both activation approaches are ineffective for a catalyst activation time of 2 h. For the in situ activation approach, 16 h of activation time are also inefficient, which can be observed when compared with results of activating the catalyst using the ex situ approach. Thus, for the insitu activation approach, higher activation times would be necessary. On the other hand, for the ex situ activation approach, it is observed that 16 h are enough for obtaining an efficient catalyst

activation (Fig. 7). The stirring speed used for the ex situ activation approach was 120 rpm. No higher stirring speed was used for avoiding the diminution on the particle size distribution.
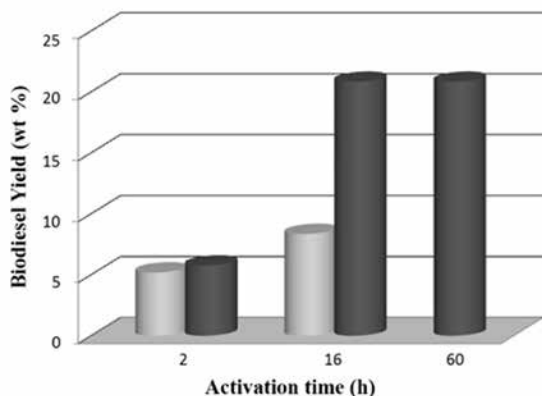

Figure 7. Shape effect (gray bars: in situ and black bar: ex situ) and activation time of the CaO in the methyl esters production. CaO activation temperature=25°C, reaction temperature=60°Ccatalyst mass=25 g, methanol flow during activation of reactants during the reaction of 0.5 ml/min.

3.6 Addition of Co-solvent

Taking into account that alcohol and oil present a low mutual solubility, it is important to consider the mass transfer limitations between the phases. That is the reason why using an adequate co-solvent could improve reaction yields by minimizing mass transfer limitations. Fig. 8 shows the effect of adding ethyl acetate (molar ratio co-solvent/oil = 4.71) and tert-Butanol (molar ratio co-solvent/oil = 9). In Fig. 8, it is observed that the co-solvent addition increases the methyl ester yields; thus, the co-solvent improves the interaction of reactants with the catalyst. In Fig. 8, it is also noticed that when comparing the two co-solvents used in this study, higher methyl ester yields were obtained with ethyl acetate (31 %). It is expected that an adequate co-solvent increases the electrostatic interaction between the mixture constituents. When dielectric constant of the co-solvents evaluated in this work, i.e., ethyl-acetate and tert-Butanol, is compared with the dielectric constant of co-solvents used in different works, i.e., dimethyl ether, iso-propylether, tetrahydrofurane, hexane and toluene (Guan *et al*., 2009; Liu *et al*., 2007; Royon *et al*., 2007), it is observed that the closer value of the dielectric co-solvent constant to the dielectric constant of the oil or the dielectric constant of the alcohol tends to decrease the methyl ester yields.
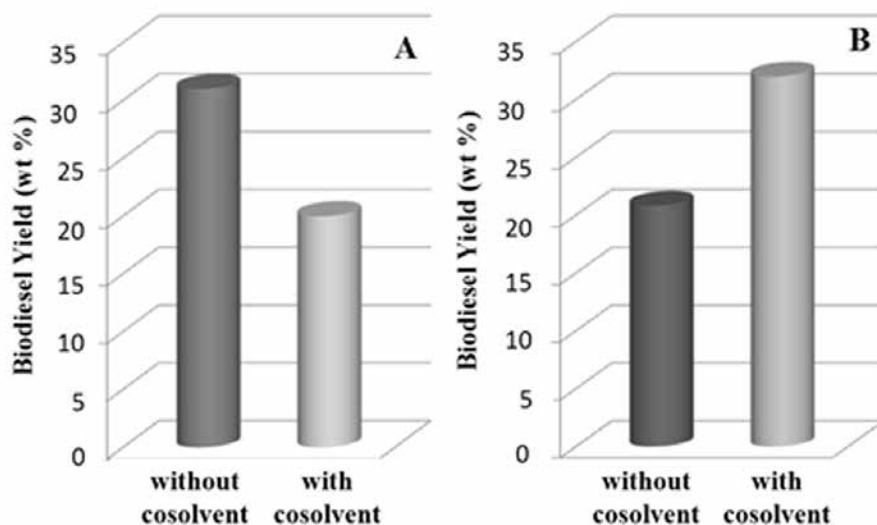

Figure 9. Comparison for continuous(A) and discontinuous(B) systems when ethyl acetate is used as co-solvent. In A: reaction time = 1h, 0.5% by weight of CaO, molar ratio Alcohol/CaO = 72.24, activation time = 1.5 h. In B: residence time =1h, activation time =16h ex situ catalyst mass = 25.27g. For A and B: Activation temperature=25°C, reaction temperature=60°C, molar ratio methanol/oil=10.
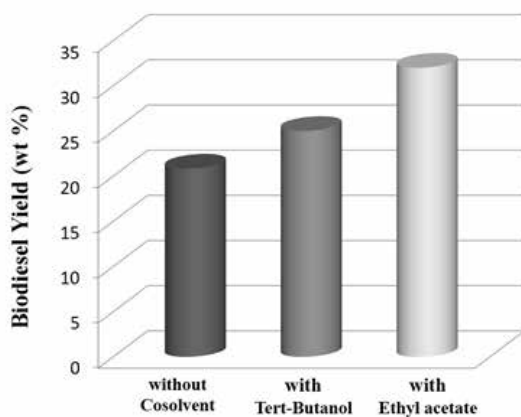
Figure 8. *Effect of the addition of co-solvent on the yield to methyl esters with 16 h activation ex situ, Activation temperature =25°C, reaction temperature =60°C, Catalyst mass =25.27g, reaction flow 0.5 ml/min.*

In the Fig. 9, the continuous and discontinuous systems are compared, when using co-solvents or in absence of co-solvents. It is observed that the discontinuous system with co-solvents present a methyl ester yield diminution. This is because the magnetic stirring used in the discontinuous system during the reaction seems to be enough for getting an adequate contact phases between methanol, oil palm and catalyst. Thus, adding the co-solvent generates a reactant dilution that is translated into a modification of interactions between reactants and catalytic surface, affecting the reaction rates. On the other hand, in the continuous system, the use of a co-solvent improves the phase contact between reactants and the catalytic surface, hence increasing the methyl ester yields. It is important to mention that in a continuous system the co-solvent and the methanol should be recovered and reused in the reaction; for this reason, the appropriate way of doing this should be studied.

4. Conclusions

In this study, the biodiesel production from oil palm in a packed bed reactor with continuous flow with calcium methoxide as catalyst was analyzed at laboratory scale aiming to find some adequate reaction conditions. CaO activation with methanol at room temperature (25 °C) prior to the reaction increases the basic sites with basic strength of 7.2 <

H< 15.0, due to the methoxide ion formation in the catalyst surface.

Using ethyl acetate in a continuous reaction system with packed bed increases the biodiesel yields because it eliminates the mass transfer limitation between reactant phases. It is convenient to activate the catalyst by the ex situ approach because longer activation times will be necessary using the in situ activation approach.

5. Acknowledgements

6. References

Albis Arrieta, A.R., Parra Garrido, J.A. & Sánchez Castellanos, F.J. (2005). Transesterificación del aceite de palma con metanol por catálisis heterogénea. *Ingeniería e Investigación 25*, 71-77.

Balat, M., & Balat, H. (2010). Progress in biodiesel processing. *Applied Energy 87*, 1815-1835.

Becerra, M., Centeno, A. & Giraldo, S.A. (2010). Búsqueda de catalizadores sólidos básicos para la producción de biodiesel. *Información Tecnológica 21*, 57-66.

Becerra, M., Centeno, A., & Giraldo, S.A. (2011). Triglyceride transesterification in heterogeneous reaction system with calcium oxide as catalyst. *Revista Facultad de Ingeniería Universidad de Antioquia 57*, 7-13.

Canakci, M. (2007). The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresource Technology 98*, 183-190.

Granados, M.L., Alba-Rubio, A.C., Vila, F., Alonso, D.M., & Mariscal, R. (2010). Surface chemical promotion of Ca oxide catalysts in

biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. *Journal of Catalysis 276*, 229-236.

Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., Moreno-Tost, R., Santamaría, J., & Fierro, J.L.G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental 73*, 317-326.

Guan, G., Sakurai, N., & Kusakabe, K. (2009). Synthesis of biodiesel from sunflower oil at room temperature in the presence of various cosolvents. *Chemical Engineering Journal 146,* 302-306.

Kawashima, A., Matsubara, K., & Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology 100*, 696-700.

Kouzu, M., Kasuno, T., Tajika, M., Yamanaka, S., & Hidaka, J. (2008). Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Applied Catalysis A: General 334*, 357-365.

Liu, X., Piao, X., Wang, Y., Zhu, S., & He, H. (2008).Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel 87*, 1076-1082.

Liu, Y., Lotero, E., Goodwin Jr, J.G., & Mo, X. (2007). Transesterification of poultry fat with methanol using Mg-Al hydrotalcite derived catalysts. *Applied Catalysis A: General 331*, 138-148.

Lutz, H.D., Möller, H., & Schmidt, M. (1994). Lattice vibration spectra. Part LXXXII. Brucite type hydroxides M(OH)2 (M = Ca, Mn, Co, Fe, Cd) --- IR and Raman spectra, neutron diffraction of Fe(OH)2. *Journal of Molecular Structure 328*, 121-132.

Rep, M., Palomares, A.E., Eder-Mirth, G., Van Ommen, J.G., Rösch, N., & Lercher, J.A. (2000). Interaction of methanol with alkali metal exchanged molecular sieves. 1. IR Spectroscopic study. *Journal of Physical Chemistry B 104*, 8624-8630.

Royon, D., Daz, M., Ellenrieder, G., & Locatelli, S. (2007). Enzymatic production of biodiesel from cotton seed oil using t-butanol as a solvent. *Bioresource Technology 98*, 648-653.

Suehara, K.-I., Kawamoto, Y., Fujii, E., Kohda, J., Nakano, Y., & Yano, T. (2005). Biological treatment of wastewater discharged from biodiesel fuel production plant with alkali-catalyzed transesterification. *Journal of Bioscience and Bioengineering 100*, 437-442.

Tanabe, K., Misono, M., Ono, Y., & Hattori, H. (1989).Determination of acidic and basic properties on solid surfaces. *Studies in Surface Science and Catalysis 51*, 5-25.

Xiao, Y., Gao, L., Xiao, G., & Lv, J. (2010). Kinetics of the transesterification reaction catalyzed by solid base in a fixed-bed reactor. *Energy & Fuels 24*, 5829-5833.