Upgrading the rice husk char obtained by flash pyrolysis for the production of amorphous silica and high quality activated carbon
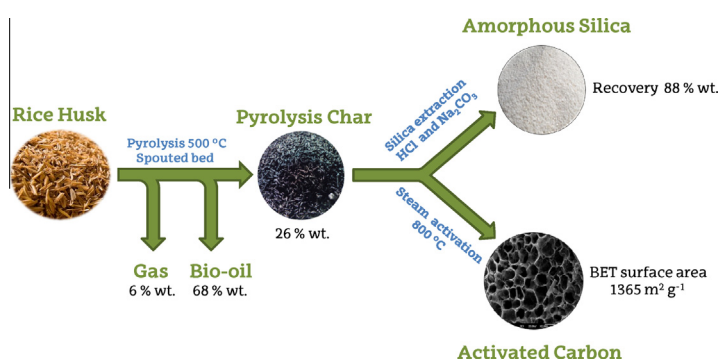
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HIGHLIGHTS

- Rice husk char is valorised for the joint production of silica and activated carbons.
- Na_2CO_3 extraction for the recovery of high amorphous silica rates (88%).
- 15 min activation for BET surface areas of up to 1365 $m^2 g^{-1}$.
- Long activation times cause growth and eventual destruction of micropores.
- Promising results for the viability of rice husk flash pyrolysis.

GRAPHICAL ABSTRACT

ABSTRACT

The overall valorization of rice husk char obtained by flash pyrolysis in a conical spouted bed reactor (CSBR) has been studied in a two-step process. Thus, silica has been recovered in a first step and the remaining carbon material has been subjected to steam activation. The char samples used in this study have been obtained by continuous flash pyrolysis in a conical spouted bed reactor at 500 °C. Extraction with Na_2CO_3 allows recovering 88% of the silica contained in the rice husk char. Activation of the silica-free rice husk char has been carried out in a fixed bed reactor at 800 °C using steam as activating agent. The porous structure of the activated carbons produced includes a combination of micropores and mesopores, with a BET surface area of up to 1365 $m^2 g^{-1}$ at the end of 15 min.

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1. Introduction

Rice husk is an agricultural waste material abundantly available in rice-producing countries. According to recent estimations the global production of rice is around 685 MT (including rice, straw and husk), and rice husk means between 0.2 and 0.33 kg per kg of rice harvested (Lim et al., 2012). Rice husk is usually burnt in open fields, and this practice involves energy waste and, moreover, causes a serious environmental problem.

Fast pyrolysis is an interesting option for the valorization of rice husk, as shown in a previous study (Alvarez et al., 2014) in which the excellent performance of a bench scale plant provided with a conical spouted bed reactor was proven to be suitable for high bio-oil production (70%). However, the economic viability of the rice husk pyrolysis process requires the valorization of the char fraction (continuously withdrawn from the reactor). Thus, the aim of this work is to study the combined production of amorphous silica and high quality activated carbon from rice husk char. Given the interesting applications of silica, its recovery improves the perspectives of the pyrolysis process and, moreover, avoids

the negative influence of the high ash content in the activated carbon.

Rice husk is an excellent source of high purity amorphous silica, which is a material used in several applications, such as the production of catalysts (Adam et al., 2012), silica gel (Prasad and Pandey, 2012) (rice husk is considered to be the cheapest route for its production) or glass (Lee et al., 2013). In addition, it is especially remarkable the possibility to use rice husk derived silica as puzzolanic agent, as reported by several authors who observed an improvement in the quality of cement when rice husk silica was added to its formulation (Ganesan et al., 2008; Givi et al., 2010). Silica is usually recovered by controlled combustion of rice husk at low temperature in order to avoid the phase change from amorphous to crystalline state (Chindaprasirt and Rukzon, 2008). Other authors have proposed an interesting alternative to recover the silica without burning the carbon matrix of the char (An et al., 2011; Liu et al., 2011). Thus, alkali carbonates have been used to leach out the silica and develop porosity in the char particle due to SiO_2 interaction with these carbonates. As observed in reaction (1), a solution of alkali silicates is formed and CO_2 is released.

$$M_2CO_3 + SiO_2 \Rightarrow M_2SiO_3 + CO_2 \qquad (1)$$
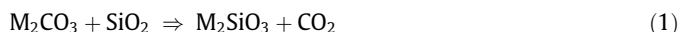
where M can be either potassium or sodium. The filtrate obtained is used to synthesize silica powders and the remaining carbonaceous matter is used as precursor for the activation process.

Any carbonaceous material with high carbon content can be used as precursor for the preparation of activated carbons (Deiana et al., 2008). In fact, many agricultural solid wastes have been used as raw materials to produce low cost adsorbents for water pollution control and decontamination processes (Ioannidou et al., 2010).

The porous carbons derived from rice husk can be applied in the adsorption of different pollutants in an aqueous medium, such as phenols (Kennedy et al., 2007), metals ions (Hsi et al., 2011b; Zhang et al., 2011) and volatile organic compounds (Hsi et al., 2011a). These studies evidence that activated carbons may have a great potential as readily available, inexpensive and effective adsorbents, with high adsorption rate, as well as capacity and selectivity for different pollutant adsorption. Furthermore, their use as catalyst support is an application with growing interest (Bedia et al., 2011; Dominguez et al., 2013; Rey et al., 2011).

Production of activated carbon from rice husk is achieved through chemical or physical activation. Chemical activation is usually performed by chemical agents, such as alkali hydroxides (NaOH/KOH) (An et al., 2011; Guo et al., 2002; Uzunova et al., 2010), inorganic acids (H_3PO_4, HCl, and H_2SO_4) (Kennedy et al., 2007; Liou and Wu, 2009) or $ZnCl_2$ (Uzunova et al., 2010). Chemical impregnation of rice husk char with KOH and NaOH followed by activation at 650–800 °C leads to activated carbons with BET surface area values in the 1500–3000 $m^2\,g^{-1}$ range and pore volume values of up to 1.88 $cm^3\,g^{-1}$ (Guo et al., 2002). Kennedy et al. (2007) used phosphoric acid as chemical agent at high temperatures (700–900 °C) and obtained BET surface area values close to 500 $m^2\,g^{-1}$.

Physical activation is commonly carried out by using steam, carbon dioxide or oxygen as activation agents, with char reacting at high temperature (usually above 800 °C). Steam and carbon dioxide are mild oxidants and at high temperature gasify the carbon atoms from the char releasing CO or $CO + H_2$. Activated carbons obtained from rice husk have low specific surface areas when physical activation is applied due to their high mineral content (Yun et al., 2003). However, Deiana et al. (2008) subjected the rice husk char to an acid treatment to remove the ashes, and the activated carbons obtained exceeded 1150 $m^2\,g^{-1}$. This result evidences the interest of reducing the high ash content to produce high quality activated carbons from rice husk char.

2. Methods

2.1. Silica extraction methodology

The char derived from rice husk is made up of carbonaceous matter and ashes (mainly silica). The method conducted to recover the silica from the rice husk char has already been developed and optimized by other authors (An et al., 2011; Liu et al., 2011). The extraction steps used are as follows:

First, 10 g of pyrolytic rice husk char were pretreated with 200 ml of HCl (1 M) to remove most of the impurities and to improve the purity of the silica. The char was introduced in a flask and the suspension was boiled for 3 h under reflux condenser and vigorous stirring. Then, the suspension was filtered and the solid was washed with distilled water until neutral pH. Finally the char recovered was dried for 15 h at 120 °C.

The next step was to remove the silica with a 15 wt.% Na_2CO_3 solution. The char and 200 ml of this solution were introduced in a flask and boiled for 4 h under reflux condenser. The suspension was filtered and the precipitate was washed with distilled water until neutral pH. Once again the precipitate has been dried at 120 °C for 24 h. The precipitate is the resulting carbon material that is going to be used in the physical activation process.

The filtrate is a solution of sodium silicate, which was subjected to a carbonation process in order to recover the silica. Thus, the solution was heated to around 80 °C, and a continuous flow of carbon dioxide was then bubbled into the solution. After 1 h, the carbon dioxide flow was stopped and the solution was cooled down. Finally, the silica precipitate was filtered and dried at 120 °C for 24 h.

2.2. Physical activation in a bench scale plant

The design is based on the knowledge acquired in previous studies in the physical activation of the char obtained in the pyrolysis of waste tyres, and a scheme of the plant used is reported elsewhere (Lopez et al., 2009b). The activation occurs in a fixed bed reactor placed inside a radiant oven that provides heat to operate at temperatures up to 1000 °C. The unit is provided with a pressure meter to ensure that pressure in the reactor is not above 1.2 atm during the activation. Both the reactor and the oven are located in a forced convection oven (hot box), and kept at 270 °C in order to ensure the complete vaporization of the water fed into the reactor to perform steam activation. Nitrogen and carbon dioxide (in case the latter is used as activating agent) are fed into the reactor by means of two mass flowmeters. Water flowrate is controlled by a high precision Gilson 307 pump, and a heating coil with an electric cartridge is located at the inlet of the hot box in order to ensure the immediate and homogeneous vaporization of the water stream. Finally, the non-reacted steam was condensed at the outlet of the reactor in a Peltier cooler.

2.3. Experimental procedure

In each experimental run 1 g of rice husk char (without silica) was placed inside the fixed bed reactor. The sample was heated at a rate of 15 °C min^{-1} under inert atmosphere (nitrogen) flow to the activation temperature (800 °C). Once this temperature has been reached, a nitrogen flow was maintained for 1 h in order to ensure the complete carbonization of the sample. When the carbonization was finished, the activating gas was continuously fed into the reactor with a flow rate of 200 $cm^3\,min^{-1}$ measured at standard conditions. The activating gas was composed of steam and nitrogen at a ratio of 75:25, respectively. The activation process was performed for four different residence times with each