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Use of sugarcane straw ash for zeolite synthesis

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Abstract
The amount of biomass combustion residue is growing nowadays due to constant increasing demands of biomass utilization. The biomass ash produced currently is disposed on agricultural fields. The presence of metals, chlorine, sulphur and other species may have significant impacts on soils and the recycling of soil nutrient. The main challenge is related to the increase of possible applications of this byproduct. Sugarcane straw ash (SCSA) was used in a study on synthesis of zeolitic material by alkaline conventional hydrothermal treatment. Different experimental conditions, such as, reaction time, alkali hydroxide concentration and liquid/solid ratio were studied. Raw ash material and synthesis products were characterized by X-Ray Fluorescence, Fourier transform infrared spectroscopy powder, X-ray diffraction, cation exchange capacity and scanning electron microscopic. The presence of zeolite hydroxysodalite confirms successful conversion of native SCSA into zeolitic material. Sugarcane straw ash utilization minimizes the environmental impact of disposal problems and further appears as an alternative for the future sustainable large-scale management of biomass ash.

Keywords: Sugarcane straw; Biomass ash; Zeolite; Hydrothermal treatment.

1. Introduction

In recent years, there has been an increasing trend towards more efficient utilization of lignocellulosic agro-industrial residues and among them, sugarcane straw and bagasse, wastes generated by the sugar and alcohol production processes.

The sugar industry is one of the most important agro-based industries in Brazil, India, and others developing countries. Brazil is the largest producer of sugarcane of the world generating 400 million tons per year, on average [1].

Sugarcane straw is the material that is removed before the cane is crushed and comprises the dried/fresh leaves and the top of the plant [2, 3]. A typical sugarcane harvest in Brazil will generate at least 90 million tonnes of straw, of which 3-5% will be turned into ashes [4].

Inappropriate dumping method of sugarcane straw ash (SCSA) creates soil pollution and also causes air pollution with an allergic problem to human being [5-7].

It has been reported that sugarcane straw ash obtained from heaps of open-air burnt straw in the vicinity of a sugar factory showed a high pozzolanic activity [8].

Villar-Cociña et al. [9] studied the pozzolanic behaviour of a mixture of sugarcane straw ash with 20 and 30% clay burned at 800 and 1000 ^{o}C and calcium hydroxide and proposed a kinetic–diffusive model for describing the pozzolanic reaction kinetics.

Other possible utilization of SCSA is the conversion into higher level product zeolitic material. Sugarcane straw ash contains aluminosilicates glass, mullite and quartz, which are the required building blocks of zeolite formation [10-12]. Zeolitic materials have high potential to be developed as efficient low cost adsorbents with application in environmental problems, particularly in liquid effluents treatment through the process of ion exchange.

Some authors have reported the conversion of bagasse fly ash into zeolites [13-19]. To the best of our knowledge, are no reports on the conversion of sugarcane straw ash into zeolites.

The objective of this study is to investigate the conversion of sugarcane straw ash, a sugar industry solid waste into zeolites by conventional hydrothermal treatment. During the hydrothermal synthesis procedure, several variables were evaluated: concentration of the activator; reaction time and solution/SCSA ratio.

2. Experimental

2.1 Materials

All the regents used were of analytical grade. The sugarcane straw was collected in Piracicaba city located at state of São Paulo, Brazil. This waste was gathered as dry straw, it was cut in order to obtain fibres between 20 and 30mm long and the material was ground by oscillating mill. Sugarcane straw ashes (SCSA) from the combustion of sugarcane straw were obtained in a muffle furnace at 700°C during 20 min.

2.2 Zeolite synthesis

The SCSA was converted to zeolite using the conventional hydrothermal treatment. SCSA was mixed with aqueous NaOH solution in a Teflon vessel in a pre-determined ratio. This mixture was heated to 100°C in oven. After hydrothermal treatment, the reaction mixtures were filtered and washed with distilled water until the washing water had pH ~ 11 and the synthesis products were oven dried at 50°C for 12 h. The synthesis conditions used with different samples such as, reaction time, alkali hydroxide concentration and NaOH solution volume/mass of SCSA ratio (L/S) are presented in Table 1.

Table 1. Synthesis conditions for alkaline activation of SCSA by using conventional hydrothermal treatment

Reaction time (h)	[NaOH] (mol L^{-1})	L/S (mL/g)	Sample
45	2.0	8	TA-1
45	3.5	8	TA-2
72	2.0	10	TA-3
72	3.0	10	TA-4

2.3 Characterization of materials

The chemical compositions of materials in the form of oxides were analyzed by energy dispersive XRFX-ray fluorescence spectrometry (RX Axios Advanced, PANalytical, Phillips spectrometer). Phase and crystallinity were confirmed by powder XRD (Rigaku Multiflex) with nickel filter CuKα radiation (λ = 1.54060 Å) scanning from 5 to 80° at a rate of 1°/min with current 40 kV and 20 mA. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on Nexus 670 Thermo Nicolet using KBr pellet method. Scanning Electron micrograph was obtained by using XL-30 Philips scanning electron microscope (SEM). The particle size of the materials was measured using a laser based particle size analyzer, namely a Malvern MSS Mastersizer 2000 Ver. 5.54. For the cation exchange capacity (CEC) measurements, the samples were saturated with sodium acetate solution (1 mol L^{-1}), washed with 1L of distilled water and then mixed with ammonium acetate solution (1 mol L^{-1}) [20]. The sodium ion concentration of the resulting solution was determined by optical emission spectrometry with inductively coupled plasma - ICP-OES (Spedtroflame - M120).

3. Results and discussion

3.1 Sugarcane straw ash characterization

The composition of biomass ash is dependent on the plant species, materials that the plant absorbed from the water or the soil during its growth, growth conditions and ash fraction. The chemical compositions of SCSA in the form of oxides are shown in Table 2. The major component was SiO_2 along with small amounts of CaO, K_2O, Al_2O_3 and Fe_2O_3. Loss on ignition (LOI) implied in high weight loss of about 60%, and is mainly attributed to the presence of organic matter in the waste sample.

Table 2. Chemical composition of the sugarcane straw ash

Oxides	% wt	Oxides	% wt
SiO_2	25.3	P_2O_5	0.44
Al_2O_3	0.68	MnO	0.38
Na_2O	0.05	TiO_2	0.06
K_2O	3.78	BaO	0.14
CaO	3.98	Cr_2O_7	0.08
SO_3	0.92	SrO_2	0.01
Fe_2O_3	1.19	NiO	0.001
MgO	0.96	ZnO	0.01
Cl	0.41	LOI	61.6

Silica is absorbed from the soil through the roots of sugarcane. Accumulated silica between the plant's cuticle and cell walls acts as a physical barrier against the penetration of pathogenic fungi and reduces water loss through transpiration [21].

The percentages of the main oxides present in sugarcane straw ash are lower than values found in the literature [10, 11]. This could be related to the different calcining temperature used and controlled or uncontrolled calcining temperatures conditions. Furthermore, the silica content is probably related to the soils where sugarcane grows, as well as to other factors, such as fertilization methods and soil management.

Generally, the ash from biomass combustion content include Ca, Si, Al, Ti, Fe, Mg, Na, K, S and P. The composition of ash affects its behavior under high temperatures of combustion and gasification reactors and is responsible for technological and environmental problems during biomass processing. Problems like clogged ash-removal caused by slagging ash, sintering, deposition, erosion, corrosion and pollutant emissions are mainly created by the presence of alkali metals, alkaline earth metals, silicon, chlorine and sulphur in the ashes. Ash weight content (in dry basis) of different herbaceous biomass types have reported values ranging from less than 2% up to 8-12 % [22].

An extended overview of the phase–mineral and chemical composition and classification of biomass ash was conducted by Vassilev et al. [23].

The powder XRD pattern of SCSA is shown in Figure 1. SCSA shows a very low crystallinity and wide band is observed between 10 and 30 (2-theta), which implies the presence of vitreous matter. This fact is attributed to glass forming constituents since the organic constituents would have been removed during combustion. It has been reported that at burning temperatures up to 800°C silica was in amorphous form and silica crystals grew with time and temperature of incineration [24].

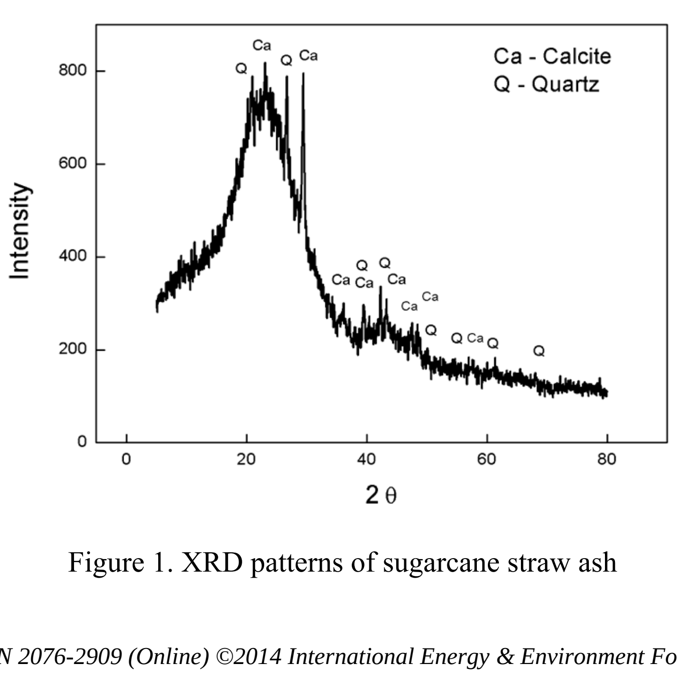

Figure 1. XRD patterns of sugarcane straw ash

Moreover, the XRD patterns suggest the presence of calcite ($CaCO_3$, ICDD/JCPDS 01-071-3699) as the main crystalline compound with quartz (SiO_2, ICDD/JCPDS 001-0649) as minor compounds. The amorphous aluminosilicate nature of SCSA makes its chemical composition difficult to characterize, but also very versatile, since the glassy phase both react and also goes into solution before the crystalline phase.

SEM micrograph of SCSA (Figure 2) seems like fibrous material containing large shallow pores with strands in each fold. The SCSA contain noncrystalline glass phase, with a loose structure and possess smooth surface particle because the surface is covered by an aluminosilicate glass phase. SCSA also possesses irregular shapes and surfaces.

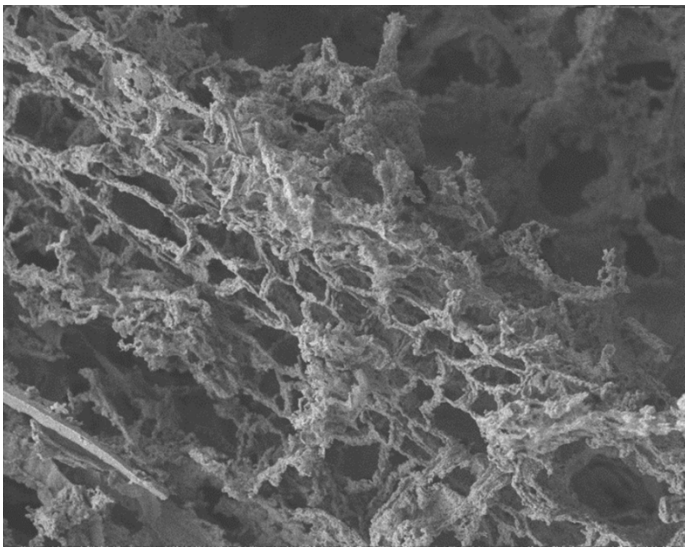

Figure 2. Scanning electron microscope micrographs of SCSA

The particle size distributions are important for predicting the size of ash particles and the tendency to impact surfaces. Figure 3 shown the absolute and cumulative, respectively, particle size distributions for the sugarcane straw ash (SCSA).

Relevant parameters are again listed in Table 3. These distributions specify that the majority of particles (90%) lie below 246.239 µm. The surface area determined by wet method was 0.0894m^2 g^{-1}.

It must be noted that fine-grained materials are more effective, when utilized for heavy metals retaining, a procedure that is also strongly dependent on the nature of the contaminated.

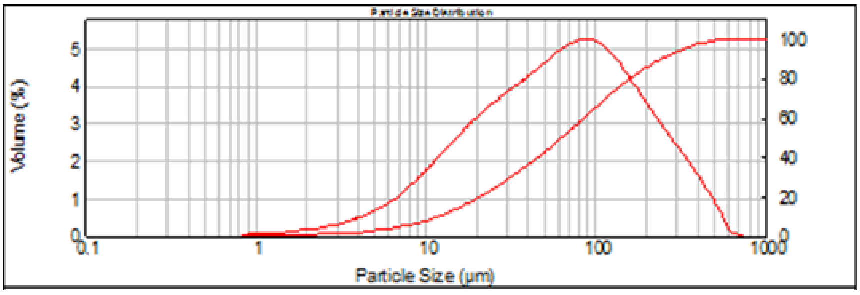

Figure 3. Particle size distribution of the sugarcane straw ash

Table 3. Parameters characteristics of size distribution of sugarcane straw ash

	Particle diameter
D_{10} (µm)	11.293
D_{50} (µm)	63.888
D_{90} (µm)	246.239
D ([3,2])	26.665

Classic alkaline conversion of ash is based on the combination of different activation solution/ash ratios, with temperature, pressure, and reaction time to obtain different zeolite types. The applied technique mainly aims at the dissolution of Al-Si bearing phases of the ash and the subsequent precipitation of the zeolitic materials.

The ash activation is usually carried out varying the activation agent (mainly KOH and NaOH), temperature (20-250°C), conversion time (2 h a 7 days), solution concentration (0.1– 8 mol L^{-1}), pressure (the vapor pressure at the temperature selected), and solution/sample ratio (1-20 mL g^{-1}) [25-27].

In the present study, experimental conditions shown in Table 1 were selected on the basis of conditions from previous reports in the literature [25]. NaOH was selected as an activation solution, since its solutions present higher conversion efficiency than the respective KOH under the same conditions. The NaOH concentrations and temperature are typical for a pure alkaline activation, taking place at low temperatures and intermediate activation periods.

As the chemical analysis results indicated (Table 2), the SCSA ash contains very little Al_2O_3, so longer reaction times (45-72 h) are required to obtain zeolitic material without adding of aluminum or preliminary fusion with alkali.

Samples TA-2 and TA-4 synthesized using more concentrated NaOH solutions (NaOH > 2 mol L^{-1}) showed colloidal properties and the solid-liquid separation by filtration was very difficult. Therefore this condition was excluded as a parameter of synthesis.

The XRD patterns of the two samples TA-1 and TA-3 appeared in Figure 4. The common crystalline phases identified in TA-1 and TA-3 from the d-spacing values are quartz and calcite, both of them are present in the unmodified sugarcane straw ash as major content (Figure 1). This significantly demonstrates that under the given experimental conditions, these phases have not been digested completely.

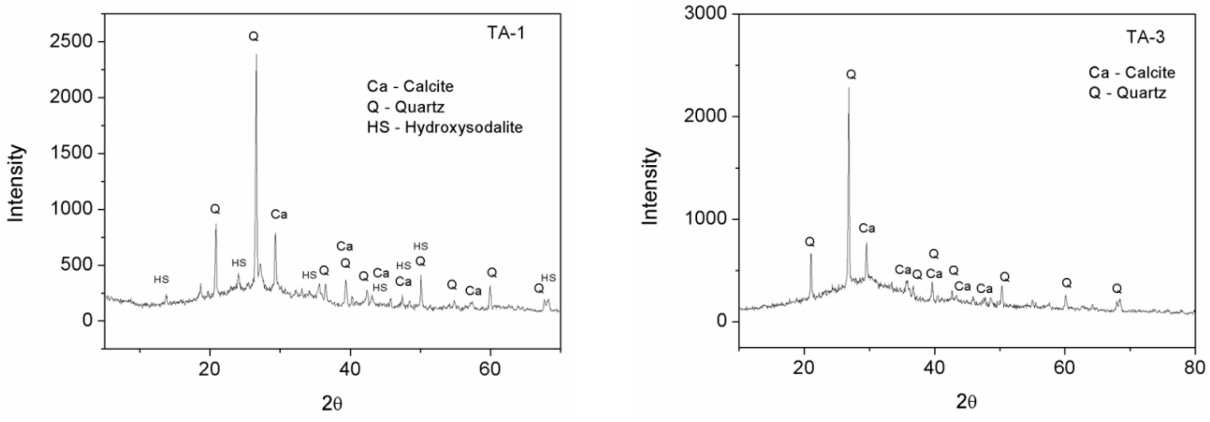

Figure 4. XRD patterns of the synthesis products obtained by hydrothermal treatment of sugarcane straw ash: TA-1 and TA-3

The high quantity of amorphous material in the SCSA (Figure 1) was found to reduce signals of crystalline material present and this can be confirmed by the increase of intensity of calcite and quartz peaks after the hydrothermal treatment (Figure 4).

During the ageing process, the amorphous phase undergoes dissolution in the alkaline media before new crystalline phases are formed and this can be confirmed by the disappearance of the broad diffraction hump that had appeared in SCSA the XRD pattern (Figure 1).

Several new sharp diffraction peaks obtained in TA-1 which were not observed in PXRD of TA-3. The observed newly peaks with d-spacing values of 14, 20, 24.7, 35, 43.4, 45.7 and 50° are ascribed to formation of zeolitic units in TA-1. The zeolite hydroxysodalite (JCPDS 011-0401) was positively identified in TA-1. Thus, under treatment conditions of sample TA-1, quartz phases and some parts of mullite get digested and consequently these phases involve in the conversion of ash into zeolite.

The activation of the studied SCSA with treatment conditions of sample TA-3 did not produce noticeable quantities of crystalline zeolites. This fact indicated that when higher crystallization time and/or higher solution/ash ratio are applied, impurities of other compounds may effect on the formation of zeolite.

Hydroxysodalite (HS) is crystalline aluminosilicate with a three dimensional channel network, belonging to clathrasil group. It exhibits similar structure of sodalite consisting of six-member oxygen aperture where framework charges are balanced with hydroxide anions.

HS has a pore size of 2.65 Å, which provides access to small molecules, e.g., helium (~2.6 Å), water (~2.7 Å), ammonia (~2.5 Å), making it a potential membrane material in separation of small molecules. Further, it is attractive as a functional material for a wide range of applications, such as removal of heavy metals and dyes from water, desalinating seawater and other salt solutions, optical materials, hydrogen storage, hydrogen separation, catalysts, and pigment occlusion [27-31].

The cation exchange capacity (CEC) and selectivity are definitely the most important characteristics of zeolites, because a substantial part of water treatment processes are based on the selective adsorption of metal cations, ammonium or polar organic compounds. In addition, cation exchange properties of zeolites can be exploited to modify their surface chemistry such that other classes of compounds can also be retained [29, 31].

The CEC rose from 0.245 meq g^{-1} for the unmodified Sugarcane straw ash to 0.602 meq g^{-1} for the modified product TA-1. The alkaline hydrothermal treatment increased CEC value of the ash due to particle modification from smooth surface to plate-and rod-shape crystals, which was indicated by the XRD analysis as hydroxysodalite zeolite. Moreover, most of raw biomass ash has low metal adsorption capacity because they do not contain suitable functional group for effective adsorption.

FTIR spectroscopy has been widely performed as an effective tool to explain the alteration of chemical structure of lignocellulosic substrates. Figure 5 shows the spectrum of treated (TA-1) and untreated sugarcane straw ash (SCSA).

The spectra of the untreated and thermally treated sugarcane straw ashes are very similar. The stretching at 3433-3415 cm^{-1} is attributed to both the silanol groups (Si-OH) and adsorbed water on the surface in SCSA and TA-1.

The weak band at 1626 cm^{-1} is attributed to the bending mode of H_2O molecules. The band at 1082 cm^{-1} (SCSA) was shifted to 1008 cm^{-1} (TA-1), which confirms the tetrahedral coordination of aluminum in the zeolite framework. The peaks at 779-796 cm^{-1} are indicative of quartz and amorphous silica. Bands in the region 465-460 cm^{-1} are mostly attributed to internal tetrahedron vibrations of Si-O and Al-O of the materials. The lack of absorption bands in the range 3600-3700 cm^{-1}, characteristic of Al-OH-Al stretching, suggests that discrete, poorly crystalline Al-rich phases are not present.

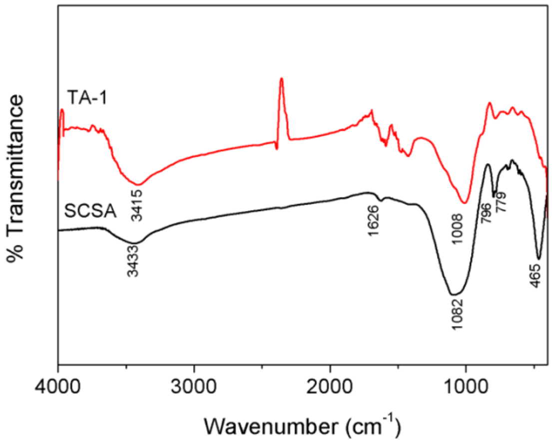

Figure 5. FTIR spectra of untreated (SCSA) and treated sugarcane straw ash (TA-1)

5. Conclusion

The presented studies revealed that the zeolitic material (zeolite hydroxysodalite) was successfully developed from the low cost sugarcane straw ash (SCSA) in the absence of organic templates, without addition of aluminum solution and without fusion prior to hydrothermal treatment.

The formation of the zeolite structure was confirmed by XRD. The efficiency in the conversion of SCSA was affected by the experimental conditions, such as, reaction time, alkali hydroxide concentration and solid/solution ratio. The conversion of SCSA into zeolitic material both contributes to the mitigation of environmental problems and turns this biomass waste of sugar industry into an attractive and useful material, which will be used in the future as an ion exchanger in removing pollutants from wastewater.

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