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Synthesis of (E)-13-*n*-hexyloxacyclicotridec-10-en-2-ona (macrolactone) by transesterification of castor oil using heterogeneous catalysts based on zinc oxide

INGENIERÍA QUÍMICA

Síntesis de (E)-13-*n*-hexiloxaciclicotridec-10-en-2-ona (macrolactona) por transesterificación de aceite de ricino mediante catalizadores heterogéneos basados en óxido de zinc

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Abstract

This work reports the results obtained from the transesterification of castor oil with methanol under soft conditions (low temperature and atmospheric pressure), employing basic solids as Ba/ZnO, Mg/ZnO, and K/ZnO. It was found that the different systems exhibit high catalytic activity for the transformation of castor oil, but the Ba/ZnO system showed a highest tendency toward cyclation of ricinoleic acid to form a product known as macrolactone, namelly (E)-13-*n*-hexyloxacyclictridec-10-en-2-ona. The catalytic systems were analyzed through FT-IR, TEM, SEM, X-ray diffraction, temperature programmed reduction, analysis of surface area and the esters obtained from the reaction were analyzed by gas chromatography coupled to mass spectroscopy (GC-MS).

Keywords: Lactones, castor oil, ricinoleic acid, basic catalysts, zinc oxide

Resumen

Este trabajo recoge los resultados obtenidos a partir de la transesterificación de aceite de ricino con metanol en condiciones suaves (baja temperatura y presión atmosférica) y el empleo de sólidos básicos Ba / ZnO, Mg / ZnO y K / ZnO. Se encontró que los diferentes sistemas presentan una buena actividad catalítica para la transformación del aceite de ricino, pero el sistema Ba/ZnO mostró una mayor tendencia a la ciclación del ácido ricinoleico para formar un producto conocido como macrolactona, específicamente (E)-13-*n*-hexiloxaciclicotridec -10-en-2-ona. Los sistemas catalíticos fueron analizados a través de FT-IR, TEM, SEM, difracción de rayos X, la reducción de la temperatura programada, el análisis de superficie y de los ésteres obtenidos a partir de la reacción se analizaron mediante cromatografía de gases acoplada a masas (GC-MS).

Palabras Claves: Aceite de ricino, aceite ricinoleico, catalizadores básicos, lactonas, oxido de zinc

1. Introduction

The study of vegetable oils transesterification in general is an issue that is being studied for some time, and researchers are interested in finding efficient systems for performing this reaction Fraile et al., (2009), Nassreddine et al., (2008), Verziu et al., (2009), Borges et al., (2011), as well as improve process Silva et al., (2011), Alba-Rubio et al., (2010).

Transesterification of vegetable oils leads to combustible products known as biodiesel. These products, generated from materials of renewable base are used to run diesel motors. Chemically, they constitute methyl and ethyl esters, with long-chain of fatty acids. When oxygenated, these chains provide the motor a cleaner combustion.

The transesterification reaction for the oil has been carried out by ultrasound, using different oxides, among which barium yielded the best results S. Gryglewicz (1999). Also, Lee et al., (2004) investigated gamma-alumina (-Al2O3) catalysts doped with sodium and sodium hydroxide, revealing a catalytic activity similar to that found in homogeneous catalysts. Another solid employed for these reactions has been strontium oxide Liu et al., (2007). These researchers achieved a transformation close to 95% in only 30 minutes. Yang and Xie (2007) and Macleod et al., (2008) investigated basic and amphoteric oxides, finding high conversions in both cases and additionally noted that a greater force of basicity for the solid was related to the catalytic activity.

Castor oil is obtained from the Ricinus communis plant, which contains approximately 40-50% of oil, of which 90% of the triglycerides belong to the ricinoleic acid (C18OH), which has a hydroxyl group at 12 position and makes it susceptible to cycling and forming a compound generically denominated as macrolactone (Figure 1).

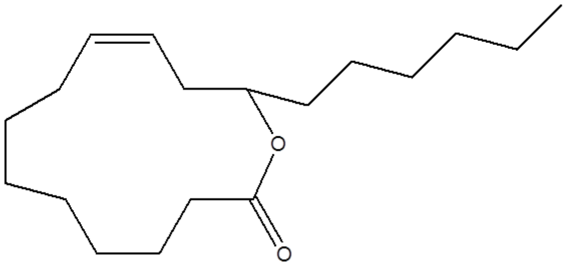


Figure 1. Representation of macrolactone (E)-13-n-hexyloxacyclicotridec-10-en-2-ona from ricinoleic acid.

Lactones are widely found in a broad variety of fruits and their role is important in the fragrance and flavorings industry. A comparison of the odor properties of lactone enantiomers was reported by Yamamoto et al., (2002). These researchers used a ruthenium complex $Ru_2Cl_4[p\text{-tolyl-binap}]_2NEt_3$ as catalyst, finding small differences in the quality of odor of the enantiomer pairs of 2-*n*-hexyl- in comparation to 2-*n*-heptylcyclopentanones, as well as the differences found in the corresponding -undeca and -dodecalactones.

In general, as far as obtaining macrolactones from enzymatic catalysis, in the literature we can find several works Cheetham (1998), Lee et al., (1994), (1996), (1998), Aguedo et al., (2004). Additionally, -decalactone has been isolated from fruits and foods, Maga (1976), initially, this lactone was obtained from fruits, but increased demand has required looking for other sources like microbiological processes Welsh et al., (1989). Several strains of *Trichoderma sp.* have also been investigated, but the most widely used microorganism in the production of fragrances is the *Sporidiobolus salmonicolor* (*Sporobolomyces odorus*), which was reported by Tahara et al., (1973) to produce decalactone. Other researchers have used Sporidiobolus to biosynthesize 4-decanol, which smells like peach, by using ricinoleic acid (12-hydroxy-9-octadecanoic acid) MacLeoda et al., (2008), Feron et al., (1996), (2000).

Regarding homogeneous and heterogeneous catalysis, Neaţu et al., (2008) used an heterogenized rhodium complex in the synthesis of functionalized lactones and Shiina (2004) in turn, used a Lewis acid like $TiCl_2(ClO_4)_2$ for carboxylic esters and -lactones synthesis from benzoic anhydride and reported that the complex is an effective catalyst in the obtaining of macrolactones with high output and at room temperature. Also reported is the synthesis of spiro-,-lactones by oxidation of 3'- and 6-hydroxy alkenes employing solids like copper sulfate Das et al., (1994), (1995), but there are no reports of -□,-lactones from the ricinoleic acid by heterogeneous catalysis.

In this study, we conducted transesterification of castor oil with methanol to obtain methyl esters from the ricinoleic acid by using alkaline and alkaline earth metal type heterogeneous catalysts and zinc oxide, finding for system containing barium a very interesting compound known as macrolactone and denominated (E)-13-*n*-hexyloxacyclictridec-10-en-2-ona.

2. Experimental

The Castor oil used for the catalytic reactions was purchased from SIGMA, St. Louis, USA, absolute methanol, potassium nitrate, magnesium nitrate, barium nitrate and zinc oxide as support-catalyst from Aldrich. The acidity index and the peroxide index were determined from the Colombian technical norm 218 (NTC-218) to know the amount of free fatty acids in castor oil, as well as the rancidity.

2.1 Preparation of the catalyst

Catalysts based on Ba, Mg, and K were prepared using impregnation methodology by depositing a solution of Ba, Mg, and K nitrate salts (0.5M) on zinc oxide (ZnO) and at room temperature for 3 hours. Thereafter, the water is evaporated by heating on a plate at 60 ºC for 6 hours under constant agitation. Then the solid is dried in an oven at 110 ºC during 12 h, and, lastly, the catalyst is calcined in a TERMOLYNE 21100 with air flow at 10 L/h at 450 ºC during 4 h.

2.2 Methods

The quantities used for the transesterification reaction were 16.8 ml castor oil, 12.3 mL methanol, and 0.6 grams catalyst at 2% in mass. Reagents were added in a 100-mL glass reactor with three holes at 70 ºC. The system was kept in reflux for the 12 h. After this time, it was cooled for 15 minutes to separate the phases obtained and then analyze them.

The reaction products were characterized by gas chromatography coupled to mass spectroscopy and under conditions of Split injector at 300 ºC, FID detector at 300 ºC with a temperature ramp of 50 ºC (1min), 230 ºC (2 min), and 300 ºC (20 min). Helium was used as carrier gas, using a pressure of 12.1 Psi, with a flow of 1.0 mL/min and a 30-m polymethylsilane phase HP5 column at 5%.

Catalysts were characterized through X-ray diffraction (XRD), in a RIGAKU 2200 diffractometer with CuKα radiation = 1.54056 Å at a step every 0.02 degrees and fixed time of 0.3 seconds within a range of 20 – 80 (2). Temperature programmed reduction (TPR) was determined in a Micromeritics autochem 2910 with TDC detector and the surface area by an SE Micromeritics ASAP 2010. The size and morphology of the impregnated particles were determined using a Scanning Electron Microscope (SEM) TOPCON SM-300 and a Transmission Electron Microscope (TEM), Jeol JEM 1200EX. Infrared, to know the functional groups in the surface of different catalysts, the sample was analyzed in a Nicolet IR-200 infrared spectrophotometer with EzOmnic 32 software – 32 scans were performed at a resolution of 16 cm^{-1}/s.

3. Results

3.1 Characterization of catalytic systems

3.1.1 FT-IR Analysis

The spectrum of samples is characterized by very broad IR bands at 400-600 cm^{-1} with shoulder at 453 cm^{-1}, and for all samples it can be attributed to the vibrations of Zn-O, Nakamoto (1970). Mg and K (1%) / ZnO catalysts (Figure 2 -4, 6) do not show strong changes compared with the support and there is no evidence of nitrates, but in the 1% barium catalyst, the spectrum shows the presence of a peak at 1384 cm^{-1}, which could attributed to the vibration of nitrates N-O. When the percentage is increased to 2% for K / ZnO solid (Fig. 2 -3), we can see bands corresponding to nitrate and the rest of samples showed an absorption band at 1384 cm^{-1} and the intensity of this band is very sharp and pronounced. According to Tamura et al., (2004) the bands at 1384 and 829 cm^{-1} correspond to the deformation of NO_3^- ion, which is very small in K / ZnO catalysts. However the presence of this band can be seen that the calcination temperature was not sufficient to remove nitrate. For all catalysts, there was not observed the absorption bands that describe the NO_2^- (1550 and 1320 cm^{-1}) showing that the result of the decomposition of nitrate oxide was M_XO_2 metal, where MX corresponds to metal instead of having an incomplete decomposition M_XNO_2, or just did not show decomposition of nitrates, as evidenced by other authors Xie and Li (2006).

Additionally, based on figure 2, we see that as increases the percentage of metal loaded, there is a shift of the band corresponding to the vibrations of the Zn-O at 430 cm^{-1}. The changes observed in the FT-IR spectrum of ZnO particles may indicate that there is an interaction between the added metal and support and/or can be related to the changes on geometrical shape and size of these particles, as shown by Musić et al., (2007), Andrés-Vergés et al., (1988, 1990) who investigated the relationship between the shape of the IR spectrum on one side, and the physical shape and aggregation of ZnO particles on the other. All these modifications can lead to a change in their electronic and catalytic properties.

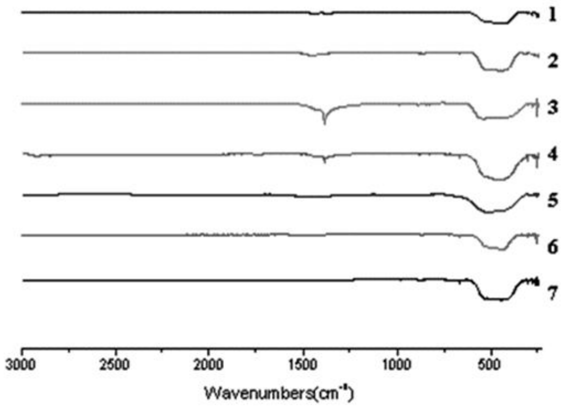


Figure 2. FT-IR Mg/ZnO, K/ZnO and Ba/ZnO. 1) Ba 2%, 2) Ba 1%, 3) K 2%, 4) K 1%, 5) Mg 2%, 6) Mh 1%, 7) ZnO

3.1.2 XRD Analysis

Figure 3 shows only the XRD analysis for the Ba/ZnO catalyst, where no characteristic peaks are observed corresponding to the metals,given that the other solids presented the same tendency. Note the presence of the zinc oxide crystalline phase, as well as that of Ba metallic species. When increasing the percentage of salt in the solid, the metal peaks increase. This shows us that there was presence of barium related crystalline species.

The solids show low-intensity incidence angles related to the crystalline system employed. For the system containing barium, the incidence angles were 43 and 45 θ. The ZnO peaks are the most intense at 19, 34, 45, and 47 θ, because of the greater proportion of zinc oxide.

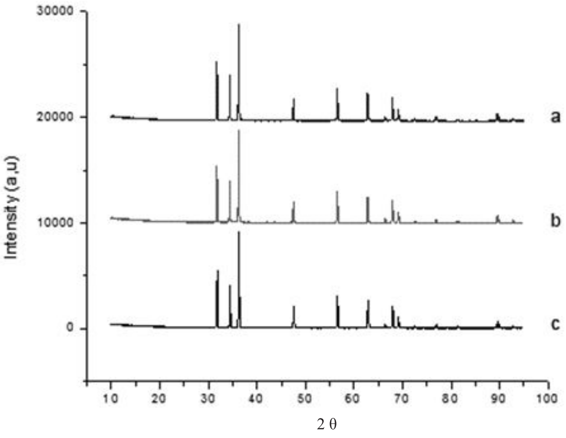


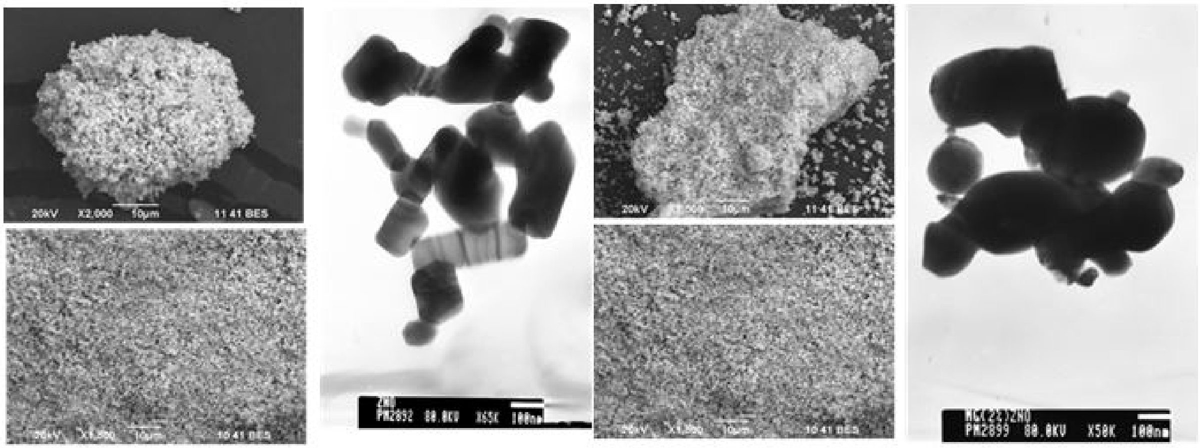
Figure 3. XRD pattern for the zinc oxide loaded with Ba. a) 2 %, b) 1%, c) ZnO

3.1.3 SEM and TEM Analysis

According to SEM analysis, it appears that the support ZnO (Fig. 4(a)) does not have a compact structure and its surface is not smooth, solid appearance having agglomerated and porous appearance. In order to further corelated the XRD results, Fig. 4(b) and 5(a) and 5(b) shows the TEM image for the sample with 2% of metal. The mean particle size determined from the TEM data is slightly larger than the mean crystalline size of support (ZnO) determined from the analysis of

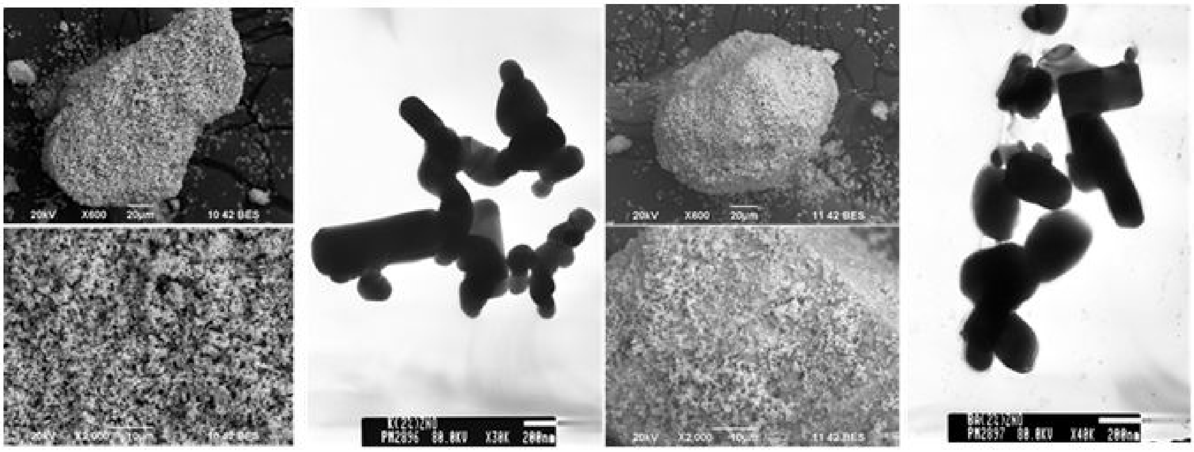
XRD (which was 98 nm, with an acicular morphology) and suggests the occurrence of structural disorder. This structural disorder is expected to occur on the particle surface because of the lattice symmetry breaking and the low coordination atoms at the particle surface. It show that the particles are not homogeneous, which can generate spaces between the particles. On the analysis of several images we have concluded that particles with the diameter from 50 to 200 nm and length of up to 50 nm are nanostructures predominantly formed and the growth of ZnO crystals occurs in direction [0 0 1] like was showing for A.A. Vostrikov et al. (2009), that the rate of crystal growth in direction [0 0 1] is maximal since vertexes of coordination polyhedrons fall on face (0 0 1).

When the support is impregnated with a metal, the solid structure change and becoming more compact and the final solid has a defined shape. The stacking of the particles changes, depending on the type of metal impregnated. The solid of magnesium (Figure 4(b)) for example, have a wurtzite structure and a grouping of particles increasing size and particle are more spherical.



(a) (b)

Figure 4. SEM and TEM of (a) ZnO, (b) Mg(2%)/ZnO



(a) (b)

Figure 5. SEM and TEM of (a) K(2%)/ZnO, (b) Ba(2%)/ZnO

The solids of potassium (Figure 5(a)) and barium (Figure 5(b)) have a compact rock structure and the surface has small clusters. K (2%) / ZnO (Fig. 5(a)) catalyst is becoming irregular with a porous surface.

3.2 Transesterification reaction

Castor oil employed in the transesterification reaction had a degree of acidity (acidity index), and rancidity (peroxide index) of 1.2 and 0.8%, respectively, showing that according to standards it is in optimal conditions to be used as raw matter.

On the other hand, the reaction was carried out in homogeneous medium by using sodium methoxide (MeONa) as catalyst. With this catalyst, we obtained a conversion close to 95%, with ricinoleic ester as the main product.

On the other hand, the values for the conversion of castor oil employing (Mg, Ba, and K /ZnO) heterogeneous systems reported yields above 87%, as shown in Table 1. K/ZnO catalysts at 1 and 2%, revealed a 90% conversion and selectivity for ricinoleic ester of 75 and 87%, respectively. Except to magnesium, it was noted that when increasing the metal percentage, the selectivity for ester was increased; Mg/ZnO catalysts at 1 and 2%, presents in general a lower selectivity towards the ester.

Table 1. Conversion and selectivity of the solids employed in the transesterification reaction of castor oil.

System	Conversion	Selectivity		
		Ester	Mono and di-ester	Lactone
K/ZnO 1%	87	75	25	0
K/ZnO 2%	90	87	13	0
Mg/ZnO 1%	89	60	20	20
Mg/ZnO 2%	87	50	35	15
Ba/ZnO 1%	95	42	16	42
Ba/ZnO 2%	93	81	10	9

Regarding Ba/ZnO-based systems at 1 and 2%, these revealed a 94% conversion, but present a different selectivity behavior, given that the systems presented the formation of a new product at 15.7 minutes as retention time by GC (Figure 6), suggesting the formation of an (E)-13-*n*-hexyloxacyclicotridec-10-en-2-ona or macrolactone (Figure 1), which is obtained by cycling of the ricinoleic acid availing of the hydroxyl group in position 12 and the acid carboxyl group.

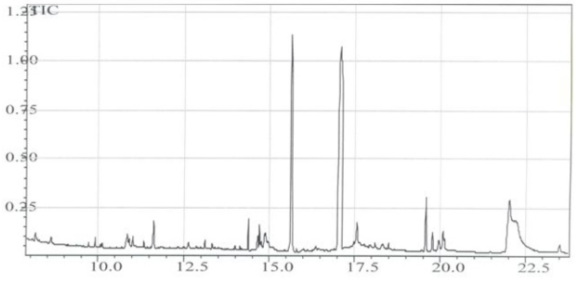


Figure 6. Gas chromatography spectrum of castor oil transesterification using Ba/ZnO catalysts at 1%

In general, there are no reports of obtaining this compound through heterogeneous catalysts and of the few works reported about its synthesis using catalysis, we can mention (R)-lactone synthesis from ricinoleic acid carried out by homogeneous catalysis by using $TiCl_2(OTf)_2$ or $TiCl_2(ClO_4)_2$ and trimethylsilyl-□-(trimethylsiloxy) carboxylate in the presence of TFBA and catalytic amounts of $TiCl_2(ClO_4)_2$ at room temperature, Shiina (2004)

To collect more evidences about the formation of (E)-13-*n*-hexyloxacyclictridec-10-en-2-ona, we used GC-Mass analysis and the results indicate the macrolactone formation, due to the fragmentation mechanism presented by the molecule with a base peak of 98 m/z (Figure 8), which corresponds to that found in the GC-Mass chromatogram.

From the afore mentioned, it may be said that the formation of (E)-13-*n*-hexyloxacyclictridec-10-en-2-ona depends on the metal used and on the interaction with the support, particularly barium – ZnO and this may be due to the presence of a divalent metal, which facilitates the insertion of the carboxyl function on the metal, compared to that observed with the monovalent metal.

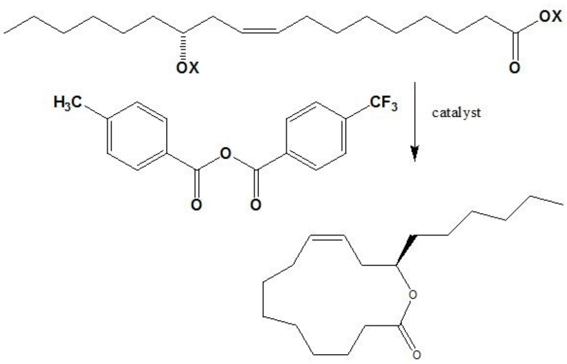


Figure 7. (R)-lactone synthesis of ricinoleic acid using TFBA. From I. Shiina (2004)

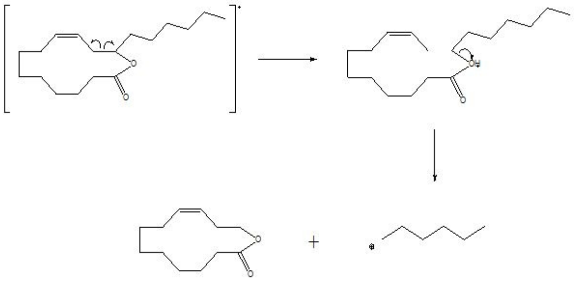


Figure 8. Macrolactone fragmentation mechanism

3.3 Surface area and temperature-programmed reduction (TPR) Analyses

Regarding the systems evaluated, the results found are shown in Table 2. A first aspect to be noted is that the surface area of all the solids is extremely low. Bearing in mind that the surface area of zinc oxide, starting material, is of approximately 40 m^2/g it can be observed that the areas of the catalysts fall to values smaller than 4m^2/g, due essentially to the calcination temperature at which the catalyst is subjected, which makes lose surface area. However, it is noted that the conversion percentages reached for all the solids has been considerably high; hence, such small area has not kept the reactions from taking place and there must be a basic metal-support interaction that leads to achieving an active species for this reaction.

Now, although a reducing medium is not employed in the transesterification reaction, it is important to evaluate the metal-support interaction by the temperature programmed reduction technique (TPR), where the catalyst surface is reduced revealing the different states of oxidation.

Table 2. Values obtained from characterization of solids through different techniques.

Technique	Mg/ZnO		K/ZnO		Ba/ZnO	
	1%	2%	1%	2%	1%	2%
Surface Area m^2/g	3.7	3.9	2.6	2.1	0.6	__
Pore Volume mm^2/g	$3*10^{-2}$	$2*10^{-2}$	$1.4*10^{-2}$	$3*10^{-2}$	0.8	1.4
TPR (ºC)	> 900	> 900	410	470 480	440 480	450 480 495

Thus, what is observed for the systems employed is that in the first place Mg/ZnO, which presented the lowest catalytic results in the transformation of the triglyceride to the methyl ester, is the solid with the highest reduction peak above 800 ºC, indicating that a poor interaction between magnesium and the zinc oxide. However, for the K/ZnO and Ba/ZnO systems, which show a completely different behavior to that observed in magnesium, the metal joined to the oxide interacts with the support and somehow modifies its crystalline structure, because, on the average, the highest temperature peak dropped from 900 ºC to 450 ºC, meaning that the zinc oxide is most easily reduced. It must be noted that although in both systems the reducibility of the oxide is modified, the interaction behaves differently for the two systems, given that the potassium system leads to the exclusive formation of methyl ester, while the barium system leads to obtaining a cyclic ester or macrolactone, this must be essentially due to the presence of a divalent metal, which can facilitate the adsorption of the carbonyl group and to facilitate in-situ reaction with the OH group.

Finally, for the system that present the highest formation of macrolactone, Ba/ZnO 1%, it can be noted that it has an extremely small area of 0.6 m^2/g, and a small pore volume (0.8-1.4), which indicates as it was previously stated that the reaction takes place superficially. This behavior may be explained by analyzing the electronic properties of barium and its interaction with the ZnO support, when achieving effective adsorption with the triglyceride and breaking the bonds permitting the ester formation. In addition, there must be a high electronic effect, given that the area is extremely small and reactions are achieved in the carbonyl group and the hydroxyl group along with the formation of macrolactone. Also, this result reveals that M/ZnO systems, in general, did not need a big area to activate the carbonyl function; therefore, there must be a more active species, which is in charge of efficiently interacting with the reagents. This should be explained through a more profound study of the issue, on which the researchers are already working.

4. Conclusions

From the point of view of assessing agro-industrial resources, we studied the transesterification of castor oil through heterogeneous solids doped with alkaline and alkaline earth metals to obtain products with greater added value like esters of fatty acids, which have great industrial application.

Ba, Mg, and K catalysts revealed high catalytic activity against the alcoholysis reaction for castor oil toward the conversion of methyl esters, although the reaction was not complete given that sub-products like mono- and diglycerides were obtained. We had the formation of a product from the cycling of ricinoleic acid known as macrolactone and, more specifically, the (E)-13-*n*-hexyloxacyclotridec-10-en-2-ona, and its existence was evidence via GC-Mass. Additionally, the Ba/ZnO solid at 1%, presented the highest selectivity for the (E)-13-*n*-hexyloxacyclicotridec-10-en-2-ona (macrolactone). An explanation for such is the high interaction between the metal and the support corroborated by surface area, TPR, and XRD analysis.

5. Acknowledgements

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