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**Continuous production of biodiesel from low grade feedstock in presence of Zr-SBA-15: Catalyst performance and resistance against deactivation**

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1 **Abstract**

2 Zirconium-containing SBA-15 materials have been used in the production of fatty acid  
3 methyl esters from low grade oleaginous feedstock. Its resistance against deactivation  
4 has been assessed by means of studying the effect of conventional impurities present in  
5 lipid wastes over the catalytic performance of this material. Alkaline metal cations like  
6 potassium could interact with Brønsted acid sites, causing their neutralization by ion  
7 exchange and a limited, but not complete, deactivation of the material. Additionally,  
8 organic unsaponifiable compounds like retinoids or phospholipids –being studied in this  
9 work as retinol and lecithin respectively-, strongly interact with the catalyst surface,  
10 leading to a strong deactivation of the material, though reversible, since they are fully  
11 regenerated by calcination in air. Catalytic assays in continuous mode in a fixed bed  
12 reactor suggest a higher resistance of Zr-SBA-15/bentonite pellets against catalyst  
13 deactivation. Bentonite clay, which has been used as binding agent for the preparation  
14 of the particulate catalyst, seems to be the responsible for this behavior, acting as poison  
15 scavenger and preventing the access of the impurities to the catalytic acid sites and  
16 consequently their deactivation.

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20 **Keywords:** Biodiesel, Heterogeneous Acid Catalysts, Zirconium, Zr-SBA-15, Low  
21 Grade Feedstock, Fixed Bed Reactor

22

1 **1. Introduction**

2 Biodiesel consists of a mixture of fatty acid alkyl esters obtained from renewable  
3 resources, typically from vegetables oils and/or animal fats, by alcoholysis -mainly  
4 using methanol- of triglycerides present in lipids, conventionally using a basic or an  
5 acid catalyst. Currently, the most extended process for biodiesel production involves the  
6 transesterification of high-grade, refined oleaginous feedstock with methanol using  
7 homogeneous alkaline catalysts, because of their superior catalytic performance at low  
8 reaction temperatures compared to acid catalysts. However, this operation mode has  
9 several important disadvantages, such as the need of using high-grade feedstock, with  
10 low amounts of impurities –typically free fatty acids (FFA), water or unsaponifiable  
11 matter-. In this way, these raw materials usually represent a substantial fraction of the  
12 processing cost for biodiesel, reducing its profitability. As an alternative, lower-grade  
13 feedstock could be used as starting raw materials, but in this case, the processing costs  
14 are moved from the feedstock to the conditioning stages needed for the treatment of the  
15 feedstock to decrease the amount of the impurities, and the purification of biodiesel  
16 through the removal of salts formed during the neutralization of homogeneous catalysts.  
17 Moreover, conventional processes are quite sensitive to water content in the feedstock  
18 and other impurities, making even worse the above described drawbacks of this  
19 technology [1].

20 Overcoming these disadvantages has been the focus of scientists' efforts which have  
21 crystallized in the development of new production technologies with higher profitability  
22 and environmental sustainability. In addition, some environmental politics drive  
23 investments in the biofuels sector in the same direction. As an example, the EU  
24 Directive 2009/30/CE, which stiffens the legislation in terms of greenhouse emissions by  
25 means of conventional fuels substitution by biofuels, suggests the use of waste

1 feedstock as starting raw materials for their production. In this way, it is of major  
2 importance studying alternative non-edible waste feedstock which could be used for the  
3 sustainable production of biodiesel.

4 During the last years, development of heterogeneous catalysts for biodiesel production  
5 has been a very active research area [2] since the use of heterogeneous catalysts  
6 involves several advantages which are not present in their homogeneous counterparts,  
7 such as the production of a higher grade biodiesel and glycerol, the ability to be used in  
8 continuous fixed bed reactors, no waste water generation because the catalyst removal is  
9 not required, fewer purification steps and, therefore, fewer complex facilities [1]. In  
10 particular, heterogeneous acid catalysts could be of great interest to improve biodiesel  
11 production process, because these, besides the multiple advantages described for  
12 heterogeneous systems, can also simultaneously drive both esterification and  
13 transesterification reactions, being not required the conditioning stages for the use of  
14 low grade feedstocks with high acidity. In this way, heterogeneous acid catalysts make  
15 possible designing integrated process based on packed bed continuous flow reactors  
16 with enhanced productivity, easy catalyst separation and minimum purification steps as  
17 compared to conventional biodiesel production processes [3]-[5]. Moreover, techno-  
18 economic studies suggest that heterogeneous acid catalyzed processes are more  
19 profitable than conventional procedures applied to the production of biodiesel [6].  
20 However, the industrial implementation of such catalysts in commercial biodiesel  
21 production still needs important improvements, mainly devoted to the stability of the  
22 catalysts and resistance against deactivation in presence of high amounts of several  
23 impurities which are plenty in low-quality oleaginous raw materials (water, metals and  
24 unsaponifiable matter).

1 In this context, Zr-SBA-15 has revealed to be an interesting catalyst for the production  
2 of biodiesel. Recently, we have demonstrated that this catalyst show high catalytic  
3 performance in biodiesel production from low-grade waste cooking oil in a continuous  
4 packed bed reactor [7]. However, there are still some lacks of information about the  
5 response of this material to the presence of some impurities accompanying the  
6 oleaginous feedstock, which could act as potential catalyst poison. This work sheds  
7 some light on the catalytic behavior of Zr-SBA-15 material in biodiesel production from  
8 low-grade raw materials, assessing the influence of several natural substances present in  
9 oleaginous feedstock on the stability of the catalyst against deactivation. Finally, this  
10 investigation provides some answers about the good resistance of this material against  
11 catalyst poisoning in long time-on-stream experiments for the transformation of  
12 mixtures of low-grade oleaginous feedstock.

13

## 1 **2. Materials and Methods**

### 2 **2.1. Materials**

3 Crude palm oil (*CPO*, Gran Velada), category-1 animal fat (*AF-1*, Ibergrasa), waste  
4 cooking oil (*WCO*, obtained from the canteen of the university), pork lard (*Lard*,  
5 Ibergrasa), mixed animals fats (Chicken-Beef-Pork, *MAF*, Ibergrasa), and methanol  
6 (ACS grade, Aldrich) were used as feedstock in acid catalyzed methanolysis tests.  
7 Oleaginous feedstocks were filtered to remove suspended solids prior to their use as the  
8 sole conditioning step for these materials. Tetraethylorthosilicate (TEOS, 98 %,   
9 Aldrich) and zirconocene dichloride ( $\text{Cp}_2\text{ZrCl}_2$ , ABCR) were used as silicon and  
10 zirconium precursors, respectively, together with Pluronic P-123 ( $\text{PEO}_{20}\text{-PPO}_{70}\text{-PEO}_{20}$ ,  
11 Aldrich) as the structure directing agent for the synthesis of Zr-SBA-15. Natural  
12 bentonite, a montmorillonite-type clay (Süd-Chemie) was used as binding agent and  
13 methyl cellulose (Aldrich) was employed as additive to control the plasticity of the  
14 mixed catalyst-clay-water in the agglomeration of Zr-SBA-15.

### 15 **2.2. Synthesis of Zr-SBA-15 material**

16 Zirconium-functionalized SBA-15 material was prepared according to the method  
17 described in literature [8]. In a typical synthesis, Pluronic 123 (4 g) was dissolved in a  
18 hydrochloric acid aqueous solution (125 mL of 0.67N) at room temperature. After  
19 complete dissolution, 1.2 g of zirconocene dichloride were added and the resultant  
20 suspension was stirred for 3 h and heated to 40°C. TEOS (8.63 g) was added to the  
21 synthesis media under vigorous stirring, which continued for 20 additional hours  
22 keeping constant the synthesis temperature at 40°C. The resultant suspension was  
23 hydrothermally aged at 130°C under static conditions for 24 h. The materials were  
24 finally recovered by filtration and air-dried overnight. Surfactant was removed by  
25 calcination at 450°C in air during 5 hours.

### 1 **2.3. Agglomeration of Zr-SBA-15**

2 Agglomeration of powder Zr-SBA-15 was accomplished with the aim to get a  
3 particulate material to be used in a packed bed reactor while keeping low the pressure  
4 drop during operation. Agglomeration of Zr-SBA-15 was performed following a  
5 method previously reported in literature [8]. Powdered Zr-SBA-15 (65 g) was mixed  
6 with bentonite (25 g), acting as binding agent, methyl cellulose (10 g), which increased  
7 the plasticity of the mixture, and ultra-pure water. The mixture was loaded into a  
8 kneading machine (Lleal) and the dough was kneaded during 3 h to achieve a  
9 homogeneous mixture. The resultant material was extruded to form uniform rods  
10 (diameter 1.0 mm) which were dried in a climatic chamber with controlled atmospheric  
11 humidity. The resultant material was calcined in air at 450°C during 5 h. Finally, the  
12 rods were cut into particles of 1.0 mm.

### 13 **2.4. Catalyst characterization**

14 The textural properties of the synthesized catalyst samples were calculated from N<sub>2</sub>  
15 adsorption-desorption isotherms recorded at 77 K in a Micromeritics TRISTAR 3000  
16 unit. Surface area was calculated applying the B.E.T. method and pore size distributions  
17 by applying the B.J.H. method using the K.J.S. correction. Total pore volume was  
18 assumed to be that recorded at  $p/p_0 = 0.985$ . Structural properties were assessed by  
19 means of X-ray powder diffraction (XRD) experiments performed on a Philips X'Pert  
20 diffractometer using the Cu K $\alpha$  line in the 2 $\theta$  angle range 0.6-5.0°, with a step size of  
21 0.02° for low angle analysis and a step size of 0.04° in the 2 $\theta$  angle range of 5.0-50.0°  
22 for high angle analysis. Bulk zirconium contents were determined by Inductively  
23 Coupled Plasma-Atomic Emission Spectroscopy (ICP-OES). Acid capacity was  
24 measured by ammonia temperature programmed desorption in a Micromeritics 2910  
25 (TPD/TPR) equipment fitted with a TCD detector. X-ray photoelectron spectroscopy

1 (XPS) experiments were performed using a Kratos AXIS HSi instruments fitted with a  
2 charge neutraliser and Al K $\alpha$  X-ray source. Spectra were recorded at normal emission  
3 using analyser pass energy of 40 eV and X-ray power of 225 W. Prior to the analysis,  
4 samples were outgassed at 10<sup>-11</sup> bar overnight. Binding energies were referenced to the  
5 C1s line (284,8 eV) and deconvolution curves were achieved using the Casa XPS  
6 software.

## 7 **2.5. Catalytic experiments**

8 Catalytic experiments performed in presence of powder Zr-SBA-15 were accomplished  
9 in a batch reactor. The experiments were carried out in a 25 ml stainless-steel autoclave  
10 (Autoclave Engineers) fitted with temperature controller, mechanical stirrer and a  
11 pressure transducer. In a typical experiment, 5 g of low-grade oleaginous feedstock,  
12 methanol (50 methanol to oil molar ratio) and the catalyst (12.45 wt% catalyst loading)  
13 are placed together inside the reactor vessel. The system is then hermetically closed and  
14 the temperature (209°C) and stirring conditions (2000 rpm) set up. The reaction was  
15 allowed to proceed for 6 hours before cooling down the reactor using an ice-water bath.  
16 The resultant suspension was filtered using a nylon-membrane filter to recover the  
17 catalyst and minimize solid losses –for catalyst reuse experiments-. The excess of  
18 methanol was removed by rotary evaporation under vacuum at 60°C at 0.2 bar. The  
19 recovered catalysts samples were double-washed with methanol and n-hexane in an  
20 ultrasound bath for the removal of both polar and non-polar surface-adsorbed  
21 compounds. Alternatively, recovered catalysts were thermally treated at 450°C in air  
22 atmosphere, depending on the experiment, to completely burn out the adsorbed organic  
23 substances.

24 Catalytic reaction experiments with agglomerated Zr-SBA-15 were driven in a  
25 continuous up-flow fixed-bed reactor (120 cm length, 0.9 cm ID). The inner



1 temperature of the reactor (209°C) was controlled by an external wrapping metallic  
2 resistance, whereas the pressure of the system (70 bar) was controlled by means of a  
3 needle valve placed in the reactor exit, to ensure liquid phase conditions. The catalytic  
4 bed was initially loaded with 28 g of particulate catalyst and used for all the reaction  
5 tests. Methanol and oil were fed to the inlet of the reactor using HPLC pumps, allowing  
6 an effective control of the methanol to oil molar ratio (50) and residence time of the  
7 reactants stream inside the reactor of 30 min. The effluent solution coming from the  
8 reactor was expanded in a flash vessel at 65°C under vacuum (0.2 bar) to remove some  
9 of the methanol excess and allowed to decant in a tank to separate the FAME and  
10 glycerol layers. FAME layer was then recovered and rotaevaporated to eliminate the  
11 remaining methanol.

12 The molar yield of transformation of fatty acid alkyl chains (comprising both FFA and  
13 glycerides) into fatty acid methyl esters ( $Y_{\text{FAME}}$ ) was calculated by analyzing crude  
14 reaction samples by means of  $^1\text{H}$  NMR analysis in a Varian Mercury Plus 400 unit in a  
15 similar way to that described by Whalen et al. [9].

## 16 **2.6. Biodiesel characterization**

17 The biodiesel product was thoroughly washed twice with distilled water in a separation  
18 funnel and the resultant product dried at 40°C and 0.5 bar for 12 h to remove traces of  
19 moisture. The methyl esters produced were characterized using the quality standard  
20 ISO-14214, in terms of composition (FAME content, acid value, presence of alkaline  
21 metals and phosphorus, presence of mono-, di-, and triglycerides, presence of methanol  
22 and glycerol), density, viscosity, flash point, cetane number, iodine value, and cold  
23 properties such as cold filter plugging point (CFPP).

24

### 1 **3. Results and discussion**

#### 2 **3.1. Catalytic tests in presence of low grade feedstock: influence of catalyst poisons**

3 The first purpose of the present work was to evaluate the properties of the starting  
4 oleaginous raw materials which could exert any influence on the catalytic behavior of  
5 Zr-SBA-15 catalyst. Table 1 lists the main properties calculated for CPO, WCO, AF-1,  
6 Lard and MFA, such as density, viscosity, acid value, metals content, water and  
7 unsaponifiable matter. The exhaustive characterization of these raw materials revealed  
8 the presence of several impurities which could adversely interfere in the catalytic  
9 activity and stability of Zr-SBA-15 to produce fatty acid methyl esters (FAME). In  
10 particular, high content of free fatty acids (FFA), alkaline and alkaline earth metals,  
11 phosphorous, unsaponifiable matter and moisture have been observed. Hence, the  
12 processing of these raw materials in the production of biodiesel by means of acid-  
13 catalysis is expected to be difficult [10] and could probably lead to some catalyst  
14 poisoning during the methanolysis reaction tests.

15 The catalytic activity of Zr-SBA-15 material in the production of methyl esters from  
16 low-grade oils and fats was evaluated in batch-mode using previously optimized  
17 reaction conditions: 209°C, 45.80 methanol to oil molar ratio, 12.45 wt% catalysts  
18 loading, 2000 rpm stirring rate [11]. Figure 1 displays the yield towards FAME  
19 achieved for the different raw materials in three sets of experiments: using the fresh  
20 catalyst, after a first reuse with intermediate catalyst washing with methanol and n-  
21 hexane, and after a second reuse with intermediate thermal treatment (450°C in air). Zr-  
22 SBA-15 provided very good behavior under the optimized conditions for all the  
23 experiments leading to molar FAME yields around 92% after 6 h. Nonetheless, with  
24 regard to the first reutilization experiment after catalyst washing, the material evidenced  
25 a slight deactivation, with a 5% FAME yield decay –on average-. However, initial

1 catalytic activity was fully recovered in the third consecutive reaction experiment, after  
2 the calcination treatment, which suggests that the catalyst deactivation observed during  
3 the first recycling test was a reversible process, most probably linked to the adsorption  
4 of organics onto or around the catalytic sites [11], regardless the starting raw material  
5 used in the catalytic test.

6 With the aim to fully understand the deactivation phenomena observed in the previous  
7 experiments, some catalytic tests were performed in the methanolysis of CPO, by  
8 modifying this time the starting raw material with the addition of several of the natural  
9 substances and impurities detected in the low grade feedstocks: alkaline metals such as  
10 Na and K -through the addition of NaCl and KCl-, P -which was added in the form of  
11 lecithin- and unsaponifiable compounds such as cholesterol and retinol, a chemical  
12 present in high concentration in several oleaginous feedstock, such as crude palm oil  
13 [12]. As in the previous catalytic tests, the activity and stability of the Zr-SBA-15  
14 material were evaluated in two consecutive reactions runs, one of them performed in  
15 presence of the fresh catalyst and the second one after washing the used material with  
16 methanol and n-hexane. Figure 2 depicts the results (FAME yield) obtained from the  
17 described experiments.

18 First use of the catalyst in presence of unmodified CPO provided good catalytic results,  
19 yielding FAME productivity above 80% of the maximum available after 3 h. Recycling  
20 tests evidenced the same catalytic activity decay (~5%) previously observed for tests  
21 performed during 6 h. These FAME yield values were used as reference to compare  
22 with in the study of the deactivating capability of the previously described potential  
23 poisons. At this respect, most of the catalytic tests carried out in presence of doped CPO  
24 showed similar reaction results, suggesting lack of deactivating capability for most of  
25 the tested substances. However, there is a substance which displays a much higher

1 deactivating capability than any other one among the tested potential poisons: lecithin.  
2 Lecithin is the common name given for phosphatidylcholine, a phosphatide of fatty acid  
3 diglycerides linked to the choline ester of phosphoric acid. This is a natural substance,  
4 present in both animal and vegetal lipids, which is a key building block of cell  
5 membrane bilayers. The first use of the catalyst in presence of lecithin-containing CPO  
6 yielded 65-70% FAME, depending on the initial phosphorus loading, a much lower  
7 yield than that obtained for the reference tests in absence of potential poisons. These  
8 low FAME yields, together with the drop observed in the recycling tests, make obvious  
9 the deactivation of the zirconium-based material in presence of this natural substance.  
10 This fact seems to be linked to the high affinity of zirconium oxides for phosphates.  
11 Several authors have described the strong adsorption of these ions onto the surface of  
12 zirconium oxide particles [13], and consequently, the deactivation of the Zr-SBA-15  
13 material could be related to the preferential adsorption of the phosphate group of  
14 lecithin onto the zirconium acid sites, in an analogous way to that described by Su. In  
15 this way, Lewis acid sites would be blocked and the access of the glycerides to these  
16 catalytic centers hindered, limiting the extension of the reaction.  
17 With regard to the experiments performed in presence of sodium or potassium chloride  
18 (500 mg/kg), cholesterol and retinol (each at 5%wt), negligible differences with the  
19 results achieved for the reference catalytic tests were detected, suggesting an absence of  
20 catalytic poisoning, at least for these substances at the tested concentration levels.  
21 Increasing the amount of these substances up to 1000 mg/kg for the alkaline cations and  
22 to 10%wt in the case of the organic chemicals produced almost the same results, unless  
23 for the potassium and retinol, which significantly reduced the FAME yield achieved  
24 when present at these concentration levels.

1 In the case of potassium, the deactivating effect could be related to the partial  
2 neutralization of the Brønsted acid sites present in Zr-SBA-15 materials [14], since  
3 Lewis acid sites do not present ion exchange capability and thus, alkaline cations such  
4 as sodium or potassium should not interfere with this type of acid sites. The fact that Zr-  
5 SBA-15 activity is conditioned by the presence of potassium but not of sodium could be  
6 related to the higher solubility of potassium chloride in methanol at high temperatures,  
7 in contrast to that found for sodium chloride, whose solubility in methanol is scarce at  
8 temperature levels such as those used in the catalytic tests [15]. In this way, the  
9 interaction between sodium and the Brønsted acid sites is limited, and thus the  
10 neutralization of the same does not occur during the reaction test.

11 On the other hand, the deactivating effect of retinol seems to be caused by a similar  
12 process to that found for lecithin, the retention over the catalyst surface. Bearing in  
13 mind the lipophilic nature of retinol and its low affinity for silica [16], the deactivation  
14 of Zr-SBA-15 materials by retinol could be caused by the interaction of retinol with the  
15 zirconium acid sites. However, this fact has not previously been described, and  
16 nevertheless the interaction and deactivation capability of retinoids seems to be weaker  
17 than that observed for the phosphatidylcholine.

18 In order to fully understand the deactivating effect of the different substances used as  
19 potential poisons for Zr-SBA-15 in the methanolysis transformation of oleaginous  
20 feedstock into methyl esters, several analytical techniques were applied for the  
21 characterization of the physicochemical properties of the used samples of the  
22 mesostructured materials.

23 Results obtained from the thermogravimetric analysis performed on used samples of Zr-  
24 SBA-15 suggest a negligible influence of retained matter, since the weight loss during  
25 the thermal analysis was quite similar for every sample (ranging from 14-17% wt). This

1 similar result, regardless the potential poison in whose presence the catalytic material  
2 was used, suggests that the amount of glycerides/FAME retained by the catalyst is much  
3 higher than the held amount of lecithin or retinol, shadowing their presence in  
4 thermogravimetric curves. In this way, although lecithin and retinol deactivation  
5 capabilities have been ascribed to the selective adsorption of these substances onto the  
6 catalytic acid sites, their presence cannot be ascertained from TG analysis.

7 In order to get better insights in the effect of the different substances acting as poisons  
8 in the surroundings of zirconium acid sites, XPS spectra were recorded for the used Zr-  
9 SBA-15 samples (Figure 3). Zr-3d XPS spectra evidenced the presence of two groups of  
10 signals corresponding to two different types of zirconium species in all the samples. In  
11 the case of a fresh sample of Zr-SBA-15 these two chemical environments lead to two  
12 Zr3d core level signals: one located at 184.0 eV (and its spin-orbit component at 186.5  
13 eV) and the second one located at 182.9 eV (and its spin-orbit component at 185.3). The  
14 former is usually ascribed to the presence of isolated  $Zr^{4+}$  species in silica framework  
15 [17][18], whereas the last indicates the presence of zirconium dioxide nanodomains  
16 [19]. These spectra remain almost unchanged when using the Zr-SBA-15 catalyst in  
17 presence of large amounts of sodium and cholesterol (not shown), confirming the  
18 absence of interaction between these substances and the zirconium sites. On the  
19 contrary, spectra corresponding to samples used in presence of potassium, retinol and  
20 lecithin evidenced some changes with regards to the Zr3d XPS spectrum achieved for  
21 the fresh catalyst. In the case of potassium and retinol, XPS is slightly shifted towards  
22 lower binding energies but, in essential, the recorded spectrum remains almost the same  
23 than in the fresh catalyst. A different behavior is found when the catalyst is used in  
24 presence of lecithin, which leads to a great change in the chemical environment of  
25 zirconium atoms. This is the chemical exerts the highest influence, among the tested

1 substances, on the modification of the XPS Zr3d core level spectrum of Zr-SBA-15. In  
2 this case, both signals, those attributed to isolated zirconium and zirconia are, by far,  
3 more shifted towards lower binding energy values than in the rest of the cases under  
4 study. This modification is accompanied by the transformation of the two signals  
5 detected for Zr-SBA-15 into a single one, suggesting that the interaction of the lecithin  
6 with the catalyst occurs through the zirconium atoms. This strong modification of the  
7 XPS spectra could be related to the interaction of hydroxyl functionalities at zirconium  
8 sites, leading to an ionic complexation of phosphate/phosphonate groups with the  
9 zirconium atoms, in a similar way to those described by Blanchard and co-workers on  
10 the immobilization of phospholipids onto zirconated surfaces [20]-[22]. This interaction  
11 has been described to be energetically favourable and chemically stable, and it supports  
12 the previous mentioned conclusions about the preferential interaction of phosphate ion  
13 with the zirconium sites to be the major cause of catalyst deactivation in presence of  
14 lecithin. With regards to the influence of the different substances in O 1S XPS spectra,  
15 again two different environments were detected, one attributed to oxygen atoms in silica  
16 (~532.5 eV) and the other one to oxygen atoms bonded to zirconium sites (~530.5 eV).  
17 In this case, unlike retinol and lecithin, potassium does not exert any influence on the O  
18 1s XPS spectra. On the other hand, organic impurities lead to a displacement of both  
19 signals to lower energy bindings, indicating that the interaction of these substances with  
20 the catalyst surface occurs, not only with zirconium sites, but also with the silica matrix,  
21 at least with the oxygen atoms of the catalyst support. In this way, the deactivation  
22 phenomena detected when performing the methanolysis tests in presence of retinol and  
23 lecithin can be ascribed to the adsorption of these substances onto the catalyst support –  
24 in the case of retinol- as well as on the catalytic acid sites –clearly evident in the case of  
25 lecithin-.

1 The individual study of the different impurities accompanying low grade oleaginous  
2 feedstock indicated that some of them –potassium chloride, retinol and lecithin- caused  
3 catalyst deactivation by different reasons. Neutralization of Brønsted acid sites by ion-  
4 exchange was ascribed to be the main influence of potassium chloride. On the contrary,  
5 adsorption onto the surface of the catalyst, as well as onto the catalytic sites, was the  
6 major cause in the case of unsaponifiable organic compounds. However, the extension  
7 of the catalyst deactivation was not large in the case of methanolysis tests performed in  
8 presence of real low-grade feedstock. Moreover, calcination revealed to be a suitable  
9 method to fully recover the starting catalytic activity of Zr-SBA-15 material, suggesting  
10 that most of the catalyst deactivation was reversible. Under these assumptions, a deeper  
11 insight on the catalytic stability of Zr-SBA-15 material in biodiesel synthesis was  
12 accomplished, this time by performing the methanolysis tests in a continuous packed  
13 bed reactor.

### 14 **3.2. Catalytic tests in presence of low grade feedstock: assays in a packed bed** 15 **reactor**

16 Table 2 depicts the physico-chemical properties of both the powder and the  
17 agglomerated Zr-SBA-15 material to be used in the fixed bed reactor. Whereas the  
18 powder sample displays values for the textural and structural parameters typical from  
19 SBA-15 mesostructured materials, the agglomerated sample displays slightly reduced  
20 textural properties, acid loading and metal content, most likely due to the dilution of the  
21 Zr-SBA-15 material with the clay used as binding agent [7]. However, previous  
22 experiments have demonstrated that the observed reductions in the physico-chemical  
23 properties are not high enough to jeopardize the catalytic activity of the Zr-SBA-15  
24 material in a packed bed reactor.



1 The catalytic activity and stability of Zr-SBA-15 material was assessed in the  
2 transformation of category-1 animal fat and waste cooking oil mixtures, ranging from  
3 10 to 30 wt% animal fat in the overall mixture. Since category-1 animal fat is a solid  
4 under ambient conditions, this was mixed with WCO, after melting at 65°C, prior to its  
5 injection in the fixed bed reactor. Results from the catalytic transformation of these  
6 mixtures are depicted in Figure 4. Bentonite agglomerated Zr-SBA-15 material displays  
7 an excellent catalytic behavior in terms of activity and stability in the production of  
8 biodiesel from AF-1:WCO mixtures during, at least, 45 hours on stream experiments.  
9 This catalytic activity and stability is even more outstanding considering that the  
10 different experiments were accomplished in presence of the same catalyst sample. After  
11 almost 150 hours on stream, the Zr-SBA-15 material provided a product stream with  
12 96% FAME yield on average, without evidence of catalyst poisoning, even although the  
13 amount of sodium, potassium, phosphorus and unsaponifiable matter, was progressively  
14 incremented in the feed stream insofar as the amount of AF-1 was increased in the  
15 mixture. This outstanding stability of the agglomerated material in continuous operation  
16 mode in the fixed bed reactor could be ascribed to the bentonite used as binding agent.  
17 Clays have been described to be excellent adsorbents for the purification of vegetable  
18 oils [23], being able to retain inorganic metal ions –such as iron and copper-,  
19 phosphorus as well as some unsaponifiable isoprenoids and chlorophyll [24]-[26].  
20 Bearing in mind this adsorption activity of clays, bentonite could act as a poison  
21 scavenger, preventing the deactivation of the Zr-SBA-15 materials by capturing the  
22 different substances before these reach the catalytic sites. A prove of this behavior can  
23 be the low phosphorus content found in the product stream, which is substantially lower  
24 than that coming from mixing AF-1 and WCO.

1 The properties of the product stream (after a simple washing stage with ultra-pure  
2 water) were assessed according to the European Standard UNE-EN 14214 and listed in  
3 Table 3. FAME content in final product was close to that specified in UNE-EN 14214  
4 (96.5%wt), an outstanding result in view of the properties of the used low-grade raw  
5 materials. In the case of the density and viscosity, values are within the range set by the  
6 standard, regardless of the composition of the starting raw material. Note that both  
7 parameters decrease with increasing the amount of AF-1 in the initial mixture, due to its  
8 lower density and viscosity as compared to WCO, so that there is a clear direct  
9 influence of the starting feedstock on the final properties of the biodiesel product. Flash  
10 points were above 160°C, discarding the presence of residual alcohol, also confirmed by  
11 the direct measurement of methanol content (<0.2% wt). Phosphorus and other metals  
12 (Na, K, Ca, Mg) contents, were lower, in every sample, than those set by the UNE-EN  
13 14214. In conclusion, the obtained biodiesel products meet most of the requirements  
14 established by the European standard. Values exceeding the limit could be solved with a  
15 small addition of additives, or mixing low-grade raw materials with oils and fats with  
16 complementary properties, or blending different biodiesel batches so that the final blend  
17 fulfills specifications.

18

#### 1 **4. Conclusions**

2 Zirconium-containing SBA-15 materials have revealed to be excellent catalysts for the  
3 transformation of low-grade oleaginous feedstock into biodiesel through the  
4 methanolysis of triglycerides and free-fatty acids present in the raw materials. However,  
5 these materials seem to be sensitive to the presence of certain kinds of impurities,  
6 present in waste lipids, which can act as catalyst poisons. Alkaline metals, such as  
7 potassium, could interact with Brønsted acid sites causing a partial, but limited,  
8 deactivation of these heterogeneous acid catalysts. In a similar way, organic  
9 unsaponifiable compounds, such as retinoids or phospholipids –like retinol and lecithin,  
10 respectively-, strongly interact with the silica surface -the catalyst matrix- in the case of  
11 retinoids, or with the zirconium sites, like lecithin does. These interactions cause the  
12 partial blockage of the zirconium acid sites preventing the reactants to access them and  
13 avoiding the progress of the chemical transformation, being one of the most probable  
14 cause of catalyst deactivation when these substances are present. On the contrary,  
15 methanolysis catalytic tests performed in a fixed bed reactor suggested a stronger  
16 resistance of Zr-SBA-15/bentonite pellets against catalyst deactivation. These pellets are  
17 able to provide a sustained FAME yield over 96% during more than 150 hours on  
18 stream, even starting from such a low grade raw material as WCO/AF-1 mixtures  
19 containing up to 30%wt animal fat. The reason for the higher resistance against  
20 deactivation could be ascribed to the clay used as binding agent –bentonite- which  
21 could act also as poison scavenger during the reaction, avoiding the access of poisons to  
22 the catalytic acid sites.

23

1 **5. Acknowledgements**

2 The financial support from the Spanish Ministry of Science and Innovation through the  
3 project CTQ2008-01396 and from the Regional Government of Madrid through the  
4 project S2009-ENE1743 are gratefully acknowledged. RSV also thanks the Spanish  
5 Government for a FPI grant.

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1 **Figure captions**

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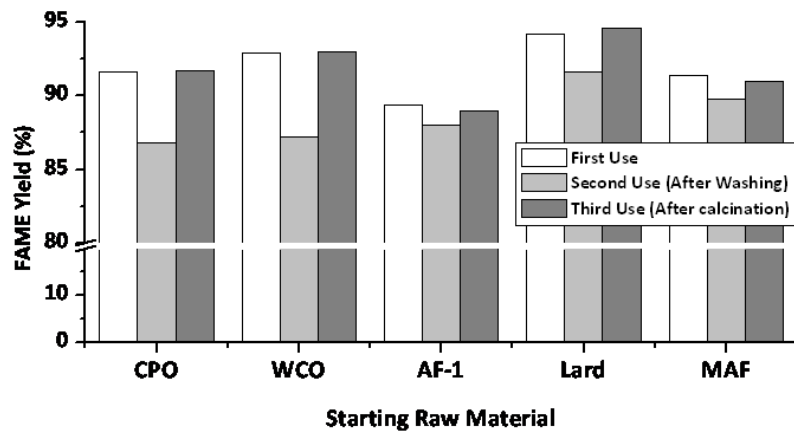
3 **Figure 1.** FAME yield obtained in the batch-mode methanolysis of various low-grade  
4 feedstocks in presence of fresh and used Zr-SBA-15 samples under optimized reaction  
5 conditions. Reaction conditions: Time = 6 h; 45.80 methanol:oil molar ratio; 12.45 wt%  
6 catalyst loading; stirring rate 2000 rpm.

7 **Figure 2.** Results from batch-mode methanolysis reaction tests, performed in presence  
8 Zr-SBA-15 material, carried out over CPO doped with some impurities (NaCl, KCl,  
9 Lecithin, cholesterol and retinol). Time = 3 h; 45.80 methanol:oil molar ratio; 12.45  
10 wt% catalyst loading; stirring rate 2000 rpm.

11 **Figure 3.** Zr-3d and O-1S XPS spectra recorded for Zr-SBA-15 catalysts used in  
12 methanolysis tests performed in presence of some impurities in the reaction mixture.

13 **Figure 4.** FAME yield obtained in the transesterification of AF-1/WCO mixtures  
14 (ranging from 10 to 30 wt% in AF-1) with methanol performed over agglomerated Zr-  
15 SBA-15 material in a packed bed reactor operating under steady-state conditions.  
16 Reaction conditions: 209°C, 50 methanol:oil molar ratio, and 30 minutes residence time.

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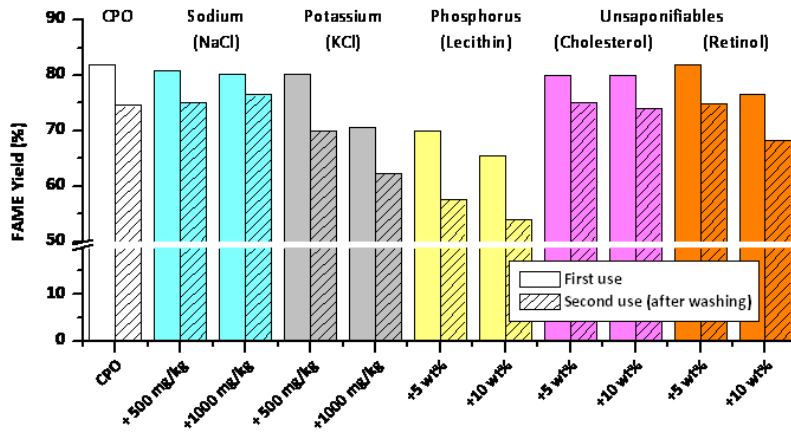


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Figure 1

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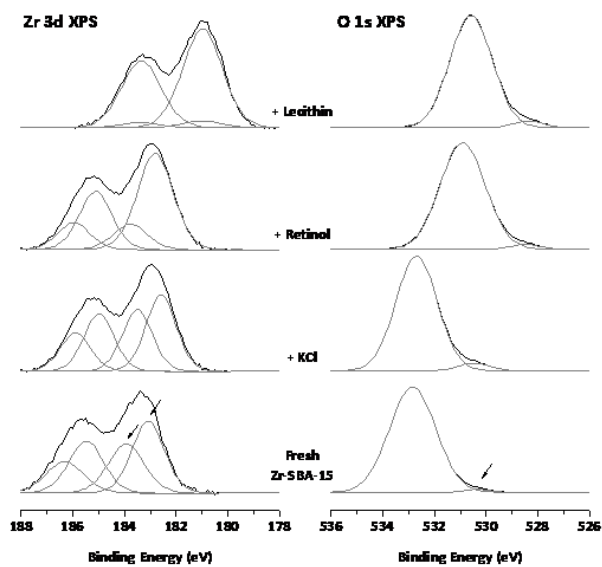




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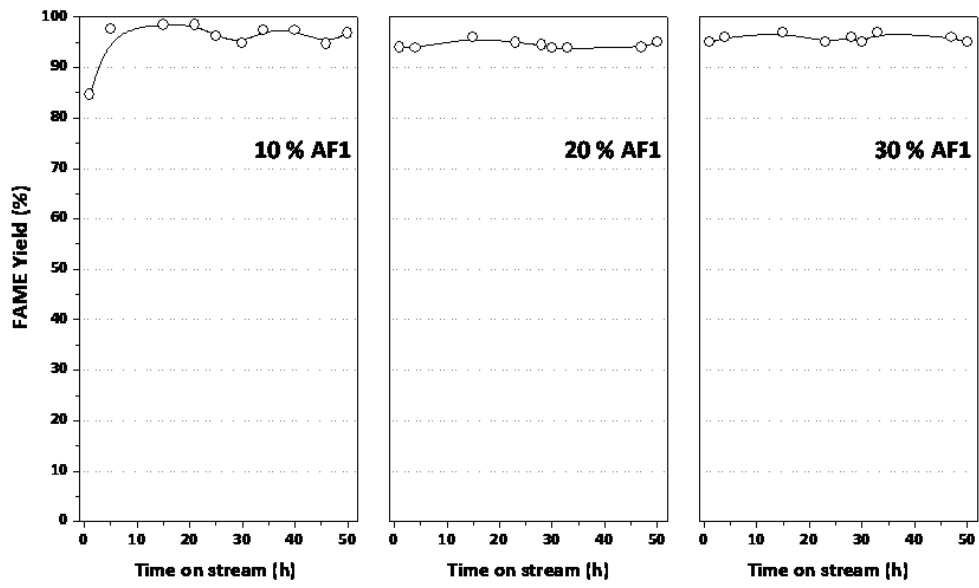
Figure 2

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Figure 3  
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Figure 4

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1 **Table 1.** Properties of crude palm oil used as feedstock for methyl ester production.

Property	Analytical Method	Unit	Value				
			CPO	AF-1	WCO	Lard	MAF
Acid value	UNE EN ISO 660:2000	$\text{mg}_{\text{KOH}} \cdot \text{g}^{-1}$	21.45	33.45	4.06	0.47	3.57
Density at 40°C	UNE EN ISO 3675:1999	$\text{kg} \cdot \text{m}^{-3}$	908	829	918	894	920
Viscosity at 40°C	UNE EN ISO 3104:1996	$\text{mm}^2 \cdot \text{s}^{-1}$	42.9	47.4	66.5	48.7	52
Metals content	ASTM D5185:2013	$\text{mg} \cdot \text{kg}^{-1}$					
	P		13.1	85.9	3.1	72.6	302.8
	Na		15.7	154.4	2.8	n.d.	83.8
	K		n.d.	144.2	n.d.	0.4	10.8
	Mg		4.9	0.1	n.d.	0.4	10.8
	Ca		5.3	2.6	0.5	4.5	123.3
Fatty acid profile	UNE EN ISO 5508:1996 and 5509:2000	Wt %					
	Myristic acid (14:0)		0.8	3.1	0.2	1.4	2.1
	Palmitic acid (16:0)		43.3	28.1	9.3	26.6	26.6
	Palmitoleic acid (16:1)		0.0	0.0	0.5	3.0	3.4
	Stearic acid (18:0)		5.2	20.0	3.9	14.2	16.7
	Oleic acid (18:1)		39.7	41.6	54.5	47.0	42.1
	Linoleic acid (18:2)		10.5	6.0	29.7	6.2	7.6
	Linolenic acid (18:3)		0.4	0.5	0.3	0.4	0.6
Water content	UNE EN ISO 12937:2001	$\text{mg} \cdot \text{kg}^{-1}$	687	1170	1398	288	956
Unsaponifiable matter	Plank and Lorbeer, 1994	Wt %	2.5	22.6	1.0	2.9	9.8

2 n.d.: not detected (below detection limit). CPO: Crude palm oil; AF-1: Category-1 animal fat; WCO: Waste cooking oil; Lard: Pork fat; MAF: Mixed animal fats (chicken, pork, and beef).

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1 **Table 2.** Physico-chemical properties of Zr-SBA-15-based catalysts, before and after the agglomeration treatment.

Zr-SBA-15	Zr <sup>a</sup> (% wt)	H <sup>+</sup> <sup>b</sup> (meq·g <sup>-1</sup> )	S <sub>BET</sub> <sup>c</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>p</sub> <sup>d</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	D <sub>p</sub> <sup>e</sup> (Å)	a <sub>0</sub> <sup>f</sup> (Å)
Powder	9.7	0.27	531	1.41	128	136
Agglomerated	7.1	0.18	335	0.80	124	134

<sup>a</sup> Metal loading calculated by means of ICP-OES; <sup>b</sup> Acid loading calculated by NH<sub>3</sub> temperature programmed desorption analysis; <sup>c</sup> Specific Surface area calculated by the B.E.T. method; <sup>d</sup> Total pore volume recorded at p/p<sub>0</sub>=0.985; <sup>e</sup> Mean pore size calculated as the maximum of the B.J.H. pore sizes distribution applying the K.J.S. correction; <sup>f</sup> Unit cell size calculated as  $2/(\sqrt{3} \cdot d_{100})$ , where d<sub>100</sub> is the Bragg's lattice parameter obtained as  $(d_{100} + \sqrt{3} \cdot d_{110} + \sqrt{4} \cdot d_{200})/3$ .

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1 **Table 3.** Quality parameters of biodiesel samples analysed by ISO 14214 standard.

<b>Parameter</b>	<b>0% AF-1</b>	<b>10% AF-1</b>	<b>30% AF-1</b>
Methylesters, (% wt)	97.1	95.2	96.2
Density (15°C), (kg·m <sup>-3</sup> )	894	891	886
Viscosity (40°C), (mm <sup>2</sup> ·s <sup>-1</sup> )	5.9	5.7	5.2
Flash Point, (°C)	160	167	172
Cetane number	54	-	-
Copper stripcorrosion	1a	1a	1a
Acid value, (mg·g <sup>-1</sup> )	2.4	1.8	1.0
Iodine value (g·100 g <sup>-1</sup> )	100.8	86.0	91.0
Methanol, (% wt)	0.02	0.02	0.01
Monoglycerides (% wt)	0.55	0.84	0.96
Diglycerides (% wt)	2.11	2.39	1.75
Triglycerides (% wt)	0.21	1.58	1.08
Free glycerol (% wt)	0.02	0.01	0.02
Total glycerol (% wt)	0.39	0.49	0.40
Na + K, (mg·kg <sup>-1</sup> )	1.8	1.5	2.1
Ca + Mg, (mg·kg <sup>-1</sup> )	0.4	1.0	1.0
P, (mg·kg <sup>-1</sup> )	1.7	0.2	0.3
CFPP, (°C)	0	+ 7	+ 13

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