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### STRONTIUM ZIRCONATE AND HYDROXIDE MATRICES WITH HIGH PERFORMANCE AS HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION

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#### ARTICLE INFO

#### ABSTRACT

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# Strontium Zirconate (ZrSrO<sub>3</sub>) and hydroxide (Sr(OH<sub>2</sub>)) were synthesized, characterized and investigated as catalyst for preparing biodiesel. Both matrices were characterized by SEM, XRD, FTIR, TG and BET. Vegetable oil and methanol were used to prepare biodiesel and reaction conditions optimized by experimental design. Analysis showed that ZrSrO<sub>3</sub> matrix sample, synthesized by citrate route, is composed by ZrSrO<sub>3</sub>, Zr<sub>0.93</sub>O<sub>2</sub>, SrCO<sub>3</sub>, Sr(OH)<sub>2</sub>, and Sr(OH)<sub>2</sub>.H<sub>2</sub>O phases. ZrSrO<sub>3</sub> used as catalyst produced high ester content biodiesel, 98.0%. (OH)-matrix, obtained by co-precipitation, presented low solubility in methanol and best performance than ZrSrO<sub>3</sub>, because 97.6% of ester was obtained using less catalyst and a shorter time to react. When using ethanol as reactant, SrOH-matrix presented results in ester yield around 90%, while ZrSrO<sub>3</sub>-matrix produced only 9%. A comparison between both matrices recommend us to adopt strontium-matrix as a promising novel and efficient heterogeneous base catalyst to biodiesel production.

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# **INTRODUCTION**

Biodiesel is an important renewable liquid fuel that is obtained from processing either vegetable oil or animal fat through a reaction named transesterification that depends on a catalyst to occur in suitable short time (KNOTHE and STEIDLEY, 2005). Main catalysts employed in the transesterification processes are based either in acid or basic homogeneous or heterogeneous materials. Most of the conventional catalysts employed in the biodiesel industry are homogeneous base material such as sodium hydroxide or acid like sulfuric acid, despite they present many problems during the purification steps and polluting byproducts formation. (ABREU et al., 2005) The most significant benefit of using heterogeneous catalysts, especially in transesterification, is that non-polluting byproducts are formed, and the catalysts can be easily removed from the reaction medium due to their immiscibility with both reactants and products. In addition, heterogeneous catalysts can minimize corrosion and environmental problems due to the alkaline or acid characteristics besides to reduce further purification procedures. (SUNITA et al., 2008) An improved heterogeneous catalyst for biodiesel production must presents some desired behavior: thermal and chemical stability; high conversion

rate; tolerate high content of FFA (Free Fatty Acid); non-affected by the low quality of the raw material and furthermore is desirable that it present amphoteric character. However, materials with these characteristics are difficult to be synthesized, but despite that, several catalysts have been developed and studied in order to improve their characteristics and performance. Most of these materials are based on either earth alkali or transition metals as oxide or mixed oxide. (DI SERIO et al., 2008; ALBUQUERQUE et al., 2008). Specific metal oxides like strontium and zirconium have showed good catalytic activity as catalysts for biodiesel production. (ZABETI et al., 2009; JITPUTTI et al., 2006) Strontium oxide is a solid base catalyst very much studied as catalyst for biodiesel production and have always presented good results for converting oil to alkyl ester since it is thermal and chemically stable according to Liu et al., (2007) and Carvalho et al., (2013) Zirconium oxide is a well-known solid acid catalyst for transesterification reaction despite it does not work efficiently under mild conditions like strontium oxide does. (ZABETI et al., 2009; JITPUTTI et al., 2006) Mixed oxides described as perovskite (ABO<sub>3</sub>) has presented great results for several reactions as catalyst (VOORHOEVE et al., 1975) and in a promising way for transesterification. Recently, we have reported that the strontium zirconate matrix is an efficient catalyst for transesterification reaction whit high catalytic activity. (LIMA et al, 2012) In the present study, strontium zirconate synthesized by the citrate route was characterized in order to comprehend the synergic effect of the matrix phases for transesterification reactions. Over this research, it was identified all crystalline phases present in the matrix and how each one does behaves itself in the methyl transesterification reaction. Strontium hydroxide phase was identified in the zirconate matrix as an active site and then it was synthesized by co-precipitation method to be compared with zirconate matrix.

# **MATERIAL AND METHODS**

All reactants here employed were purchased from commercial sources and were used as received. Zirconium oxynitrate (Sigma-Aldrich), strontium nitrate (Sigma-Aldrich), citric acid (Sigma-Aldrich), sodium hydroxide (Merk), ammonium hydroxide (Merk), refined soybean oil (Soya), methanol (99.8%, Synth), ethanol (99.8%, Synth) and deionized water (Thermo Scientific) were used without further treatment.

Catalyst preparation: SZCRA-matrix: Strontium Zirconate was synthesized by the citrate route (VOORHOEVE et al., 1975) from zirconium oxynitrate and strontium nitrate aqueous solutions used as precursor, both in a 0.5 molL<sup>-1</sup> concentration. Citric acid (1.5 mol L<sup>-1</sup>) aqueous solution and concentrated ammonium hydroxide were used. Under slow stirring, citric acid solution was added in a stoichiometry 1:3 metal/acid ratio. Clear and transparent solutions were obtained after all reactants have been added. The solution was continuously stirred at 400 rpm and the temperature was slowly increased up to 100 °C in order to remove 75% of the initial water. After this procedure, a viscous and spongy resin was obtained, which neither turbidity nor precipitate was observed during this process. The resulting resins were taken to furnace at 130 °C for one hour. This material was milled and thermally treated in a furnace at 400 - 450 °C in environment atmosphere to eliminate volatile and organic constituents.

Catalyst characterization: Powder X-ray diffraction analyzes were performed in a Shimadzu X-ray diffractometer equipped with a graphite monochromator using CuK $\alpha$  radiation ( $\lambda = 0.1541$ nm) (Shimadzu, Tokyo, Japan). Data were collected at the 20 range of 10-80°, with a step size of  $0.02^{\circ}$  at a scanning speed of 3 step min<sup>-1</sup>. Phase quantification was done using Rietveld method with GSAS (TOBY, 2001) software. The BET method was used to measure surface area (SBET) and the mesopore volume (Vmeso) using the tplot method. The distribution of pore size was calculated from the adsorption branch using the Barret-Joyner-Halenda (BJH) model. Scanning Electron Microscopy (SEM) images were recorded at 10 kV on a JEOL Model 7500F microscope. The FTIR spectra were collected by using KBr pellets in the transmission mode recorded from 4000 to 400 cm<sup>-1</sup>, with 32 scans and resolution of 4 cm<sup>-1</sup> on a Thermo Nicolet spectrometer 6700 model. TG data were obtained in a TA Instruments thermo-balance model SDT Q600 using air flow at 50 mLmin<sup>-1</sup> and a heating program as 10 °Cmin<sup>-1</sup> from 30 to 500 °C where spent 3 minutes stabilizing. The heating kept going on from 500 °C to 1000 °C using a 5 °Cmin<sup>-1</sup> heating rate.

**Experimental design:** Reaction conditions and reactant mass were optimized after experimental design experiments in way that both SZCRA-matrix and (OH)-matrix phases were employed as catalyst for this procedure. It was designed a central composed experiment for both catalyst in three levels for all variables. Pareto chart, response surface, and contour curves were tools used to evaluate experimental results.

**Catalytic activity analysis:** The biodiesel was prepared in a threeneck flask in a reflux system. Reaction time, alcohol/oil molar ratio, temperature and catalyst percentage were defined by the experimental design. Refined soybean oil and methanol were used. The properly amount of catalyst and alcohol were added into the reaction flask under stirring followed by oil addition and then the resulting suspension was heated up to 60 °C. Biodiesel conversion was evaluated in terms of ester content, which was analyzed by gas chromatography (GC) according to EN/ISO 14103 [Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) –Determination of



Figure 1. X ray diffractograms of the SZCRA (a) and OH-matrixes (b) analyzed by Rietveld method

The resulting material was slightly ground into powders and heating treated at 900 °C for one hour. (OH)-matrix: A like-hydroxide catalyst based on strontium was obtained by co-precipitation route which was carried out following the methodology described by Rossignol et al., (1999). Strontium nitrate solution (0.5 mol L<sup>-1</sup>) was added into a flask under stirring and, following, a sodium hydroxide solution (1.5 mol L<sup>-1</sup>) was dropwised slowly into the mixture. The solution remained at 80 °C during 120 minutes under slow stirring. The precipitate was separated by filtration, washed with cool water to prevent crystals dissolution, and dried overnight at 100 °C.

Ester and linolenic acid methyl esters contents] in a Shimadzu GC-2010, with FID detector.

## **RESULTS AND DISCUSSION**

**Catalysts:** Recently, we have reported the catalyst based on the strontium zirconate matrix as an efficient catalyst for transesterification obtaining around 98% of ester yield. (LIMA et al, 2012).

 Table 1. SZCRA-matrix and OH-matrix samples phase quantification obtained by Rietveld refinement and the textural properties of samples analyzed by BET and BJH method

Card number <sup>a</sup>	Phase	SZCRA-matrix (%) <sup>b</sup>	OH-matrix (%) <sup>c</sup>
(1) 650-ICSD	$ZrSrO_3$	51.0	-
(2) 15195-ICSD	$SrCO_3$	24.5	20.6
(3) 63016-ICSD	$Sr(OH)_2.H_2O$	11.2	78.3
(4) 15167-ICSD	$Sr(OH)_2$	6.0	-
(5) 72698-ICSD	$Zr_{0.93}O_2$	7.2	-
(6) 24689-ICSD	$Sr(OH)_2.8H_2O$	-	1.1
Surface area (SBET) $(m^2 e^{-1})$		26.85	6.64
Porous volume (Vmeso) $(cm^3g^{-1})$		0.21	0.05
Porous size (BET) (Å)		394.72	390.53

<sup>a)</sup>ICSD <sup>b)</sup>  $\chi^2 = 1.849$ ;  $R_{wp} = 12.12\%$ ;  $R_p = 8.69\%$  <sup>c)</sup>  $\chi^2 = 8.191$ ;  $R_{wp} = 14.38\%$ ;  $R_p = 10.17\%$ 



Figure 2. SEM micrographs of (a) SZCRA and (b) OH-matrices

Hitherto any approach about zirconate matrix compound phases were done in order to analysis its activity or synergic effect, despite it was found carbonate and hydroxide in the catalyst bulk. Here in this paper, we have performed a quantitative study on zirconate matrix composition based on the Rietveld method to each found phase like SrZrO, SrOH and SrCO<sub>3</sub>. Figure 1 shows, firstly, the diffraction patterns of the SZCRA matrix where the presence of five different phases is confirmed and, in the second chart, a (OH)-matrix sample analysis presents three phases of it. The numbers between parentheses in the Figure 1 are assigned to the Bragg peaks positions, (JCPDS, 2003) while the blue line is the refinement residue. The well-fitted superimposition of the experimental and calculated patterns in the Figure 1 is in a good agreement with the reliability parameters of the refinement. Refinement reliability parameters as  $\chi^2$ test (chi square test)and R<sub>wp</sub>(weighted profile R-factor) are presented on the bottom of Table 1 in which are also displayed the obtained results in percentages for each phase found in SZCRA and (OH) matrices. Both parameters show that the refinement is reliable because its ideal values have to be as smaller as possible, despite for complex systems,  $\chi^2$  is supposed remains around 5 and  $R_{wp}$  in the range of 10-20%. A complex system was identified by the Rietveld refinement in the SZCRA-matrix, in which five crystalline phases were quantified. They had been showed ZrSrO<sub>3</sub>, Zr<sub>0.93</sub>O<sub>2</sub>, SrCO<sub>3</sub>, Sr(OH)<sub>2</sub>, and Sr(OH)<sub>2</sub>.H<sub>2</sub>O phases. Results of quantification for each phase were presented in the Table 1, as well as, the ICSD card number of the corresponding phase. According to the Rietveld refinement results, ZrSrO<sub>3</sub> was quantified as majority phase (~51%). In the citrate route, an initial acid medium favors the precipitation of some strontium citrate because of its stability. The presence of this precipitated material during the initial precipitation stage interferes directly on the stoichiometric ratio to formation of the strontium zirconate phase. As there was a deficit of strontium in solution during complexation process due to the precipitation of strontium citrate, the excess of remained zirconium was complexed in order to produce a nonstoichiometric zirconium oxide (Zr<sub>0.93</sub>O<sub>2</sub>). Hydroxide phases Sr(OH)<sub>2</sub> and Sr(OH)<sub>2</sub>.H<sub>2</sub>O should not be present in zirconate matrix due to the thermal decomposition processes, since it was heated up to 900 °C. However, some inner oxygen atoms on the catalyst particle surface can adsorbs water molecules and, then, lead it to the hydroxide and hydrated phases formation onto the surface.

This like-hydration reaction is expected to occur on oxide surface, but these water molecules may also be diffused through first atoms layer resulting in structural water in the perovskite structure. Under these conditions, structural water can remain trapped in there even at high temperatures(LUTZ et al., 1981). Hydroxide phases were quantified about 17% in SZCRA-matrix sample. Pure strontium zirconate phase has not presented activity as catalyst for transesterification when used under mild conditions in this research, but Zr<sub>0.93</sub>O<sub>2</sub> is a known solid acid catalyst for transesterification and esterification of glycerides and fatty acid under high time and temperature conditions(ZABETI et al., 2009). Despite studies about catalytic activity to transesterification process using strontium hydroxide are rare, the compound presents alkali character and it could be acting as basic catalyst material. Therefore, as SrZrO3 phase has not showed activity, it is predictable a synergic interaction between all phases (SrZrO+SrCO+SrOH) over SZCRA-matrix that promoted the catalytic activity to transesterification reactions. The (OH)-matrix sample synthesized exhibited Sr(OH)2.H2O, Sr(OH)2.8H2O and SrCO<sub>3</sub> phases. Strontium hydroxide was the majority product, of which the monohydrated phase represents around 78% and strontium carbonate represents around 20% of the total catalyst mass. In both catalysts matrix (OH and Zirconate), the amount of strontium carbonate was relatively high. Inner carbonate formation and the noncontrolled atmosphere during calcination step can also be one of the main reasons responsible for the carbonates formation(FURNO et al., 1997). Robbins et al. (1995) have reported that carbonate phase is present into the matrix bulk before and after calcination at 950 °C.

It is possible to find considerable amount of carbonate especially in complex matrix where a fresh oxide surface combines itself with atmospheric CO<sub>2</sub> resulting in the carbonate phase (ROBBINS et al., *1995)*. Although this occurrence represents a reduction of strontium availability in reaction medium during the catalyst synthesis, it did not inhibit the high catalytic activity of any matrix. Due to its high percentage in the sample, commercial pure SrCO<sub>3</sub> was tested in transesterification reaction, but it did not presented catalytic activity. Concerning to the catalysts morphology, the presence of large agglomerates was observed in both matrices as can be observed in the micrograph of SZCRA and OH matrices. Figure 2(a) shows a frame of SZCRA-*matrix* grain agglomerate in which can be seen smaller

particles, less than 100 nm, over a bigger one multilayer grain. This variety of size can be assigned to the effect of calcinations that drove the primary particle to agglomerate in grains of several dimensions. (OH)-matrix grain image shows particles size around 5 µm being structured by smaller pellets auto-assembled due to the coprecipitation method formation process, Figure 2(b). BET and BJH method analysis showed that (OH)-matrix surface area and porous volume are very much smaller than in SZCRA-matrix (see Table 1). When porous volume has decreased in OH-matrix, its surface area have been reduced too, however the porous size kept in the same dimension for both samples (around 390 Å). Despite SZCRA-matrix has presented big particles as a agglomerated, its high porosity make it to dispose a high surface area too, being around 26 m<sup>2</sup> g<sup>-1</sup> against only 6.6 m<sup>2</sup> g<sup>-1</sup> in OH-matrix. Infrared spectra of SZCRA and OH matrices are presented in the Figure 3. Bands in the region between 500 cm<sup>-1</sup> and 650 cm<sup>-1</sup> are expected and assigned to metal-oxygen bonds that absorbs in this wavelength region. (LUTZ et al., 1981) Bands in 1440 cm<sup>-1</sup> in both matrices spectra are attributed to carbonates groups. (BACCE et al., 2001).

decomposition behavior diverse of other matrices for same materials. It is expectable to find hydration and crystallization water in the bulk of the material according to XRD analysis. In generally, the thermogravimetric curve profile presents three main mass losses. Dehydration process in the interval starting below 100 and going up to 500 °C is the first decomposition range. A mass loss (3.7%) is observed between 500 and 750 °C, which can be attributed to decomposition of strontium hydroxide hydrate associated to a small sum of organic residue remained originated from reactants. Despite this decomposition, a small amount of this hydroxide was found in the material even after heat treatment at temperature above 900 °C. This is justified by the fact of the complex phase mixture has trapped and stabilized inner this components phases. (DISNESCU and PREDA, 1973) had investigated the system SrO-H<sub>2</sub>O thermal decomposition and verified that SrO was formed above 700 °C, however water molecule absorption can leads to formation of strontium hydroxide again. Therefore, the stabilization of strontium hydroxide phase can be assigned to the low energy demanded by synthesis system, as well as the non-controlled atmosphere during



Figure 3. Infrared spectra of SZCRA-matrix (solid line) and (OH)-matrix (dot line) in pellets. Highlighted bands at 3600 cm<sup>-1</sup>, assigned to hydroxyl groups



Figure 4. Thermogravimetric curve of a) SZCRA-matrix and b) OH-matrix

Two sharp bands located at  $3610 \text{ cm}^{-1}$  and  $3591 \text{ cm}^{-1}$  are assigned to the stretching vibration of non-hydrogen-bonded hydroxide ions called as free OH<sup>-</sup> ions. (LUTZ et al., 1981; SILVERSTEIN, 1997) The presence of the two bands in this region suggests, at least, two different coordination sites for the free OH<sup>-</sup> ions in the catalyst structure, probably related to surface and inner coordination sites. These bands associated with the broad band around 2880 cm<sup>-1</sup>, attributed to water deformation from water of crystallization trapped into the solid structure, agrees with the XRD results and the Sr(OH)<sub>2</sub> phase formation in this sample. Thermogravimetric analysis of SZCRA-*matrix* and (OH)-*matrix* are presented in Figure 4(a) and (b), respectively. The first one has confirmed to be a complex matrix since it is composed by five different phases what can generate calcination. This mass loss is not observed in the Figure. 4(b) at the same temperature because it is supposed it has been moved up due complexity of the SZCRA-matrix once (OH)-matrix is very much simple. The last mass loss found in SZCRA-matrix thermogram is attributed to  $CO_2$  releasing (D'ASSUNÇÃO, GIOLITO AND IONASHIRO, 1989)as a carbonate structure decomposition. It was lost around 8.75% weight in this heating step. Above 900 °C was not observed mass loss for any sample up to heating reach 1000 °C. Strontium hydroxide matrix prepared and dried at 100 °C over 10 hours was analyzed producing a thermal decomposition curve which agrees with a like-mono hydrate material. Figure 4(b) presents thermogravimetric and derivate curves in which are highlighted three mass loss regions. A mass loss of 10% is the first region in the interval from 70 to 130 °C which is assigned to the loss of one mol of

water caring strontium hydroxide to dehydrated state. Second great mass loss occurs between 470 and 520 °C and is a referent to 8.6% of mass what is identified as the stage in which hydroxide strontium is transformed in strontium oxide through loss of one mol of hydrogen. Additionally, in this stage has started carbon dioxide elimination. So it is predictable that matrix had been lost <sup>1</sup>/<sub>4</sub> mol of CO<sub>2</sub>. The last mass loss is found around 900 °C, like seen in SZCRA thermogram, and is inherent to elimination of 14.4% of mass as CO<sub>2</sub>. The oxogroups on the oxide surface are less susceptible to hydrolysis reaction than other more reactive surface groups, and react to carbon dioxide molecules in order to produce a rich-SrCO<sub>3</sub> surface. That way, just SrO remained at the end of the analysis.

Catalytic performance: Two aspects deserve different approaches: catalyst synthesis procedure and its performance after reaction conditions optimization by using experimental design. In this sense, is important to take in account that both matrices were synthesized by different procedures. The main parameter to evaluate the catalytic activity of any material for a transesterification reaction is the ester content yield. Catalytic behavior of both catalysts is efficient enough to produce biodiesel with quality in accordance with international parameters quality control, where the minimum acceptable ester content is 96.5%. After performed all designed experiments, response surface were built in terms of ester yield and that parameter which most influenced the reaction efficiency. In both cases these parameters were reaction time and catalyst amount. Figure 5 shows both response surfaces built with results from experimental design of reactions using SZCRA-matrix and OH-matrix as catalyst. According to the response surface behavior, reaction using SZCRA-matrix demanded 3% of catalyst w/w, 40% of alcohol w/w, 60 °C and 140 min to obtain 98 % of ester content, while for (OH)-matrix was necessary only 0.5% of catalyst, 40% of alcohol, 60 °C and just 60 minutes of reaction time to reach 97.6% of ester content.



Figure 5. Response surface of optimization for reaction conditions using (a) SZCRA and (b) OH-matrixes

Figure 6 presents a chart in which are displayed and compared the best conditions optimized for SZCRA,  $SrCO_3$  and (OH) matrices. In terms of % alcohol and temperature, all of the catalyst behaved similarly. (OH)-*matrix*has presented the best performance, because beyond it demands less catalyst (<0.5% w/w) and a shorterreaction time (60 min.) to complete the process than when using SZCRA or SrCO3 (140 and 180 min, respectively). Actually, SrCO<sub>3</sub> showed itself to be inactive to transesterification catalysis since the ester content obtained was only 1.6%. This test was performed just to check whether SrCO<sub>3</sub> affects or not the matrices activity, due to its relatively high percentage into samples (>20% w/w).



Figure 6. Comparison of the best conditions optimized for SZCRA, SrCO<sub>3</sub> and (OH) matrices and its ester content yeild

Although no records were found about solubility of strontium hydroxide in methanol, qualitative tests carried out in our laboratory showed low solubility when compared to their solubility in water (1.77 g/100 mL H<sub>2</sub>O at 20 °C). After all reaction to produce biodiesel, it was always observed a sediment material on the flask. The catalyst solubility study was realized by monitoring the conductivity of a strontium hydroxide solution in methanol. Conductivity results have showed a dependency in terms of catalyst concentration, nonetheless, these results can also be considered as catalytic activity indicator. Even after one week, the mixture of strontium hydroxide with methanol had a large amount of sediment. The relation between conductivity and catalyst percentage could be correlated with the ionization of methanol, or its deprotonation and subsequent formation of the methoxide, which is essential to the transesterification process. Based on this experimental observation, biodiesel production was performed without the presence of the catalyst. It was carried out the following procedure: an amount of methanol was added over strontium hydroxide and left one hour under ultrasound stirring. Then, the methanol/catalyst mixture was centrifuged and the supernatant was put into the oil to perform the transesterification procedure. Tests results of this reaction were similar of those in presence of the catalyst. That is a very important result, since it brings us the possibility of biodiesel production by using only "activatedmethanol", and avoiding leaching and loss of catalytic material over the purification processes to obtain the final biodiesel. In order to analysis remaining catalyst in the final biodiesel were performed metal quantification in both samples, SZCRA and (OH)-matrices, where was confirmed the significant leaching of strontium to the final biodiesel. As biodiesel is a complex matrix, the percentage of strontium found on it is not only due to the dissolved ions, but as well as due to the catalyst-matrix residues not removed during the purification processes of biodiesel, such as centrifugation and washing. Nevertheless, the presence of metals in fuel to diesel engines can not be considered a problem exactly, because metals such as Mg, Sr, Co, Cr, Ce, Fe and others, have been used as base to the composition of FBC (Fuel Born Catalyst) additive for fuel employed to help clean up exhaust gas filter of internal combustion engines. (STEPIEN et al., 2015; RICHARDS et al., 2006; KESKIN et al.,

2008; KANNAN, KARVEMBU and ANAND, 2011) However, it is necessary to attempt that there are restrictive limits of metal specified on the worldwide legislation. That maximum limits established for sodium (Na) and potassium (K), for example, are mandatory in way to prevent soap formation along the engine fuel injection system. That way, it does require a more careful study of the strontium combustion interference in biodiesel and engines performance. The studied catalyst matrices had presented excellent potential to reaction using ethanol instead of methanol. Ethanolysis tests using SZCRA-matrix has showed itself very promising because reaction obtained 9% of ester. This is a low conversion, but it might means that a deeper study about reaction conditions and optimization could lift it up to suitable results, since Zr oxides are acid catalysts and can work under severe conditions. Notwithstanding, (OH)-matrix have presented results in ester yield around 90%. Further researches are being performed to optimize this process.

## CONCLUSIONS

Strontium zirconate matrix synthesized by the citrate route (SZCRAmatrix sample) showed high catalytic activity to produce biodiesel via transesterification reactions. XRD analysis showed that SZCRA sample is composed of ZrSrO<sub>3</sub>, Zr<sub>0.93</sub>O<sub>2</sub>, SrCO<sub>3</sub>, Sr(OH)<sub>2</sub>, and Sr(OH)<sub>2</sub>.H<sub>2</sub>O phases. The ester content of the biodiesel produced using that catalyst was 98.0%. However, as pure SrZrO<sub>3</sub> phase has not showed activity, a synergic interaction between all phases over SZCRA-matrix have promoted the catalytic activity to transesterification reactions. Strontium hydroxide was synthetized and compared with SZCRA-matrix. Obtained results come to set strontium hydroxide (OH-matrix) as a novel and efficient heterogeneous base catalyst. This matrix presented best performance than SZCRA-matrix, because beyond to use less catalyst, it needs less reaction time to produce a biodiesel with more than 97% of ester content. Experimental observations showed that synthetized strontium hydroxide possess very low solubility in methanol. Nonetheless, even if considering it as a homogeneous catalyst, under environmental and technological viewpoint, it is more suitable than common sodium or potassium-based homogeneous catalyst since the wastewater and biodiesel contains less metal than those one produced by conventional reaction. Therefore, strontium zirconate and strontium hydroxide matrices showed themselves as promising catalysts to biodiesel production. As strontium hydroxide presented characteristic of heterogeneous catalyst, its reuse becomes more feasible due to the simplicity of the sample. Future studies regarding to the reuse of the catalysts will be necessary to a better understanding of the active sites recovery conditions.

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