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New heterogeneous catalyst for the esterification of fatty acid produced by surface aromatization/sulfonation of oilseed cake

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HIGHLIGHTS

- Simple sulfonation of biodiesel waste cake in mild conditions produces a new and active heterogeneous acid catalyst.
- The catalytic activity is comparable to H_2SO_4 and the catalyst can be reused several times.
- The catalyst combines a carbon-sulfonic acid surface with a very hydrophilic cellulose surface responsible for water removal.

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ABSTRACT

In this work, an efficient heterogeneous acid catalyst for the esterification of oleic acid was prepared directly from oilseed cake by a simple sulfonation with concentrated H_2SO_4. Characterization by SEM/EDS, IR, Raman, TG, TG/MS, potentiometric titration showed that treatment with H_2SO_4 for 1, 2 and 4 h at 120 °C partially dehydrates the cake to form a carbon/cellulose composite which is sulfonated to produce strong $—SO_3H$ acidic sites. These surface sites were active for the esterification of oleic acid with yields ca. 84%, 88% and 94% in the presence of 5, 10 and 20 wt% catalyst, respectively. These results are comparable to 98% yield obtained with 1 wt% H2SO4 and higher than 75% observed for a high surface area (880 $m^2\,g^{-1}$) sulfonated activated carbon with similar number of —SO3H active groups. These results are discussed in terms of two effects: (i) the number of sulfonic surface acidic groups and (ii) the presence of a hydrophilic cellulosic fraction in the catalyst that adsorbs/traps water formed in the reaction shifting the esterification equilibrium and improving the yield.

1. Introduction

The transesterification reaction to produce biodiesel in the presence of basic homogeneous catalysts, e.g. KOH, NaOH or methoxides, has been extensively investigated in the last decade [1–4]. It is well established that this alkaline catalyzed transesterification is strongly affected by the presence of free fatty acids [4,5]. The presence of these acids in concentrations higher than ca. 2% can hinder the reaction and form surface active molecules with significant complications in the purification step due to the formation of stable emulsions [6].

An alternative route to deal with acidic oils is typically a previous esterification in the presence of H_2SO_4 as catalyst [7]. However, sulfuric acid is corrosive and cannot be recovered [8,9]. In this respect, the development of an active acid heterogeneous catalyst to produce biodiesel using acidic oils is of considerable interest. Heterogeneous catalysts can be easily removed and reused avoiding the washing step which simplifies the process [10–13].

Different types of acidic materials, such as zeolites [14–16]; mesoporous silica [17–19], resins [20,21], oxides, e.g. zinc, titanium, strontium oxides [22–24], zirconia [25–28], supported carbon nanotubes [29] and minerals such as a mordenite, kaolins, halloysite [30–32] have been investigated as catalyst for the esterification reaction. Also promising carbon based acid catalysts have been prepared by pyrolysis followed by sulfonation with sulfuric acid, using different precursors such as carbohydrates, lignin [33,34], sugar cane bagasse [35], fibers [36], biochar [37], resin

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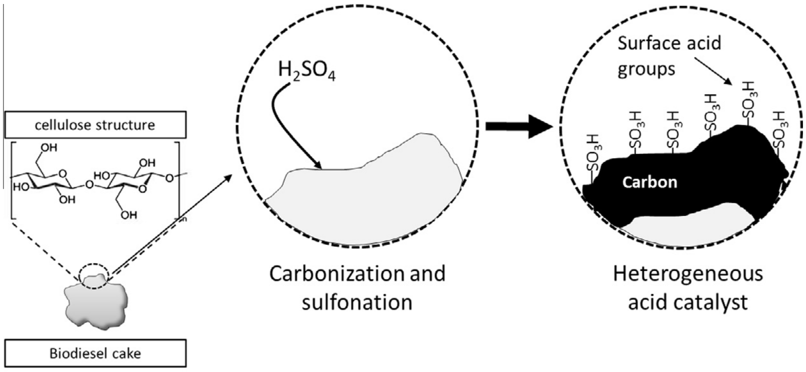

Fig. 1. Representation of the partial aromatization/sulfonation reaction of the biodiesel cake to produce the composite acid catalyst.

[38], bean vermicelli [39], de-oiled canola [40], polymers [41], D-glucose and sulfonated ordered mesoporous carbons [42–46]. These catalysts have shown great potential to replace the traditional homogeneous H_2SO_4 catalysis.

In this work, we present a new and simple reaction procedure to prepare an active heterogeneous catalyst from oilseed cake, a biodiesel byproduct. Biodiesel cakes are solid materials obtained after oil extraction by mechanical pressing, consisting mainly of lignocellulosic fibers. The high concentrations of lignocellulosic material, deficiency of proteins and the presence of some toxic compounds strongly limit the use of some biodiesel cakes in feed blends for ruminant animals [47,48]. The active acid catalyst can be produced by the direct reaction of the cake with sulfuric acid according to the simplified scheme shown in Fig. 1.

The reaction with concentrated sulfuric acid with the lignocellulosic waste seems to promote surface reactions likely based on dehydration with aromatization followed by sulfonation producing the acid catalytic sites. The synthesis, characterization and use of this heterogeneous acid catalyst for the esterification of oleic acid in bench and pilot/ultrasound scale are described below.

2. Material and methods

Different biodiesel cakes obtained after extraction of sunflower, castor, jatropha, curcas and macaw palm oil can be used as solid lignocellulosic precursor. In a typical procedure the biodiesel cake (1 g, ground to particles smaller than 2 mm and dried overnight at 80 °C) was mixed with concentrated H_2SO_4 (min 98%, 8 mL, Synth®), under stirring, at room temperature for 1 h (sample CK1rt) and at 120 ± 5 °C for 1, 2 and 4 h (samples CK1, CK2 and CK4, respectively). Due to the exothermicity of the reaction, the process should be well controlled in order to avoid overheating and dissipate possible hot spots generated on the precursor surface. Caution should be taken to control after the reaction the black solid was extensively washed with water (until reaching pH ~ 7) and dried at 80 °C for 12 h. Raman spectroscopy measurements were made using a Senterra Raman spectrometer from Bruker using a CCD detector, equipped with an optical microscope (OLYMPUS BX51) and a laser at 633 nm. Thermal analyses (TG/DTG) were performed in a Shimadzu 60H under nitrogen flow (100 mL min^{-1}) and heating rate of 10 °C min-1 up to 900 °C. Scanning Electron Microscopy (SEM/EDS) results were obtained in a Quanta 200 – FEG – FEI 2006. FTIR spectra were obtained with KBr pellets in a Perkin Elmer FTIR GX instrument. Potentiometric titration was carried out in an automatic titrator Metrhomn 670 with a mixture of 25 mg of the sample dispersed in 0.01 mol/L of HCl and 0.1 mol/L of NaCl and titrated with 0.010 mol/L of NaOH solution. The thermogravimetric-mass spectrometry (TG–MS) analysis were performed in a NETZSCH TGA model STA 449 F3, coupled to a mass spectrometer NETZSCH Aëolos model QMS 403C. About 20 mg of the sample was used an argon flow in the purge and protective lines, both at 20 mL/min, and with heating rate of 10 °C min^{-1} up to 900 °C. Gaseous species released from the sample during the heating were drawn into an alumina tube fixed inside the furnace of the thermobalance close to the sample, connected to a capillary silica column heated at 300 °C. The gases were then directly sucked into the ionization chamber of the mass spectrometer.

The catalytic activity of the materials was tested in the esterification of pure oleic acid in a round bottom flask fitted with a reflux condenser at 60 °C for 2 h, with a ratio of 12:1 methyl alcohol:oleic acid and different catalyst concentrations (5, 10 or 20 wt%, with respect of oleic acid concentration). After the reaction the catalyst (ca. 1 g) was washed with ethanol (30 mL at room temperature) and dried at 80 °C for 4 h and tested in the reuse experiments. The conversion of methyl esters was analyzed by the Ca 5a-40/AOCS method and confirmed by 1H NMR. (RMN Bruker Advance DPX 200). The signals used as references were of the methoxy groups in the methyl ester (3.7 ppm) and of the α-carbonyl methylene groups present in the oil and biodiesel (2.1 ppm) [49]. A calibration curve from the 1H NMR spectra of oil/biodiesel mixtures using the 3.7 ppm and 2.3 ppm area ratio was obtained.

The catalytic activity of the materials was also investigated at a pilot plant scale using an ultrasound promoted reactor (see Supplementary Material – Fig. 1S) [50].

Commercially available activated carbon (from coconut shell, 880 $m^2\ g^{-1}$, Sulfal) was used as a catalyst in a control reaction study. The activated carbon was sulfonated using the same conditions used for preparation of CK2 (sulfonation with concentrated H_2SO_4 for 2 h at 120 °C under stirring and washed with water (pH ~ 7) and dried at 80 °C for 12 h). The water absorption capacity of the CK2 material was determined by the "tea bag" method by weighing the water retained by the material [51].

3. Results and discussion

Biodiesel cakes from different sources, e.g. sunflower, castor, jatropha curcas and macaw palm are composed mainly of lignocellulosic fibers. In contact with sulfuric acid the lignocellulosic material becomes completely black suggesting a strong dehydration process to form polyaromatic/carbon on the surface. The reaction with H_2SO_4 was carried out at room temperature for 1 h (sample CK1rt) and at 120 °C for 1, 2 and 4 h (samples CK1, CK2 and CK4 respectively).

Raman analyses (Fig.2) for all the obtained solids after reaction with sulfuric acid at 120 °C, showed two typical bands for carbonaceous materials: the D and the G band. The G band (at 1590 cm^{-1}) is typical for well-formed and organized graphitic structures whereas the D band (near 1350 cm^{-1}) indicates the presence of

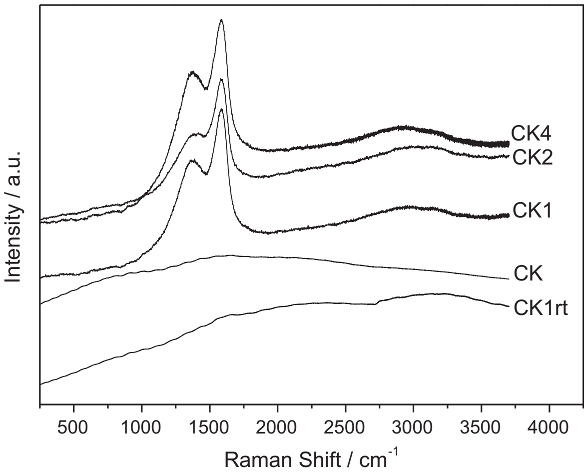

Fig. 2. Raman spectra of CK samples after reaction with concentrated H_2SO_4.

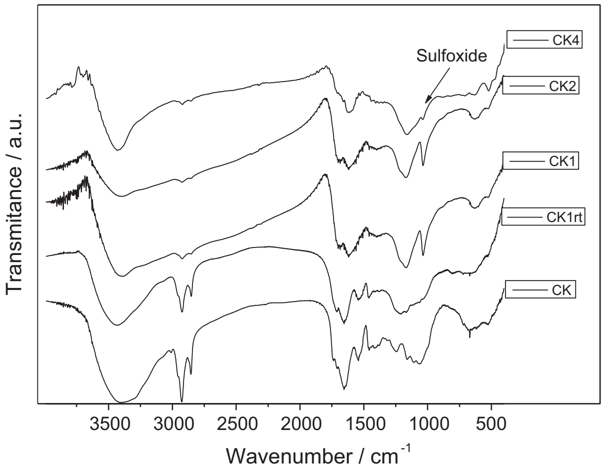

Fig. 4. FTIR spectra of the materials CK, CK1rt, CK1, CK2, CK4.

defects or amorphous carbon [52] confirming the carbonization process of the cake material. These bands are not observed in the material obtained at room temperature, CK1rt, indicating no significant reaction with H_2SO_4. Moreover, due to exothermicity of the reaction at 120 °C local temperatures might significantly raise to generate hot spots which can contribute to the pyrolysis process.

TG and DTG analyses (in N_2) of the dry cake before reaction (Fig. 3) showed a weight loss between 200 and 500 °C of *ca.* 80% associated to the decomposition of lignocellulose to produce mainly CO_2, H_2O and other small volatile molecules [53]. Similar TG profile was obtained for the sample CK1rt. On the other hand, the materials after reaction at 120 °C showed weight losses of only ca. 35–50%. These smaller weight losses are likely related to the decomposition of the remaining lignocellulose present in the materials.

FTIR spectra (Fig. 4) of the cake showed typical absorptions observed in lignocellulosic materials. The intense band at 3340 cm^{-1} is assigned to the O—H stretching vibration, bands at 2893 and 1431 cm^{-1} characteristic of C—H stretching and bands at 1190 and 1000 cm^{-1} are related to the saccharide structure [54]. After acid dehydration a significant change in the IR spectrum was observed with strong changes in the absorptions at 1190 and 1000 cm^{-1} and a narrowing of the band at 3340 cm^{-1}. On the other hand, new bands appeared, i.e. 1029 and 1160 cm^{-1}, related to the symmetric stretching vibrations of O=S=O in —SO_3H groups [38,55–57] and another at 620 cm^{-1} related to the bending vibration of –OH groups hydrogen bonded to -SO_3H [57], mainly in CK1 and CK2 samples. In addition, intense absorptions are observed between 1500 and 1800 cm^{-1} likely related to aromatic C=C (~1600 cm^{-1}) and C=O from various functional groups as carboxyl (1729 cm^{-1}) and quinone (1550–1680 cm^{-1}) [58].

Fig. 5 shows the potentiometric titration curves of the CK catalysts with NaOH. The number of acidic sites and p*K*a obtained are displayed in Table 1.

It can be observed that the CK and CK1rt showed total groups concentration of 1.2–1.7 mmol g^{-1}, mainly as weak acidic groups. As the cake was treated with H_2SO_4, more acidic groups were formed, 3.0–3.3 mmol g^{-1}. It can be observed that very acidic groups are formed with p*K*a lower than 2. These groups are likely related to —SO_3H.

It is interesting to observe that longer reaction times, i.e. 4 h, led to a decrease of the number of acidic groups. This is probably related to the hydrolysis/decomposition of the surface groups [51].

SEM analyses (Fig. 6) suggests that the surface texture of the cake does not change significantly after H_2SO_4 reaction. In fact, the BET surface area (ca. 0 m^2 g^{-1}) and porosity of the precursor CK also did not change after H_2SO_4 treatment. EDS data clearly showed the presence of sulfur after reactions with H_2SO_4 due to the sulfonation reaction.

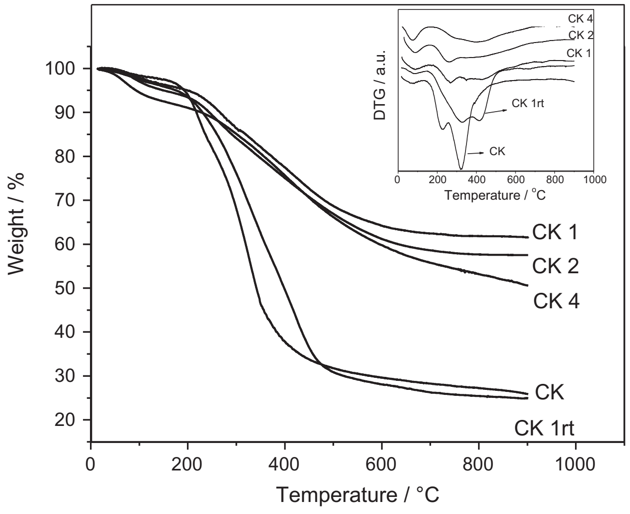

Fig. 3. TG and DTG analyses of the materials CK, CK1rt, CK1, CK2, CK4, under nitrogen atmosphere.

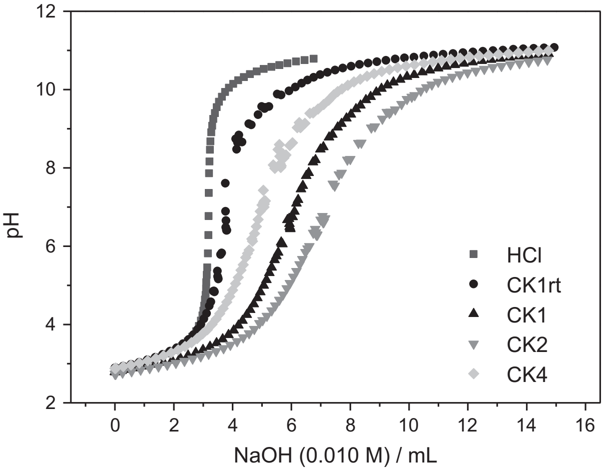

Fig. 5. Potentiometric titration of the materials CK, CK1rt, CK1, CK2, CK4.

Table 1
Results of potentiometric titrations for biodiesel cake, before and after reaction with H_2SO_4.

Sample	Acidic functional groups ($mmol\ g^{-1}$)				Total of acids ($mmol\ g^{-1}$)
	($pKa < 2.5$)	$4 < pKa < 6$	$6 < pKa < 8$	$8 < pKa < 10$	
CK	–	0.45	0.53	0.22	1.2
CK1rt	–	0.47	0.04	1.20	1.7
CK1	0.43	0.83	0.34	1.36	3.0
CK2	0.68	0.91	0.74	0.93	3.3
CK4	–	1.00	0.51	1.10	2.6

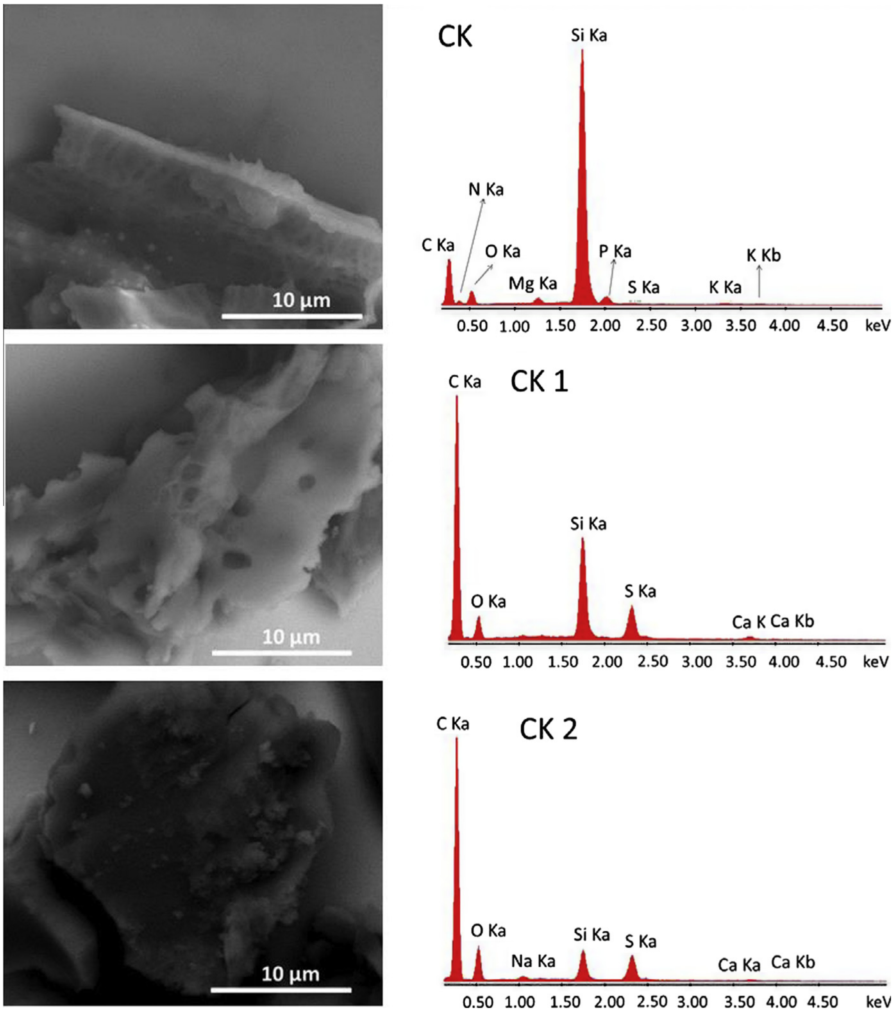

Fig. 6. SEM/EDS images of the materials CK, CK1and CK2.

The CK and CK2 samples were also characterized by TG/MS. Fig. 7 shows the TG/MS profiles for some specific molecules. It is possible to observe that the CK sample loses m/z 18 near 100 °C related to adsorbed water. It can also be observed a water loss 150–350 °C related to cellulose decomposition. After sulfonation for 2 h (CK2) the TG/MS profiles suggests the presence of some adsorbed water but the cellulose decomposition signal is much less intense, suggesting that H_2SO_4 has previously dehydrated the cake. The profile for m/z 44 signal also decreases in intensity after sulfonation which is also likely due to deoxygenation reactions caused by sulfuric acid. It is interesting to observe an intense m/z signal 64 related to SO_2 produced in the sulfonated CK2 material which suggests the presence of —SO_3H groups.

The esterification of oleic acid was investigated using the sample CK2 since it showed the highest concentration of surface acid sites. Different catalyst concentrations were used, i.e. 5, 10 and 20 wt% relative to oleic acid. The esterification yields after 2 h reaction are shown in Fig. 8 (see SM Fig. S3 results for ester yields vs reaction time).

It can be observed yields near 84, 88 and 94% in the presence of 5, 10 and 20 wt% of catalyst, respectively. It is interesting to observe that the use of the classical homogeneous reaction with 1 wt% H_2SO_4 showed yield near 98%. Sulfuric acid (H_2SO_4) is very acidic with pKa of −3 (first ionization) and 2 (second ionization) [59] and potentially affords 2 H^+ for the reaction. Catalyst concentration of 1wt% H_2SO_4 corresponds to 20 mmol H^+/100 g of oleic acid. For the CK2 heterogeneous catalyst it can be considered as catalytically active sites sulfonic acid surface groups which should have pKa near between −2 and −3 (see for example benzene sulfonic acid with pKa of −2.8) [59]. According to titration results

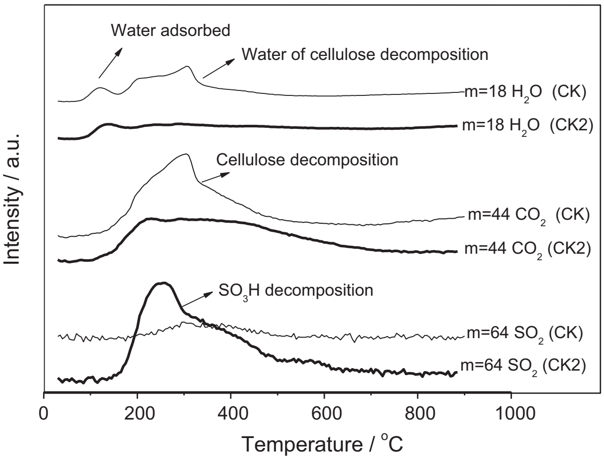

Fig. 7. TG/MS profiles of the samples CK and CK2.

the surface groups with p*K*a < 2.5 corresponds to ca. 0.68 mmol g^{-1} for the catalyst CK2 (see Table 1). Therefore, 5, 10 and 20 wt% of catalyst in the reaction corresponds to 3.4, 6.8 and 13.6 mmol H^+/ 100 g oleic acid. It is interesting to observe that the CK2 shows similar catalytic activity with even lower concentration of catalytic species. It is also interesting to compare the CK2 catalyst (near no surface area ca. 0 $m^2\ g^{-1}$) with a high surface area activated carbon (890 $m^2\ g^{-1}$) sulfonated under the same conditions (2 h at 120 °C with H_2SO_4 concentrated). This catalyst showed total acid concentration of 3.15 mmol g^{-1} however with lower esterification yield, 75%, compared with the CK2. Turnover number calculation after 2 h reaction showed for the catalyst CK2 (20%) 4.6 $mol_{ester}\ mol_{site}$ whereas the activated carbon AC-SO_3 showed TON of 3.9 $mol_{ester}\ mol_{site}$. This result suggests that some catalytic acid sites of the activated carbon are not active for the reaction likely due to the location inside the not accessible small micro pores.

Catalyst reuse was carried out with the sample CK2 at 10 wt% under mechanical stirring without any treatment between the reactions (Fig. 9).

After the first use the yield decrease from 88% to *ca*. 66%. In the subsequent cycles there was a decrease of the 10% in ester yield every cycle. The catalyst used in the 4th reaction was regenerated by ethanol washing characterized by thermal analysis in nitrogen atmosphere (see SM Fig. S4). It is possible to observe a weight loss of 4% at temperatures below 150 °C, relating to the loss of water/alcohol adsorbed. In addition, the material still lost 35% weight at temperatures between 150 and 300 °C. This loss can be attributed to the contamination of the catalyst by oleic acid or biodiesel.

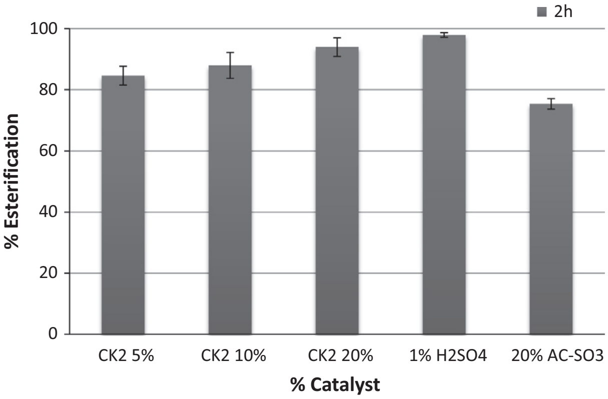

Fig. 8. Esterification yield of oleic acid using the catalyst CK2, H_2SO_4, and sulfonated commercial activated carbon (AC-SO3) by mechanical stirring after 2 h reaction.

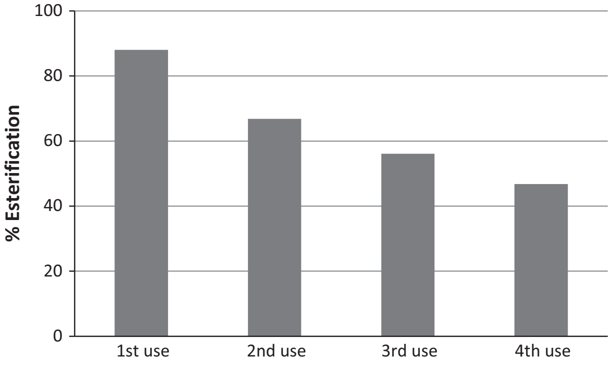

Fig. 9. Esterification yields for different reuses with 10 wt% of CK2 after 2 h reaction with mechanical stirring.

Preliminary scale up experiments in ultrasonic reactor produced by the company Biominas (see reactor in SM, Fig. S1) were carried out for the esterification of oleic acid (Fig. 10).

It can be observed for pilot scale ultrasound stirring similar ester yields obtained by mechanical stirring bench experiments. Reactions in the presence of 5, 10 and 20% showed similar behavior as in mechanical stirring bench experiments (see SM – Fig. S5). The 20% CK2 heterogeneous catalyst showed esterification yield higher than 90% which was comparable to 1% H_2SO_4 used as control.

The reuse of the catalyst CK2 (10%) under ultrasound stirring showed a decrease from 86% to 81%, 56% and 48% for the 1st, 2nd, 3rd and 4th reuse.

Previous works used sulfonated carbons as heterogeneous catalysts for the esterification of fatty acids. The carbons used were produced by pyrolysis of different vegetable precursors such as lignin [33], cane bagasse [35], mung bean [39], canola [40] and sugars [60]. In all these studies, the precursors had to be previously carbonized at high temperature (400–800 °C) under controlled atmosphere and only after pyrolysis underwent sulfonation. The obtained results showed only moderate yields of ca. 80% which could be increased to higher than 90% at high temperatures and prolonged reactions (5–24 h).

The catalysts prepared in this work did not need a preliminary carbonization step and the sulfonation was carried out directly on the lignocellulosic precursor waste under mild reaction conditions. Another feature of the CK catalysts is that the carbonization and sulfonation is only partial and part of the lignocellulosic structure remains in the material as suggested by IR and TG analyses. This lignocellulosic structure has a high concentration of surface OH groups and shows a strong hydrophilic character. This hydrophilic surface can have the effect of water adsorption which can be

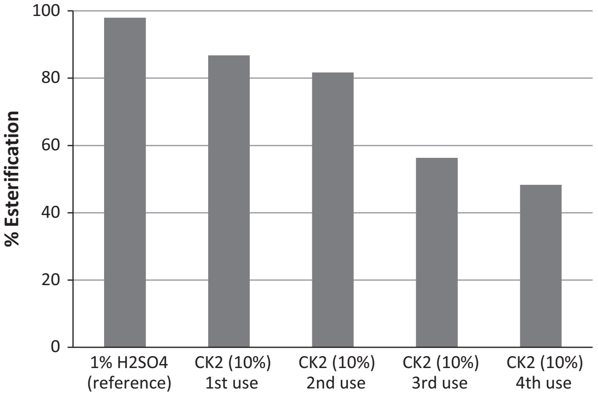

Fig. 10. Esterification yield of oleic acid using the catalyst H_2SO_4 (1%) and CK2 (10%, 2 h, methanol/oleic acid 12:1) in ultrasonic reactor and reuse experiments.

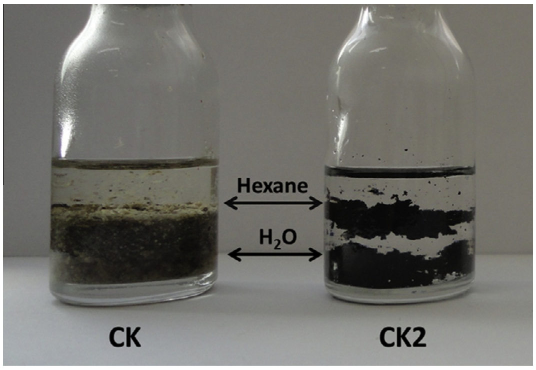

Fig. 11. Behavior of materials CK and CK2 in contact with a biphasic mixture of water and hexane.

beneficial for the esterification reaction since the water molecules are directly involved in the reaction equilibrium.

In fact, water absorption experiments showed that the CK2 material can absorb a high amount of water, i.e. 30 $g_{H2O}/g_{catalyst}$. (see SM – Fig. S6). This water absorption can be a potential advantage over the homogeneous H_2SO_4 catalyst that does not have any effect on the H_2O formed in the reaction. On the other hand, the carbonized surface has a more hydrophobic character which is important for the interaction/interface with the oil or oleic acid. Fig. 11 shows the behavior of materials CK (cake without sulfonation) and CK2 in the presence of water/hexane two phases mixture. It is possible to observe that the cake CK, before sulfonation, presents a hydrophilic character and immediately goes to the aqueous phase. For the CK2 (after the sulfonation) the material initially stays at the interface water/hexane suggesting an amphiphilic character due to the combination of hydrophilic cellulose fraction with the carbonized surface. However, after few minutes the black solid migrates to the aqueous phase due to the wetting of the hydrophilic surface. The reaction medium is an emulsion of the hydrophobic oleic acid and the hydrophilic methanol. An amphiphilic catalyst is very important to contact these reactants and promote the reaction. The hydrophilic surface is important to interact with the polar methanol.

4. Conclusion

Cakes obtained after oil extraction can be converted by a simple process of aromatization/sulfonation with H_2SO_4 into a new type of heterogeneous catalyst for the esterification of free fatty acids. The produced catalyst showed activities comparable to the homogeneous H_2SO_4 catalyst and could be recovered and reused several times. The catalytic activity is discussed in terms of sulfonic groups ($-SO_3H$) combined with an amphiphilic surface composed of carbon (more hydrophobic) which interacts well with the fatty acid and non-decomposed cellulose (more hydrophilic) which is responsible for water adsorption during the esterification reaction. Preliminary tests, showed that this heterogeneous catalyst can also be used in the production of biodiesel from low quality/high free acidity oils with the important advantage of eliminating the washing step.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2015.02.027.

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