Fuel Processing Technology 127 (2014) 133–139

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

The use of experimental design and response surface methodologies for the synthesis of chemically activated carbons produced from bamboo

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ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form 7 May 2014
Accepted 12 May 2014
Available online 7 July 2014

Keywords:
Activated carbon
Bamboo
Experimental design
Response surface

ABSTRACT

The experimental design and response surface methodologies were used for the synthesis and characterization of eight chemically activated carbons produced from the bamboo species *Guadua amplexifolia*. The synthetic method was performed following a fractional factorial design having as factors for the activation temperature and time, carbonization temperature and chemical activation agent. Experimental results showed production yields ranging from 1.5 to 24.5%, average point of zero charge of 1.5 and 10.3, adsorption capacity as high as 1872 mg of iodine/g of activated carbon and high content of carboxylic and lactones surface groups. According to the statistical analysis obtained from the analysis of variance, the activation agents (H_3PO_4 and NaOH) played the most significant roles in the physicochemical properties. In addition, the use of the response surface plots proposes the routes to enhance the physicochemical characteristics obtained in the present work.

1. Introduction

The synthesis, modification, characterization and application of activated carbons (ACs), especially those obtained from lignocellulosic resources, are widely studied by a significant number of researchers worldwide. In this sense, wood and coconut shells are the most common precursors for the large scale synthesis of AC, yielding a world production of more than 300,000 t/year [1]. The selection of the precursor for the development of AC as low-cost material depends upon many factors. The lignocellulosic material should be preferably freely available, inexpensive and non-hazardous in nature having high contents of carbon and low amounts of inorganic materials [2].

Nowadays, the raw materials used for preparation of AC are increasingly from a lignocellulosic origin. From here, several precursors have been selected: nut and almond shells [3–7], rice straw and husk [7–9], sugarcane bagasse [9,10], olive stones [7,11], bamboo [12–15], wheat bran [16], corncob [17], apricot stones [18], oil palm tree [19] and much more. One of the advantages of bamboos as AC precursor is their relative fast growing rate since they provide a renewable source of raw material. Bamboos are a group of woody perennial plants in the grass family *Poaceae*, subfamily *bambusoideae* including more than 1200 species and more than 100 genders [28]. To the gender *Guadua* belongs more than 20 species, of which *Guadua amplexifolia*, is geographically distributed in the rain forest from the south of Mexico to the north of Colombia and Venezuela. However, the Mexican variety has thornless hollow culms [29]. Despite the fact that bamboos have favorable mechanical properties, high flexibility, low cost and fast growing rate, their principal use has been limited to handcrafts or construction materials [30].

It is well known that the material selected as carbon precursor and the manufacturing process provide important features in the structure and properties of the produced AC. Some characteristics such as the production yield, adsorption capacity and the surface oxygenated acidic groups can be tuned during the activation procedure by selecting carefully the synthesis conditions [11,13,14].

Activation processes of carbonaceous materials can be classified into two categories: physical (also known as thermal) and chemical [20]. During physical activation, the precursor material as such or the previously carbonized can undergo to gasification with water steam, carbon dioxide or the same combustion gases produced during the carbonization [14,21]. On the other hand, chemical activation consists of impregnating lignocellulosic or carbonaceous raw materials with chemicals such as $ZnCl_2$, H_3PO_4, HNO_3, H_2SO_4, NaOH, or KOH. Then, they are carbonized (a process now called "pyrolysis") and finally, washed to eliminate the activating agent [13,22]. The application of a gaseous stream such as air, nitrogen, or argon is a common practice during pyrolysis which generates a better development of the material's porosity [20–22]. Although not common, potassium carbonate [23], or formamide [24] has been also used as activating agents.

The activation of lignocellulosic materials with H_3PO_4 has become a widespread method for the large-scale manufacture of AC. The use of H_3PO_4 has some environmental advantages such as easy recovery, low energy cost and high carbon yield. H_3PO_4 plays two roles during the preparation of AC: i) acts as an acid catalyst to promote bond cleavage,

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http://dx.doi.org/10.1016/j.fuproc.2014.05.035
0378-3820/

hydrolysis, dehydration and condensation, accompanied by cross-linking reactions between phosphoric acid and biopolymers and ii) may function as a template because the volume occupied by phosphoric acid in the interior of the activated precursor is coincident with the micropore volume of the activated carbon obtained [25].

On the other hand, alkaline hydroxides (KOH, NaOH) have been used as activation agents in the preparation of AC with high specific surface [15,26]. Activation using NaOH has shown to be more interesting agent due to the possibility of reducing chemical costs and environmental load when compared with KOH activation [27].

In this work, we describe the synthesis and physicochemical characterization of eight chemically activated carbons (CACs) produced from the bamboo specie *Guadua amplexifolia* as precursor. Proximal and lignocellulosic analyses were done to know the characteristics of the raw material. Activation procedure was performed following a fractional factorial experimental design. The physicochemical characteristics (point of zero charge, density, moisture, adsorption capacity, surface oxygenated acidic groups and yield) were analyzed by using the analysis of variance. From here, it was possible to identify the influence of the synthesis parameters on the final characteristics of these CACs and later on, their possible improvement by using the response surface methodology.

2. Experimental

2.1. Selection, preparation and characterization of the AC precursor

Bamboo (*G. amplexifolia*) dry canes were reduced into strips ≈ 5 cm (length) and ≈ 0.5 cm (width). Cellulose, hemicellulose and lignin contents were determined using the Van Soest extraction procedures [31]. Moisture (ASTM D2867-09), volatile matter (ASTM D5832-98), ash content (ASTM D2866-94), fixed carbon and waxes (Soxhlet extraction) were analyzed. In addition, a Vickers microhardness tests were performed based on ASTM D1037 (1999) by applying a load of 1 N during 10 s on the specimen, by using a Vickers microhardness tester Mitutoyo HM-124.

2.2. Carbonization stage

Bamboo thermal decomposition was studied in terms of global mass loss using a Perkin Elmer TGA-6000 thermo gravimetric analyzer. 10 mg of bamboo was placed in a platinum crucible and heated from 25 to 700 °C with a heating rate of 3 °C/min in air atmosphere. From here, the temperature to carbonize bamboo was set at 300 and 350 °C. Samples were carbonized in a Felisa furnace in air atmosphere during 30 min. Then, furnace was switched off and cooled down to 25 °C. Carbonization yield was obtained by weight difference.

2.3. Activation procedure

A fractional factorial experimental design (FFED) type 2^{4-1} was followed to activate the carbons obtained from the carbonization stage. This method evolves two levels: low (−) and high (+) and four factors: activation temperature (A), activation time (B), carbonization temperature (C) and chemical activation agent (D), see Table 1. The selection of this fractional design allows one to work with eight samples rather than sixteen of the complete experimental design type 2^4 [32] having the same number of factors and levels.

For the experimental procedure, a known carbon sample, indicated by FFED, was impregnated with the ratio of 2:1 (chemical agent:carbon) at 80 °C during 5 h. Later, the samples were heated at 110 °C for 12 h to remove excess moisture. As following step, the impregnated carbon was thermally treated (activation) in a furnace during the activation temperature and time selected from the FFED. This step was performed at air atmosphere. All the experiments were randomly run in order to minimize possible systematical bias during the experimental procedure [32].

Table 1
Fractional experimental design 2^{4-1}.

Factors				Levels	
				Low (−)	High (+)
A. Activation temperature (°C)				500	700
B. Time (min)				60	120
C. Carbonization temperature (°C)				300	350
D. Activation agent				H_3PO_4	NaOH
Run	Basic design				Treatment
	A	B	C	D = ABC	
1	−	−	−	−	(1)
2	+	−	−	+	ad
3	−	−	−	+	bd
4	+	+	−	−	ab
5	−	−	+	+	cd
6	+	−	+	−	ac
7	−	+	+	−	bc
8	+	+	+	+	abcd

To label the obtained CAC, as a result of the different experimental treatments, a nomenclature type CACr will be used; where r corresponds to the number of run indicated by the FFED.

2.4. Physicochemical characterization of the CAC

Properties of CAC were obtained from the following analysis: moisture (ASTM D 2867-09), volatile matter (ASTM D5832-98), apparent density (ASTM D 2854-96), adsorption capacity measured as iodine number (ASTM D 4607-94), point of zero charge (ASTM D 3838-80) and Surface Oxygenated Acidic Groups (SOAGs) by Boehm's method [33]. Results from this stage will be analyzed by using the analysis of variance (ANOVA) and response surface plots (RSPs) for a FFED 2^{4-1} [32] by using the Design Expert Software (version7.1.5) from Stat-Ease Inc., USA.

3. Results

3.1. Characteristics of the Guadua Amplexifolia species

The results of the proximal and lignocellulosic analyses performed on the bamboo species are shown in Table 2. Here, some results collected from the literature, as comparison, are also included.

As observed in Table 2, the *G. amplexifolia* bamboo has the typical composition present in most of the lignocellulosic materials used for production of activated carbons. The high content of volatile matter and low amount of ash suggests that the bamboo structure is appropriate to obtain activated carbon. Finally, the *G. amplexifolia* microhardness was 10.4 HV, at load of 1 N, which is ≈ 40% harder than common oaks [37].

3.2. Carbonization stage

Thermogram obtained from the Thermogravimetric analysis (TGA) of the raw *G. amplexifolia* bamboo, is presented in Fig. 1. The TG plot shows a first weight loss corresponding to the moisture elimination (≈5%) from heating the material from 25 to 150 °C. The second stage of 150–400 °C, which has the highest weight loss (56.14%), corresponds to primary carbonization or active pyrolysis, the result of elimination of volatile matters and tars. Based on the literature survey [21,27,36,38], this stage can be divided into two parts corresponding to the decomposition of hemicelluloses (180–270 °C) and celluloses (270–400 °C). The third stage starting at the 400–550 °C range indicates the decomposition of a structure with high stability [21]. Above 550 °C (passive pyrolysis), the weight loss was small indicating that the basic structure of the char has been formed.