Procedure to obtain activated carbons from Pecán nutshell

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ABSTRACT

In the present study, activated carbons were obtained from vegetable Pecán nutshell by physical activation with water vapor, for which an electric furnace and a steam generator were adapted to a tubular rotary pyrolysis reactor where the carbonization of the particles was carried out to proceed immediately to activation. The activation temperature was from 600 to 800 °C and the activation time was from 0.5 to 2.0 h. The activated carbons obtained were characterized by: specific surface area, pore size distribution, pH and moisture content. The obtained N_2 isotherms were adjusted to the Langmuir equation. The minimum specific surface area reached was 246 m^2/g and the maximum value was 542 m^2/g. The BJH model was used to analyze the results of pore distribution, observing a bimodal behavior where mesoporosity prevails and microporosity remains in second place. The pH varied from 6 to 13 and the moisture content was determined from 1.01 to 6.45%. The temperature and activation time for the largest specific area of 542 m^2 / g were 800 ° C and 2 h, with a pH of 13.

RESUMEN

En el presente trabajo se obtuvieron carbones activados a partir de desechos vegetales mediante activación física con vapor de agua, para lo cual fueron adaptados un horno eléctrico y un generador de vapor a un reactor tubular rotatorio de pirolisis donde se llevó a cabo la carbonización de las muestras para en seguida proceder a la activación. El desecho vegetal utilizado fue cáscara de nuez de Pecán de México. La temperatura de activación fue de 600 a 800 °C y el tiempo de activación fue de 0.5 a 2.0 horas. Se caracterizaron los carbones activados obtenidos mediante pruebas de: área específica, distribución de tamaño de poros, pH y contenido de humedad. Las isotermas obtenidas se ajustaron a la ecuación de Langmuir. El área específica mínima alcanzada fue de 246 m^2/g y el valor máximo fue de 542 m^2/g. Se empleó el modelo BJH para el análisis de los resultados de distribución de poros observando un comportamiento bimodal donde prevalece la mesoporosidad y quedando en segundo término la microporosidad. El pH varió de 6 a 13 y el contenido de humedad se determinó desde 1.01 a 6.45 %. La temperatura y tiempo de activación para la mayor área específica de 542 m^2/g fueron 800°C y 2 h y con un pH de 13.

1. INTRODUCTION

In this work, we study the procedure for the manufacture of activated carbon from the Pecan nut shell (Carya illinoensis Koch) that is grown in the states of Chihuahua and Coahuila Mexico, where the first is the first nut producer of the country, with an annual production of 80 413 Tons, being the first world place as a nut producer [1]. In 2014 the mexican production was 126 799 Tons of walnut which represents 20% more than the year 2013. It has a price of MX $ 55 000 per ton and the international market is 63% of the national production that is destined to the USA, with which around 370 million dollars are obtained annually and 1.8 Ton per hectare can be cultivated.

In the state of Coahuila, Mexico has 13 000 hectares of cultivation [2] and is the center of origin.

Other states of Mexico also contribute to national production such as the state of Durango, Nuevo León, Sonora, Hidalgo, Aguascalientes and the total was 76,627 Tons in 2010. As you can see, the raw material for the manufacture of activated carbon to process the shell is guaranteed.

To develop the production process of activated carbon from the Pecan shell, this work has been initiated, the development of research for the manufacturing process of activated carbon.

Of the existing processes [3], carbon produced by carbonization has a relatively small internal specific area for adsorption applications. To increase the specific area, the carbon can be activated by the action of oxidizing agents, such as water vapor, air or CO_2 at high temperatures, said activation is known as physical activation or thermal activation. Oxidizing gases more easily attack the oxidizable portions of the coal, resulting in the development of a porous structure and a large internal surface.

It is known [4] that activated carbons are carbonaceous materials whose structure and properties are more or less similar to the structure and properties of graphite, which is composed of planes formed of carbon atoms arranged in regular hexagons, similar to those of aromatic compounds. The distance between carbon atoms in a plane is 1.42 Å. The planes have a parallel arrangement whose distance from each other is 3.35 Å and this arrangement is the most common or typical, although in some graphites a certain fraction of the planes form a rhombohedral arrangement.

The structure of activated carbon is not ordered as well as the structure of graphite. Two types of structures have been observed by X-ray studies; the first type is composed of elementary crystallites, which are in two dimensions analogously to graphite, are composed of planes of carbon atoms arranged hexagonally. The structure differs from that of graphite in that the parallel planes are not perfectly oriented with respect to a common perpendicular axis, the angular

displacement of one plane with respect to another is randomly overlapping each other irregularly. This structure has been called "turbostractic structure".

The orientation between the elementary crystallites is completely random, their dimensions mainly depend on the carbonization temperature. These crystals usually have a length of 2-12 Å and width (or diameter if there is a circular section) of 20-23Å. From this it is believed that the crystallites are equivalent to 3 parallel planes of graphite, whose diameter is about 9 times the width of a carbon hexagon. The dimensions of elementary crystallites can increase with high temperature treatments.

The second type of structure is formed considering that the carbon hexagon cells have a messy cross-section, which is due to the deflection of the graphite planes. This structure is probably stabilized by hetero atoms, first of all by oxygen, as has been observed in carbons prepared from materials with a high oxygen content. It seems that a good number of carbons develop both types of structures.

In this work, we have designed, built and evaluated an installation consisting of a rotary kiln, a steam condenser and a steam generator to carry out the activation of carbon. We have evaluated the carbons by studying the effect of: the temperature 600 ° C, 700 ° C and 800 ° C, the activation time from 0.5 h to 2h, on the specific BET area and the texture, keeping the particle size constant between 0.8 at 2 mm and the constant steam flow. In addition, weight loss, pH and moisture percentage have been measured.

2. EXPERIMENTAL

2.1.- Materials

2.1.1. Pecan nut shell.

This shell came from the crops of the state of Coahuila, Mexico, which was cleaned, crushed in a hammer mill (Lasser-Mexico) and then sifted between the US Mesh sieves: 10 and 20, this means that the particle sizes varied between 0.8 to 2 mm.

2.1.2. Installation to obtain activated carbon

The installation consisted of the following elements (Figure 1 (a) and Figure 1 (b)): Steam generator, coupling of the pipe with steam to the pyrolysis reactor, rotating supports of the tube-reactor, furnace, condenser, collector of vapors and condensed liquids.
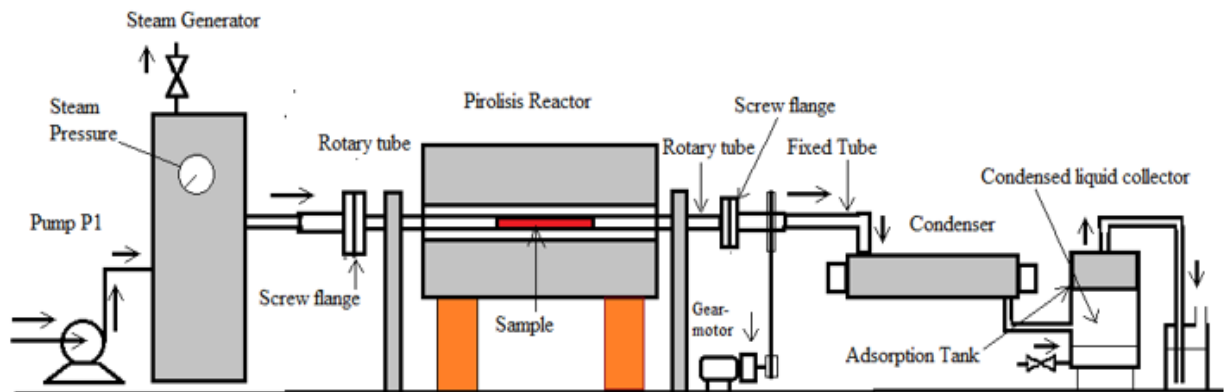

Figure 1(a). Pyrolysis reactor to produce activated carbon from Pecan nut shell using steam vapor.
Figure 1(a). Reactor de pirolisis para producir carbón activado a partir de cascara de nuez de Pecan usando vapor de agua.

Figure 1(b) Pyrolysis reactor to produce activated carbon from Pecan nut shell.

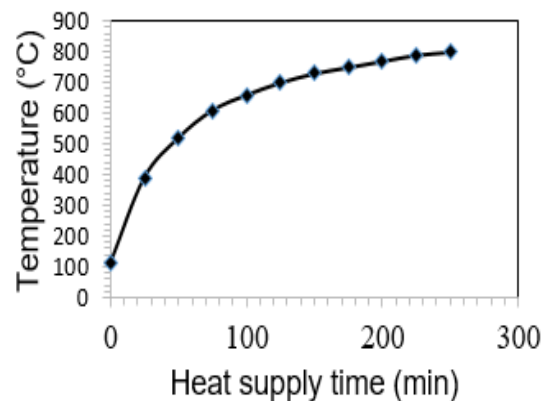**Figure 1(b)** Reactor de pirólisis para producer carbon activado a partir de cascara de nuez.

Figure 2. Temperature as a function of the time of power supply to the pyrolytic reactor.
Figure 2. Temperatura en función del tiempo de suministro de energía al reactor pirolítico.

2.1.3. Pyrolysis reactor

The reactor was formed by 4 electrical resistance connected in series-parallel to reach 800 ° C. The voltage was 120 volts, with a maximum current of 30 amp. The power reached in the oven was 1097 W without opening the fuses to reach the maximum temperature. The oven had to be lined with two layers of additional fiberglass 2 cm thick each. The temperature profiles as a function of the heat energy supply time are shown in Figure 2. As can be seen in about 4 hours, the temperature of 800 ° C can be reached.

The pyrolysis tube was 1.5 inches in diameter and 40 cm long in 316 stainless steel. The temperature control was West 2800 brand aided by two relays or 110 volt contactors.

2.1.4. Steam generator

A Susman brand electric steam generator (Mod. MBA9) was used with a steam flow of 27 lb of steam per hour and a maximum pressure of 90 Psig. A pump with a pressure of at least 38 psig was required for its operation. Pumps F&Q brand (Mod. HT100) with an expense of 30 L / min, Power of 250 W to be able to raise the water to 30 m.

2.1.5. Condenser

A stainless steel, shell-type condenser and tubes 55 cm long and 11.5 cm in diameter with 48 inner tubes of 8 mm in diameter were used. The condenser was previously washed with a 10% acetic acid solution. The coolant was ice water and with it the temperature of the condensate was less than 40 ° C.

2.1.6. Liquid separator and adsorber

A condensate receiving tank was constructed of 8.5 by 12 inch stainless steel. each. The upper part of the tank was filled with the same activated carbon to adsorb the pyrolysis gases with water vapor.

2.2.- Methods

The effect of treatment temperature and residence time on a steam flow was studied. The temperatures studied were 600, 700 and 800 ° C while the times were: 0.5, 1.0, 1.5 and 2.0 h.

At first it was considered to study the effect of the particle size of solid samples, however, according to the literature, no major changes are observed [5,6]. The sizes studied pass the 10 mesh and are retained in the 20 mesh and the nut shell mass was maintained at 50 g.

The analyzes that were made were humidity according to ASTM D 2867-91 [7] and pH determination according to ASTM D [8] 3838-80 (reapproved 1990).

The BET area measurements were carried out on an ASAP 2400 analyzer (Micromerithics) using as adsorbate N_2 at 77 K. Pretreatment was given at 350 ° C at a vacuum of 1×10^{-3} torr for 18 h. To determine the pore size distribution, the BJH method was applied [9].

3.- RESULTS AND DISCUSSION

3.1.- Reaction time effect

As the contact time between the water vapor and the nut shell increases, the BET area increases to 1 h (Figure 3), especially when temperatures are high (700 and 800°C). However, when the treatment was at 600°C, the area decreases. This fact is related to the formation of more volatile compounds and micropore formation during the time from 0 to 1h.

At higher times no major attack or pore formation that could increase the area is experienced, rather it remains constant and at 600°C the energy to carry out pyrolysis is not enough. Therefore, the weight loss observed (Figure 4) is related to the above, since the greatest weight loss corresponds to the treatment at 800 ° C and a longer residence time for 700 and 800 ° C, however for in the case of 600 ° C no significant weight loss is observed.
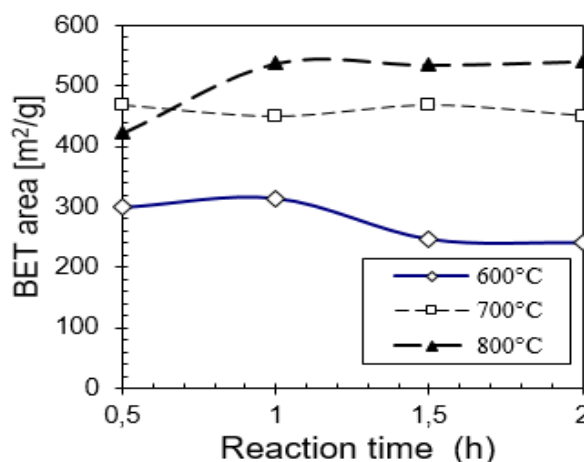

Figure 3. Effect of reaction time over the BET area during the pyrolysis of the Pecan nut shell at three reaction temperatures.
Figura 3. Efecto del tiempo de reaccion sobre el área BET durante la pirolisis de la cascara de nuez de Pecan a 3 temperaturas.
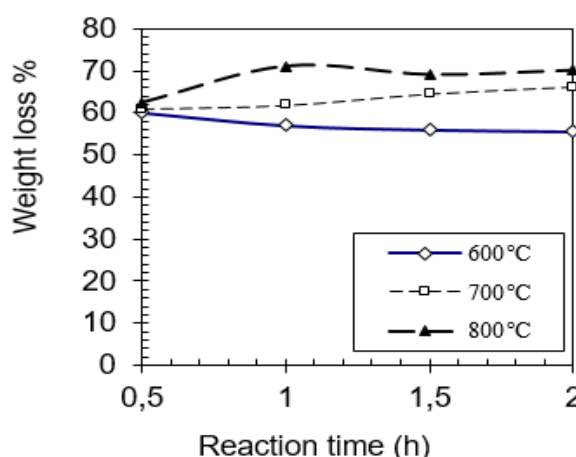

Figure 4. Effect of reaction time on weight loss during pyrolysis of the Pecan nut shell at three reaction temperatures.
Figura 4. Efecto del tiempo de reaccion sobre la pérdida de peso durante la pirolisis de la cascara de nuez de Pecan.

The shape of the BET area curve, from 0 to 1 h, coincides with the case in which the pistachio shell is activated in N_2 or with CO_2 [10] although in these cases the area is almost double. In general, larger average pore diameters were obtained (Figure 5) as

the treatment temperature increased and almost no variation was observed depending on the residence time, this is explainable since it is known that from the micropore formation they are generated the mesopores [10].
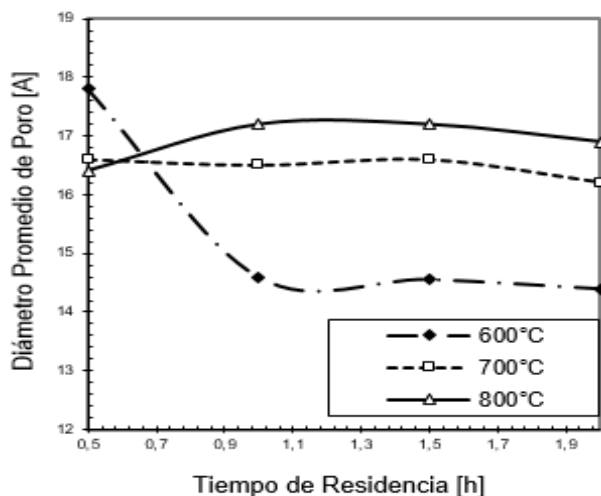

Figure 5. Average pore diameter as a function of reaction time.
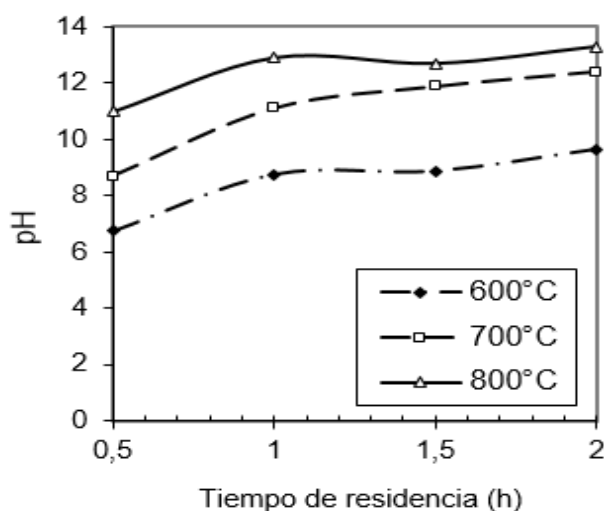**Figura 5.** Diámetro de poro promedio como una función del tiempo de reaccion.

Figure 6. pH as a function of the reaction time at three temperatures.
Figura 6. pH como una función del tiempo de reaccion.

Although this type of nutshell showed that it is "harder" than other types of shells and wood sawdust [11].

3.2. Effect of Reaction temperature on the pH

In the case of pH analyzes, carbon basicity was observed (Figure 6) which increases as the treatment temperature and residence time increases. This phenomenon could be related to the presence of –OH groups, aromatic groups (-C = C-) and corboxylates C = O, C-O that have been found by infrared spectroscopy [10]. In the case of sawdust the weight loss was 88% while for this shell it was 70% which shows that this shell contains a higher content of lignocellulosic compounds difficult to react and that the high BET area values of sawdust (1500 m^2/g) could be related to the lower structural "hardness" of the precursor.

CONCLUSIONS

When the reaction or pyrolysis time increases, during the steam activation of the Pecan nut shell, the BET area increases. It was observed that at times greater than 1 h they do not improve said area.

A greater variation was found in the BET area, pore diameter, weight loss and pH due to the temperature increase from 600 to 800 ° C.

BET areas of no greater than 542 m2 / g were obtained with a high degree of mesoporosity, pH values greater than 7 and weight losses greater than 50% were observed.

Given the greater "hardness" of this type of shell compared to wood sawdust, lower weight losses (20% less) were found, but also less area.

The increase in the pH of the carbon obtained could be related to the presence of surface groups of the type –OH and carboxylates

The best operating conditions to obtain a carbon by physical activation with steam for this shell are: Activation temperature 800 ° C and reaction time of 1h, which will give us a weight loss of up to 70%.

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