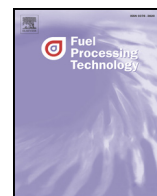




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Mineral sorbents for downstream sodium capture in biomass gasifiers

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ABSTRACT

The concentration of alkali metal vapors (especially sodium and potassium) ordinarily reaches more than 10 ppm during agri-based biomass gasification, leading to several problems, as: corrosion of turbine blades, decreased catalytic activity and undesirable deposition on downstream equipment. Adsorption on aluminosilicates is thought to be an interesting option to reduce alkali concentration in syngas thus generated. Therefore, in this work, six samples of mineral sorbents were exposed to sodium vapors at high temperatures and under moisture conditions. Before and after sodium vapor exposure, samples were characterized by various analytical techniques, textural analysis, TGA, XRD and XRF, aimed at better understanding of the binding mechanisms and assessing their ability to remove sodium from the gas phase. The combination of all techniques allowed the confirmation of the sorption mechanisms, which is chemisorption in most cases, with the formation of silicates and aluminosilicate salts. Sorbents with higher Al content, such as green clay and bauxite, showed potential for the application of capturing alkali metal vapors at high temperatures in the presence of steam by fixing sodium as nepheline (NaAlSiO₄). Sorbents with higher silica content (e.g., diatomite and kaolin) showed irreversible fixation of Na, which could not be recovered even upon acid leaching. The presence of elements other than Si and Al (e.g. Ca) also plays an important role in Na sorption.

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1. Introduction

The gaseous mixture produced from biomass gasification has been pointed out as a reliable and clean way of producing renewable energy. It contains hydrogen, carbon monoxide, carbon dioxide, methane, aliphatic and aromatic hydrocarbons, as well as impurities [1,2]. Due to the high temperatures required for gasification, alkali metals present in biomass are often released in the product stream. This contamination in the gas phase may be also augmented from other alkali and alkaline earth metal sources present in the gasifier, especially from refractory materials and ceramics used in the cleaning operations of the outlet gas [3].

The concentration of these alkali metals (especially sodium and potassium) can reach more than 10 ppm in syngas obtained from biomass gasification. Salo and Mojtahedi [4] reported that alkali metal concentrations of up to 0.1 ppm wt. may cause corrosion of turbine blades. In addition, alkali metal vapors are known to dramatically decrease the activity of cobalt-supported Fischer–Tropsch catalysts [3]. Some other problems associated with the presence of potassium and

chlorine vapors released during the biomass gasification process are [5]: (i) agglomeration in fluidized beds, (ii) reaction between potassium and other components of the ash leading to unwanted substances; (iii) corrosion of the reactor constituent material; (iv) clogging and fouling in pipes; (v) reduction of thermal conversion efficiency and (vi) increase in costs for equipment maintenance. Hence, cleaning the biomass gasifier produced gas is essential to avoid corrosion and deposition of inorganic alkali compounds in downstream equipment. Alkali concentrations must be reduced to acceptable levels according to the destination of the produced syngas.

Several studies have been reported in the literature [6–16] regarding methods and technologies to abate alkali metal vapors in syngas obtained from biomass gasification. Sorption on aluminosilicate-based sorbents has been frequently pointed out as an effective method for this purpose [4,11,17]. The sorption capacity of these materials for alkali vapors at high temperatures depends basically on their composition and physical properties, as well as the water/solid ratio and atmospheric conditions (oxidizing or reducing). Some studies reported in the literature have shown that the presence of water plays a critical role on the occurrence of physical or chemical adsorption [7–10,14–17]. Steam is always present in the gas produced from biomass gasification and therefore the effects of humidity on the sorption of alkali vapors should be carefully taken into account. Most of the previous studies have focused on either the

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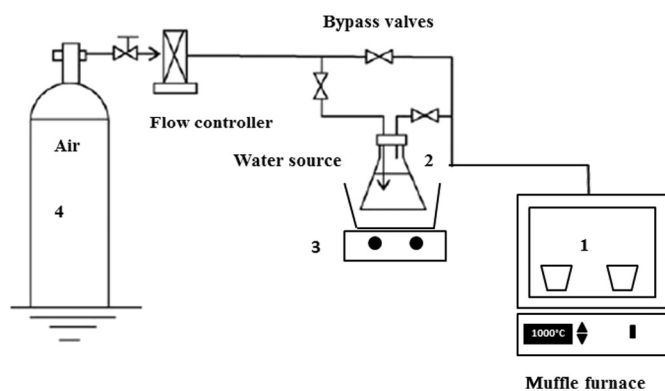


Fig. 1. Experimental apparatus for the gravimetric tests. Legend is as follows: 1 – muffle furnace; 2 – saturator; 3 – heating system; and 4 – air cylinder.

Table 1
Characterization techniques used in this work and their respective purposes.

Technique	Purpose
XRD	Obtain information on the structure and composition of the main phase of the adsorbents and correlate the observed changes due to the exposure to NaCl humid vapors with the adsorption mechanism
XRF	Determine the chemical composition of the sorbents in terms of oxides and identify the effects of the composition (mainly Al_2O_3 and SiO_2) on the adsorption of alkali
SEM/EDS	Detect the presence of sodium on the surface and indicate the occurrence of adsorption by comparing the analysis before and after exposure of the samples to NaCl humid vapors
TGA	Evaluate the thermal stability of the samples under the conditions of test and hydrophilicity/hydrophobicity, which is an important parameter for the analysis of adsorption under humid conditions
ICP-OES	Assess the amount of alkali adsorbed on each sample by comparing the amounts released and irreversibly bound after and before the exposure to NaCl humid vapors

detection of alkali in the gasifier outlet gas or on the selection of sorbents for the removal of alkali metal vapors [6–16]. However, the relation between the retention mechanisms as a function of the solid composition and the presence of water is not fully understood.

The aim of this work is to characterize different sorbents by means of various analytical techniques (XRF, XRD and SEM–EDS) and textural and thermogravimetric analyses, before and after controlled exposure to sodium vapors, in order to shed some light on the sorption mechanisms and to correlate the evaluated characteristics with the sample performance in removing sodium from the gas phase.

2. Experimental

2.1. Materials, reagents and samples

All sorbent samples used in this study are naturally occurring minerals composed of varying amounts of silica (SiO_2) and alumina (Al_2O_3). All samples were kindly supplied by Brasil Minas (Brazil), except bauxite,

which was provided by the Department of Geology at the Federal University of Ceará (UFC). All samples were used without prior purification or manipulation.

To minimize risks of contamination, whenever necessary, all plastic and glassware were washed with tap water, immersed in Extran (48 h), rinsed with tap and deionized water and immersed in 20% (v/v) HNO_3 for at least 24 h. Before use, these materials were thoroughly rinsed with ultrapure water.

2.2. Exposure to NaCl humid vapors

The experiments for exposing the fresh mineral sorbents to sodium humid vapors were carried out using sodium chloride as the alkali metal source (5 g NaCl) placed in different crucibles inside a muffle furnace. The samples were heated at a rate of $25\text{ }^\circ\text{C min}^{-1}$ up to $1000\text{ }^\circ\text{C}$ and kept at this temperature for 5 h inside the muffle. The alkali metal source, NaCl, was purchased from VETEC Química Fina LTDA. (Brazil) and presented >99% purity. A muffle furnace Model EDG 3P-S 3000 (EDG Equipamentos, Brazil) and an analytical balance with 0.0001 g precision Model AB 204-S/FACT – Class I (Mettler Toledo, Brazil) were employed. In order to generate a humid environment inside the muffle furnace, an isothermal water stripper was connected to the system as illustrated in Fig. 1. Deionized water was used in the saturator, which was kept at approximately $80\text{ }^\circ\text{C}$ with the aid of a silicon oil bath. The air flow rate was set to $10\text{ L}\cdot\text{min}^{-1}$. The steam molar flow rate was $0.0487\text{ kmol water/kmol air}$, as calculated with the aid of a hygrometer to determine the relative humidity and vapor pressure tables [18].

2.3. Sorbent characterization

All samples were assessed for their textural characteristics before and after exposure to humid sodium vapors by measuring N_2 adsorption isotherms at 77 K in an Autosorb-1 MP apparatus (Quantachrome, USA). From the N_2 isotherms, it was possible to determine the specific surface area, total pore volume and average pore size [19].

X-ray fluorescence analyses (XRF) were performed in an X-ray fluorescence spectrometer ZSXmini II (Rigaku, USA) operating at 40 kV and 1.2 mA. X-ray diffraction (XRD) was carried out on a diffractometer for polycrystalline sample model X'Pert Pro MPD (PANalytical, The Netherlands). The radiation source was a Co X-ray tube, with $\text{CoK}\alpha$ operating at 40 kV and 40 mA.

A Sputter Coater POLARON, model SC7620 (VG Microtech, England) was used for SEM–EDS analyses. Samples were mounted in an aluminum holder of 12.7 mm diameter and bombarded with 15 kV from a Leo 440i scanning electron microscope. The characteristic X-rays were detected with an energy-dispersive spectrometer model 6070, calibrated with copper. Both SEM (Leo 440i) and EDS (6070) were purchased from Leo Electron Microscopy Ltd (England). The electron beam current was 50 pA and the measuring time was 10 min.

For thermogravimetric analysis (TGA), a STA 40-9 CD/403/5/G (NETZSCH, Germany) apparatus was employed. The experimental procedure consisted of weighing 30 mg of each sorbent in platinum crucibles. All tests were performed at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$, from room temperature until $850\text{ }^\circ\text{C}$, under an argon (99.999%, supplied by White

Table 2
Composition of the mineral adsorbents obtained by XRF calculated as oxides.

Adsorbents	Mass (%)										$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio
	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	SO_3	TiO_2	ZrO_2	MgO	MnO	
Bauxite	66.13	20.50	0.11	0.25	7.01	0.19	5.59	0.18	–	–	0.5
Diatomite	4.91	91.96	0.33	0.85	1.12	–	0.79	0.04	–	–	31.8
Green clay	15.65	51.40	6.57	4.74	15.88	0.39	2.10	–	2.43	–	5.6
Kaolin	12.08	75.37	8.75	–	2.31	–	1.36	–	–	–	10.6
Palygorskite	6.05	35.61	0.31	47.3	9.71	–	0.97	0.04	–	–	10.0
Natural zeolite	7.74	45.17	2.01	12.4	4.44	13.7	–	–	–	13.66	9.9

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