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Comparative Study of Quick Lime and CaO as Catalysts of Safflower Oil Transesterification

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Abstract: This work aimed to contrast the performance of quicklime and CaO reagent grade as heterogeneous catalysts for the safflower oil transesterification reaction. Quicklime was characterized by TGA analysis, XRD, atomic absorption, nitrogen physisorption and by Hammett method. In the safflower transesterification reaction, four main variables were studied: addition reagents order, reagents dosage, type of catalyst and methanol-oil molar ratio. The addition reagents order was not found to be determinant on time for reaching equilibrium or maximum methyl esters yield. On the contrary, reagents dosage was found to negatively affect reaction rate and methyl esters yield. It was found that quicklime performs better than CaO and this was ascribed to an increased basicity found in the former. From the results can also be inferred that the use of quicklime as catalyst of the transesterification reaction allows the decrease of the process cost by reducing both, the reaction time and the required amount of alcohol.

Keywords: safflower oil, methyl esters, alcoholysis, quick lime, biodiesel.

1 Introduction

Over the last years, the relevance of minimizing pollutant gases has motivated the research on alternative energy sources other than petroleum such as eolic energy, hydroelectric, solar energy, biomass and biofuels. Among them we find biodiesel at the top. Biodiesel basically is a mixture of Fatty Acids Methyl Esters (FAME) obtained from renewable sources, mainly by transesterification of either

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vegetable oils or animal fats, followed by glycerol separation (sub-product). Transesterification becomes necessary since fats cannot be used directly, in most cases, to drive modern high-speed engines without fundamental changes in their design. This is due to important differences in physicochemical properties between fats and the standard hydrocarbon fuel (Schlick, Hanna, and Schnstock 1988).

Transesterification, also known as alcoholysis, is a chemical reaction of an oil or fatty acid with an alcohol under the presence of a catalyst to produce esters and glycerol. This global reaction implies a sequence of reversible reactions where triglycerides (TGs) are converted into diglycerides (DGs) and these DGs are converted into monoglycerides (MGs). Finally, these MGs are transformed into glycerol. In each step an ester is produced and therefore three molecules of ester are produced for every molecule of TG. Methanol and ethanol are the most used alcohols due to its low cost, however, methanol stands out over ethanol since presents less esteric impediment at attacking carbonile groups and this is responsible for the higher selectivity obtained with such an alcohol (Sarin 2012).

In general, to accelerate the triglycerides transesterification reaction, the use of a catalyst, alkaline or acid, is recommended. An alkaline catalyst can reach high purity and high yields of biodiesel in a short period of time. However, alkaline catalysts are strongly sensitive to the presence of water and free fatty acids (FFA) in the raw materials. This environment is expected to cause saponification over the ester. In fact, if the oil contains more than 0.5% of weight of FFA, the oil is not suitable to be used as a reactant during the alkaline process, since the alkaline catalyst will react with the FFAs to produce soap. This reaction is undesirable since decreases the biodiesel yield and inhibits the separation of esters and glycerol. The acid catalyzed process is an alternative when the raw material contains more than 0.5% in weight of FFA. However, the acid catalyzed process requires an excess of methanol, high pressure, high temperature and a higher cost on stainless steel equipment. Albeit the catalyst used for the transesterification reaction can be homogeneous or heterogeneous, the former is preferred since provides high reaction rates. Unfortunately, the process carried out with a homogenous

catalyst exhibits higher production costs due to the necessity of several separation steps and high amounts of water discharges. In contrast, heterogeneous catalysts are potentially cheaper and solve many of the problems of homogeneous catalysts (Li et al. 2013). Therefore, the scientific community has dedicated important efforts to develop heterogeneous catalysts that overcome the difficulties implied by the use of homogeneous catalysts. In this context, the heterogeneous catalyst can also be acid or basic. Lewis acid catalysts exhibit a slower reaction rate due to limitations on mass transfer between methanol and oil. However, basic heterogeneous catalysts present more advantages than disadvantages like: they are not corrosive, are environmental benign, are easily disposed, are more easily separated from the liquid products and can be designed to obtain higher activity, selectivity and large periods of useful life. Actually, there is in the literature a vast number of papers dedicated to assess the performance of different alkaline heterogeneous catalysts in the vegetable oils transesterification reaction. Some tested catalysts are alkaline oxides (Mootabadi et al. 2010), many alkali metal compounds alumina-supported (Zabeti, Daud, and Aroua 2010) and zeolites (Shu et al. 2007). Nevertheless, in most of the alkaline catalysts the active ingredients are easily corroded by methanol and shows short useful life (Liu et al. 2007). Among, heterogeneous alkaline catalysts, calcium oxide (CaO) outstands due to its relative low cost, high basicity ($H_b = 26.5$) and low solubility in methanol. Several works have been developed to improve the reaction rate by using CaO (reagent grade) as catalyst (Tang et al. 2011). However, CaO is easily deactivated by carbon dioxide (CO_2) and calcium hydroxide ($Ca(OH)_2$) at the catalyst surface in just a few minutes of exposure to air. This is why in many commercial cases CaO requires to be calcined at high temperature in order to remove the inactive layer before being use, likewise different ways of catalyst preparation using a solvent treatment have been reported with satisfactory results (Huang et al. 2013).

Other advantage of using CaO as catalyst is that it has the characteristic of being able to be reused, regenerated and its high selectivity to methanolysis, then the process can be stopped at any step (Calero et al. 2014).

Through literature, it can be observed that the preferred used CaO is reagent grade. This, however, is an important variable that might lead to reduce the overall process cost. In this sense, other sources rather natural of CaO like egg shell (Buasri et al. 2013) and sea sand have been explored (Muciño et al. 2014).

In this work, the use of quicklime as source of CaO to catalyze the transesterification of safflower oil is not only assessed but also compared to that of CaO reagent grade.

Quicklime is also known as burnt lime, a reference to its manufacturing process, or simply lime. To make it, limestone ($CaCO_3$) is broken up and shoveled into a kiln (a kiln is a high temperature oven), which is heated to very high temperatures 1,000 K. The high temperatures release carbon dioxide (CO_2) from the stone, turning it into calcium oxide. After it is cooled down, the compound can be ground into a powder and packaged for sale.

Quicklime is a rather cheap source of CaO for catalysis compared to analytical reactant CaO source. In this context, quicklime have been reported to be used by Kouzu et al. (2009) in the methanolysis of rapeseed oil conducted in a fixed-bed reactor located in the circulating stream of a batch reaction system, and by Miladinovic et al. (2014) who performed a kinetic study of quicklime-catalyzed sunflower oil methanolysis.

Albeit quicklime has already been tested as a transesterification reaction catalyst, the variables assessed in this work are the type of oil, the influence of catalyst amount, methanol-to-oil molar ratio, addition order of raw materials and the catalyst calcination temperature. The response variable at all cases is the FAME content.

2 Material and methods

2.1 Materials

Food-grade Safflower oil highly monounsaturated was used, which consisted of palmitic acid 5%, stearic acid 1.9%, oleic acid 76%, linoleic acid 15.7%, linolenic acid 0.1% and others 1.3% was supplied by AarhusKarlshamn México SA de CV. The methods in the current European Union Quality Standard (EN-14214) were followed to determine viscosity, acid value and water content of the safflower oil. These parameters are reported in Table 1. Quick lime was purchased from a rural market. CaO Calcium oxide 99.9% trace metal basis was purchased from Aldrich Chemistry. Anhydrous methanol (99.96%) was supplied by J.T. Baker. Heptane (HPLC) was purchased from Fermont Co. Methyl heptadecanoate

Table 1: Safflower oil properties.

Property	Value
Acid value (mg KOH/g)	0.12
Water content (wt%)	0.05
Viscosity at 40 °C (cSt)	39.05

Source: Muciño et al. (2014)

(Analytical standard) was purchased from Fluka analytical Co. The gas chromatography reference standard for fatty acid methyl esters was purchased in Supelco. Methyl heptadecanoate was purchased in Sigma Aldrich (puriss. p.a., standard for GC, $\geq 99.7\%$) and was used for quantifying methyl esters.

2.2 Catalyst preparation

Quick lime was triturated, meshed and recovered between 0.12 mm and 0.84 mm mesh, then calcined at 900 °C during 8 h in order to perform the CO_2 (CaCO_3) and H_2O ($\text{Ca}(\text{OH})_2$) desorption and obtain CaO. Calcium oxide from Aldrich Chemistry was used as purchased without further processing since the reagent was free of CaCO_3 and $\text{Ca}(\text{OH})_2$. Relatively large exposure to air was avoided in order to prevent contamination.

2.3 Catalyst characterization

X-ray diffraction (XRD) analysis was performed using a Bruker diffractometer and a Cu $K\alpha$ radiation source at 35 kV and 35 mA. Data were collected over 2θ range of 20–100° with a step of 0.029193 degrees and speed of 26.5 sec/step.

Differential Scanning Calorimetry and Thermogravimetric Analysis (TGA) was conducted in a SDT Q600 Simultaneous TGA/DSC, TA Instruments equipment under nitrogen flow at a heating rate of 10 °C/min.

Nitrogen physisorption (MultiPoint BET) was conducted in an Automated Gas Sorption and data were analyzed with ASiQwin Quantachrome Version 2.02.

Atomic absorption analysis was performed using a Varian equipment AA240FS Fast Sequential Atomic Absorption Spectrometer with Calcium (422.7 nm) and Magnesium (285.2 nm) lamps. Samples were first dissolved in hydrofluoric acid and diluted to the measurement interval.

2.4 Basicity determination

Basicity and base strength were determined using Hammett indicators following a similar methodology proposed by (Take, Kikuchi, and Yoneda 1971) and Ono (Ono et al. 2011). To determine the basic strength, 100 mg of catalyst were added to 5 mL of benzene adding three drops of indicator and stirring for 4 h.

The added indicators (0.1% w/w) were bromothymol blue, phenolphthalein and 2,4-dinitroaniline. Basicity was quantified by adding 1 gram of catalyst in 15 mL of benzene, three drops of indicator and then stirring for 2 h. Subsequently, the resulting slurry was titrated with benzoic acid dissolved in benzene 0.05 M to see a color change of the indicator already adsorbed onto the solid.

2.5 Reaction procedure

Transesterification reactions were carried out in a 250 mL glass reactor with a condenser and hot plate as depicted in Figure 1. In a typical experiment, stirring rate, methanol-oil molar ratio, quantity of catalyst, order of reagents addition, raw materials source and temperature were controlled. The magnetic stirring rate was 1,000 rpm. Experiments were performed with a methanol-oil molar ratio of (6:1), (9:1) and (12:1). The catalyst loading was 3.4% (w/w) with respect to the reaction mixture, and the reaction time was 5 h.



Figure 1: Experimental set-up.

The reaction procedure follows 11 different experiments (Table 2):

Table 2: Experiments description and codes.

Code	Experiment
A	Mix alcohol (methanol) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add oil (Safflower) at the same temperature., methanol-oil molar ratio (6:1)
B	Mix oil (Safflower) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add alcohol (methanol) at the same temperature, methanol-oil molar ratio (6:1).
C	Mix alcohol (methanol) and catalyst (Sigma Aldrich reagent grade CaO) were heated at a temperature of 55 °C for 15 min then add oil (Safflower) at the same temperature, methanol-oil molar ratio (6:1).
D	Mix alcohol (methanol) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add a flow 1 mL/min oil (Safflower) at the same temperature, methanol-oil molar ratio (6:1).
E	Mix oil (Safflower) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add a flow 1 mL/min of alcohol (methanol) at the same temperature, methanol-oil molar ratio (6:1).
F	Mix alcohol (methanol) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add oil (Safflower) at the same temperature, methanol-oil molar ratio (9:1).
G	Mix alcohol (methanol) and catalyst (quicklime) were heated at a temperature of 55 °C for 15 min then add oil (Safflower) at the same temperature, methanol-oil molar ratio (12:1).
H	Mix alcohol (methanol) and catalyst (Sigma Aldrich reagent grade CaO) were heated at a temperature of 55 °C for 15 min then oil (Safflower) at the same temperature, methanol-oil molar ratio (9:1).
I	Mix alcohol (methanol) and catalyst (Sigma Aldrich reagent grade CaO) were heated at a temperature of 55 °C for 15 min then add oil (Safflower) at the same temperature, methanol-oil molar ratio (12:1).

After the transesterification reaction, catalyst was separated from the products (glycerin and methyl esters) by centrifugation. Residual methanol was evaporated in a rotavapor (R-215 Buchi Switzerland) under vacuum.

2.6 Biodiesel characterization

Methyl esters samples were taken at 20 min, 30 min, 1 h and then hourly up to 5 h. These sample were analyzed using gas chromatography in concordance with norm UNE-EN 14103 in a Varian CP-3800 gas chromatograph with flame ionization detector (FID), with a DB-5HT capillary column (length 15 m × diameter 0.230 mm × layer

thinness 0.10 μm), Methyl heptadecanoate was used as chromatograph standard. Helium was used as carrier gas.

The concentration of Ca and Mg in the produced biodiesel was determined by using a Varian 720-ES Series ICP Optica Emission Spectrometer.

2.7 Methanol: oil dispersion image

A digital image of methanol drops in oil was acquired by using a Motic BA400 microscope with WFPL 10X/22 mm lens. Digital camera moticom 2,300 3.0 M Pixel and software Motic Images Plus 2.0.

3 Results and discussion

3.1 Catalyst characterization

In order to establish the adequate calcination temperature, quick lime was analyzed by DSC/TGA and the results are shown in Figure 2. Three characteristic stages can be distinguished in the resulting TGA curve. The first one, at around 120 °C, can be ascribed to the loss of physisorbed water on the sample surface. The second stage, at 380 °C, corresponds to the decomposition of calcium hydroxide $\text{Ca}(\text{OH})_2$. Finally, the third stage, from 550 °C and onwards corresponds to the decomposition of calcium carbonate, CaCO_3 . The global mass loss from 0 °C to 900 °C is 2%; beyond this temperature mass loss is not significant. This is why in this work 900 °C was elected as calcination temperature. This is related to previous results in literature that refers that higher temperatures reduce the surface area and increases the pore

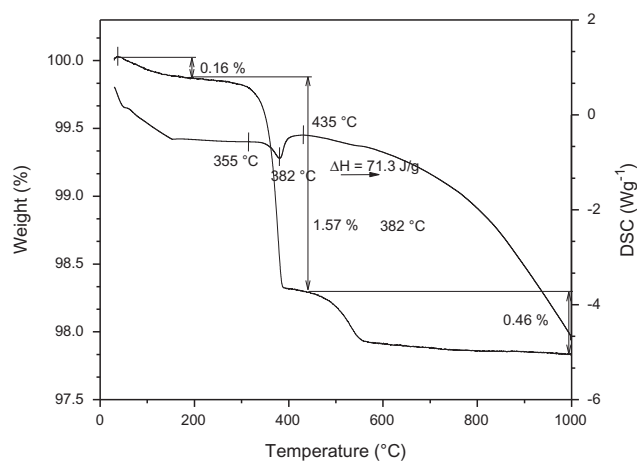


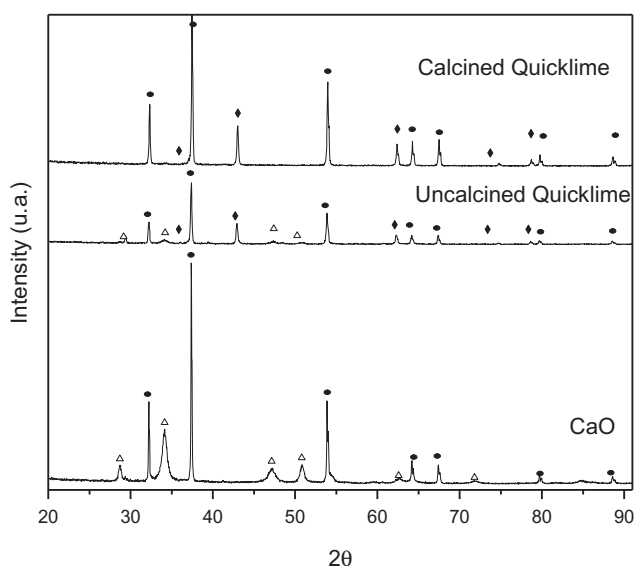
Figure 2: DSC/TGA analysis of Quick lime sample.

Table 3: Temperature weight loss for quick lime.

Temperature ranges	Compound
120–380 °C	Absorbed and free water
380–550 °C	Ca(OH) ₂
550–900 °C	CaCO ₃

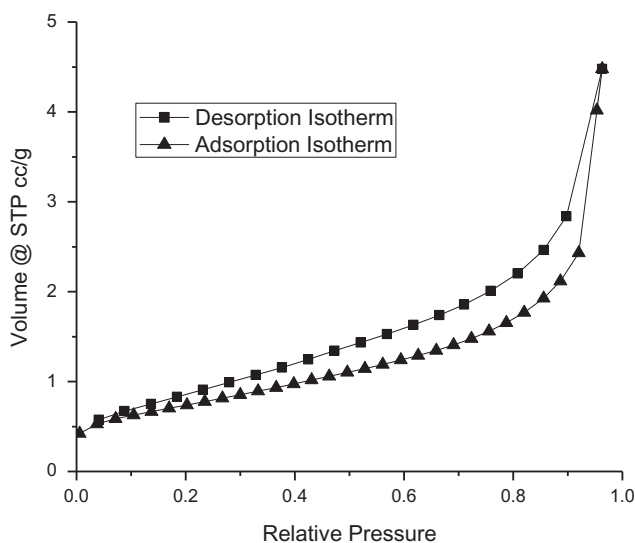
diameter, which consequently results in higher basicity. Table 3 summarizes the aforesaid.

Calcium oxide CaO (reagent grade) was analyzed by X-ray Diffraction (XRD) and its diffractogram is shown in Figure 3. Diffraction signals that correspond to CaO and Ca(OH)₂ are mainly observed.

**Figure 3:** XRD of CaO, calcined and uncalcined Quick lime (● CaO, Δ Ca(OH)₂, MgO).

Quick lime was analyzed by X-ray Diffraction (XRD) and the diffractogram is also shown in Figure 3. Unlike CaO reagent grade, quicklime presents diffraction signals that can be ascribed not only to CaO and Ca(OH)₂ but also to MgO. Structurally, this is a difference of paramount importance since MgO is also reactive in the transesterification reaction (Leclercq, Finiels, and Moreau 2001). From TGA analysis, the presence of CaCO₃ was also expected, however, this compound could not be observed by XRD most probably due to its low concentration and to the noise signal.

Finally, calcined quicklime was also analyzed by X-ray Diffraction (XRD) (see Figure 3). In this case, neither Ca(OH)₂ nor CaCO₃ were detected. This suggests that the calcination process is effective removing these compounds

**Figure 4:** Calcined quicklime N₂ adsorption-desorption isotherm.

and converting them into CaO. MgO remains without been affected.

The textural properties of quicklime were determined by nitrogen physisorption. Figure 4 shows the resulting adsorption-desorption isotherm. This isotherm corresponds to a IV type isotherm (mesoporous solids). Table 4 summarizes the textural properties established by nitrogen physisorption data obtained from Figure 4 using software ASiQwin version 2.02 (Quantachrome Instruments).

Table 4: Calcined quicklime textural properties.

	Value
Surface Area	1.313 m ² /g
Pore Volume	0.001383 m ³

The values in Table 4 have the same order of magnitude than those previously reported (Micic et al. 2015) for CaO when calcined at 900 °C (Surface area = 2.4 m²/g and Pore Volume = 0.009 m³/g).

Atomic absorption was used in order to quantify the percentage of Ca and Mg in quicklime. With these values was possible to calculate the weight percentage of calcium oxide and magnesium oxide. These results are summarized in Table 5. The remained 4.8% can be ascribed

Table 5: Quicklime composition.

Compound	Weight percentage
Calcium oxide	92.2
Magnesium oxide	3.0

to the presence of some other compounds like calcium carbonate that are in such a low concentration that are not evident by XRD.

Hence, the main difference regarding chemical composition between the calcined quicklime and the CaO reagent grade is the presence of magnesium oxide since CaO reagent is claimed to be 99.9% pure.

Table 6 summarizes the basic strength values calculated as described in Section 2.4. These values indicate that the basic strength of the active sites in quicklime and in the CaO reagent grade is practically the same. Because of the calculated basic strength value, the presence of strong basic sites in both catalysts can be claimed. It is worth pointing out that this type of sites are required for the vegetable oil transesterification (Ramos et al. 2008). The amount of basic sites is directly correlated to the basicity value and this is up to one order of magnitude higher in the quicklime than in the reagent grade CaO. This can be ascribed to the presence of MgO and the absence of calcium hydroxide, which is in the reagent grade CaO.

Table 6: Basic strength and Basicity (CaO and calcined quicklime).

	Basic strength (H_-)	Basicity (mmol/g)
Calcined quicklime	$9.8 \geq H_- \geq 15$	0.228
CaO	$9.8 \geq H_- \geq 15$	0.073

3.2 Transesterification of safflower oil

Reaction experiments described in Section 2.4 were performed twice and Fatty Acid Methyl Ester (FAME) profiles as function of time are shown in Figures 5, 6 and 7. By comparing the FAME profiles of experiments A and B in Figure 5, it can be concluded that the reagents addition order does not affect the time at which equilibrium is reached (about 4 h). Initial production rate (given by the slope of each profile at zero time), however, is found to be dependent on reagents order addition. This suggests the safflower oil transesterification catalyzed by quicklime follows an Eley-Rideal elementary reaction mechanism where the methanol adsorption may be the rate limiting step. This is in agreement with reaction Scheme 1.

The comparison of the FAME profiles obtained from experiments A (Mixed at first: methanol-quicklime) and C (Mix at first: methanol-reagent CaO), leads to conclude that calcined quicklime is a more effective catalyst than CaO reagent grade and this can be ascribed to the basicity

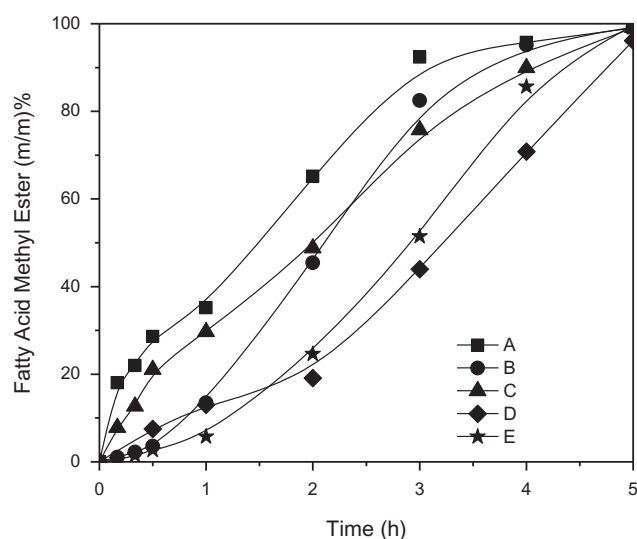
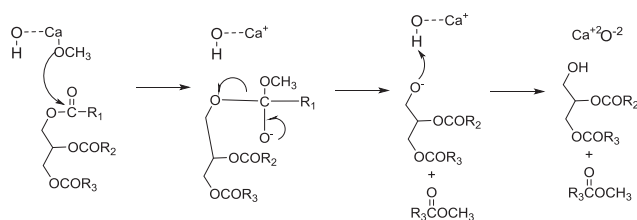


Figure 5: Effect of I) addition reagents order: A (methanol-quicklime, oil) and B (oil-quicklime, methanol) II) Type of catalyst: A (quicklime) and C (reagent CaO) III) reagents dosage flow of 1 mL/min: D (addition order: methanol-quicklime, oil) and E (addition order: oil-quicklime, methanol) on FAME profile as function of time. Methanol-oil ratio = 6, $T = 328$ K, rpm = 1000, $W = 3.4$ % w/w.



Reaction Scheme 1: CaO-Catalyzed transesterification mechanism (Boey, Maniam, and Abd Hamid 2011).

differences reported in Table 6 and therefore to the presence of MgO.

By contrasting the produced profiles in experiments A (no oil dosage) and D (oil dosage of 1 mL/min), B (no oil dosage) and E (oil dosage of 1 mL/min), it can be concluded that the dosage of reagents negatively affects not only the initial production rate but also the time to reach equilibrium.

The importance of the methanol-oil molar ratio is evidenced by Figures 6 and 7. It can be observed that this variable affects both, the reaction rate and the final methyl esters yield. The trend is different for every catalyst though. Regarding CaO, it can be observed in Figure 6 that increasing the methanol-oil molar ratio has a positive effect on rate. Conversely, it is observed in Figure 7 that the transesterification catalyzed with quicklime performs the best with the lowest tested methanol-oil molar ratio (6:1). This implies an improvement on process time of about 1 h compared to the 12:1 methanol-oil molar ratio.

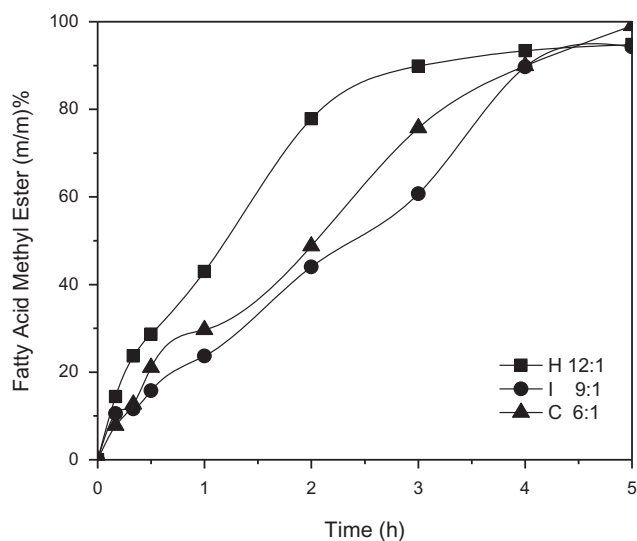


Figure 6: Effect of methanol-oil molar ratio on FAME profiles as function of time. C: methanol-oil molar ratio = 6, H: methanol-oil molar ratio = 9; I: methanol-oil molar ratio = 12. Reaction conditions: catalyst = CaO reagent grade, $T = 328$ K, rpm = 1000, $W = 3.4$ % w/w.

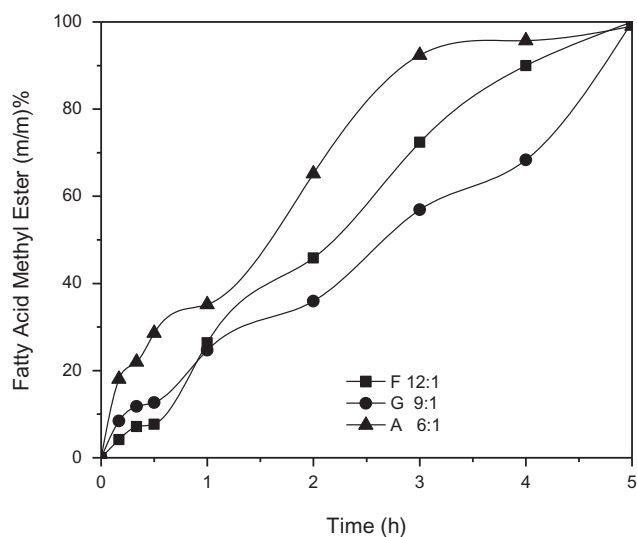


Figure 7: Effect of methanol-oil molar ratio on FAME profiles as function of time. A: methanol-oil molar ratio = 6, F: methanol-oil molar ratio = 12, G: methanol-oil molar ratio = 9. Reaction conditions: catalyst = calcined quicklime, $T = 328$ K, rpm = 1000, $W = 3.4$ % w/w.

Albeit calcined quicklime contains MgO, a reaction mechanism similar to that previously reported for CaO could be expected. The reaction mechanism is depicted in reaction scheme 1 and is consistent with the ER mechanism suggested by the above presented experiments.

According to the results shown in Figure 5 (A and B) and to the mechanism depicted in reaction Scheme 1, it is

fundamental that the catalyst is first accessible to methanol and then oil must become close enough to the chemisorbed methoxide group for the transesterification reaction to take place. This suggests that any factor affecting any of these steps will affect the FAME production rate. Taking this into account helps to explain the effect of methanol:oil molar ratio. Figure 8 shows a digital image of methanol drops in an oil continuum where the catalyst is mainly inside the methanol drops. From this image, it can be inferred that the probability of methanol to find a catalyst particle will increase with its concentration and this explains the maximum production rate with the methanol:oil molar ratio of 12:1 when using CaO reagent grade catalyst. On the contrary, the maximum production rate with the calcined quicklime is when using the 6:1 methanol:oil molar ratio. This difference can be ascribed to the higher basicity in calcined quicklime than in CaO reagent grade. The transesterification reaction being more rapid implies that methyl esters are formed more rapidly also and the fact of these working similarly to a co-solvent could be admitted.

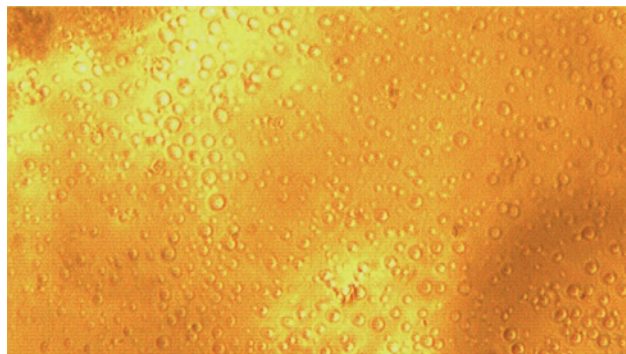
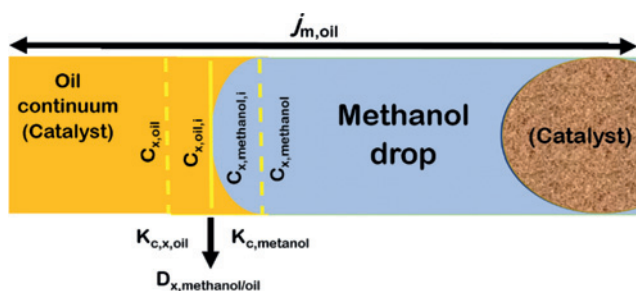


Figure 8: Digital image of methanol drops in an oil continuum, methanol-oil molar ratio = 6.

When methanol:oil molar ratio increases not only the probability of methanol finding a catalyst particle increases but also a larger species mass transport pathway is formed. The model of drops of methanol in oil continuum is suitable to explain this phenomenon in which the diameter of the drop of methanol is the mass resistance pathway that triglycerides should travel to become near the catalytic surface and react with the chemisorbed methoxide species. The model is depicted in Scheme 2 and is based on that proposed by Likozar et al. (2014). This may explain why the 12:1 molar ratio leads to a slower FAME production than the 6:1 molar ratio when calcined quicklime is the catalyst. The aforesaid suggests that a certain balance must be kept among all the reaction participants,



Scheme 2: Drop model methanol in an oil continuum, where C is the concentration of component x , x is any specie involved in transesterification reaction, K is the overall mass transfer coefficient of component x , D is the distribution coefficient of component x , j_{m} is the molar flux of component x and i is the interface between methanol and oil.

oil:alcohol and number of active sites, so that if one is altered another one can be modified in order to restore such a balance. Otherwise a detrimental effect on reaction rate is observed. This is the case of the molar ratio 9:1 for both catalysts.

Finally, it is worth noticing that quicklime used in this work is significantly more accessible than CaO reagent grade not only from an economical point of view but also from an availability angle. A drawback, however, is the leaching of the active species that limits its reuse with the same efficiency. By ICP spectrometry, the concentration of calcium and magnesium in the produced biodiesel was determined to be 143 and 2.66 mg/L, respectively. In addition, at the end of reaction it was also observed that part of the spent catalyst combined with glycerol and turned into calcium glyceroxide. This compound has been shown to also act as catalyst albeit with less efficiency (Kouzu et al. 2010).

4 Conclusions

A performance comparison in the transesterification of safflower oil between quicklime and CaO reagent grade was conducted. It was concluded that quicklime performs the best due to an increased basicity given by the presence of MgO and the absence of Ca(OH)₂. The use of quicklime compared to CaO reagent grade not only lowers the price of the transesterification process by making it faster but also by reducing to half the amount of methanol. Regarding the other studied variables, it can be concluded that the addition reagents order does not affect neither the time to reach equilibrium nor the maximum FAME yield. On the contrary, dosage of reagents does have a negative effect on FAME production rate.

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