Journal of Analytical and Applied Pyrolysis 122 (2016) 216–223

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

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

María L. Nieva Lobos[a,b], Paola Campitelli[c], María A. Volpe[b], E. Laura Moyano[a,*]

[a] INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Cordoba, Argentina
[b] Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Bahía Blanca, Argentina
[c] Laboratorio Coloides de Suelo y Enmiendas, Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Córdoba, Argentina

ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form
19 September 2016
Accepted 24 September 2016
Available online 28 September 2016

Keywords:
Kraft pulp
Pyrolysis
Anhydrosugars
Biochar
Phytotoxicity

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.

1. Introduction

Pyrolysis of biomass is a viable route for producing gases, liquids and solids that can 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-

* Corresponding author.
E-mail address: lauramoy@fcq.unc.edu.ar (E.L. Moyano).

http://dx.doi.org/10.1016/j.jaap.2016.09.021
0165-2370/

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_2O_3 (wt.%)[d]	0.30
CaO (wt.%) [d]	6.30
Na_2O (wt.%) [d]	1.48
Fe_2O_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 SiO_2, 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% HNO_3 0.5% HCl mixture followed by digestion for 24 h before Q-ICPMS measurements. Standards and blanks were prepared using the same mixture (1% HNO_3–0.5% 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:

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

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

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
		400	13 ± 1	25 ± 2	62 ± 4	–	98	–	2
T-KP	SiO_2[g]	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.