



Research paper

Influence of the biomass components on the pore formation of activated carbon

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ABSTRACT

Uncontrolled management of agricultural wastes have strongly contributed to the increase of greenhouse emissions and pollution. On the other hand, these residues can be used as a sustainable source for the production of activated carbon. Currently, biomasses rich in lignin are the most widely used, due to the high yields and large surface areas attainable. The aim of this study is to understand the influence of each biomass component on activated carbon properties. Alpha-cellulose, xylan, kraft lignin, and mixtures with different ratios of the single components were used as model substances to represent biomass. These materials were pyrolyzed and subsequently activated with KOH to expand the surface area. TGA results showed no interaction between components during pyrolysis but there was a strong influence of the composition of the mixture on the activated carbon properties due to the different thermal stabilities of each char. The activated carbon with the largest apparent surface area was obtained from cellulose with 2220 m² g⁻¹ and pure xylan showed the lowest with 1950 m² g⁻¹. T-plot calculations showed that more than 90% of the surface area was composed by micropores. To understand the microporosity, CO₂ isotherms were measured. The surface areas calculated were lower but followed the same trend as those obtained from the isotherms with N₂.

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1. Introduction

With attainably high surface areas and porosity volumes, lignin or lignin-rich biomass presents a highly interesting feedstock-material in producing activated. Additionally, woody biomass yields a considerably higher amount of product compared to grassy biomasses [1]. This leads to the assumption that not only the presence of lignin is important, but also the whole composition or the structure needs to be considered. However, whether lignin has the most appropriate structure for porosity development, especially microporosity, is a question which still remains. Additionally, the influence of the other biomass components (cellulose and hemicellulose) on porosity formation requires a more thorough research. The main scope of this work is to understand how biomass cell-wall components affect surface area and porosity formation.

The first important criterion is concerned with steam activation

of carbon materials. Cagnon et al. [2] studied the contributions of biomass compounds to the porosity of steam activated carbons using model compounds and biomasses with different proportions of hemicellulose, cellulose and lignin. They identified that only the model compounds and those biomasses with high lignin contents (coconut shell, olive stones treated with sulfuric acid and soft wood) were able to form a fairly high micropore volume during the pyrolysis stage. Biomass with a high percentage of extractives showed no evidence of microporosity at all. Nonetheless, after steam activation, most biomasses had developed a moderate microporous structure, whereas those with high lignin content had the highest micropore volumes. The only exception was apple pulp, which showed the highest micropore volumes despite its low lignin content.

The findings of Cagnon et al. [2] are consistent with several studies conducted with palm oil stones or coconut shells. Guo et al. [3,4] pyrolyzed palm oil stones and obtained relatively high surface areas (approximately 300 m² g⁻¹). Additionally, the type I N₂ isotherms of all the chars indicated the presence of a microporous structure, which corresponded to approximately 60% of the whole surface. The same group [5] activated these palm oil stones with

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CO₂ after a previous impregnation with KOH and H₂SO₄. They again found a microporous structure by means of the N₂ isotherm, and in both cases the microporous volume had increased proportionally to the impregnation ratio. In a different work [6], palm shell and coconut shell with lignin contents of 53.4% and 30.1%, respectively, were pyrolyzed at 850 °C and attained surface areas of 260 m² g⁻¹ and 183 m² g⁻¹. By subsequently activating these chars at 850 °C with CO₂, coconut shell had exhibited a faster activation rate in comparison to palm shell, due to its higher cellulose and hemicellulose content.

It is well known that coconut shell and wood are the most widespread natural precursors for the production of activated carbon, however successful trials have been conducted with wheat straw [7,8], rice husks and rice straw [9–11], sugar beet bagasse and pulp [12,13], as well as with sugarcane bagasse [14,15]. These agricultural residues are similar in that their lignin content is considerably lower than that of nut shells, fruit stones, or wood. Another characteristic of these biomasses is the low surface areas and porosity that develop during the pyrolysis process. Nanda et al. [16] studied Timothy grass residue and wheat straw residue for the production of biochar for soil amending. They pyrolyzed the substrates at 600 °C for 4 h to obtain surface areas and total pore volumes smaller than 5 m² g⁻¹ and 7 mm³ g⁻¹, respectively. Rice straw biochar was carbonized by Hammes et al. [17] in a staged pyrolysis process with a maximum temperature of 450 °C and residence time of 5 h to obtain a surface area of 5.9 m² g⁻¹. Bornemann et al. [18] pyrolyzed Phalaris grass at different temperatures and determined that surface area increased with temperature. Independent of the carbonization temperature, the charcoals did not develop a measurable microporosity. The low surface areas shown for grassy biomasses like rice or wheat straw are usually related to their inherently high ash content [19]. Nevertheless, high surface areas can be achieved by leaching out the minerals as shown by Alvarez et al. [20]. They obtained a rice husk char with a surface area of 487 m² g⁻¹ and activated carbons with surface areas larger than 800 m² g⁻¹. Guo et al. [21] also leached the minerals from rice husk and used the organic residues to chemically produce activated carbon with KOH, obtaining surface areas larger than 1000 m² g⁻¹. Their finding supports the idea that minerals in biomass may hinder the surface area development. Even so, the presence of an effect from high hemicellulose and cellulose contents in grassy biomasses should not be overlooked.

The question remains as to what extent do the components of biomass play a role during activation? The reaction steps during the activation of biomass with H₃PO₄ have been studied to some extent. Jagtoyen and Derbyshire [22] proposed that H₃PO₄ stabilizes cellulose and inhibits the formation of levoglucosan through a mechanism during which phosphate esters form by the phosphorylation of cellulose. Guo et al. [23] examined the influence of temperature, impregnation ratio, and of the precursor on the formation and type of surface groups that can be formed during the activation of biomass with H₃PO₄ by means of Boehm titration. This technique helps to quantify acid surface groups by exposing the activated carbon to three different basic solutions: NaOH is the strongest base and neutralizes all Brønsted acids (phenols, lactonic groups and carboxylic acids), Na₂CO₃ neutralizes lactonic and carboxylic groups, and NaHCO₃ reacts only with carboxylic acids [24,25]. The surface group concentrations are quantified from the difference between the base consumption. In the study by Guo et al. [23], cellulose, xylan and kraft lignin were used as model compounds for biomass. They observed that xylan and cellulose were significantly more reactive towards H₃PO₄ than lignin, therefore they presented a higher volume of mesopores. They determined as well that the surface groups are either temperature-sensitive, formed due to the low temperature hydrolysis of the raw

precursors in acidic surroundings, or temperature-insensitive, which are phosphorous containing compounds formed after the reaction of the raw material and H₃PO₄. Furthermore, they also concluded that all the carbons contained the same type of functional groups, however the abundance of each group type depended on the precursor. Acidic groups, especially strong and weak acidic groups, were present in higher concentrations in cellulose activated carbon than in kraft lignin.

Due to the formation of highly developed porous structures, many studies concentrate on activation with alkali compounds, especially with KOH. The process begins as a solid-solid reaction, followed by a liquid-solid reaction at higher temperatures. During the heating stage, potassium penetrates the carbon layers creating a lamellar structure of carbon-potassium-carbon layers (intercalation) [26]. Lillo-Ródenas et al. [27–29] proposed a mechanism for the interaction between KOH and carbon (Equation (1)), however this reaction cannot be thermodynamically proven at low temperatures. On the other hand, at temperatures higher than 570 °C, the Gibbs energy becomes negative. Especially during activation processes under nitrogen, hydrogen is diluted dropping its partial pressure to less than 0.1 MPa, therefore the Gibbs energy can become negative at even lower temperatures [30]. Nevertheless, it is clear that the alkali salts react directly with the carbon that results from the carbonization process and not with the substrate [31]. This explains why it is more effective to conduct a two-step (carbonization followed by the activation) rather than a one-step activation.



Khezami et al. [32] studied the feasibility of producing activated carbon from biomass model compounds and obtained adsorbents that could remove pollutants from aqueous as well as from gaseous sources. They measured high surface areas, especially for carbonized xylan, followed by wood, cellulose and finally lignin. It must be highlighted that biomasses with high lignin content are the most promising precursors for the production of activated carbon (e.g. coconut shell) and the reason is not only the high yields, but also the large surface area that is attainable. The results presented by the group of Khezami show the complete opposite: in this case lignin had developed the poorest surface area compared to the other biomass main components. The authors of the work presented here believe that the reason is the performance of the carbonization (first) step previous to the actual chemical activation with KOH. The precursor materials were carbonized at 300 °C, which is very low temperature to allow the formation of a fully carbonized structure. Xylan and cellulose decompose in a narrow temperature range of 220–315 °C and 315–400 °C, respectively. On the other hand, lignin decomposes slowly and over a wide temperature range between 100 and 900 °C. At 300 °C, only xylan undergoes a relatively complete decomposition and therefore has a stable and carbon-rich structure [33].

The second step of the activation conducted by Khezami et al. [32] occurred at 700 °C in the presence of KOH, however this activation wasn't solely an activation but also a further carbonization of undecomposed cellulose and lignin. This "mixed" set of reactions may have affected the pore development of the activated carbons produced by this group. By taking this into account, the aim of this present research was to study the biomass components with complete carbonization (T = 600 °C) prior to activation. This temperature was not high enough to allow a full decomposition of the kraft lignin, however this did not prevent the formation of a wide surface area as well as a highly microporous structure.

With regards to climate change, increasing greenhouse emissions, and the pollution caused by inadequate treatment of

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