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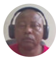

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Synthesis and IR Characterization of Activated Carbon Acid Catalysts from Cassava Peels and their Use in Esterification of Free Fatty Acid in Palm Kernel oil

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Authors' contributions:

This work was carried out in collaboration among all authors. Author LTB designed the study and performed the statistical analysis. Author KMT wrote the protocol and wrote the first draft of the manuscript. Authors MTN, SJK and TJK managed the analyses of the study. Author BPN managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The present study reports the preparation of four solid acids (CS, CPS, CAS and CPAS) from cassava peels and investigates their catalytic activities in the esterification of free fatty acid (FFA) in palm Kernel oil (PKO). The activated carbon obtained from carbonization was directly sulfonated with sulfuric acid (CS) or treated first with phosphoric acid before sulfonation (CPS). Another part of activated carbon was pyrolyzed at 800°C and treated as in the two previous cases (CAS and CPAS). The FTIR spectra of CS, CPS, CAS and CPAS showed characteristic absorption peaks of functional groups such as O=S=O (1031 cm^{-1}), OH (3849 and 3405 cm^{-1}), C=C (1555-1574 cm^{-1}), S=O (1042,1031 cm^{-1}) and P=O (754 cm^{-1}), which confirm the presence of sulfonic, carboxylic and phosphoric groups on the surface of the activated carbon acids prepared. The total acid densities of the catalysts range from 2.26 to 3.49 mmol/g whereas the -SO_3H densities were from 0.92 to 2.20

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mmol/g. Amongthe four catalysts prepared, their effectiveness in the esterification of free fatty acid in palm kernel oil with a conversion rate from 70 to 90%, depended mostly on the sulfonic acid density on the catalyst, CPS showed the highest total and $-SO_3H$ acid densities with 3.49 and 2.2 mmol/g respectively and a highest free acid fatty conversion rate of 90%. Thus, CPS was more efficient than CS, CPAS and CAS. All the catalysts prepared could be reused in the esterification reaction with a mild decrease in the conversion rate.

Keywords: Solid carbon acid; cassava peels; esterification; palm kernel oil.

1. INTRODUCTION

Activated carbons have attracting recently a lot of interest in catalysis and separation chemistry. They have been used as good and efficient adsorbent in removal of organic and inorganic pollutants from gaseous and liquid media [1-7]. Their chemical activation with mineral acids resulted in solid acid catalysts used as replacement of homogenous acids used in chemical reactions such as hydrolysis of cellulosic material, esterification of fatty acids and transesterification of esters [8-18].

Activated carbons are obtained mostly from incomplete carbonization of natural products (sugar, starch, cellulose) [11]. Recently, sulfonated incompletely carbonized of natural organic matter is attracting interest of researchers as solid acids because of their high catalytic performance for various liquid-phase acid-catalyzed reactions such as esterification of free fatty acid [12]. In addition solid acid catalysts could also be reused several times with less loss of their catalytic activity [11].

The texture and chemical characteristics of solid carbon acids depend on the nature of raw material, the activation method, and the activation agent used. Treatment of activated carbon with phosphoric acid was shown to facilitate formation of the porous structure which allows easy impregnation of other functional groups [7,19].

Cassava peels are wastes generated in the processing of cassava roots. They makes up to 10% of total mass of the root. They are usually discarded in nature and constitutes an environment problem despite the fact that, they can be used for manufacturing animal feed, bio fertilizer as well as raw material for biogas production [20].

Several studies have been reported on the use of cassava peels activated carbon as adsorbent in treatment of industrial waste water[3-5], very few however deals with sulfonated cassava peels as acid catalyst in chemical reactions.

We here report the preparation and characterization of four solid acids from cassava peels and we investigate their use as catalysts in the esterification of Free Fatty Acid (FFA) in Palm Kernel Oil (PKO).

2. EXPERIMENTAL DETAILS

2.1 Materials

Cassava peels were collected at Mbanza-Lemba market (Kinshasa). They were first washed to remove sand and then sun dried, crushed to powder in a blender and kept in a dry container. Palm kernel oil (PKO) was purchased also at Mbanza-Lemba market.

2.2 Catalysts Preparation

Cassava peels powder was put in crucible and placed in a muffle furnace (Nabertherm B180). The furnace was brought to 500°C and heated at different times: 15,30,45,60 and 90 minutes [9-15]. The carbon char obtained at each time after cooling, were submitted for FTIR analysis to find the optimal carbonization time. Cassava peels carbon char from best carbonization time was divided in 4 parts to prepare different solid acid catalysts. The first part was used to prepare sulfonated carbon acid (CS) as follows:4 g of carbon char were introduced in a 500 mL Erlenmeyer and 30 mL of concentrated sulfuric acid was added slowly during 30 minutes. The reaction mixture was heated in an oil bath at 160°C during 15 hrs. Upon cooling, distilled water was added slowly and the black powder obtained was filtered and washed several times with distilled water until the filtrate reached neutral pH. The sulfonated carbon (CS) material obtained was dried in an oven at 105°C for 12 hrs. The second part was first treated with phosphoric acid 40% before sulfonation with sulfuric acid. In a typical run, 4 gr of carbon precursor was added to 30 mL of 40% H_3PO_4.

The mixture was stirred during 6 hrs at room temperature, then filtered and washed with distilled water until the filtrate reached neutral pH. The obtained material was dried in an oven at 105°C during 12 hrs and submitted for sulfonation with concentrated sulfuric acid as described above to give phosphated and sulfonated activated carbon acid (CPS). The third and fourth parts of carbon precursor were first heated at 800°C in a muffle furnace for 5 minutes. The obtained material was treated directly with sulfuric acid to give thermally activated carbon acid (CAS) or treated with phosphoric acid prior to sulfonation with sulfuric acid to give thermally phosphated and sulfonated carbon acid (CAPS).

2.3 Characterization of Catalysts

The FTIR spectra of biochar and different carbon acids were recorded in a Brüker Fourier Transform infrared spectrometer by using KBr pellets from 4000 to 500 cm^{-1}. The sulfonic acid densities of different activated carbon, CS, CPS, CAS and CAPS were determined by titration according to the method described by Liu et al. [14]. 50 mg of solid carbon acid were mixed with 15 mL of 2 M NaCl solution. The mixture was sonicated during 30 minutes for facilitating the exchange of Na^+ with proton in sulfonic group. The filtrate from the mixture was titrated with 0.02 molar of NaOH, using phenolphthalein as indicator. Total acid sites were determined by adding 50 mL of 0.05 M NaOH solution to 50 mg of solid acid catalyst. The mixture was shaken for 15 h then filtered. The filtrate was titrated withstandard solution of 0.05MHClusing phenolphthalein as indicator. The amount of NaOH which reacted with the catalyst allowed to calculate acid sites number. All the measurements were done in triplicate and average values are reported in Table 1..

2.4 Catalytic Activities

The esterification reaction of FFA in PKO with ethanol was used to assess catalytic activities of the four solid acids. In a typical reaction: a known amount of PKO and ethanol (1 to 6 ratio) were mixed into a three-neck round bottom flask on sand bath and equipped with reflux condenser, a magnetic stirrer and a thermometer. Once the mixture reached the reaction temperature, the catalyst was added and the mixture was continuously stirred and heated at 70°C during 5h. Each catalyst sample was dried at 100°C for 1h before use. After esterification reaction, the unreacted oil phase was isolated and FFA was measured by titration of the sample with a 0.1 M KOH solution. The conversion rate of FFA was determined from the ratio of the acid value before and after esterification by using the following formula: $FFA conversion(\%) = \left(1 - \frac{AV_f}{AV_i}\right) x100$

Where AV_i is the initial acid value of palmitic acid, and AV_f is the final acid value of palmitic acid after the esterification reaction.

Each catalyst was removed after esterification reactionby vacuum filtration, washed three times thoroughly with water and ethanol before drying in oven at 105°C for 2 h and then reused many times as described previously to assess its stability and reusability.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization of the Solid Acid Catalysts

Fig. 1 shows FTIR spectra of carbon char from cassava peels carbonization at 500°C after heating at different times (from 15 to 90 minutes). One can observe that the intensity of the aliphatic C-H bond stretching vibration decreases from 2925 cm^{-1} to 2516 cm^{-1} for 15 min to 30 min of carbonization respectively. But when carbonization time increased from 45 to 90min, that vibration band disappeared. The same observation was made for aliphatic C=C bond, indicating that these two bonds (C-H and C=C) are cleaved during the pyrolysis. The characteristic vibration peaks of the aromatic C=C bond remained after carbonization, these vibration frequencies decrease slightly as carbonization decreases (1582 cm^{-1}, 1580 cm^{-1}, 1579 cm^{-1}, 1578 cm^{-1}, 1577 cm^{-1} and 1574 cm^{-1}). This could be due to the dissociation of –C-O-C-, leading to polycyclic aromatic carbon rings and amorphous carbon structure Li et al. [21]. According to Lingtao et al. [22], intensity decreasing could indicate the conversion of benzene ring into polycyclic aromatic carbon. Additionally, the vibration peaks (750-798 cm^{-1}) observed was attributed to C-H aromatics out-of-plan bending vibration. The stability of aromatic ring causes these bonds to be stable at all carbonization times. The vibration band at 1377 cm^{-1} corresponding to the bending vibration of CH_3 disappears after 90 min of carbonization, showing that this group is eliminated during a long time of the carbonization process. It is noteworthy seen that even though cassava peels carbonization was done at 500°C and between 15 min to 90 min, vibration bands of O-H (H-bonded) and C-O (alcohol, ethers, esters and carboxylic acids) have not disappeared. This could be due to the high composition of lignin in cassava peel [23]. The present results are closed to those of Derkacheva and Sukhov [24], which showed that the complete lignin spectral band was set in the range from 740 to1840 cm^{-1}.

Fig. 2 shows the FTIR spectra of all cassava peels carbon acids (CS, CPS, CAS and CPAS) two strong bands at 1175 and 1350 cm^{-1} could be assigned respectively to symmetric stretch and asymmetric stretch of S=O of sulfonic acid.. This shows clearly that sulfonic acid group is present on the surface of all catalysts. The vibration band around 1700 cm^{-1}could be attributed to the stretching vibration of C=O bond; it corresponds to the -COOH groups; while, the broad band at 3429 cm^{-1} could be assigned to the stretching vibration of –OH. In CPS FTIR spectrum, the strong band at 2320 cm^{-1} (P-H) and 1300 cm^{-1} (P=O) and a medium band at 752-820 cm^{-1} (P-O) are assigned to the phosphoric acid. The results show the presence of some functional groups such as -COOH, -SO$_3$ H and –OH after sulfonation of carbon char which led to obtain solid acids catalysts. Similar absorption bands were found in carbon acids prepared from other agricultural waste [7,17].

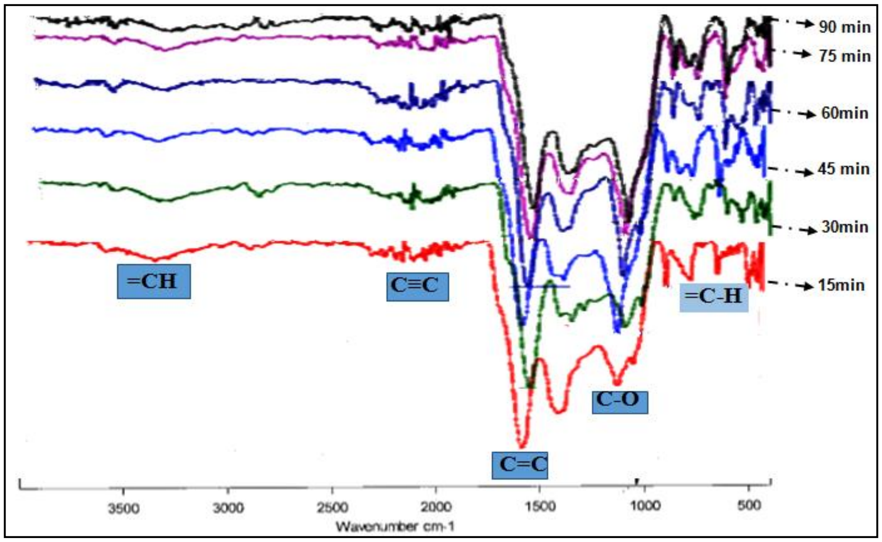

Fig. 1. FTIR spectra carbonization of carbon cassava peels at 500°C after 15, 30, 45, 60, 75 and 90 minutes

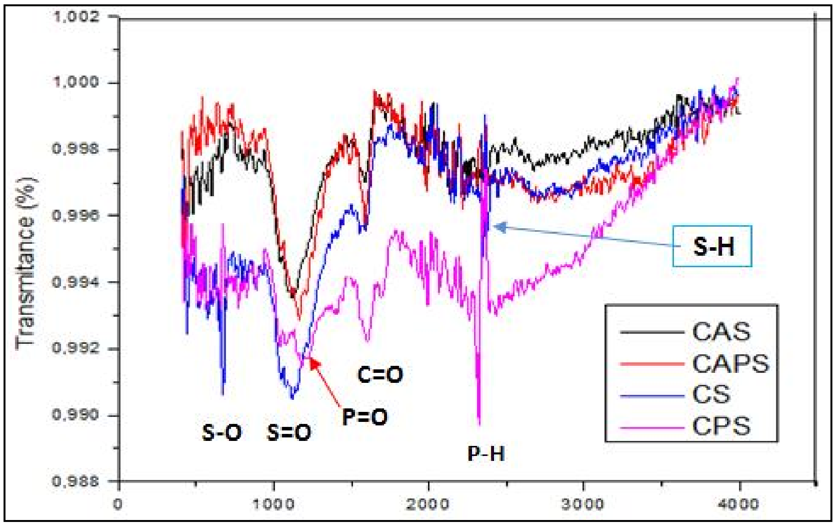

Fig. 2. FTIR spectra sulfonation of solid acid catalysts

3.2 Catalytic Activities of Catalysts

The results in Fig. 3 show that sulfonic acid densities range from 0.92 to 2.20 mmol/g while the total acid densities range from 2.26 to 3.49 mmol/g. It has been shown that total acid and -SO_3H acid densities of different catalysts decreased in the following order CPS>CS>CPAS>CAS. CPS catalyst showed the highest acid density of 3.49 and 2.20 respectively for total and -SO3H acid density. These values are higher than 1.030 reported by Li et al. [18], for acid catalyst prepared from corncobs, but lower than 4.73 for Amberlyst 15 [22]. Whereas, they were similar to those obtained for cassavas tillage carbon acid (2.65) [14], and for the rice straw carbon acid (2.64) [7]. Total acid values were high comparatively to –SO3H acid values for all catalysts, because total acid is the sum of acidity of all acidic groups such as phenolic -OH and –COOH.

Hence, CPS was found more acidic than CS while CPAS was more than CAS because of they high total acid density. The highest acid site density of CPS could be due to the pretreatment of that catalyst. It was seen that phosphoric pretreatment of carbon char promoted the formation of high porous structure (Pua et al. [25] which would then facilitate sulfonation and suggesting the attachment of more –SO_3H groups to carbon char [12]. Phosphoric acid has been shown to be an effective activating agent to develop carbon char porosity which allow more access to –SO_3H group. These observations are closed to those reported by Li et al. [18] in the case of corn cobs carbon acid which were pyrolyzed at 800°C, the obtained carbon material has less acid functional groups (CPAS and CAS). Similar observations were reported by Wangef al. [14] in the preparation of carbon based solid acid from cassava stillage.

The Fig. 3 gives acid densities of the solid acid catalysts.

3.3 Free Fatty Acid Conversion Rate by Solid Catalysts

The results on Table 1 show that CPS catalyst had a high catalytic activity to convert the free fatty acid of palm kernel oil to biodiesel. Free fatty acid conversion rate increased with catalyst concentration and the highest rate (90%) was obtained with 0.9% of catalyst. Beyond 0.9% of catalyst, there is a decreasing of free fatty acid conversion. This could mean that CPS has a high acid density due to its pretreatment. Pua et al. [25] showed that phosphoric acid increases the surface area which could promote the formation of high porous structure. This result suggests why CPS catalyst is highly active and stable. The higher conversion rate of free fatty acid of PKO is possibly due to the high density of the acid (-SO_3H) sites from sulfonation in the pores of activated carbon by treatment with phosphoric acid and pyrolysis. The Table 1 report results of acid catalyze free fatty acid conversion into biodiesel.

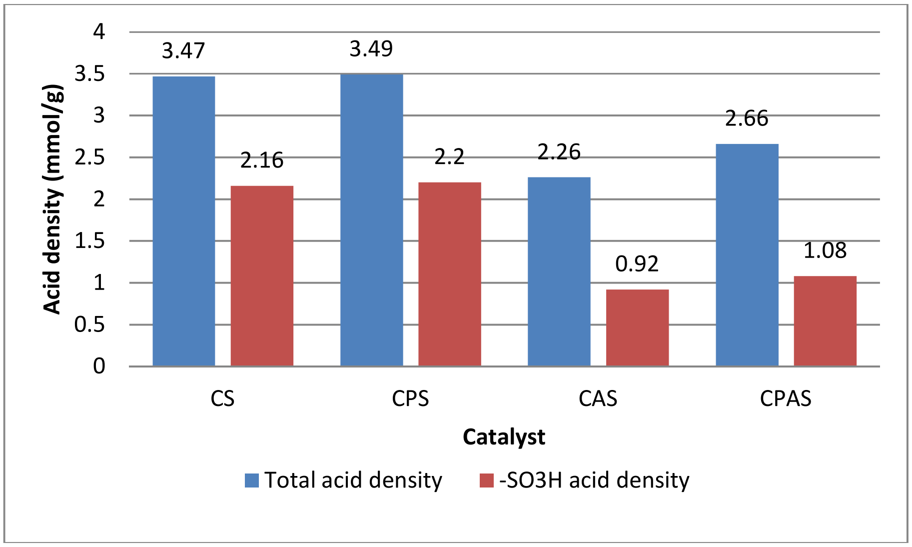

Fig. 3. Acid densities of various prepared catalysts

Table 1. Rate of conversion of free fatty acid to biodiesel

Solid acid concentration (%)	FFA conversion (%)			
	CAS	**CPAS**	**CS**	**CPS**
0.1	70	74	72	76
0.3	76	84	85	86
0.5	84	86	86	87
0.7	86	87	88	89
0.9	88	88	89	90
1.1	82	83	84	86
1.3	76	74	76	78

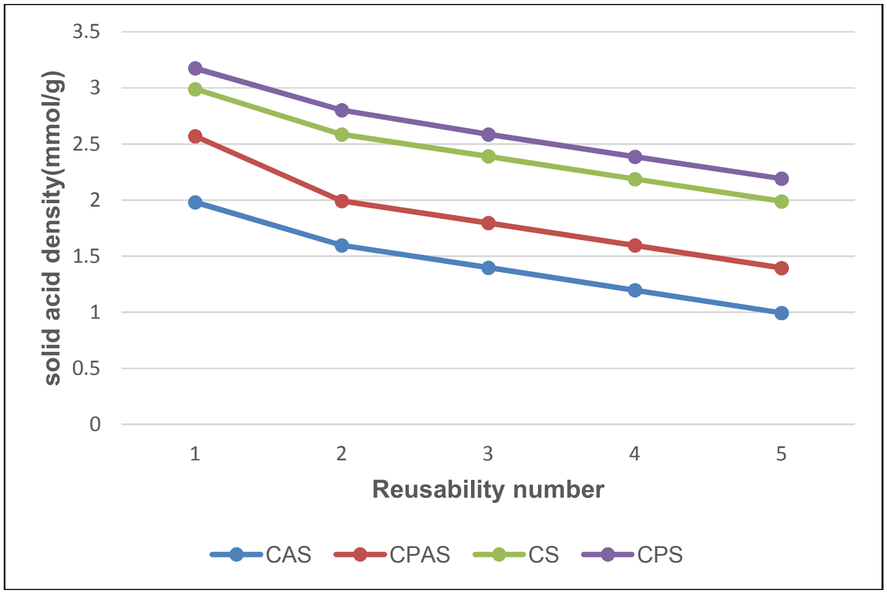

Fig. 4. Reusability of catalysts

3.4 Reusability of Catalysts

The reusability of each catalyst was evaluated after the first run under the similar reaction conditions. The used catalyst after each run was easily recovered as described previouslyin catalytic activities section. The results of Fig. 4, showed that total acid density of all catalysts decreases after each reuse due to the following reasons: possible deactivation of catalyst actives sites such as -SO_3H because of accumulated water and ethanol, deposition of reactants and products on catalysts pores and surface which could cause the hindrance of active sites [26]. Similar observations were reported by Chin et al. [27] in the case of sugar cane bagasse solid acid catalyst. For all catalysts, CPS had the highest acid density followed by CS, CPAS and then CAS. The rate of conversion decreases slightly at each successive run. For CPS the most acidic catalyst, it decreases from 86% to 74% after the fourth run.

4. CONCLUSION

In this work, four solid acid catalysts were prepared from cassava peels via carbonization at 500°C. One part was furthermore treated with sulfuric acid or with phosphoric acid and then with sulfuric acid to obtain CS and CPS respectively. Another part of carbon char were pyrolyzed at 800°C and was treated as previous to obtain CAS and CPAS. The catalysts obtained have shown to be useful for esterification as used in this work. FTIR confirmed the presence of -SO_3H,-COOH and OH functional groups on the surface of the catalysts. The total acid densities of the catalysts range from 2.26 to 3.49 mmol/g whereas the -SO_3H densities were 0.92 to 2.20 mmol/g. all the catalysts were effective in the esterification of free fatty acid in palm kernel oil with a conversion rate ranging from 70 to 90%, depending mostly on the sulfonic acid density on the catalyst. The solid catalysts were found stable and could be recovered and reused in the esterification reaction with a mild decrease in the conversion of FFA to esters. Although, CPS was found more stable than all other catalysts prepared, further work will explore the use of these catalysts in other acids catalyzed reactions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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