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Production of Biochar and Chemical Products from Banana and Coffee residues after Acid Hydrolysis

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Abstract The use of the residues from renewable feedstock, besides the production of power and heat, but also for the generation of chemicals products, has become a priority. Superior plants have considerable potential as carbohydrate, aryl and fat acids sources. However, the separation of the main constituents of the samples is necessary for several purposes in the biorefinery concept. The acid hydrolysis is a very promising technology, however it was detected carbohydrates (14-17%) in the residues after the conventional acid hydrolysis of some uncommon biomasses (e.g. coffee husk and banana stem and stalk), indicating the adjustment need of the hydrolysis conditions for different biomasses. On the other hand, it was showed that, by pyrolysis, it is possible to obtain, from the solid residue after acid hydrolysis: pyrogenic carbon (charcoal: 45-65%) for agriculture use; and valuable chemicals in the biooil fraction, such as lignin monomers (32.6-56.4%) and fat acids (30-52.5%).

Introduction

Significant amounts of residues are generated by the banana and coffee production, among of which are coffee husks and stem and stalk of banana (1). Methods such as acid hydrolysis and pyrolysis can be used for converting these feedstocks into biofuels and bioproducts (2).

Acid hydrolysis is a promising technology, which involves the hydrolysis of polysaccharides to their monomeric constituents. In this process, the efficiency system achieves yields of 70–80% to convert hexoses and pentoses into valuable chemicals, with 30% being converted to partially carbonized char (3). Pyrolysis is a process for production of fuel gases, liquids and charcoal, that can be used directly and as an intermediate pretreatment step to convert biomass into a higher energy content biofuel (4) and another bioproducts and biochar (5). After the acid hydrolysis, remains a solid residual (AHR) mainly consisting of lignin. This lignin can be pyrolysed providing high quantities of char and biooil. The last is composed of a very complex mixture of oxygenated hydrocarbons, be considered a promising substitute for various fuel petroleum (4). Already the solid residue (carbonized biomass, pyrogenic C - C_{py}) can be used for production of pellets or for agricultural use (biochar), providing numerous benefits, such as: sequester of carbon; soil conditioner; increasing agricultural productivity; suppression of methane emissions; reducing the need for fertilizers and leaching of nutrients (5). So the combination of these processes can be regarded in the biorefinery concept, where the product of a process becomes the raw material of the next process. Analytical pyrolysis combined with gas chromatography separation and mass spectrometry

(Py-GC/MS) provides a simple and reliable characterization of the components originated from lignocellulosic biomass (6), while solid state Carbon Nuclear Magnetic Resonance Spectroscopy (¹³C NMR) is a powerful technique for the characterization of the solid residues (2).

Experimental

Coffee (*Coffea arabica*) husks and banana (*Musa spp.*) stem and stalk were harvested in Brazil. The samples were chipped, milled and sieved (180–850 µm) and then submitted to proximate analysis and extractives removed (NREL/TP-510-42619). The acid hydrolysis was carried out in two-stages with sulfuric acid. In the first step (water bath, 60 min, 30 °C), sulphuric acid 72% was used. In the second step (autoclave, 60 min, 120 °C), a dilution take the solution acid to 4%. After the last step, the hydrolysates were filtered. The residual solids remaining were dried and used for subsequent pyrolysis process. In the hydrolysate were measured the lignin acid soluble and carbohydrates.

The AHR was methylated with tetramethyl ammonium hydroxide and pyrolysed in a Pyrex tubular reactor at 450 °C for 30 min. The products released by pyrolysis were continuously transferred by a helium flow (20 mL min⁻¹) into two successive chloroform (50 mL) traps kept in ice/salt baths. The chloroform solutions were concentrated by rotoevaporation under reduced pressure. The residue was redissolved in 1 mL of chloroform and transferred to a glass vial for GC/MS analysis.

The GC separations and MS were carried out according (7) and solid-state ¹³C NMR spectra according (2).

Results and Discussion

¹³C NMR of the AHR: [Figure 1] The ¹³C NMR spectra of the AHR showed an important decrease of the carbohydrates signals (O-Alkyl and di-O-Alkyl), however, the hydrolysis was not so efficient, since it is possible to detect carbohydrate signals in the residue after the hydrolysis, accounting for 14, 17 and 16% of ¹³C NMR signal for husk, stalk and stem, respectively.

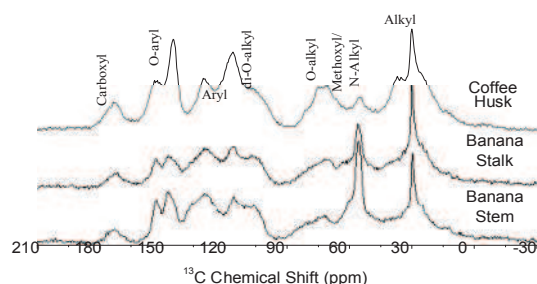


Figure 1. ¹³C NMR spectra of the Acid Hydrolysis Residues from different biomass.

Despite the fact that the extractive was tentatively removed from the samples, the alkyl region, in association with the carboxyl one, indicate the presence of fat acids: 33% of ¹³C NMR signal for husk; 36% for stalk; and 29% for stem. But the major constituent is lignin (sum of lignin monomers main signals: Methoxyl, Aryl and O-Aryl), being coffee 49%; stalk 42% and stem the richest with 52%.

Py-GC/MS of the AHR: [Figure 2] The main single pyrolytic products of AHR were long chain fat acids: palmitic acid for banana stem and stalk (20 and 26% of the pyrolytic products, respectively) and oleic acid (33%) for coffee husk, these high content of aliphatic acids was also observed in ¹³C NMR spectra. The palmitic acid (C16) and oleic acid (C18:1) can be derived from microorganisms or hydroxy acids from cutin and/or suberin (7).

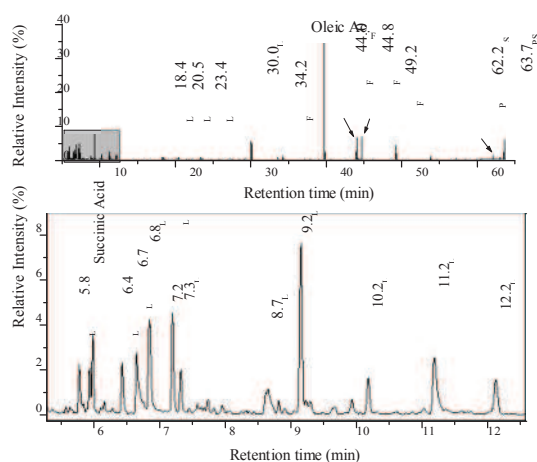


Figure 2. Gas chromatogram of the Acid Hydrolysis Residues from coffee husk. The gray square in the top graphic is the zoom area (Lignin monomers, except when indicated) showed in the bottom. Retention time index: L: Lignin monomers; F: Fat Acids; PS: Phytosterols.

However, after the sum of all the pyrolytic products from the same class of compounds (e.g.: lignin, fat acids and phytosterols), the main compounds of banana stem was lignin (56.4%), that corroborate the ¹³C NMR result, followed by fat acids (30%) and phytosterols (12.1%), while for banana stalk, fat acids accounted by 45.1% and lignin and phytosterols by 39.6 and 11.6%, respectively. The coffee husk, by its turn, showed the simplest chromatogram, with only 25 compounds those concentration was higher than 1%, against 31 compounds for stalk and 35 for stem, and showed the highest concentration of fat acids (52.5%) followed by lignin (32.6%) and phytosterols (11.1%). Several of these compounds are valuable chemicals (4,8). An interesting compounds found in coffee husk and banana stalk was succinic acid (2 and 1.3%, respectively), probably from the fruit fermentation during the coffee drying and fermentation of the wet banana stalk left in the field after the harvest.

Although the Py-GC/MS is not quantitative, it is found a general agreement among the results of ¹³C NMR and Py-GC/MS, except for carbohydrates, in general underestimated by Py-GC/MS (7).

¹³C NMR of the C_{py}: The further slow pyrolysis (450 °C during 30 min) of the AHR results in a strong simplification of the spectrum, remaining just polycondensed Aryl groups (symmetrical peak at 128 ppm) with a small amount of O-Aryl residues (153 ppm), probably phenolic C, and also small amount of aliphatic C (0-50 ppm). The pyrolysis of all tested biomass (banana stalk and stem and coffee husk) resulted in very similar spectra, indicating that the employed pyrolysis was very effective to carbonisate the samples (data not showed). The pyrolysis at higher temperatures resulted in a loss of the O-aryl signal and also increased the aromatic ring polycondensation, resulting in a graphene structure with a very high anisotropy and low electric resistance, since the ¹³C signal result undetectable (data not showed).

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