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Hydrothermal Carbonization of *Acrocomia Aculeata* for the Production of Hydrochar and Activated Carbon

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Macaúba palm (*Acrocomia aculeata* (Jacq.) Loddiges ex Mart) is a South American palm species used mainly as food and oil crop. The oil is extracted from the seed and the pulp, leaving the epicarp, endocarp, and pressed cakes as residues. The aim of this study was to explore possible applications for these residues after a carbonization process in a closed system and high pressures (hydrothermal carbonization). The different parts of the macaúba fruit as well as the pressed cakes were submitted to a 2-step hydrothermal carbonization process to obtain a carbon-rich product (hydrochar HC) and their potential as fuel and as precursor for activated carbon (AC) was studied. The HC obtained from all raw materials showed a carbon content increase ranging between 25 - 120% due to high oxygen loss. This was reflected by a calorific value increase ranging from 30% for the endocarp to up to 50% for the biomasses with high oil content and pressed cakes. The H, N and S concentrations varied slightly during the carbonization process. Based on the H/C- and O/C- ratios, the obtained HCs have a close resemblance to lignite, however the ash content is lower and the energy content higher. The surface area of the ACs increased by a factor of more than 30 as compared to the HCs. Besides its value as a fuel source, the possibility of making AC using HC as precursor was also explored. To achieve this, the HCs were submitted to a chemical activation process with KOH and characterized by means of BET analysis.

Introduction

Acrocomia aculeata (**macaúba Palm)** is a wild species commonly found in parts of South America, but is not yet cultivated. The plant produces small fruits with orange pulp and a very hard pit, which are the basis for a large variety of products that include food, fuel and cosmetics. In the course of processing, many residues accumulate including epicarp, endocarp, and press cakes. Considering carbonization processes to increase the heating value or activation processes to increase the surface area can bring additional value to the residues.

Biomass carbonization can take place under inert atmospheres (pyrolysis) or in a closed vessel with an aqueous medium (hydrothermal carbonization HTC). Both processes are followed by a carbon content and surface area increase.

The typical temperature range for HTC is between 180°C and 220°C with corresponding pressures between 20 and 40 bar, depending on water input. Under these conditions, biomass undergoes a decomposition process promoted by water as reaction medium. At elevated

temperatures and pressures, the water solubility of certain compounds increases as well as the production of ions, favouring reactions that are typically catalysed by acids (Kruse, Funke, & Titirici, 2013). The products consist mainly of very little gas and a solid fraction as well as water with soluble organic compounds (Funke & Ziegler, 2010).

ACs are carbon-rich materials with large surface areas ranging between 600 – 1000 m^2/g mostly used in water purification or air filters. Other applications have been found in medicine as adsorbant of toxins, in chemistry as catalyst or for sound absorption. There are two main paths to produce AC: chemical or physical activation. The first one uses alkali or acidic substances that react with the precursor's carbonaceous structure, enhancing the pore formation and, therfore, the surface area. The second one can be regarded as an incomplete gasification under water-steam or carbon dioxide (Marsh & Rodríguez-Reinoso, 2006).

Material and Methods

Six different derivatives of the macaúba fruit (epicarp, pulp, pressed pulp, endocarp, seed and pressed seed) were hydrothermally treated at 160°C for one hour (pre-treatment), followed by 5 hours at 220°C and 40 bar.

After filtering, washing, and drying, the HCs of the pressed cakes, the epicarp, and the endocarp were activated at an impregnation ratio of 4:1 KOH to precursor carbon under a nitrogen atmosphere at 450°C for 1 h.

The parent materials and HCs were characterized by means of ultimate and proximate analysis according to the DIN norms 51718, 51719, 51720, 51732 and 51900. The surface area was determined for the HCs and ACs based on the Brunauer-Emmett-Teller method (BET). The characterization of the parent materials is shown in Figures 1 and 2.

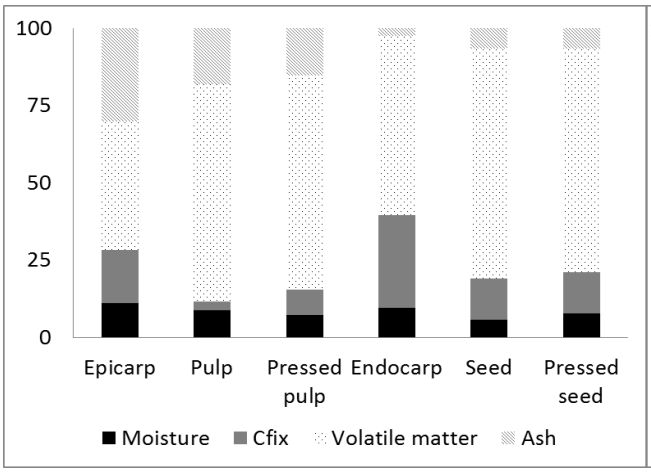

Figure 1: proximate analysis of the feedstock

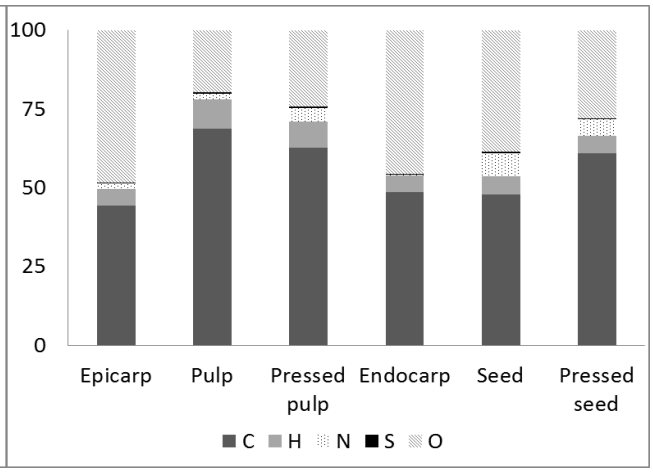

Figure 2: Elementary composition of the feedstock

Results and Discussion

The most relevant results obtained from this study were the energy content increase of the feedstock after HTC and the significant enlargement of the surface area after the chemical activation process, especially for the pressed pulp.

Figure 3 describes the decrease of the H/C- and O/C-ratios from the materials before and after HTC. The decrease of H and O is due to hemicellulose hydrolysis as well as cellulose and lignin alterations. During HTC, the ether bonds of the hemicellulose are the most reactive and a

depolymerisation to oligomers and monomers takes place (Garrote, Domínguez, & Parajó, 1999).

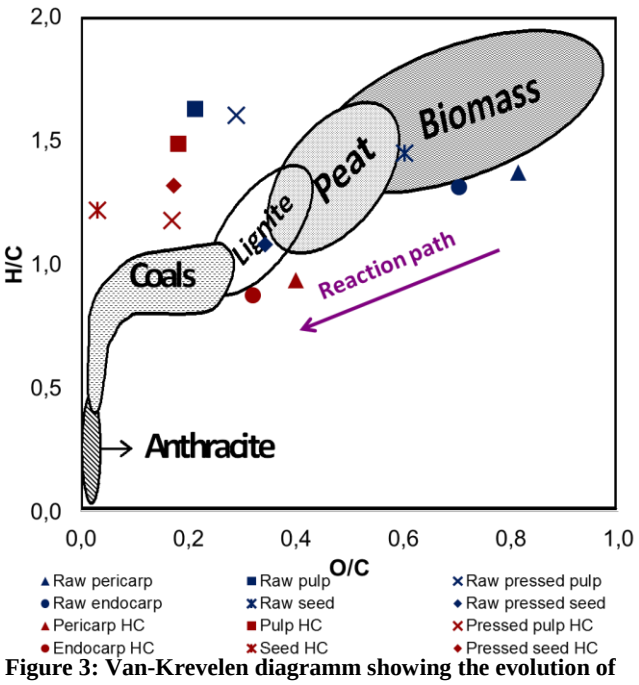

Figure 3: Van-Krevelen diagramm showing the evolution of the feedstock to HC after HTC.

In Figure 4 it can also be seen that, the amount moisture content of the HC is significantly reduced as compared to the parent material. This is also attributed to the loss of –OH groups, which are responsible for the hygroscopic properties of biomass.

The ash content of the parent material also decreased considerably, especially for the pericarp, since the mineral matter partially dissolves in water. This works in favour of using the HC in gasification or combustion processes, since corrosion, slagging, and clogging problems can be avoided or diminished. Additionally, if the purpose of HC is to be used as feedstock for the production of AC, a decrease of the mineral matter is also beneficial, since it enhances the surface area enlargement.

Changes of the biomass structure lead to an increase of the C-content and, therefore, to an increase of the heating value (Figure 5). During HTC, the molecular structure of the parent materials is rearranged and a graphene-like structure is created, although not as markedly as during pyrolysis. This more stable and resistant structure contains C-C bonds, which have more energy than C-H or C-O bonds (Abdullah & Wu, 2009).

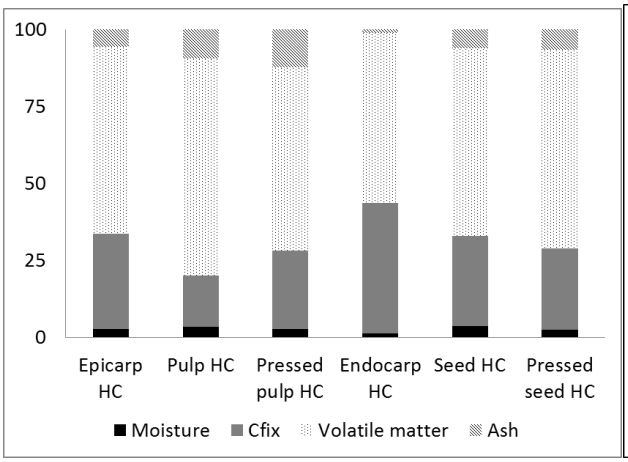

Figure 4: Proximate analysis of the HCs.

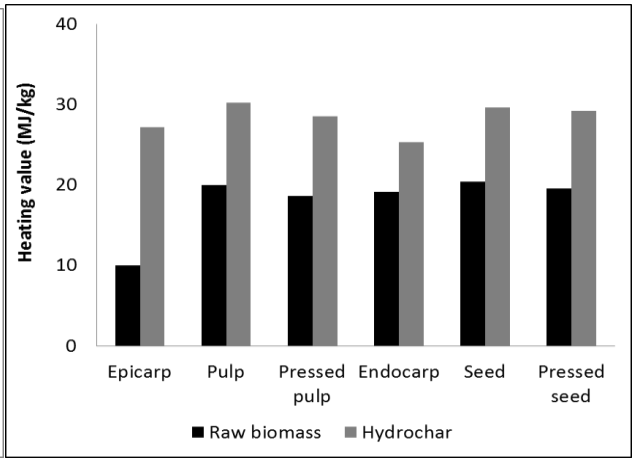

Figure 5: Comparison of the heating values between the parent materials and the HCs.

Some of the HC's were also tested as possible feedstock for the production of AC by means of chemical activation with KOH. The main result was a dramatic increase of the surface area, due to the reaction of the carbonaceous structure with KOH and the release of volatile matter during the activation process. The biomass decomposition during HTC is incomplete, since some cellulose and, especially lignin, are structurally modified but not strongly degraded nor

depolymerized like hemicellulose (Garrote, Domínguez, & Parajó, 1999). These components decompose during the activation process, resulting in higher surface area of the HC.

The pressed pulp normally has a high hemicellulose and cellulose content, which is probably why it presented the highest surface area (803,7 m^2/g). The endocarp and the pericarp, on the other hand, have a higher lignin compositions that didn't decompose during HTC, which would explain the lower surface areas. The pressed seed has a similar proximate analysis to the pericarp and the ash content of both HCs is almost the same (6,7% and 6,8% respectively). Mineral compounds clog the meso- and micropores, decreasing the surface area.

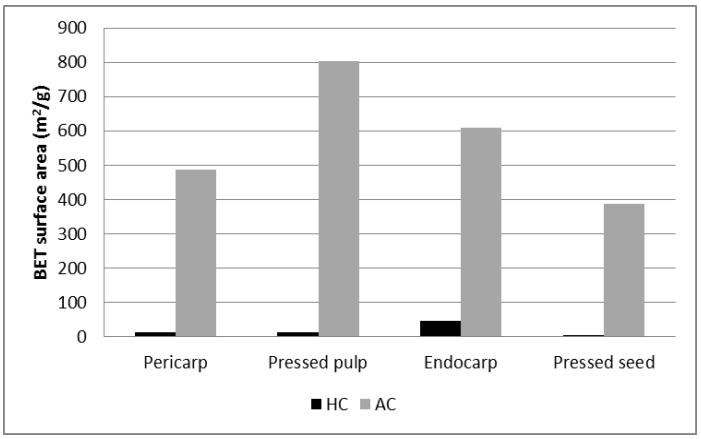

Figure 6: BET surface area of the HCs and ACs.

Conclusions and Outlook

Processing the residues of the oil extraction of the macaúba nut by means of HTC resulted in a lignite-like carbonaceous material, with high potential to be used as fuel during combustion or gasification processes. It does not only have a higher energetic content than the parent material, but also less ash content. Additionally, the reduction of the moisture content improves the storability of the material.

The HC proved to be also a suitable precursor for the production of AC. The pressed pulp showed the best results, due to its high hemicellulose content, followed by the endocarp, the pericarp and the pressed seed. The surface area evolution of these materials could have been hindered by the relative high lignin and ash contents.

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