



Catalytic and non-catalytic pyrolysis of Kraft pulp waste into anhydrosugars containing bio-oils and non-phytotoxic biochars



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ABSTRACT

The catalytic and non-catalytic fast pyrolysis process for converting Kraft pulp paper waste into bio-oil and biochar was studied. Catalysis free pyrolysis of untreated Kraft pulp resulted on good yields of bio-oil (39% at 400 °C), showing a relative high concentration of levoglucosan, while phosphoric acid-pretreated pulp produced lower yields of bio-oil (max. value 14% at 350 °C) being levoglucosenone the main component. The catalytic pyrolysis of pretreated pulp employing silica led to a high yield of the liquid fraction (57% at 400 °C) with a high selectivity to levoglucosan. The biochar produced from as received pulp could be envisaged for soil amendment. It displayed a relatively high specific surface area, showing micro and mesoporosity. Besides, no phytotoxic effect of the biochar obtained at 350 °C was recorded.

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1. Introduction

Pyrolysis of biomass is a viable route for producing gases, liquids and solids that can be employed for different purposes. The process is especially complex and consists of both simultaneous and successive reactions in which organic material is heated in a non-reactive atmosphere.

Cellulose is the dominant component of lignocellulosic biomass and an excellent raw material for pyrolysis since it does not compete with food production [1]. A large number of studies have focused on the pyrolysis of cellulose for producing valuable chemicals [2,3]. The acid treatment of starting cellulose, as well as the use of catalysts, strongly influence on the course of thermal degradation and consequently on the product distribution and on the composition of bio-oils. Acid-pretreatment promotes dehydration of the biopolymer and led to a liquid with a high concentration of furan derivatives and valuable anhydrosugars such as levoglucosan (LG) and levoglucosenone (LGO) [4,5]. LG is an interesting precursor for the synthesis of chiral natural products [6,7]. Besides it is often used as a highly specific tracer for biomass burning aerosols

[8]. On the other hand, LGO is used as a versatile chiral building block owing to its high functionality [9].

The Kraft pulp paper (KP from now on) has not been extensively studied as raw material for pyrolysis. In Kraft pulping, wood is previously debarked and subsequently a chemical treatment removes lignin, breaking down the wood into fibers. KP is an interesting material for pyrolysis, since the content of lignin is negligible. However, to our knowledge, there are no investigations on the pyrolysis of KP as a procedure to obtain valuable chemicals; studies have only been limited to analytical determinations [10,11]. Thus, it can be speculated that bio-liquid from KP would contain valuable chemicals, as in the case of cellulose.

Biochar is a solid by-product that is produced in biomass pyrolysis. There has been a growing interest on the efficient conversion to this product [12], which can be used for many purposes. Due to micropores developed during pyrolysis, biochar has large surface area and can be used for filtration and adsorption of pollutants. Most recently, the use of biochar as a sustainable soil amendment to improve soil productivity, carbon sequestration, and overall soil fertility has drawn greater attention [13,14]. The beneficial effects of biochar on plant growth have been reported when this carbonaceous material is combined with fertilizers, both organic and inorganic [15–17].

In the present work we report on the fast pyrolysis of KP (non-pretreated and acid pretreated) with the aim of obtaining bio-

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Table 1
Some physicochemical Properties of Kraft pulp.

C (wt.%) ^a	46
N (wt.%) ^a	0.03
H (wt.%) ^a	5
O (wt.%) ^b	46
S (wt.%) ^a	0.8
HHV (MJ kg ⁻¹) ^c	17.1
Ash (wt.%) ^a	2.4
Al ₂ O ₃ (wt.%) ^d	0.30
CaO (wt.%) ^d	6.30
Na ₂ O (wt.%) ^d	1.48
Fe ₂ O ₃ (wt.%) ^d	0.22
MgO (wt.%) ^d	1.02
MnO (wt.%) ^d	0.08
Mo (wt.%) ^d	0.01
Cellulose (g kg ⁻¹) ^a	81
Hemicellulose (g kg ⁻¹) ^a	9
Lignin (g kg ⁻¹) ^a	5

^a Determined on dry basis.^b Calculated by difference.^c Calculated values.^d Ash composition.

liquids rich in valuable anhydrosugars. Pyrolysis reactions are also performed with KP in contact with SiO₂, as a heterogeneous catalyst. The different bio-oils were analyzed in order to determine the influence of the different conditions on pyrolysate composition.

In addition, we have focused on the biochar formed in KP pyrolysis, for finding a proper disposal for this waste. In this context, the solid product obtained from KP pyrolysis was exhaustively characterized and evaluated as a potential soil amendment through germination and growth bioassays.

2. Materials and methods

2.1. Raw material

The fibrous fraction of a recycled pulp obtained from unbleached softwood Kraft-liner paper was used for the study. For acid impregnation, the pulp was treated with a phosphoric acid solution (Anedra, 85% w/w). Thus, 1.00 g of KP and 5 mL of 1% (w/w) phosphoric acid aqueous solution were introduced in a round-bottom flask and kept at 80 °C under magnetic stirring. Following 2 h, the mixture was filtered under vacuum and the solid was dried at 40 °C

under vacuum overnight. This raw material is named as T-KP from now on.

Characterization of fresh pulp was performed by using various analysis methods (Table 1). Elemental analyses of pulp were performed by a CHNS Elemental Analyzer 2400 Serie II Perkin Elmer. Alkali metals and other inorganic components (Ca, Na, Fe, Mg, Al, Mn and Mo) were determined by an ICP-MS Agilent 7500 CX equipment. The analysis was carried out by using a quadrupole inductive plasma mass spectrometer (Q-ICPMS) for all elements except sodium. A Thermo-Elemental X7 series (Thermo Fisher Scientific, Bremen, Germany), equipped with an ASX-100 autosampler model (CETAC Technologies, Omaha, NE), was used. CCT mode measurements were performed for Mg, Na, Ca, Mn, Fe and Mo. The element Al was measured without operating the collision cell with gas, and thus full sensitivity. All of the Q-ICPMS measurements were performed using Sc, In, and Re as internal standards. Samples were diluted 10-fold using a 1% HNO₃ 0.5% HCl mixture followed by digestion for 24 h before Q-ICPMS measurements. Standards and blanks were prepared using the same mixture (1% HNO₃–0.5% HCl). Instrumental and procedural blanks were determined together with samples, and the means of five runs were obtained for each sample. Full quantitative analysis was performed against calibration standards for each element. Precision (% CV) was below 5% considering five measures on the same sample (Table 2).

The content of cellulose, hemicellulose and lignin were obtained following the method described by Van Soest et al. [18].

Total ash content of the biomass material was determined via combustion of the biomass at 575 °C for 24 h.

The higher heating values (HHV) of feedstock and biochar, expressed in MJ/kg, were calculated using the equations 1 and 2 described by Friedl et al. [19] and an average taken from these two values:

$$\text{HHV}_{(\text{OLSmodel})} = 1.87\text{C}^2 - 144\text{C} - 2820\text{H} + 63.8\text{C} \\ \times \text{H} + 129\text{N} + 20147(1)$$

$$\text{HHV}_{(\text{PLSmodel})} = 5.22\text{C}^2 - 319\text{C} \\ - 1647\text{H} + 38.6\text{C} \times \text{H} + 133\text{N} + 21028(2)$$

Table 2
The product composition from catalytic and non-catalytic fast pyrolysis of KP and T-KP.

Sample	Catalyst	T (°C)	Yields of fractions (%) ^a			Products of liquid fraction (%) ^b			
			Liquid	Solid	Gas	LG ^c	LGO ^d	AS ^e	Others ^f
KP	none	300	27 ± 2	20 ± 1	53 ± 3	7	4	51	38
		350	34 ± 2	9 ± 1	57 ± 4	51	3	24	22
		400	39 ± 2	5 ± 0.4	56 ± 4	38	–	19	43
KP	SiO ₂ ^g	300	45 ± 3	7 ± 0.5	48 ± 3	83	15	2	–
		350	51 ± 3	2 ± 0.1	47 ± 3	72	–	14	14
		400	42 ± 3	1 ± 0.1	57 ± 4	80	–	11	9
T-KP	none	300	8 ± 0.5	37 ± 2	55 ± 4	2	89	6	3
		350	14 ± 1	32 ± 2	54 ± 4	3	90	5	2
		350 ^h	36 ± 2	11 ± 1	53 ± 3	52	19	24	5
T-KP	SiO ₂ ^g	400	13 ± 1	25 ± 2	62 ± 4	–	98	–	2
		300	39 ± 2	11 ± 1	50 ± 3	55	6	13	26
		350	43 ± 3	3 ± 0.2	54 ± 3	84	9	6	1
		400	57 ± 4	1 ± 0.1	42 ± 3	95	2	3	–

^a Values expressed as average of 3–4 measurements with their analytical errors.^b Percentages calculated based on the peak area in the GC/MS analysis.^c LG: levoglucosan.^d LGO: levoglucosenone.^e Other anhydrosugars.^f Mainly furans: 5-methyl-furan-2-one and 5-methyl-2-furancarboxaldehyde.^g 10% (w/w).^h For this experiment the treated pulp was extensively washed with water until pH was 6.

The moisture content of the untreated pulp samples (5.9–6.3%) was determined using a Mettler Toledo halogen moisture analyzer. About 1.00 g of the sample was weighed into the moisture analyzer and the moisture content was determined at 105 °C.

KP and T-KP were characterized by X-ray diffraction in a Philips PW1710 BASED instrument operating at 45 KV and 30 mA, fitted with a graphite monochromator in order to get Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$); the angle step and counting time were 0.02° (2 θ) and 1s, respectively. Besides, pulp materials were studied by Scanning Electron Microscopy (SEM) on a Jeol 100 CX2 apparatus.

2.2. Fast pyrolysis experiments

The pyrolysis was carried out in inert atmosphere in a quartz tubular reactor with a length of 25.00 cm and a diameter of 2.50 cm. The heating was performed with an external furnace having a temperature-controller device. The reactor was connected to a high vacuum pump with pressures in the 0.1–0.5 Torr range. KP or T-KP samples (1.00 g) were placed in a sliding ceramic boat, which was put into the pyrolysis furnace once the reaction temperature (300–400 °C) was achieved and the vacuum conditions were attained. Oxygen-free dry nitrogen, with a flow rate of 0.1 mL s⁻¹, was employed as an inert carrier gas to improve the transportation of products to the condensation region. Thus, the sample was subjected to pyrolysis temperature at very short residence times (<0.5 s) and the experiments last around 20 min to get the pyrolysis of full sample. The different bio-liquids were trapped at liquid-air temperature, immediately after they escaped the hot zone. The pyrolysate formed by two phases (water and oil) was diluted with acetone and submitted to several analyses or separation techniques. After evaporation of organic solvent and water, the liquid phase consisting of oil was weighed. The pyrolytic water formed during the pyrolysis process was thus removed in the evaporation of solvent. The amount of pyrolytic water was determined using the Karl Fischer titration method (Mettler Toledo analyzer, KF V10S Compact) and ranged from 6 to 10% wt. depending on pyrolysis temperature. The biochar was removed from the ceramic boat and also weighed; the gas yield was then calculated by mass balance. The yields are expressed as the average of at least three experiments to confirm reproducibility of the results reported.

In the catalytic experiments, pulp blends with addition of 10% (w/w) SiO₂ (commercial, Davisil Grade 923) were pressed and then granulated to 10–20 Mesh size particles. BET surface area, pore volume and size were calculated from N₂ isotherms at 77 K in a Nova Quantachrome 1200e equipment. The acidity of the solid catalyst was measured by titration with *N*-butylamine using an AT500N Automatic Potentiometric Titrator provided with a Pt electrode. The equivalents of the base employed for reaching the plateau of the titration curve were taken as a measurement of the total acidity of the solid. The strength of the acid sites of the silica was measured considering that the potential (E₀, mV) developed by the suspension (catalyst plus acetonitrile), following the addition of a drop of *N*-butylamine solution, was proportional to such a strength [20,21].

2.3. Gas chromatography/mass spectrometry (GC/MS) analyses

GC/MS analyses of the bio-liquids obtained in the experiments were performed in a Shimadzu GC-MS-QP 5050 spectrometer. The injector temperature was kept at 300 °C and the separation was performed using a VF-5 ms capillary column. Helium was used as a carrier gas with a constant flow rate of 0.5–1.0 $\mu\text{L}/\text{min}$. The oven temperature was programmed from 80 °C (3 min) to 280 °C (15 min) with a heating rate of 10 °C/min. The temperature of the GC/MS interface was held at 280 °C and mass spectrometer was operated at 70 eV under electron ionization. The liquid fraction was analyzed by GC/MS technique, where the peak area percent-

age of the detected products depends on the response factor of the mass spectrometer detector, turning difficult the accurate quantification of products. Having that in mind, the peak area of an individual compound was considered to be directly proportional to the concentration of such compound in the liquid pyrolysate. Thus, the peak area percentage of a compound was used to compare the change of its relative amount in the bio-oil at the different conditions.

The identification of chromatographic peaks corresponding to furan and aromatic compounds was achieved according to NIST MS library (match >95%). The identification of LG and LGO was established by comparison with authentic samples.

2.4. Physicochemical characterization of the biochar

Biochar generated in the pyrolysis of KP at 350 °C was characterized by elemental analysis in a CHNS Elemental Analyzer 2400 Serie II Perkin Elmer. The C/N and H/C atomic ratios were calculated from these results and the content in oxygen was calculated by difference, taking into account the ash content in the calculus. Ash content of biochars samples were determined by dry combustion at 760 °C for 6 h according to ASTM standards [22]. The total organic matter content was determined by ignition for 4 h at 550 °C. Heavy metals (Cd, Cr, Zn, Cu, Pb, Ni), alkali metals (Ca, Mg), P and K were determined by an ICP-MS Agilent 7500 CX equipment following the methodology described in Subsection 2.1.

2.5. Phytotoxicity germination test

The growth of Lettuce sp. (*Lactuca sativa*) seeds on the biochar aqueous extract was used for evaluating the phytotoxicity of this carbonaceous solid, because of their sensitivity to toxic substances and speed of germination.

A water extract of the biochar, obtained in KP pyrolysis at 350 °C, was prepared by shaking the fresh sample with distilled water at 1:10 w/w using a horizontal shaker for 30 min at room temperature followed by filtration. The water extract (10 mL) was then dropped into a Petri dish with a filter paper. *Lactuca sativa* seeds (25 in total) were distributed onto the filter paper. Deionized water was used as a control and all experiments were run in triplicate. Petri dishes were kept in a light camera at 20 °C. Following 7 days, the percentage of seed germination in the biochar water extract was compared with that of the water control. The number of seeds germinated was computed and the lengths of the root radical were measured. The germination index (GI) was calculated according to the method previously proposed [23]. The results were analyzed by ANOVA and Tukey's test ($p < 0.05$). The pH and the electrical conductivity (EC) values of the biochar aqueous extract were determined using an Orion Research 901 pHmeter equipped with a glass combined electrode and a DIST4 Hanna conductivity meter respectively.

3. Results and discussion

3.1. Characterization of kraft pulp samples

Table 1 summarizes the properties of Kraft pulp. For this material, carbon and oxygen content was similar, concentration of hydrogen and sulphur was low and nitrogen was detected in traces.

The composition of biopolymers indicated that cellulose is the main component although hemicellulose and lignin were also present. Composition as well as calorific values was similar to other biomasses such as bagasse with high proportion of cellulose polymer [24].

The chemical composition of ash obtained from KP is also shown in Table 1. Major constituents were the alkali metals calcium,

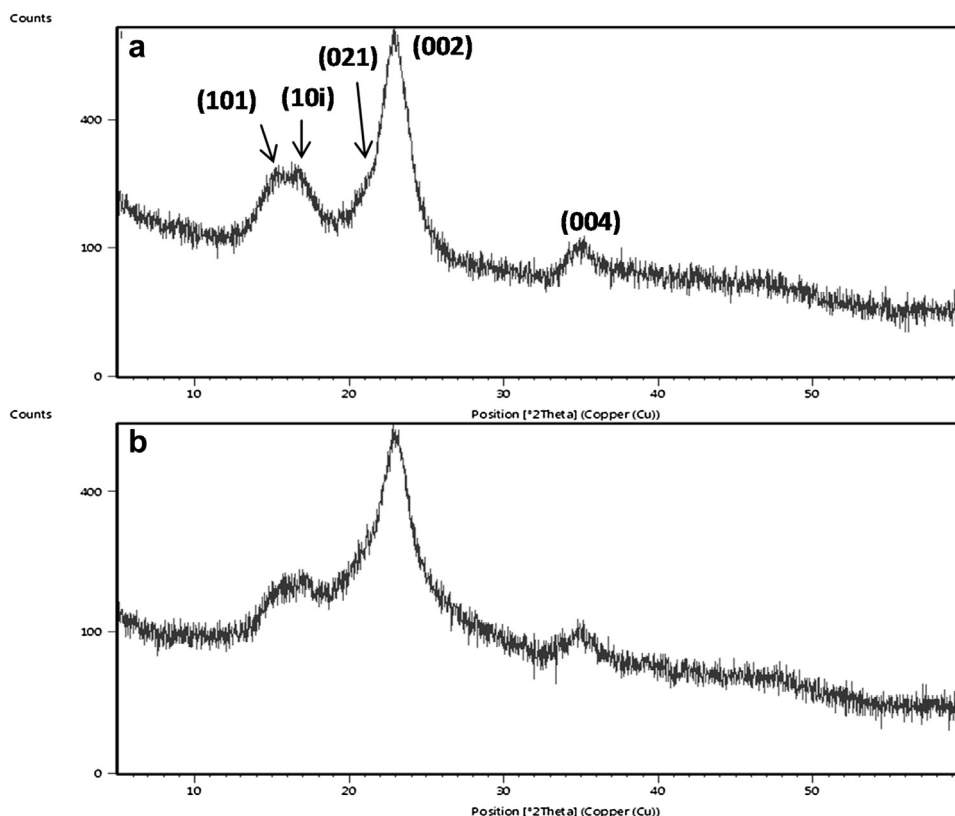


Fig. 1. XRD patterns of Kraft pulp samples: (a) KP and (b) T-KP.

sodium and magnesium. Aluminium and iron were present in similar proportions while manganese and molybdenum were minority components.

The majority of the alkali and alkaline earth metals present in the structure of biomass are reported to be in the form of water soluble salts such as chlorides, nitrates, carbonates and phosphates [25]. The contents of major and minor elements were close to the minimum values found for other cellulosic biomasses [26]. Other metals (mainly Al) were also detected, which could be originated in the process of KP production.

Fig. 1 shows KP and T-KP XRD diffraction patterns. The diffraction peaks of cellulose crystals were observed in both cases. The width of the peaks corresponding to KP is narrower than those of T-KP. Thus, the acid treatment was effective for reducing the number of ordered micro-regions of the macromolecule, increasing the relative content of amorphous regions, in agreement with previous studies [11,27].

The morphologic modification of KP upon acid treatment was also examined by SEM analysis (Fig. 2). Cellulose ribbons were clearly observed for KP together with a minimum amount of amorphous regions. On the other hand, T-KP showed a very irregular surface of the ribbons. Additionally, ribbons were shortened upon acidic treatment. A closer look at the macrofibril surface showed many terraces, steps and kinks on T-KP. This change would be attributed to the surface dehydration of the cellulose biopolymer catalysed by the acid [28].

3.2. Fast pyrolysis experiments

Catalytic and non-catalytic pyrolysis of KP and T-KP were carried out at different temperatures: 300, 350 and 400 °C. The yields of the three fractions, liquid, solid and gas are reported in Table 1 as weight percentages for the different pyrolysis experiments.

In the case of KP reactions, the liquid fraction increased with temperature at the expense of the solid fraction, the gas fraction being the predominant product at all temperatures.

The impregnation of KP with phosphoric acid diminished considerably the formation of bio-oil. This is related to the fact that the acid treatment leads to a dehydration of cellulosic material, which in some way protects the pulp against thermal attack during pyrolysis [2,4]. On the other hand, the acid-pretreatment of pulp strongly increased the production of biochar although the gases still prevailed. Interestingly, when T-KP was exhaustively washed until pH of nearly 6, the amount and composition of the bio-oil were similar to those produced in the reactions of non-treated pulp, at the same temperature. It is demonstrated that phosphoric acid remained attached to the material to be pyrolysed when an exhaustively washing was not performed after the acid-treatment.

The presence of an acid catalyst impregnated in the pulp has a significant impact on the yields and product composition during pyrolysis. A similar behaviour has been observed for the presence of acidic additives in the cellulose pyrolysis [2,3]. Based on literature, acids in contact with cellulose particles, during pyrolysis, would assist the ring-opening reactions (via β -elimination) at the expense of the transglycosylation pathway, which generate anhydrosaccharides [3,29]. We also found that the presence of phosphoric acid decreased the total amount of anhydrosugars in correlation with the diminution of bio-oil formation and char increase. Also, acid is promoting secondary dehydration reactions which convert LG into LGO, which is in agreement with previous investigations concerning pyrolysis of acid-treated cellulose [2,3,30].

Focusing the attention on the catalytic pyrolysis of KP and T-KP with SiO₂, yields to liquids were increased with a reduction of the solid fraction. The beneficial effect of silica as catalytic material was also observed in the pyrolysis of microcrystalline cellulose [5] and lignocellulosic biomasses [31]. According to our findings, an effec-

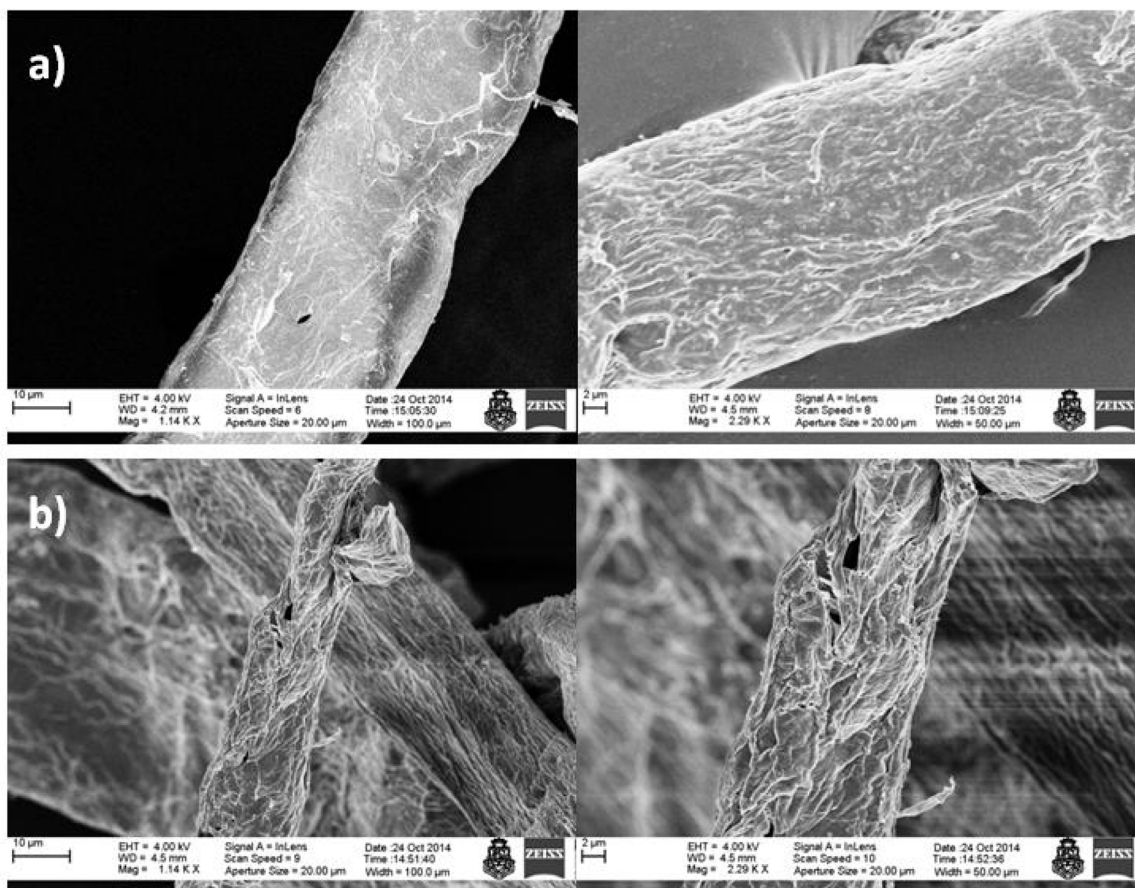


Fig. 2. SEM micrographs of Kraft pulp samples at 1.14 kx and 2.29 kx magnifications: a) KP and b) T-KP.

tive interaction between silica and cellulose probably favours the breaking of glycosidic bonds to give condensable products. It can be noted that silica inhibited the effect of phosphoric acid on the formation of biochar at the expense of bio-oil. This could be attributed to the interaction of silicon dioxide surface and phosphate groups at high temperature, as it has been described for functionalized silica [32] and other oxides [33]. Thus, the formation of silicon phosphate species would avoid the catalytic effect of phosphoric acid on the degradation of pulp to char.

To study the chemical composition of bio-oils, GC–MS analyses were conducted. Regardless of operating conditions, anhydrosugars were the main products at all evaluated temperatures (Table 1). Among these compounds, levoglucosan (LG) and levoglucosenone (LGO) were identified. In pyrolysis of fresh pulp furan derivatives were also detected to a lesser extent than anhydrosugars.

LG was predominant in the non-catalytic reactions at temperatures close to 300 °C. Below this temperature, high molecular weight sugars as well as furans were formed in high proportion. At 400 °C (and higher), the transformation of LG to other anhydrosugars was favored. The thermal behaviour of LG was studied by carrying out the verified when fast pyrolysis of pure LG was carried out between 250 and 400 °C and 0.05 Torr in our reaction system [5]. Under these conditions, the composition of the pyrolysate from LG at 250 °C was 29% of LGO, 24% of aromatics, 36% of un-reacted LG and 12% of other products. At high temperatures (>280 °C) LG was totally converted and a complex mixture of anhydrosugars and aromatic compounds was obtained.

Taking into account that in the fast pyrolysis of pure cellulose, LG was produced in high amounts (80–84% of the total products, between 350 and 500 °C), it can be seen that the nature of the cellu-

losic material notably influences the chemical bio-oil composition [5].

A greater impact on the formation of LG was observed when silica was used as catalyst in pyrolysis of KP. Thus, high proportions of this compound were obtained at all temperatures (72–83% of the total area of products determined by CG/MS).

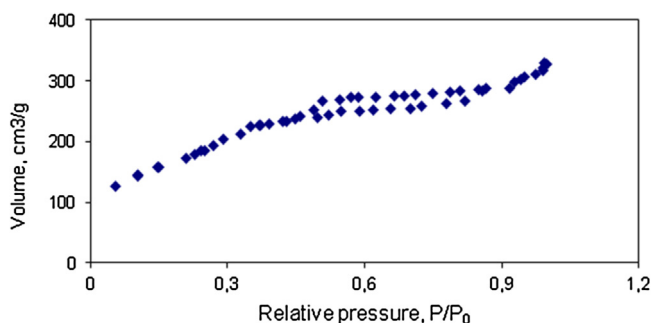
The bio-oil composition corresponding to T-KP was notably different from that observed for KP. LGO was produced almost exclusively in pyrolysis of T-KP, while its formation was rather meagre from KP. It has been established that LG undergoes dehydration and isomerization to form other anhydrosugars, including LGO [5,28,31]. According to by Dobele et al. [2], the presence of phosphoric acid alters the relative proportion of LG and LGO produced from cellulose pyrolysis. Thus, phosphoric acid, as well as other acids, enhances the dehydration of LG into LGO [3]. In our reactions, the acid-pretreatment of pulp leads to a liquid consisting of practically only one product, LGO. This is a quite interesting result, showing that the selectivity of products in the bio-liquids obtained from Kraft pulp pyrolysis is achievable.

When silica was used as catalyst in the reactions of T-KP, the composition of the bio-liquid was different from that obtained in the catalysis-free pyrolysis. In this case the main product was LG at all temperatures and the formation of LGO was depleted. Thus, the highest yield to LG was obtained for the catalytic pyrolysis of the acid pretreated pulp, at 400 °C. The production was even higher than that obtained when pure cellulose was employed [5] indicating that this pulp constitutes an ideal material for production of LG.

Some of the physicochemical properties of silica are reported in Table 3. The specific surface area is quite large, while acidity is rather low and the strength of the acid sites is very weak, as

Table 3
Physicochemical properties of SiO₂.

Catalyst	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ /g)	Acidity ^c (mEq/g)
SiO ₂ ^a	310	0.51	0.11
Spent SiO ₂ ^b	309	0.49	0.10

^a Commercial sample.^b Following a pyrolysis at 350 °C and a regeneration treatment.^c As measured by titration with *N*-butylamine.**Fig. 3.** Isotherms (77K, N₂) of the KP biochar produced at 350 °C.

deduced from the first point of the titration curve (E0). The rather inert nature of the catalytic surface of silica would prevent LG decomposition, leading to a high yield of this product. This could be explained suggesting the formation of hydrogen bonds between silanol groups of the silica and LG, preventing its transformation into LGO.

To test the possibility of reusing the silica catalyst, following pyrolysis of KP at 350 °C, the remaining solid (char plus catalyst) was calcined at 500 °C for 2 h. Although the color of the silica turned from white (fresh sample) to grey (recovered and calcined catalyst), the specific surface area, the pores size and the surface acidity were practically unaltered. These findings would suggest that this regenerated silica can be used again in the pyrolysis of fresh pulp.

3.3. Biochar characterization and phytotoxicity evaluation

The experimental conditions for pyrolysis of the present work were selected in order to maximize the yield to liquids (relatively low temperatures, short residence times and catalyst selection). Thus, the amount of solid residue was relatively low (5–20%wt.). Based on the high carbon content of biochar produced from pyrolysis of KP at 350 °C (nearly the same to obtained at 400 °C, Table S2 in SI), this material was selected to determine its bulk properties

Table 4
Characteristics of biochar produced in pyrolysis of KP at 350 °C.

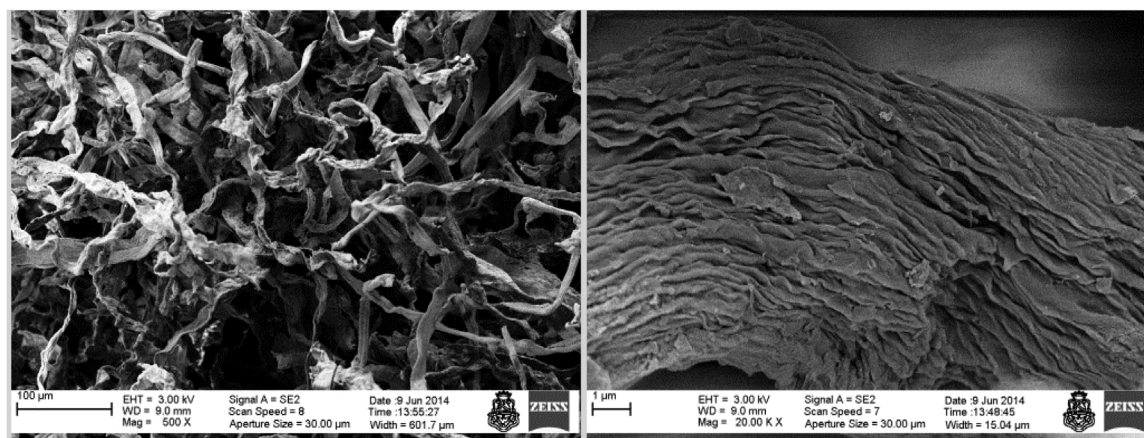
S _{BET} (m ² g ⁻¹)	223
Pore volume (cm ³ g ⁻¹)	1.2
Acidity (mEq/g) ^a	0.5
C (wt.%) ^b	71
N (wt.%) ^b	0.07
H (wt.%) ^b	2
O (wt.%) ^c	21
S (wt.%) ^b	0.4
H/C ^d	0.34
O/C ^d	0.22
Organic matter content (g kg ⁻¹)	975
Ash (wt.%) ^e	5.2
HHV (MJ kg ⁻¹) ^f	24.8
Ca (mg/kg)	12156
Mg (mg/kg)	1656
P (mg/kg)	1900
K (mg/kg)	11000
Cr (mg/kg)	15.4
Cd (mg/kg)	3.6
Zn (mg/kg)	74.1
Cu (mg/kg)	42.2
Pb (mg/kg)	6.9
Ni (mg/kg)	26.3
pH	5.18
EC (dSm ⁻¹ , 25 °C)	0.8

^a By titration with *N*-butylamine.^b On dry basis.^c Calculated by difference.^d Atomic ratios.^e On as received basis.^f Calculated values.

and performance in stimulating or inhibiting seed germination as a potential soil amendment (Table 4).

One of the main roles of biochar in the soil is to provide an increased retention of nutrients as well as to contribute with new nutrients for improving the quality of the soil. Therefore, the porosity of the biochar constitutes one of the fundamental properties, which determines nutrients and water adsorption. The presence of pores plays an important role, when applied to the soil providing habitats for different microorganisms and other biota [34].

Here, the specific surface area as well as the pore volume of the biochar obtained by pyrolysis of KP is quite good. Fig. 3 displays the corresponding isotherm; it shows a steep rise at low relative pressures, indicating that the sample was a microporous solid. In addition, for relative pressures higher than 0.4, a hysteresis loop was observed, which is associated with the presence of mesopores. These results indicate that this material presents both types of pores: micro- and mesopores. These features of biochar could

**Fig. 4.** SEM micrographs of biochar obtained from KP at 500× and 20.00 k× magnification.

contribute to increase the capacity of the soil for holding water and nutrients, thereby reducing the need for fertilizers.

The micro-structural features of the biochar were also investigated by SEM analysis (Fig. 4). Observations confirmed that the shape of the cellulose macrofibrils was maintained after pyrolysis process. Some macrofibrils remained separated presenting diameters of 10–15 μm , but other macrofibrils are agglomerated. The SEM images of an individual macrofibril at larger magnification showed that the biochar surface presented higher amount of terraces, steps and kinks than the pulp before pyrolysis.

After pyrolysis, the solid material became highly carbonaceous, with a high carbon content (71%) compared to that of the initial pulp (46%), decreasing drastically the oxygen content. Besides, the carbon content of the pulp-derived biochar was higher than biochar obtained in pyrolysis (at 350 °C) of microcrystalline cellulose (58%) [35]. The H:C and O:C ratios were similar to other biochars prepared from cellulosic and lignocellulosic biomasses [36]. These features were reflected in the calculated value of HHV, which was in the range of values obtained for other biomasses [37].

When the germination essay was evaluated using the biochar water extract, the seed germination of *L. sativa* was not affected. Thus, the germination index (GI) calculated according to Zucconi was 85.23%. Following these authors, a germination index above 60% indicates lack of phytotoxic effect [23]. Thus, the biochar from KP was not phytotoxic for seeds although any stimulating effect was determined on root and shoot growth.

The EC value is a measurement of the presence of soluble ionic compounds in the biochar, and it should be low to allow the disposal of the biochar into the soil without risking of salinization. It is known that salinization of a soil promotes low germination of seeds and there is a direct relationship between EC and GI. For the biochar here studied, EC was equal to 0.08 dS m^{-1} , this value was quite lower than the maximum value recommended, about 1.5 dS m^{-1} [38].

In addition, pH constitutes an important property of the soil, which influences the types of plants and microbes to grow, and the availability of nutrients to be absorbed. In our studies, the pH of biochar water extract was slightly acidic. While this value is rather inappropriate to neutralize acidic soils, it is in the range of traditional requirements to ensure compatibility with most plants [38].

Regarding other parameters of toxicity, the heavy metal content for the biochar was very low, although the cadmium concentration was in the upper limit value of class C for materials allowed in soil as compost and amendments [39]. Since TN was low, this solid should not be considered a material for improving the nitrogen content in the soil. Considering that the recommended value for C/N is 25/1 [39], the biochar corresponding to the present study showed a quite high C/N ratio. Additionally, the analysis of secondary nutrient profile (Ca, Mg, P and K) revealed meaningful content of these components, which is desirable for soil amendment [40]. The concentration of these nutrients is similar to reported in literature for wood-derived biochars [41].

4. Conclusion

The fast pyrolysis of Kraft pulp paper waste produced high yields of bio-liquids with a higher content of valuable anhydrosugars: LG and LGO. The relative concentration of the products strongly depended on the pyrolysis temperature and the presence of silica catalyst. LG formation was strongly favored when pyrolysis was carried out over the pulp in contact with a cheap and reusable catalyst as SiO_2 . Acid impregnation of pulp promoted the formation of LGO; however the presence of silica inhibited the effect of acid treatment, significantly improving the formation of LG at 400 °C.

Biochar, produced from the pyrolysis of KP, presented a high heating value that makes it a possible fuel candidate. Due to its high concentration in C, relatively high specific surface area and porosity, it is suitable for soil amendment. Also, a good germination index in the growth of *L. sativa* seeds demonstrated that the disposal of this material in soil would not present negative consequences.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jaap.2016.09.021>.

References

- [1] M. Kälndström, N. Kumar, M. Tenho, M. Mokeev, Y. Moskalenko, D. Murzin, Catalytic transformations of birch Kraft pulp, ACS Catal. 2 (2012) 1381–1393.
- [2] G. Dobelev, T. Dizhbite, G. Rossinskaja, G. Telysheva, D. Meier, S. Radtke, O. Faix, Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis: a promising method for obtaining 1,6-anhydrosaccharides in high yields, J. Anal. Appl. Pyrol. 68–69 (2003) 197–211.
- [3] S. Shaik, P. Sharratt, R. Tan, Influence of selected mineral acids and alkalis on cellulose pyrolysis pathways and anhydrosaccharide formation, J. Anal. Appl. Pyrol. 104 (2013) 234–242.
- [4] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapfle, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresour. Technol. 96 (2005) 673–686.
- [5] M. Nieva Lobos, M. Volpe, E. Moyano, Catalytic and catalytic free process for cellulose conversion: fast pyrolysis and microwave induced pyrolysis studies, Cellulose 22 (2015) 215–228.
- [6] V. Bailliez, A. Olesker, J. Cleophax, Synthesis of polynitrogenated analogues of glucopyranoses from levoglucosan, Tetrahedron 60 (2004) 1079–1085.
- [7] N. Merlis, E. Andrievskaya, L. Kosteljan, O. Golova, Synthesis of desoxy derivatives of 1,6-anhydro-d-glucopyranose (levoglucosan), Bull. Acad. Sci. USSR 24 (1975) 128–135.
- [8] B. Simoneit, J. Schauer, C. Nolte, D. Oros, V. Elias, M. Fraser, W. Rogge, R. Cass Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmos. Environ. 33 (1999) 173–182.
- [9] Z. Witczak, Synthesis of C-glycosyl compounds and other natural products from levoglucosone, Pure Appl. Chem. 66 (1994) 2189–2192.
- [10] M. Kleen, G. Lindblad, Quantification of lignin and carbohydrates in Kraft pulps using analytical pyrolysis and multivariate data analysis, J. Anal. Appl. Pyrol. 25 (2003) 209–227.
- [11] G. Dobelev, D. Meier, O. Faix, S. Radtke, G. Rossinskaja, G. Telysheva, Volatile products of catalytic flash pyrolysis of celluloses, J. Anal. Appl. Pyrol. 58–59 (2001) 453–463.
- [12] M.J. Antal, M. Grønli, The art, science and technology of charcoal production, Int. Eng. Chem. Res. 42 (2003) 1619–1640.
- [13] J. Lehmann, J. Gaunt, M. Rondon, Bio-char sequestration in terrestrial ecosystems: a review, Mitig. Adapt. Strat. Glob. Change 11 (2006) 395–419.
- [14] E. Marris, Black is the new green, Nature 442 (2006) 624–626.
- [15] K. Chan, L. Van Zwi, I. Meszaros, A. Downie, S. Joseph, Agronomic values of green waste biochar as a soil amendment, Austr. J. Soil Res. 45 (2007) 5954–5967.
- [16] C. Steiner, W. Teixeira, J. Lehmann, J. Nehls, J. De Macêdo, W. Blum, W. Zech, Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered central Amazonian upland soil, Plant Soil 291 (2007) 275–290.
- [17] L. Van Zwieten, S. Kimber, S. Morris, K. Chan, A. Downie, J. Rust, S. Joseph, A. Cowie, Effects of biochar from slow pyrolysis of paper mill waste on agronomic performance and soil fertility, Plant Soil 327 (2010) 235–246.
- [18] P. Van Soest, J. Robertson, B. Lewis, Methods for dietary fiber, neutral detergent fiber and nonstarch polysaccharides in relation to animal nutrition, J. Dairy Sci. 74 (1991) 3583–3597.
- [19] A. Friedl, E. Padouvas, H. Rotter, K. Varmuza, Prediction of heating values of biomass fuel from elemental composition, Anal. Chem. Acta 544 (2005) 191–198.
- [20] R. Cid, G. Pecchi, Potentiometric method for determining the number and relative strength of acid sites in colored catalysts, App. Catal. 14 (1985) 15–21.
- [21] R. Covarrubias, R. Quijada, R. Rojas, Synthesis of nanosized ZSM-2 zeolite with potential acid catalytic properties, Micropor. Mesopor. Mater. 117 (2009) 118–125.
- [22] ASTM D1762-84, Standard methods for chemical analysis of wood charcoal (1990).

- [23] F. Zucconi, A. Pera, M. Forte, M. De Bertoldi, Evaluating toxicity in immature compost, *Biocycle* 22 (1981) 54–57.
- [24] A. Demirbas, Biomass resource facilities and biomass conversion processing for fuel and chemicals, *Energ. Convers. Manage.* 42 (2001) 1357–1378.
- [25] W. Livingston in *Biomass ash characteristics and behaviour in combustion, gasification and pyrolysis systems Report*, Doosan Babcock Energy Limited (2007).
- [26] V. Stanislav, V. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification, *Fuel* 105 (2013) 40–76.
- [27] J. Zhang, J. Zhang, L. Lin, T. Chen, J. Zhang, S. Liu, Z. Li, P. Ouyang, Dissolution of microcrystalline cellulose in phosphoric acid- molecular changes and kinetics, *Molecules* 14 (2009) 5027–5041.
- [28] H. Zhao, J. Kwak, Z. Zhang, H. Brown, B. Arey, Holladay Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis, *Carbohydr. Polym.* 68 (2007) 235–241.
- [29] V. Mamleev, S. Bourbigot, M.L. Bras, J. Yvon, The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis. Interdependence of the steps, *J. Anal. App. Pyrol.* 84 (2009) 1–17.
- [30] Z. Witczak, Levoglucosenone and levoglucosans chemistry and applications, ATL Press, Mount Prospect, 1994.
- [31] F. Mendes, A. Pinho, M. Figueiredo, Evaluation of the impact of temperature and type of catalyst on the bio-oil quality obtained by biomass catalytic pyrolysis process, *Defect. Diffus. Forum* 334–335 (2013) 13–18.
- [32] M. Puziy, O. Poddubnaya, B. Gawdzik, M. Sobiesiak, M. Tsyba, Functionalization of carbon and silica gel by phosphoric acid, *Adsorpt. Sci. Technol.* 25 (2007) 8–11.
- [33] A. Domanskii, Y. Orlov, P. Rummyantsev, O. Shidlovskaya, Kinetic regularities of the interaction of aluminum oxide and silicon dioxide single crystals with phosphoric acid, *Glass Phys. Chem.* 33 (2007) 55–61.
- [34] J. Thies, M. Rilig, Characteristics of biochar: biological properties, in: J. Lehmann, S. Joseph (Eds.), *Biochar for Environmental Management. Science and Technology*, Earthscan Gateshead, London, 2009, pp. 85–105 (Chapter 6).
- [35] M. Nieva Lobos, J.M. Sieben, V. Comignani, M. Duarte, M. Volpe, Moyano biochar from pyrolysis of cellulose: an alternative catalyst support for the electro-oxidation of methanol, *Int. J. Hydrogen Energy* 41 (2016) 10695–10706.
- [36] C. Brewer, V. Chuang, C. Masiello, H. Gonnermann, X. Gao, B. Dugan, L. Driver, P. Panzacchi, K. Zygourakis, C. Davies, New approaches to measuring biochar density and Porosity, *Biomass Bioenergy* 66 (2014) 176–185.
- [37] A. Demirbas, Determination of calorific values of bio-chars and pyro-oils from pyrolysis of beech trunkbarks, *J. Anal. Appl. Pyrol.* 72 (2004) 215–219.
- [38] D. Hogg, E. Favoino, M. Centemero, V. Caimi, F. Amlinger, W. Devliegher, W.D. Hogg, J. Barth, E. Favoino, M. Centemero, V. Caimi, F. Amlinger, W. Devliegher, W. Brinton, S. Antler, Comparison of compost standards within the EU. North America and Australia, in: *The Waste and Resources Action Programme (Ed.)*, Oxon, 2002, pp. 26–61.
- [39] A. Masaguer Rodríguez, M. Benito Capa, in: J. Compostaje. Moreno Casco, R. Moral Herrero (Eds.), *Evaluación De La Calidad Del Compost*, Mundiprensa, Madrid, 2008, pp. 285–303 (Chapter 12).
- [40] IBI, *Standardized Product Definition and Product Testing Guidelines for Biochar* (2012).
- [41] G. Sigua, J. Novak, D. Watts, M. Johnson, K. Spokas, Efficacies of designer biochars in improving biomass and nutrient uptake of winter wheat grown in a hard setting subsoil layer, *Chemosphere* 142 (2016) 176–183.