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Short Communication

Pyrolysis of sunflower seed hulls for obtaining bio-oils

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HIGHLIGHTS

- An agro-industrial residue is employed for obtaining bio-oils.
- Pyrolysis of *Helianthus annuus* seed hulls is performed in a flow glass reactor.
- Levoglucosenone was obtained from hulls treated with diluted acid.

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ABSTRACT

Bio-oils from pyrolysis of as received sunflower seed hulls (SSH), hulls previously washed with acid (SSHA) and hulls submitted to a mushroom enzymatic attack (BSSH) were analyzed. The concentration of lignin, hemicellulose and cellulose varied with the pre-treatment. The liquid corresponding to SSH presented a relatively high concentration of acetic acid and a high instability to storage. The bio-oil from SSHA showed a high concentration of furfural and an appreciable amount of levoglucosenone. Lignin was degraded upon enzymatic activity, for this reason BSSH led to the highest yield of bio-oil, with relative high concentration of acetic acid and stability to storage.

1. Introduction

Twenty two thousand tons of sunflower (*Helianthus annuus*) seed hulls (SSH) are produced as a residue of edible oil industries located at Bahia Blanca city, in Argentina. At the moment, SSH are directly burned for obtaining heat power. However, this lignocellulosic agronomic residue is a promising source for renewable energy and chemicals. However transportation of biomass is expensive due to its low density. Besides, storage presents problems associated with dry losses, compositional changes and risks of fire (Hayes Daniel, 2013). For these reasons, densification arises as a way for enabling the storage and transportation of huge amounts of SSH. Pyrolysis is an interesting option for densification of biomass as bio-oils. These liquids are corrosive due to their low pH (Bridgwater, 2012), besides the spontaneous condensation of compounds coming from lignin leads to the precipitation of tar.

In this work pyrolysis of SSH was performed in a glass reactor at 400 °C under N_2 flow, for obtaining valuable chemical products to turn SSH into a valuable material. Different pre-treatments were carried out over SSH for leading to a bio-oil less complex than the traditional one, from the point of view of the chemical composition. Two routes were followed for pre-treating the biomass: acid washing with a dilute mineral acid and a biotransformation by the activity of a mushroom. The latter pre-treatment was carried out by growing of *Ganoderma lucidum* on SSH, which secretes a multi-enzyme complex that attacks lignin (Boominathan and Reddy, 1992), which is the most refractive component. It is expected that *G. lucidum* modifies the biomass, leading to a particular chemical composition of the corresponding bio-oil. It is worth noting that the bio transformation of the hulls is based on the growing of an edible mushroom which is commercialized. Besides, *G. lucidum* can be employed for pharmaceutical porpoises.

The chemical composition and the stability against aging of the obtained bio-oils were studied.

2. Methods

2.1. Materials

Sunflower seed hulls (SSH) were provided by Cargil S.A., an oleo-chemical industry located at Bahia Blanca city. Besides, two

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other biomasses were employed: (a) SSH after washing with diluted acid and (b) SSH after growing of *G. lucidum*. For obtaining (a), 10 g of hulls were washed with 200 ml of H_2SO_4 (10%, Merck, 99.9%) at room temperature during 24 h. Then the material was filtered and dried at room temperature for 24 h. This material was named as SSHA. For (b) SSH was employed as the substrate for growing of *G. lucidum* (Gonzáles Matute et al., 2010). The basal substrate formulation contained 32.5% SSH, 5.0% barley (*Hordeum vulgare*), 2.0% $CaSO_4$, 0.5% $CaCO_3$, and 60% water by weight. For further details see the work of Curvetto et al. (2004). For some experiments cellulose, from Biopack, was employed. Before pyrolysis, hulls were milled to particles with size in the 142–476 μm range. The particle size was measured with laser diffraction equipment, HORIBA LA-950, in wet medium. The moisture of the SSH was determined by an Infra-Red scale OHAUS MB45 at 130 °C. The lignin, cellulose and hemicellulose concentrations were determined following the procedure of Van Soest et al. (1991).

SSH, BSSH and SSHA were studied by a Thermo-Gravimetric (TG) and Differential Thermo-Gravimetric (DTG) analyses, employing a TA Instruments – Discovery. Firstly, the scale was purged with N_2 during 20 min to ensure an oxygen free atmosphere. Then 20 mg of each sample were heated at 10 °C min^{-1}, ranging from room temperature to 600 °C. The concentration of Na, K, Ca and Mg were measured by means of Inductive Coupled Plasma with a Shimadzu simultaneous 9000 equipment following EPA standard 200.7.

2.2. Pyrolysis

A lab-scale fast pyrolysis set was designed for the experiments. Biomass particles (3 g) and N_2 (100 ml min^{-1}) were feed into the down-flow glass reactor at the top. The reactor was vertically positioned in a furnace for heating up to 400 °C. A disc of porous glass was fixed at the bottom of the reactor in order to support the biomass and to allow vapors to leave the heated zone, avoiding secondary cracking. With the porpoise of condensing vapors, a glass immersed into a water/ice bath was positioned at the end of the reactor. A thermocouple was placed 1 cm above the porous disc. Upon reaction three products were obtained: bio-oil (collected in the condenser), bio-char (in the pyrolysis reactor) and gases.

2.3. Bio-oils analysis

The chemical composition of bio-oils was determined by Gas Chromatography in Perkin Elmer CLAURUS 500 equipment coupled with a mass spectrometer detector. The quantification of the compounds was carried out considering that the peak area was directly proportional to the concentration of each compound. Nuclear magnetic resonance (NMR) spectra of the bio-oils were recorded on a Bruker ARX-300 spectrophotometer.

3. Results and discussion

3.1. Characterization of the biomass

It is well known that Li^+, K^+ and Ca^{+2} induce higher char and lower bio-oil yields during pyrolysis (Ramirez-Corredores, 2013a). The concentrations of Na, K, Ca and Mg for the different biomasses studied in the present work are reported in Table 1. In SSH, the amount of Na was relatively low, while the one corresponding to K is high. Both treated biomasses did not present considerable changes in Na concentration, but K, Ca and Mg concentration were modified. The increase of both Ca and Mg concentrations was attributed to the additives introduced to SSH for favoring the growth of the mushroom. The acid pre-treatment decreased the concentration of K, Mg and Ca.

Table 1
Characterization of sunflower seed hulls and percentages of bio-oils, bio-char and gases.

	SSH	SSHA	BSSH		
Metal (ppm, mg/kg)					
Na	100	500	500		
K	10,000	560	8000		
Mg	1900	160	3000		
Ca	3200	400	27,000		
Chemical composition %					
Hemicellulose	18	13	9		
Cellulose	40	41	35		
Lignin	20	21	14		
Others[a]	10,6	11,15	27,46		
Weight percentages of gas, bio-oil and bio-char					
	SSH	SSHA	BSSH	Cellulose	Acid cellulose
Bio-oil	34	15	42	54	9
Bio-char	27	40	18	5	36
Gases	39	45	40	41	55

[a] Proteins, pectins, resins, etc.

The relative concentration of lignin, cellulose and hemicellulose are reported in Table 1. BSSH showed a depleted concentration of hemicelluloses due to the activity of the mushroom (Sitarza et al., 2013). The amount of lignin was also decreased (approximately 30%) by *G. lucidum* enzymatic activity, as could be expected considering that the mushroom is a white rot fungus (Postemsky et al., 2014). The lower amount of lignin in BSSH, would lead to a less complex bio-oil (Czernik and Bridgwater, 2004).

In the case of SSHA only hemicellulose was decreased by comparison to SSH, since the acid treatment partially dissolves this compound (Nitsos et al., 2013).The TGA/DTA profiles corresponding to SSH, BSSH and SSHA are shown in Fig. 1(a–c). Since lignin, cellulose and hemicellulose are intimately related in the hull structure, the thermal decomposition of each one cannot be analyzed individually. However, it should be expected that lignin decomposition occurs at the highest temperature, while the hemicellulose degradation takes place at the lowest one (Lv et al., 2010). For the case of the SSH (Fig. 1a) a peak with a maximum at 340 °C, with a shoulder at the side of lower temperature (240 °C) is observed. Besides, a minor peak at 480 °C is also detected. The treatment with acid completely modifies the thermal profile: two main peaks, centered at 190 and 380 °C respectively, were detected. Since hemicellulose was notably decreased by the treatment, it could be considered that the first peak is mainly associated with cellulose decomposition and the latter with lignin one.

For the case of BSSH, the main peak was narrower than the one corresponding to SSH and the minor peak at 480 °C was vanished (see Fig. 1). Probably this last contribution could be associated with lignin degradation.

3.2. Pyrolysis of sunflower seed hulls to bio-liquid

The weight percentages of solid, gas and liquid phases obtained after pyrolysis are reported in Table 1. For the sake of comparison the results corresponding to the pyrolysis of cellulose and acid-washed cellulose were also shown. The highest amount of liquid was produced for pure cellulose, due to the fact that this material is free from lignin. Washing cellulose with acid produced an important increase of the solid and a notable decrease of the liquid yield as previously observed (Jiang et al., 2013). This showed that the acid protects cellulose fibers against the thermal attack.

Amongst the different hulls, the minor production of bio-char was observed for BSSH. This fact would be related with the

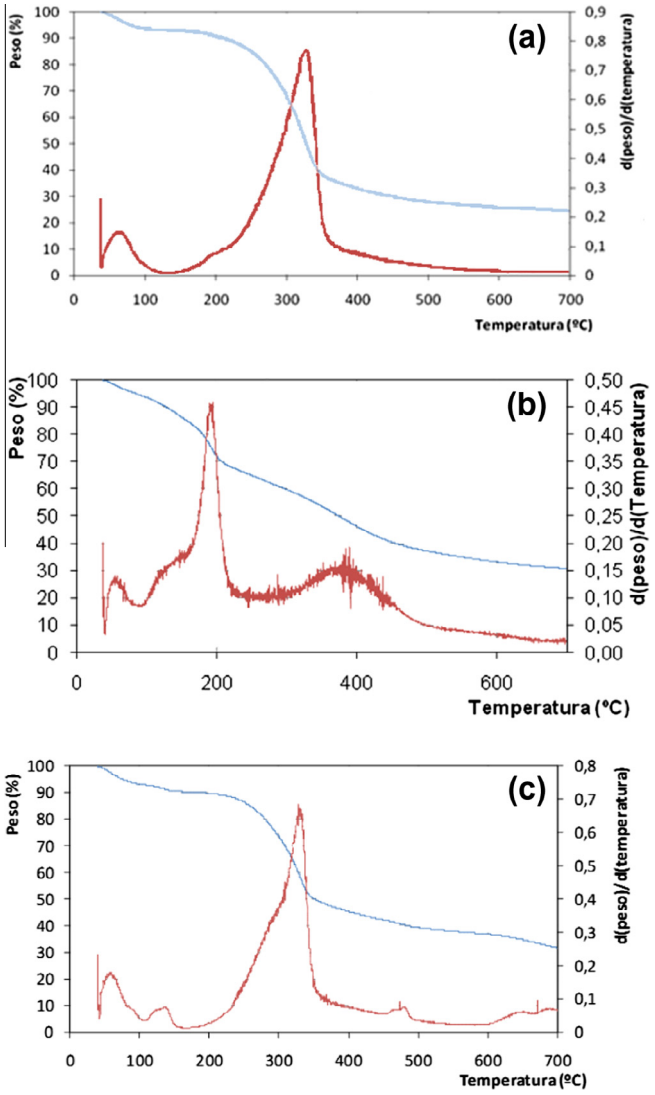

Fig. 1. TGA/DTA of: (a) SSH, (b) SSHA and (c) BSSH.

relatively low concentration of lignin in this hull. Besides, a relative high production of bio-oil was detected over BSSH. From this point of view the densification seems to be more efficient for the biotransformed material than for the other biomasses. The difference would be linked to the fact that the enzymatic activity of the mushrooms led to a degradation of the lignin structure, turning the hulls more prone to thermal attack. In spite of the notably high concentration of Ca and Mg (which are detrimental for the production of liquid), (Ramirez-Corredores, 2013a), a relatively high yield to liquid was observed. Thus, it can be concluded that the deleterious effect of Ca and Mg over the production of liquid was compensated by the degradation of lignin by mushroom enzymes.

A large number of compounds were present in the three bio-oils, as was commonly observed in this kind of pyrolysis. For the sake of simplicity, the compounds were classified into five general groups: (I) low molecular weight ketones, aldehydes and acids (less than 4 C), (II) furans, ketones, aldehydes and alcohols (more than 4 C atoms), (III) phenolic and aromatics, (IV) high molecular weight acids and esters and, (V) sugars.

The composition of the bio-oils varied with the nature of the biomass. SSH led to a liquid with a high concentration of acetic acid (group I). However, this bio-oil could not be envisaged as a source for producing this chemical, since other compounds of similar boiling point (2-methyl-4-propanol, methylglyoxal, 1-hydroxy-2-propanone) were also present, that will turn the separation process rather complicated. It was observed that this liquid was not stable and following approximately 10 h of storage at room temperature segregation of tar was detected. Even if the bio-oil was stored at −5 °C a fouling of the liquid was detected following 24 h. It is well known that this phenomenon is associated to the re-polymerization of phenolic compounds (group III).

The bio-oil from SSHA showed a relatively simple chemical composition. As can be observed in Table 2, the main component was furfural (71%), while approximately 11% of acetic acid was also present. Many of the components formerly present in the liquid from un-treated SSH were not obtained. The increase of furfural with regards to SSH would be originated in the fact that the acid activated cellulose (Ramirez-Corredores, 2013b), while the relative low amount of acetic acid in SSHA was due to the decrease in hemicellulose content. It is important to note that levoglucosenone (a high valuable sugar employed in the preparation of chiral synthons (Trahanovsky et al., 2003)) was detected in the bio-oil from SSHA. The presence of acetic acid, furfural and levoglucosenone in SSHA was confirmed with ^{13}C NMR and ^{1}H NMR analysis. Spectra were compared with standards for each compound.

Considering the differences in the boiling point of the three components of this liquid (furfural, acetic acid and the sugar), the separation process of the bio-oil would not be complicate. Furthermore, the fact that phenolic compounds were not produced led to a quite stable liquid during storage. Certainly, the aging of SSHA liquid took place in a period of time much longer than the corresponding to the bio-oil from SSH. This material remained stable even following storage of 6 months.

Notable differences were observed between the liquid from BSSH and the one originated by the pyrolysis of SSH. The amounts of group II and of group III were increased by regards to SSH. Probably, the enzymatic attack to lignin separates it from holocellulose, which structure is intimately linked to lignin in the original biomass. Consequently cellulose was more prone to the thermal attack. Carboxylic acids (group IV compounds) were practically vanished in BSSH, which is an advantage since the acids turn the

Table 2
Chemical composition of bio-oils from SSH, SSHA and BSSH (%).

Compound	Group	SSH	SSHA	BSSH
Methylglyoxal	I	2	–	–
Acetic acid	I	60	1	47
1-Hydroxy-2-propanone	I	10	–	–
2-Methyl-4-propanol	II	3	–	–
1,2-Ethanediol,diacetate	II	3	–	–
Butanedial	II	2	–	–
Furfural	II	4	7	9
1-(Acetyloxy)-2-propanone	II	2	–	3
2-Hydroxy-2-cyclopenten-1-one	II	–	–	2
Ethyl ester propanoic acid	II	–	–	2
5-Methyl-2-furancarboxaldehyde	II	–	3	3
Phenyl ester carbamic acid	II	–	–	2
4-Heptanone	II	–	–	2
3-Methyl-1,2-cyclopentanedione	II	–	–	3
2-Hydroxy-3-methyl-2-cyclopenten-1-one	II	1	–	–
2-Methoxyphenol	III	2	–	12
2-Methoxy-4-methyl-phenol	III	1	–	3
4-Ethyl-2-methoxy-phenol	III	–	–	2
2-Methoxy-4-vinylphenol	III	2	–	3
2,6-Dimethoxy-phenol	III	–	–	2
2-Methoxy-4-(1-propenyl)-phenol	III	1	–	2
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	III	1	–	3
bis-(2-Ethylhexyl)-ester-hexanedioic-acid	IV	1	–	–
Oleic acid	IV	3	–	–
Vanillin lactoside	V	1	–	–
Levoglucosenone	V	–	15	–

liquid highly corrosive and can undergo condensation with aldehydes producing solid esters.

The liquid from BSSH showed a relatively high concentration of phenolic compounds (group III). In spite of the fact that lignin concentration was relatively low in BSSH, the remaining lignin was degraded by the enzymatic activity and thus more compounds coming from its degradation were present in the liquid. This could be a negative aspect of the bio-oils from BSSH, since phenolic compounds coming from lignin were responsible for aging. However, this liquid was quite stable. Even more, the bio-oil obtaining from BSSH was much more stable to storage than the one coming from untreated material and it remained stable at room for a period of approximately 10 days. The stability of the bio-oil from BSSH could be due to the elimination of high molecular acids (group IV), which lead to spontaneous condensation reactions.

4. Conclusions

Different bio-oils were obtained from pyrolysis of sunflower seed hulls. The bio-oil corresponding to untreated hulls presented a high concentration of acetic acid but its instability to storage was high. Pre-treatments of the hulls led to liquid more stable to storage. The liquid from the hulls previously washed with acid was concentrated in furfural and also showed a relatively high amount of levoglucosenone. The pyrolysis of the hulls employed for the growing of *G. lucidum* originated a high yield to a liquid rich in acetic acid and quite stable to storage.

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