Pyrolysis of Banana and Coffee Residues after Acid Hydrolysis

Magale Karine Diel Rambo[1*], Etelvino Henrique Novotny[2], Luciano Pasqualoto Canellas[3], Natália de Oliveira Aguiar[3], Rubens Auccaise[4] and Michele Cristiane Diel Rambo[5]

1. Department of Chemistry, UFT (University of Tocantins), Araguaína 77838-824, Brazil

2. National Soil Research Center, Embrapa, Rio de Janeiro 22460-000, Brazil

3. NUDIBA (Nucleus for the Development of Biological Fertilizers in Agriculture), UENF (Darcy Ribeiro North Fluminense State University), Campos dos Goytacazes 28013-602, Brazil

4. Department of Physics, UEPG (State University of Ponta Grossa), Ponta Grossa 84030-900, Brazil

5. Federal Institute of Education, IFTO (Science and Technology of Tocantins), Palmas 77020-450, Brazil

Abstract: The use of the residues from renewable feedstock, besides the production of fuels, but also for the generation of other chemicals products, has become a priority. Superior plants have considerable potential as carbohydrate, aryl and fatty acids sources. However, the separation of the main constituents of the samples is necessary for several purposes in the biorefinery concept. The acid hydrolysis and pyrolysis processes are very promising technology, however, some adjustments in the conditions of pyrolysis are needed for different biomasses since carbohydrates were detected (14%-17%) in the residues after the conventional acid hydrolysis of these uncommon biomasses (coffee husk and banana stem and stalk). 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 with a yield of 48.5%-52.7%) for agriculture use (biochar) and valuable chemicals in the pyrolysis oil biooil fraction (that accounted by 26.4%-29.0%, free of water), such as lignin monomers (32.6%-56.4% of the bio-oil) and fatty acids (30%-52.5%).

Key words: Lignocellulosic biomass, biorefinery, acid hydrolysis, analytical pyrolysis, ^{13}C NMR (nuclear magnetic resonance).

1. Introduction

Significant amounts of wastes are generated annually in the world by the banana (95.6 Tg (teragram)) and coffee industry (7.8 Tg), including stem and stalk of banana and coffee husks [1]. Methods such as acid hydrolysis and pyrolysis can be used for converting these feedstocks into bio-fuels and bioproducts [2-6].

Acid hydrolysis is a very promising technology, which involves the hydrolysis of polysaccharides to their monomeric constituents. In this process, the efficiency system achieves hexoses recovery of 70%-80%, that are converted into valuable chemicals, with 30% being converted to partially carbonized char

(biochar), while the mass yield from pentoses sugars is also approximately 70%, with the remainder being incorporated in the biofine char [7].

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 solid biomass into a higher energy content biofuel [3].

After the acid hydrolysis, about 30% of mass remains as solid residual mainly consisting of lignin [8]. This lignin can be pyrolysed, providing high quantities of char and bio-oil [2]. The last is a very complex mixture of oxygenated hydrocarbons, considered as a promising substitute for various fuel petroleum, such as fuel oil and phenol [3, 9, 10]. Several classes of chemical compounds are present in the pyrolytic biooil such as acids, alcohols, carbonyl compounds, esters, furans, lactones phenols and

*Corresponding author: Magale Karine Diel Rambo, Ph.D., research fields: lignocellulosic residues, biorefinery and chemometrics. E-mail: magalerambo@mail.uft.edu.br.

derivations of phenol, and a small percentage of polyaromatic hydrocarbons [3, 10, 11]. The chemical composition of the bio-oil significantly depended on the pyrolysis temperature [12].

Already the carbonized biomass obtained through pyrolysis processes [13] can be used for production of pellets [14], briquettes, agricultural use (biochar), etc. [2, 15]. The use of the carbonized biomass in the soil (biochar) can provide numerous benefits, such as: sequester of carbon, soil conditioner, plant growth, increasing agricultural productivity, suppression of methane emissions, reducing emissions of nitrous oxide, reducing the need for fertilizers and also reduction of the leaching of nutrients [15-19].

Py (pyrolysis) can be combined with off-line GC (gas chromatography) separation and MS (mass spectrometry) providing a simple and reliable characterization of the components originated from lignocellulosic biomass [20, 21], as well as samples of any origin, while solid state ^{13}C NMR (nuclear magnetic resonance) is a powerful technique for the characterization of the solid residues [22].

The aim of this work was to investigate the Py of solid residues after acid hydrolysis of three lignocellulosic biomasses and the properties/potential of the bio-products in platform chemicals and for agricultural use. These residues can be regarded in the biorefinery concept, where the product of a process becomes the raw material of the next process.

2. Experiments

2.1 Samples

Coffee husks (*Coffea arabica*) and banana (*Musa* spp.) residues (stem and stalk) were harvested in the southeast region of Brazil during the year of 2012. The samples were chipped, milled and sieved (180-850 μm). The sieve fraction was stored until the physico-chemical analysis. Proximate analysis [23-24] and extractives process removed [25] were performed before the acid hydrolysis. All analyses were performed in duplicate.

2.2 Hydrolysis Process

The hydrolysis processes were carried out using standard NREL (National Renewable Energy Laboratory) methods [26] in two stages with sulfuric acid. In the first step, sulfuric acid at 72% was used and in the second moment, a dilution took the solution acid to 4%. This last stage occurs in an autoclave (60 min, 120 ºC) and the first in a water bath (60 min, 30 ºC).

After the secondary hydrolysis, the hydrolysate was cooled to room temperature. Following this, the hydrolysate solution is filtered through a filter-crucible (medium porosity) using vacuum suction and the hydrolysate retained for subsequent analysis. The solid residue that does not pass through the filter crucible contains all the acid insoluble material, that can then be pyrolyzed.

In the hydrolysate were measurement the ASL (lignin acid soluble) and carbohydrates content using chromatographic methods described in Section 2.3. The ASL was analyzed with the UV-Vis (ultraviolet-visible spectroscopy) spectrophotometer on the diluted hydrolysate, at wavelengths of 205 nm.

The AIR (acid insoluble residue), after the acid hydrolysis, was dried (105 ºC overnight), and then ashed to determine the AIA (acid insoluble ash). The difference between AIR and AIA contents gives the KL (Klason lignin).

So, the TL (total lignin) content was the sum of the soluble (ASL) and insoluble lignin (KL).

2.3 Chromatography Analysis

The monosaccharides analysis in the hydrolysate (arabinose, galactose, rhamnose, glucose, xylose and mannose) was performed by HPAEC-PAD (high performance anion exchange chromatography with pulsed amperometric detection) using ED (electrochemical detector) 40, with a CarboPac-PA 10 column and precolumn. Sugar separation occurred in 25 min with deionised water as the eluent, a flow rate of 1.1 mL/min. After 25 min, the column was regenerated involved a 30 s ramp to an eluent concentration of

240 mM NaC$_2$H$_3$O$_2$ in 400 mM NaOH, and after this again return to deionised water as eluent.

One solution containing a known concentration of fucose was used as the internal standard.

2.4 Pyrolysis Process

For the pyrolysis process, the residue remaining after the hydrolysis process was used. Two procedures were evaluated, the first one using the raw AIR, seeking to simulate the industrial pyrolysis and the other, analytical, where the AIR was methylated with TMAH (tetramethyl ammonium hydroxide) in methanol (25%) and pyrolised in a Pyrex tubular reactor at 450 °C for 30 min. The pyrolysis vapors and aerosols released by pyrolysis were continuously transferred by a helium flow (20 mL·min^{-1}) into two successive chloroform (50 mL) traps kept in ice plus salt baths. The chloroform solutions were concentrated by rotoevaporation under reduced pressure. The water content was determined by Karl Fisher titration. The residue from methylated AIR was redissolved in 1 mL of chloroform and transferred to a glass vial for GC-MS (gas chromatography-mass spectrometry) analysis. The treatments (biomass and methylation) were arranged in a completely randomized design with four repetitions and the yield results were analysed by MANOVA (multivariate analysis of variance).

The GC separations were carried out with a GC-MS QP (quadrupole) 2,010 Plus instrument (Shimadzu, Tokyo, Japan) equipped with an Rtx-5MS (Restek, 30 m × 0.25 mm; film thickness = 0.25 m) WCOT (fused silica capillary columns). Chromatographic separation was achieved with the following temperature program: 60 °C for 1 min (isothermal), raised at 7 °C·min^{-1} to 100 °C and then at 4 °C·min^{-1} to 320 °C followed by 10 min at 320 °C (isothermal). Helium was the carrier gas at 1.90 mL·min^{-1}, the injector temperature was 250 °C, and the split injection mode had a split flow at 30 mL·min^{-1}. Mass spectra were obtained in EI (electron ionisation) mode (70 eV), scanning in the range of m/z 45-850

with acycle time of 1 s. Compound identification was based on comparison of mass spectra with the NIST (National Institute of Standards and Technology) library database, published spectra and real standards. For quantitative analysis, due to the large variety of detected compounds with different chromatographic responses, external calibration curves were built by mixing methyl esters and/or methyl ethers of the following molecular standards: tridecanoic acid, octadecanol, 16-hydroxyhexadecanoicacid, docosandioic acid, sitosterol and cinnamic acid. Increasing amounts of standard mixtures were placed in a quartz boat and moistened with 0.5 mL of TMAH (25% in methanol) solution. The same thermochemolysis conditions as for compost samples were applied to the standards.

2.5 Solid-State ^{13}C NMR Analysis

Solid-state ^{13}C NMR spectra were obtained using a Varian INOVA (11.74 T) spectrometer with ^{13}C and ^{1}H frequencies of 125.7 MHz and 500.0 MHz, respectively. A variable-amplitude cross-polarization pulse sequence was employed. The experiments were performed using MAS (magic-angle spinning) of 15 kHz, cross-polarization time of 1 ms, acquisition time of 15 ms, recycle delay of 500 ms, the cross polarization time was chosen after variable contact time experiments, and the recycle delays in CP (cross-polarization) experiments were chosen to be five times longer than the longest ^{1}H spin-lattice relaxation time (T$_1$H) as determined by inversion-recovery experiments. High-power TPPM (two pulse phase-modulation) proton decoupling of 70 kHz was employed.

3. Results and Discussion

3.1 Characterizations of the Raw Biomasses

The results of the proximate analyses (Fig. 1) of the biomass residues presented ash values between 2%-6% and moisture values between 5%-10%, all with standard deviation less than 0.6%. Low levels of moisture and ash are important parameters if direct
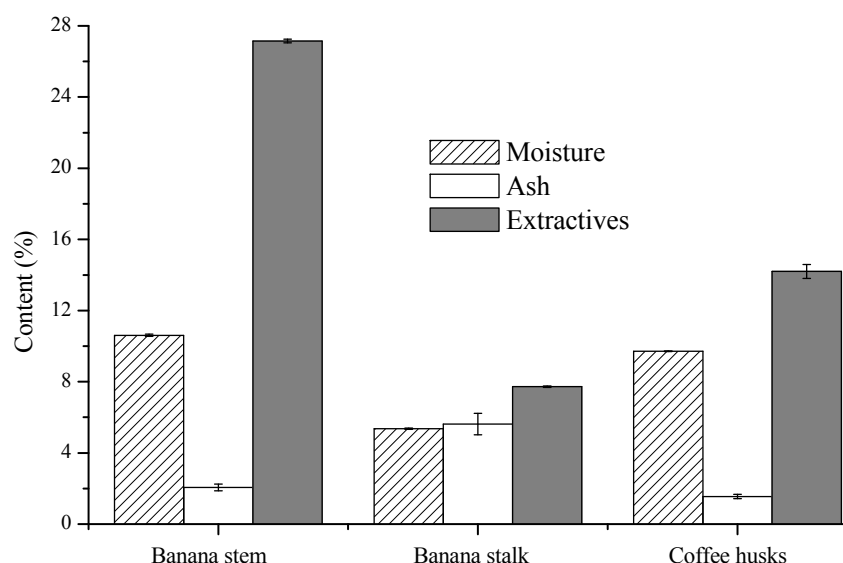
Fig. 1 Proximate analyses and extractives content of the biomasses residues (bars represent standard deviation of the mean).

burning or pyrolysis is the goal, because high ash and moisture content can cause problems in the hydrolysis and pyrolysis process. The ash content affects the acid hydrolysis by increasing the acid consumption while the moisture absorbs heat that would otherwise be available, reducing the calorific value [27].

It is well known that extractives affected the analysis of hydrolysis and pyrolysis products because they can precipitate under the strong acidic conditions, increasing erroneously the lignin products [28, 29]. So, biomasses with high extractives content, such as banana stem (27.15 ± 0.1), can affect the hydrolysis and pyrolysis analysis.

3.2 Characterizations of Hydrolysis Products

The chemical composition of the acid hydrolysis products are showed in Figs. 2 and 3. The carbohydrates composition analyses for the biomasses residues after the hydrolysis process give a total sugar and total lignin contents above 35% and 10%, respectively, for all biomasses residues. Tsai et al. [30] evaluated coffee residue as a potential feedstock for preparing char fuel, and found a total of 47.2% of carbohydrate (wt.%) and 39.4% of lignin in the hydrolyzate feedstock. Bok et al. [31] found 53% of

sugars and 33.3% of lignin in coffee residues after the hydrolysis, aiming to investigate characteristics of biooil and optimum conditions of fast pyrolysis of coffee grounds. The great difference, mainly in the TS (total sugars) values between biomasses [30-33] and biomass of this work, is probably due to the acid hydrolysis, since the total sugars remaining, evaluated by NMR in the AIR (approximately 14%) in coffee husks stalk for example, accounting with the TS content (35%), is close with the results in Refs. [30-33].

For banana residues, Fernandes et al. [32] found in pseudostem 62.4% of holocellulose and 8% of lignin, while Soffner [33] found 47.6% of holocellulose and 7.4% of lignin after acid hydrolysis. Very similar values were found for lignins for all banana residues, and for TS the data in Refs. [32, 33] are in concordance with this work only with the stalk residue.

The chemical composition of the biomasses in question is favorable due to the high carbohydrates content, providing chemicals inputs with high added value, while the solid residue, consisting mainly of lignin, can be pyrolyzed provides value-added bioproducts.
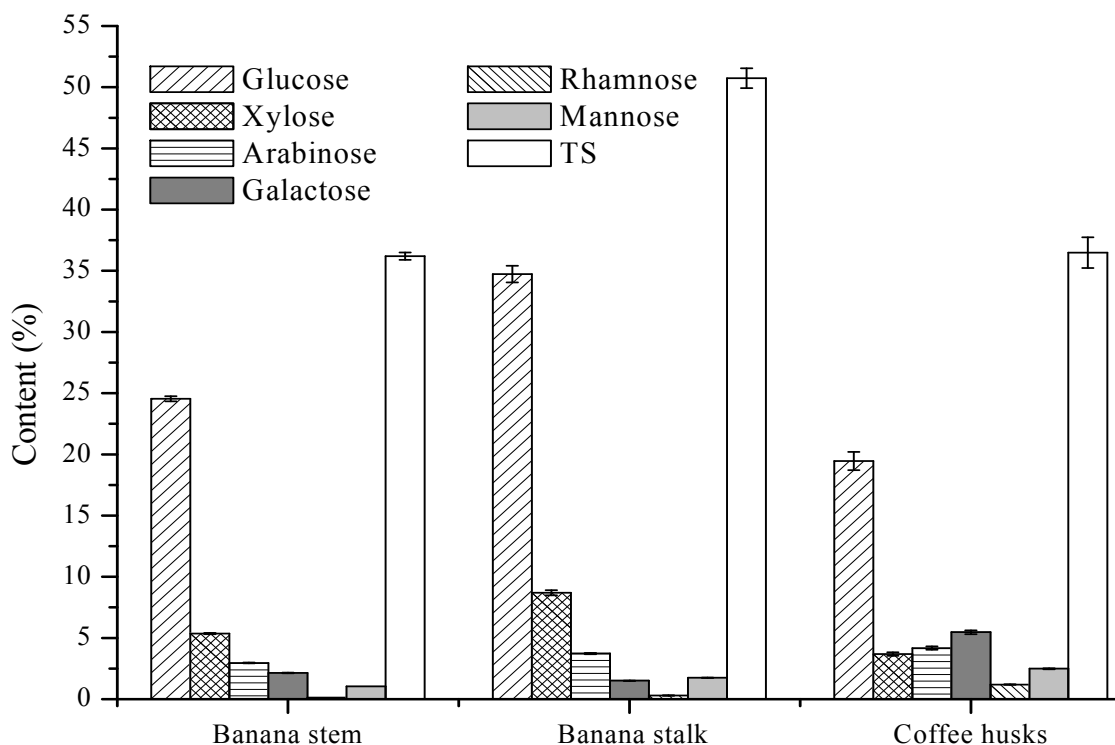
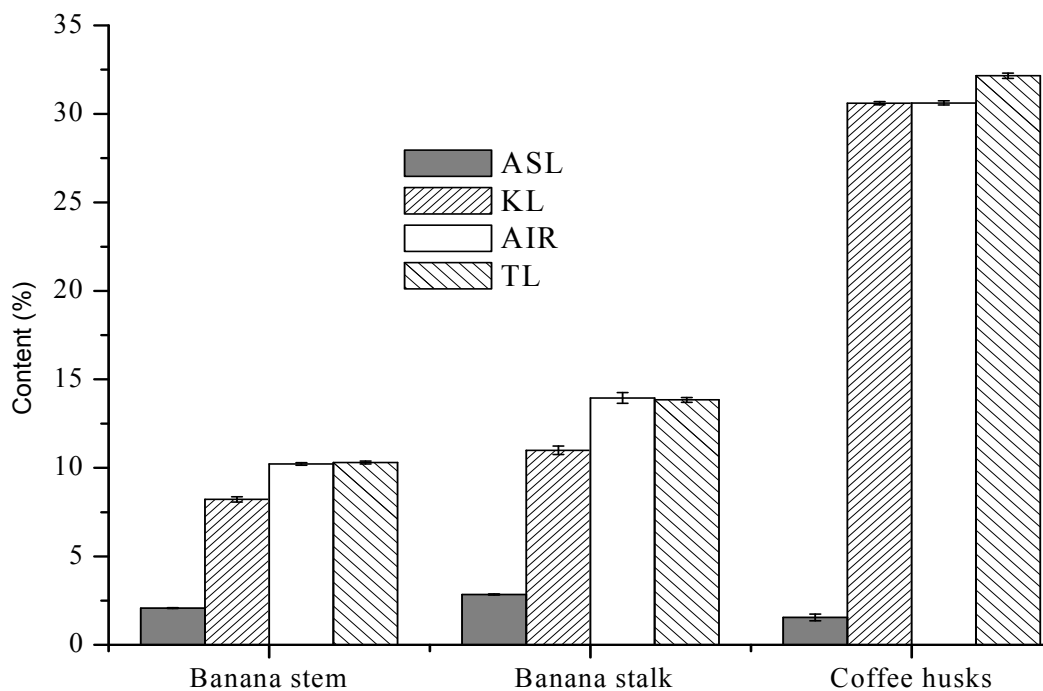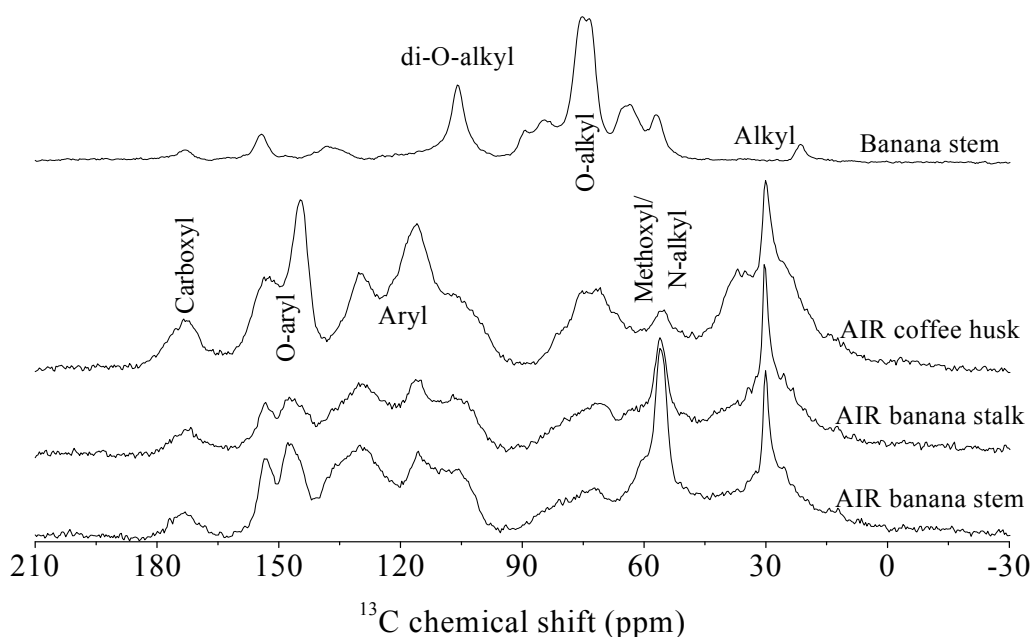**Fig. 2   Analysis of sugars after the acid hydrolysis (bars represent standard deviation of the mean).**

Fig. 3   Analysis of lignin content after the acid hydrolysis (bars represent standard deviation of the mean).

Fig. 4 ^{13}C NMR spectra of original feedstock (banana pseudostem) and of the AIR from coffee husk and banana stalk and stem.

3.3 ^{13}C NMR Analysis of the AIR

The solid residues obtained after the hydrolysis filtration process were submitted to solid state NMR analysis and their spectrums are shown in Fig. 4.

The ^{13}C NMR spectra of the AIR showed an important decrease of the carbohydrates signals (O-alkyl and di-O-alkyl) compared to the original biomasses (Fig. 3), however, the hydrolysis process used by NREL 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 ^{13}C NMR signal for coffee husk, stalk and stem, respectively.

Few studies have investigated the incomplete acid hydrolysis of carbohydrates. Zhou and Runge [34] have taken SEM (scanning electron microscopy) images of residues after acid hydrolysis to verify the hypothesis that the acid hydrolysis was incomplete. The SEM images of the AIR concluded that the solid residues are highly likely to be non-hydrolyzed carbohydrates. The incomplete hydrolysis occurs due to "pseudo-lignin" formation during acid hydrolysis, where inaccessible char could form from cellulosic

materials during the first-step of the acid hydrolysis [35], and so the pseudo-lignin which can resist to acid hydrolysis could form and cover the surface of carbohydrate particles. Thus, these particles survived during acid hydrolysis and were left as solid residues [36-37].

Despite the fact that the extractive was tentatively removed (ethanol 95%) from the samples, the alkyl region, in association with the carboxyl one, indicates the presence of fat acids: 33% of ^{13}C NMR signal for husk, 36% for stalk and 29% for stem. Solvents of different polarities are required to remove different types of extractives, and since, in the present work, only ethanol was used, the extraction efficiency may have been affected.

But, as expected, 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%.

3.4 Characterizations of Pyrolysis Products

The yield of pyrolytic products is showed in Fig. 5. The samples derivatization (methylation with tetramethyl ammonium hydroxide) resulted in the
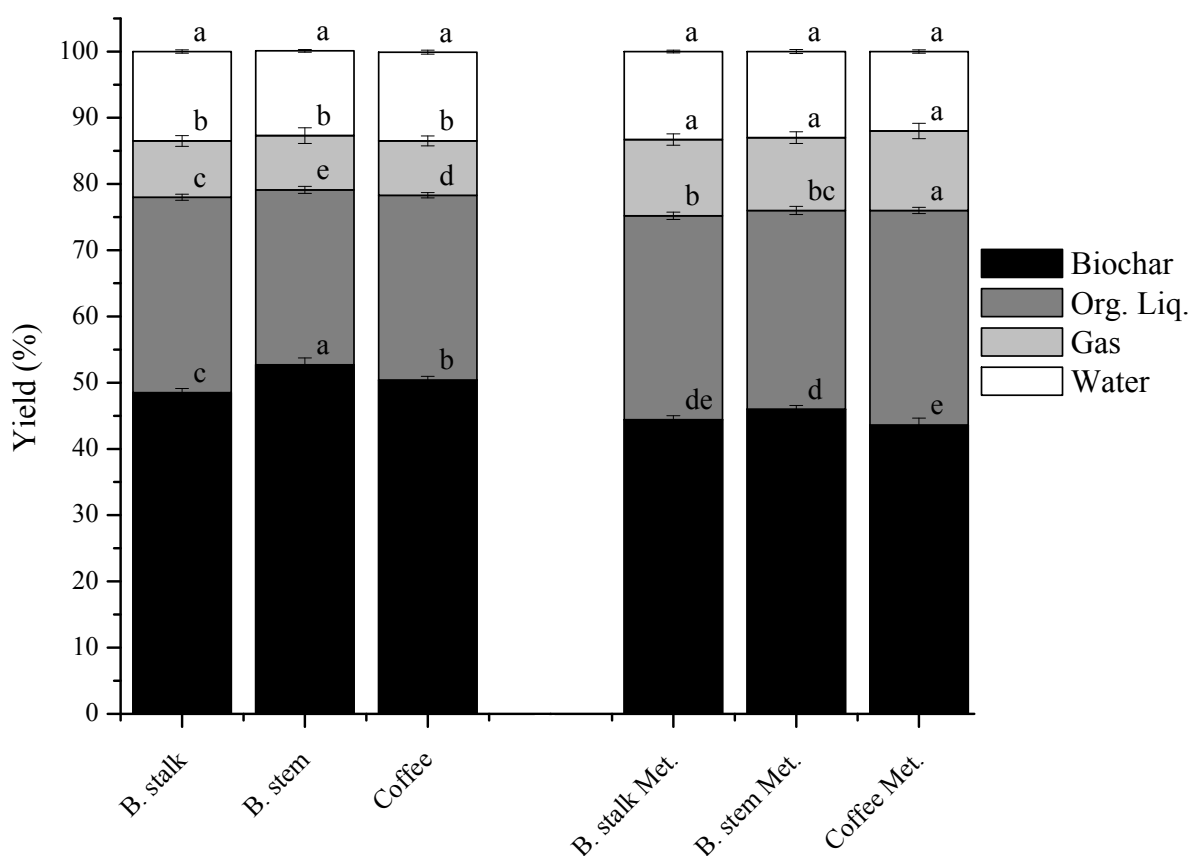
Fig. 5 Pyrolytic products yields from different biomass: coffee—coffee husk; B.—banana; Met.—methylated; Org. Liq.—organic liquids free of water. The gas yield was estimated by difference. Columns with the same letter, for each pyrolitic products, are not significantly different by the Tukey test at *P* < 0.05. Bars represent standard deviation of the mean.

decrease of biochar yield with subsequent increase of all the another pyrolytic products, except water, indicating the efficiency of methylation to increase volatile products generation after derivatization.

The biochar yields from the different biomass had close direct relationship with the lignin contents of the AIR, according estimated by ^{13}C NMR, specially from raw AIR, besides negative correlations were observed for biochar yield versus organic liquids and gas (*R* = -0.9821 and -0.9769, respectively). On the other hand, the increase of pyrolysis efficient for organic liquids production after methylation could be associated to the fat acids content determined by ^{13}C NMR, since banana stalk AIR was the richest sample in fat acids and banana steam the poorest, and this order is in accordance with the efficiency increase under

methylation (116%, 114% and 106%, relative to the raw biomass for banana stalk, coffee husk and banana stem, respectively) indicating that these compounds are prone to be methylated by TMAH and are evolved in the condensable phase.

The resulting products from fast pyrolysis (aqueous liquid and bio-oil) of lignocellulosic biomass can be identified by GC-MS. The compounds found in the bio-oil fraction are numbered in Fig. 6. There were approximately 18 main identifiable pyrolysis products.

The main single pyrolitic products of AIR were identified as methyl ester of long chain fatty acids: palmitic acid for banana stem and stalk (20% and 26% of the pyrolitic products, respectively) and oleic acid (33%) for coffee husk, these high content of aliphatic

(a)

(b)
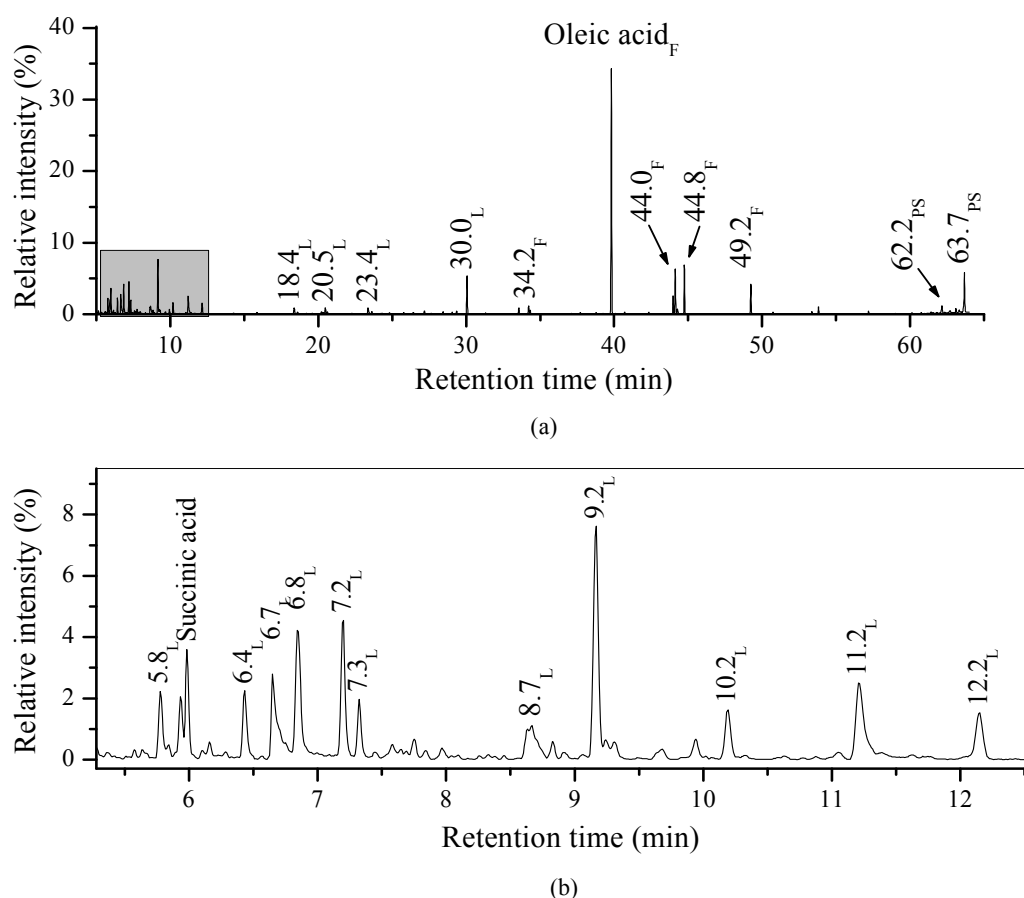
Fig. 6 Gas chromatogram of the acid insoluble residues from coffee husk. The gray square in (a) is the zoomed region (lignin monomers, except when indicated) showed in (b). Retention time index: L—lignin monomers; F—fatty acids; PS—phytosterols.

acids were also observed in ^{13}C NMR spectra. The palmitic acid (C16) and oleic acid (C18:1) can be derived from microorganisms or hydroxy acids from cutin and/or suberin [38].

However, after the sum of all the pyrolitic products from the same class of compounds (e.g., lignin, fatty acids and phytosterols), the main compounds of banana stem were lignin (56.4%), that corroborate the ^{13}C 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 considered valuable chemicals [3, 9, 11, 21, 39]. Succinic acid was found in coffee husk and banana stalk (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 ^{13}C NMR and Py-GC-MS, except for carbohydrates, in general underestimated by Py-GC-MS [38, 39].

The further slow pyrolysis (450 ^{o}C during 30 min) of the AIR 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
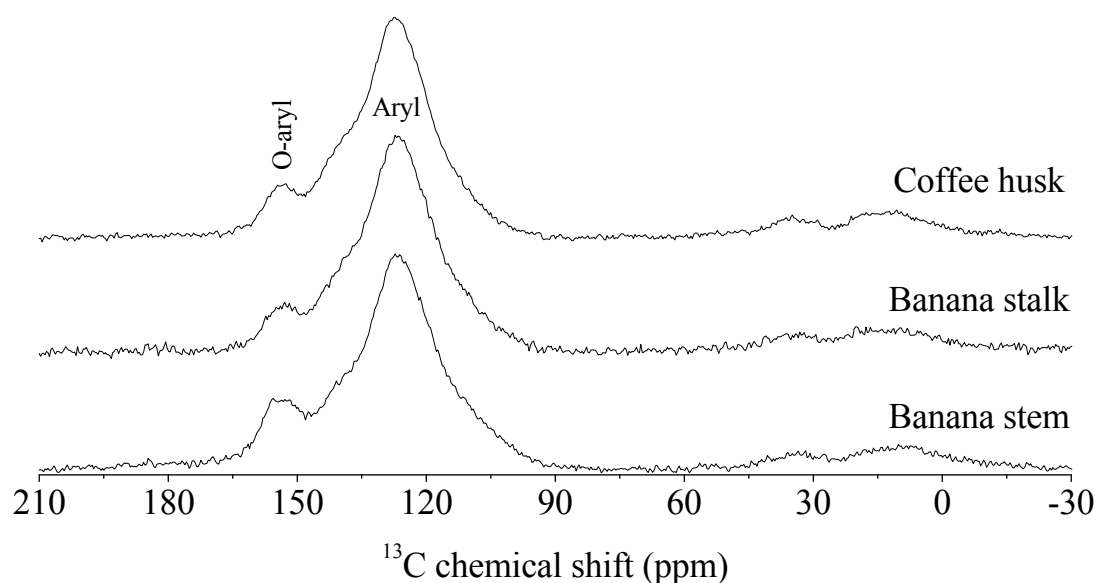
Fig. 7   **^{13}C NMR spectra of the acid insoluble residues pyrolysed (biochar) from coffee husk and banana stalk and stem.**
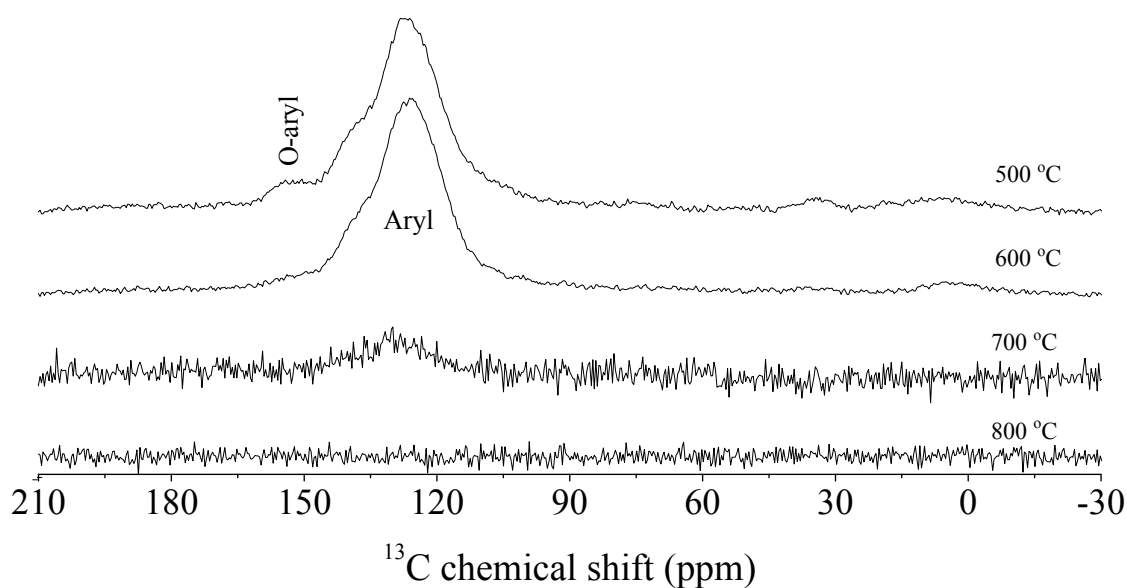

Fig. 8   **^{13}C NMR spectra of the acid insoluble residues from coffee husk pyrolysed at different temperatures.**

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 (Fig. 7), the presence of O-aryl groups could be interested seeking for a soil amendment material, since the reactivity of the material should be higher than only polycondensed aryl groups obtained under more severe carbonisation conditions.

The pyrolysis at higher temperatures resulted in a successive decreases of the O-aryl signal and also a successive increase of aromatic ring polycondensation, up to a graphene structure with a very high anisotropy and low electric resistance [40], since the ^{13}C signal result undetectable at 800 °C (Fig. 8).

And then, the increase of pyrolysis temperature results in the increase of the recalcitrance of the obtained biochar and it is an important strategy when the goal is C sequestration in the soil.

4. Conclusions

The Py-GC-MS was used to determine the thermal degradation products of various biomasses (banana stalk, pseudosteam and coffee husk), indicating that the employed pyrolysis was very effective to producing phenolic molecules which may serve as high value products. Some carbohydrates derivatives were detected in the solid residue, probably associated to pseudo lignin, but one modification of the NREL method is being tested for the biomasses in question, changing the primary hydrolysis time looking for the improvement of sugars recovery.

The liquid bio-oil and biochar produced by fast pyrolysis from residues of acid hydrolysed biomasses has the potential to supply a number of valuable chemicals and their potential has been increasingly for biorefining processes. The biochar is the most useful product, with properties for applications in agriculture, as a soil conditioner and for carbon sequestration.

About the potential of bio-oil, there are limitations, because it is a mixture of complex compounds and these will require larger scale development to prove feasibility and viability to separate the products, without counting the high cost of the process.

Pyrolysis could potentially be used to obtain energy and bioproducts from biomass residues, but more research is needed to optimize pyrolysis parameters to obtain desirable bio-oil and biochar characteristics and to refine them.

Acknowledgments

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